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The crystal and molecular structures of selected organometallic compounds and some direct methods

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THE CRYSTAL AND MOLECULAR STRUCTURES OF SELECTED ORGANOMETALLIC COMPOUNDS AND SOME DIRECT METHODS

by

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INTRODUCTION

The term "organometallic" is used to describe a wide range of compounds in which the organo-group is bonded directly to a metal atom. In addition, this term is often used to indicate compounds in which the organo-group is bonded to such atoms as silicon, boron, or phosphorus. The four compounds, $Si_7C_{26}H_{55}$, $Pd(P(CH_3)_2C_6H_5)_2Cl_2$, $Pr(N(C_2H_2O_2)_3)3H_2O$, $Dy(N(C_2H_2O_2)_3)4H_2O$ all fall into this category. An attempt was made to select compounds for study for which there was relatively little structural information available or the information was inconclusive and a crystal structure study would remove the ambiguity.

The silicon compound was selected for study due to the dearth of structural information available on multiple Si-Si bonding. In fact, this is, to my knowledge, the first crystal structure report of a compound with multiple Si-Si bonds. The silicon atoms were found to have a normal tetrahedral type configuration with little evidence for d-orbital contribution to the bonding despite the presence of a carbon-carbon double bond adjacent to the trisilane moiety. In the case of the palladium structure, information available on the structure was inconclusive. This study determined the configuration of the compound to be cis, square-planar with a significant lengthening of the Pd-Cl bond and a shortening of the Pd-P bond. The amount of structural information available for the

rare earth complexes is limited; especially on structural changes across an entire series of rare earths complexed to one particular ligand. The purpose of the study of the lanthanon(III)-nitrilotriacetate complexes was to provide good structural information on the nature of the changes in the complexes across the series and to determine the causes of these changes. The two structures, which are presented here, show a gross structural change from nona-coordinate to octa-coordinate with additional, minor changes in bond distances. The results indicate that these changes are probably due to the decreased metal-ion size.

In addition, we have attempted to extend the normal "direct methods" by use of a new phase relationship called the "quadruple product". The method has been tried successfully on $Cs_3Sb_2Cl_9$.

STRUCTURE OF 2[TETRA(TRIMETHYLSILYL)CYCLOHEXENE-1-YL]HEPTAMETHYLTRISILANE

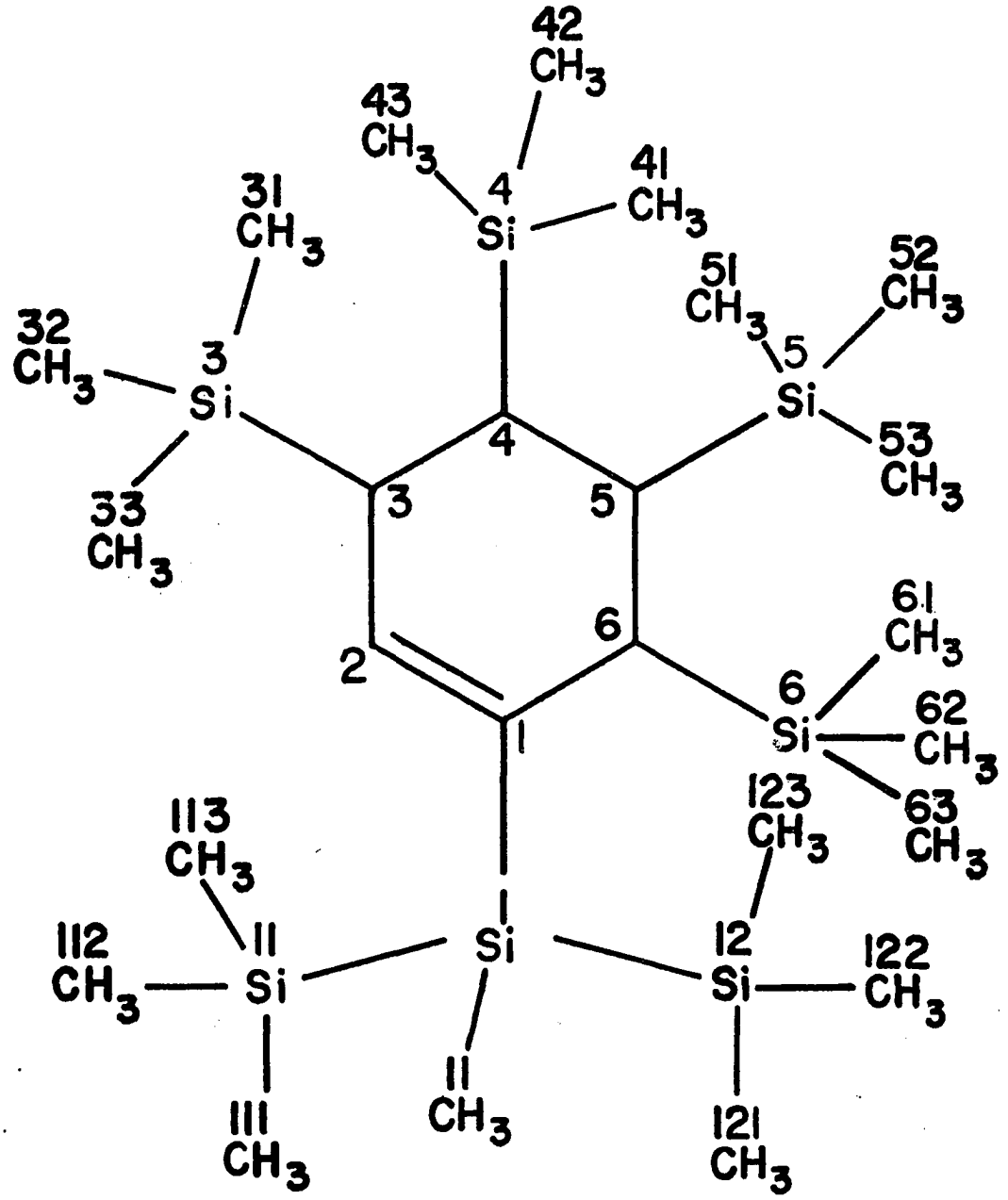
Introduction

Although the structures of inorganic silicon compounds as well as a number of organic siloxanes and silsesquioxanes have been studied extensively, relatively little structural information is available for organosilicon compounds which contain Si-Si bonds. Gas phase electron diffraction was used to investigate the structures of disilane[1] and hexamethyldisilane[2], but the only compound of this type to be investigated by single-crystal X-ray diffraction techniques prior to the present study was bistetramethyldisilanilenedioxide, $((CH_3)_4Si_2O)_2$[3]. The title compound, 2-[tetra(trimethylsilyl)cyclohexene-1-yl]heptamethyltrisilane, hereafter referred to as TTCH, is of interest because of the trisilane moiety. The molecular configuration and the numbering scheme used in this investigation are seen in Figure 1. TTCH was obtained as the major product[4] in the reaction of phenylmethyldichlorosilane and chlorotrimethylsilane with metallic lithium in tetrahydrofuran, and was unambiguously characterized only after this structural investigation.

Experimental

A sample of TTCH, mp 121°, was kindly supplied by Professor Gilman of this department. After recrystallization

Figure 1. The molecular structure of TTCH (the ring carbons are numbered from 1 through 6 and the silicon atoms which are bonded to them have the same number as the carbon to which they are attached. Substituents on each silicon atom are identified by moving the silicon number one digit to the left)


42
CH3
43
CH3
4
Si
41
CH3
31
CH3
32
CH3
3
Si
33
CH3
51
CH3
52
CH3
5
Si
53
CH3
4
3
5
2
6
1
61
CH3
6
Si
62
CH3
63
CH3
123
CH3
113
CH3
112
CH3
11
Si
111
CH3
Si
11
CH3
12
Si
122
CH3
121
CH3

from a 1:1 solution of methanol and ethyl acetate, many small, colorless crystals were obtained and were used without further purification. Weissenberg and precession photographs made with CuKα and MoKα radiation, respectively, indicated orthorhombic symmetry. Systematic absences observed for 0$\underline{k}\underline{l}$ reflections with $\underline{k} + \underline{l}$ odd, and for $\underline{h}0\underline{l}$ reflections with $\underline{h}$ odd, limited the choice of space groups to $Pna2_1$ or Pnma. Accurate unit cell parameters were obtained from a least-squares refinement based on the 2θ values for 16 reflections which had been carefully measured on a General Electric diffractometer using CrKα radiation. The α_1 and α_2 components were unresolved. Hence the wavelength used was the weighted mean of α_1 and α_2, $\lambda = 2.291$ Å. The unit cell parameters and their standard deviations based on the elements of the least-squares inverse matrix are $\underline{a} = 24.081 \pm 0.008$, $\underline{b} = 9.839 \pm 0.007$, $\underline{c} = 15.973 \pm 0.009$ Å, and $V = 3784$ Å^3. The density as measured by flotation in a methanol-glycerol mixture was 0.97 g/cm^3; the density calculated with $Z = 4$ was 0.98 g/cm^3. A General Electric XRD-5 X-ray unit equipped with a single-crystal orienter and scintillation counter was used with MoKα radiation ($\lambda = 0.7107$ Å) in the moving-crystal-moving-counter mode (θ, 2θ coupling) to measure intensities. A 100-sec scan covering 1.67° in 2θ was used for each reflection. The take-off angle was 1.0°. Since the backgrounds were seen to be a function of θ only,

the backgrounds for individual reflections were obtained from a plot of background versus 2θ. One crystallographically independent octant of data was measured within a 2θ sphere of 45° ($\sin\theta/\lambda = 0.538$) beyond which no reflections were observed to have intensities significantly above the background. These data, after correction for noncharacteristic radiation streaks[5] and Lorentz-polarization factors, were reduced to structure factors. The crystal used for intensity measurements had approximate dimensions 0.2 x 0.2 x 0.4 mm. The minimum and maximum transmittances were 91% and 97% based on $\mu = 2.50\ cm^{-1}$. Consequently no absorption correction was made. In an attempt to account for systematic as well as random errors standard deviations were assigned to the intensity data according to the formula:

$$\sigma(I) = [C_T + C_B + C_S + (0.04C_T)^2 + (0.04C_B)^2 + (0.06C_S)^2]^{1/2}$$

where C_T, C_B, and C_S are, respectively, the total counts, background counts, and streak counts. The quadratic terms correspond to estimated systematic errors of 4% in intensity and background measurements, and 6% in the streak correction. The estimated standard deviation for each structure factor was obtained by the method of finite differences[5]

$$\sigma(F) = ([I + \sigma(I)]^{1/2} - I^{1/2})/(Lp)^{1/2}$$

where Lp is the Lorentz-polarization factor. Of the 1423

measured reflections, 198 had $F < 3\sigma(F)$ and were excluded from the refinement.

Since the general multiplicity of the centrosymmetric space group, Pnma, is 8, four molecules of TTCH could occupy one unit cell in this space group only if each possessed either a center of symmetry or a mirror plane. The improbability of either symmetry in TTCH molecules indicated the noncentrosymmetric space group $Pna2_1$. The successful solution of the structure verified this space group assignment. The Si atoms were located by the use of a three-dimensional, superposition procedure starting with a well resolved peak in the Harker section of the sharpened Patterson map (the thermal parameter, B, used for sharpening was 2.0 $\AA^2$). In the resultant map, a center of symmetry relating two images was readily found. Utilizing one additional superposition and a knowledge of the space group symmetry, six of the seven Si atoms were located. Because of the large number of apparently equal peaks in the three-dimensional electron density map, the final silicon atom, Si_5, could not be distinguished from the many, as yet unassigned, carbon peaks. A centrosymmetric projection of this Fourier map along the c-axis, however, clearly yielded the $\underline{x}$ and $\underline{y}$ coordinates of Si_5. The $\underline{z}$ coordinate was readily obtained by searching the three-dimensional map along the line defined by $\underline{x}$ and $\underline{y}$. Subsequent three-dimensional Fourier syntheses revealed

the locations of all of the carbon atoms. Calculations were performed on IBM/360 models 50 and 65 computers using a series of unpublished programs developed at Iowa State University, the Oak Ridge least-squares program[6], and the block-diagonal least-squares program of the National Research Council of Canada[7]. Scattering factors for neutral silicon and carbon atoms were those of Hanson *et al.*[8]. Only the *x* and *y* parameters of Si_{11} were varied in the least-squares refinement in order to fix the origin of the polar unit cell. The full-matrix isotropic refinement converged to a conventional R, $R = \Sigma||\underline{F}_o| - |\underline{F}_c||/\Sigma|\underline{F}_o|$, of 0.116. The function minimized was $\Sigma\underline{w}(|\underline{F}_o| - |\underline{F}_c|)^2$ in which the weight, *w*, was $1/\sigma^2(\underline{F})$. The anisotropic refinement of 287 positional and temperature factors necessitated use of the block-diagonal approximation. In the final stages of refinement a modified weighting function was used in order to remove the dependence of $\langle\underline{w}(|\underline{F}_o| - |\underline{F}_c|)^2\rangle$ on F_o. The modified weighting function was $w = 1/(\sigma^2(F) + 0.005F^2)$. Convergence was achieved with a conventional R factor of 0.07 and a weighted R factor, $R_w = (\Sigma\underline{w}(|\underline{F}_o| - |\underline{F}_c|)^2/\Sigma\underline{w}F_o^2)^{1/2}$, of 0.10. The standard deviation of a reflection of unit weight was 1.009. A consideration of the isotropic and anisotropic R factors permits rejection at the 0.005 level of the hypothesis that all atoms vibrate isotropically[9]. A difference map was calculated in an attempt to determine the positions of the hydrogens. How-

ever, due to the large thermal vibrations in the molecule, the hydrogen atoms could not be located. Final positional and thermal parameters along with their estimated standard deviations are listed in Figure 2. The neglect of interatomic correlations in the block-diagonal approximation leads to underestimation of the standard deviations. Experience in this laboratory has shown that the block-diagonal standard deviations and quantities calculated from them should be multiplied by 1.2 for comparison with full-matrix values. Calculated structure factors are compared with the observed values in Figure 3.

Results and Discussion

The molecular structure of TTCH is shown in Figure 4 which was prepared by the computer utilizing Johnson's ORTEP program[10]. TTCH absorbs in the ultraviolet with a maximum at 241 mμ[11] whereas trisilanes usually absorb at 215 mμ[12]. Such a shift toward the visible is common in the spectra of silanes which have phenyl or vinyl substituents and has been explained in terms of pπ-dπ interactions with the unoccupied 3d orbitals on silicon[13,14]. Accordingly the carbon-carbon double bond in TTCH was placed vinylic to the trisilane moiety by Gilman et al.[4]. The carbon-carbon double bond of the cyclohexene system is unambiguously located between C_1 and C_2 on the basis of interatomic distances. Thus the structure proposed by Gilman et al.[4] is verified.

Figure 2. Fractional atomic coordinates and anisotropic temperature coefficients (10^4 x σ is given parentheses. β's are times 10^4 and have the form exp $[-(\underline{h}^2 \cdot \beta_{11} + \underline{k}^2 \cdot \beta_{22} + \underline{l}^2 \cdot \beta_{33} + \underline{kl} \cdot \beta_{23} + \underline{hl} \cdot \beta_{13} + \underline{hk} \cdot \beta_{12})]$)

ATOM	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
SI 1	-0.0173(2)	0.4391(6)	0.3002(4)	14(1)	134(7)	60(3)	11(9)	-4(3)	4(4)
SI 11	-0.0854(2)	0.2947(6)	0.3541(-)	16(1)	157(8)	101(4)	-8(12)	9(4)	-14(5)
SI 12	-0.0302(2)	0.6653(5)	0.3455(5)	21(1)	114(7)	66(3)	-2(10)	1(4)	2(5)
SI 3	0.1297(2)	0.1504(6)	0.4857(4)	25(1)	124(7)	66(4)	27(10)	-12(4)	-8(5)
SI 4	0.2050(2)	0.5079(6)	0.5019(4)	19(1)	143(7)	62(3)	-31(10)	-15(4)	-3(5)
SI 5	0.2005(2)	0.6148(6)	0.2787(5)	17(1)	160(8)	74(4)	43(11)	10(1)	-4(5)
SI 6	0.1301(2)	0.2862(6)	0.2092(4)	18(1)	169(8)	58(3)	-32(10)	-1(4)	24(5)
C 1	0.0554(6)	0.3917(16)	0.3328(11)	18(3)	115(21)	37(9)	-39(26)	-18(9)	34(14)
C 2	0.0619(6)	0.3504(16)	0.4112(12)	6(3)	133(24)	59(11)	8(30)	-22(9)	21(14)
C 3	0.1180(6)	0.3369(18)	0.4571(13)	14(3)	147(25)	72(12)	-29(32)	-1(11)	-7(15)
C 4	0.1697(6)	0.4194(16)	0.4142(11)	17(3)	95(22)	50(10)	54(28)	-20(10)	-17(14)
C 5	0.1486(6)	0.5090(16)	0.3394(11)	13(3)	124(21)	43(9)	-11(28)	-6(9)	1(14)
C 6	0.1047(6)	0.4360(17)	0.2817(14)	10(3)	118(22)	81(13)	-18(34)	16(11)	16(14)
C 11	-0.0246(8)	0.4398(25)	0.1813(14)	27(5)	310(44)	56(13)	-62(42)	-16(13)	16(24)
C 31	0.2062(8)	0.1025(19)	0.4837(17)	32(5)	140(26)	116(18)	38(43)	-34(18)	13(19)
C 32	0.0999(11)	0.1218(27)	0.5892(17)	54(8)	236(40)	76(15)	94(45)	27(19)	14(30)
C 33	0.0934(8)	0.0335(20)	0.4144(19)	25(4)	142(29)	128(19)	28(42)	-4(15)	12(19)
C 41	0.1702(10)	0.6748(24)	0.5245(15)	41(6)	232(38)	76(16)	-68(42)	-11(16)	23(26)
C 42	0.2820(7)	0.5208(29)	0.4790(16)	12(3)	400(50)	87(15)	33(50)	-22(13)	-42(22)
C 43	0.1999(9)	0.4151(23)	0.6029(14)	30(5)	233(37)	65(13)	-19(39)	-29(14)	-2(23)
C 51	0.2652(7)	0.5210(24)	0.2431(16)	13(3)	277(39)	106(17)	56(45)	12(13)	14(19)
C 52	0.2235(10)	0.7722(22)	0.3355(17)	48(6)	165(32)	103(17)	20(44)	53(20)	-84(24)
C 53	0.1659(8)	0.6967(26)	0.1788(16)	24(5)	308(45)	87(17)	100(48)	-1(14)	51(25)
C 61	0.0714(9)	0.1635(22)	0.1983(16)	34(5)	193(35)	92(16)	-92(43)	-12(17)	16(22)
C 62	0.1873(9)	0.1820(19)	0.2461(15)	32(5)	130(26)	85(15)	-64(34)	2(14)	10(19)
C 63	0.1477(9)	0.3565(30)	0.1009(15)	29(5)	406(55)	58(14)	-36(49)	30(14)	68(28)
C 111	-0.1553(10)	0.3457(30)	0.3133(33)	27(5)	310(51)	297(48)	175(89)	-31(27)	-84(27)
C 112	-0.0673(17)	0.1144(30)	0.3257(29)	98(15)	224(46)	232(41)	175(75)	158(42)	-202(44)
C 113	-0.0856(13)	0.2938(37)	0.4675(20)	62(10)	459(73)	87(19)	-119(65)	41(25)	-97(45)
C 121	-0.1044(9)	0.7105(25)	0.3359(19)	33(5)	237(39)	117(19)	48(48)	4(19)	37(25)
C 122	-0.0065(9)	0.6859(23)	0.4564(14)	38(6)	217(35)	59(12)	-62(37)	-16(19)	44(24)
C 123	0.0147(9)	0.7800(23)	0.2772(17)	31(5)	206(34)	93(19)	68(43)	19(17)	27(23)

Figure 3. Observed and calculated structure factors (each group of data contains, going from left to right, h, l, F_o, w, F_c while the data are headed by the value of k. Structure factors are in electrons times 10. A negative F_o indicates a reflection which is considered unobserved)

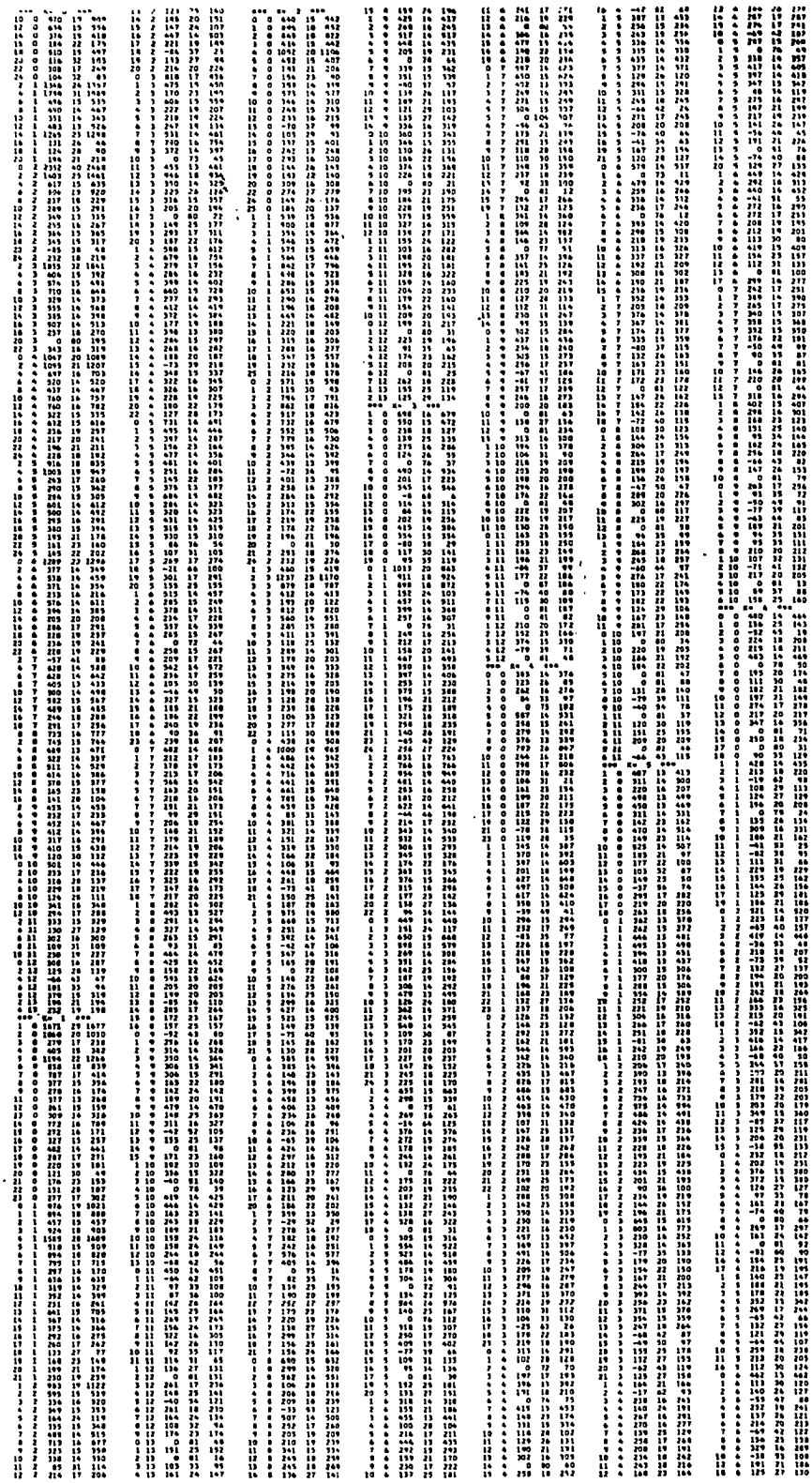
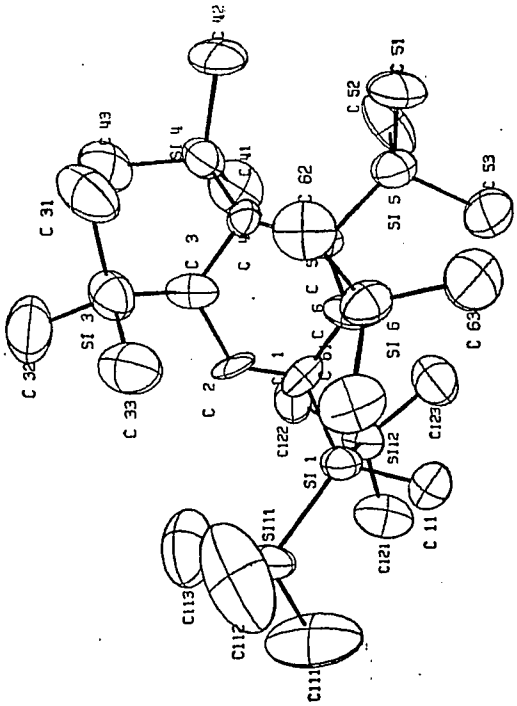
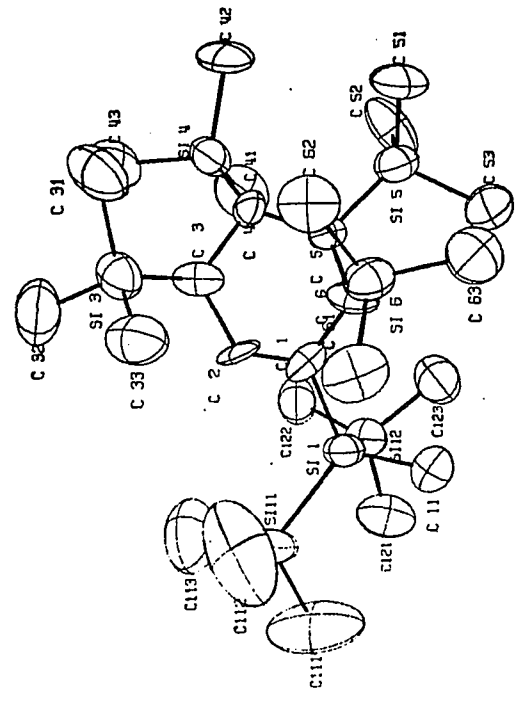


Figure 4. Stereoscopic representation of TTCH (anisotropic thermal vibration is indicated by 50% probability ellipsoids)


S2
S1
C52
C43
Si4
C41
C62
C31
Si5
C53
C3
C4
C5
Si3
C6
Si6
C63
C32
C1
C6'
C33
C2
C122
C123
Si12
Si1
C11
Si111
C121
C113
C112
C111


S2
S1
C52
C43
Si4
C41
C62
C31
Si5
C53
C3
C4
C5
Si3
C6
Si6
C63
C32
C1
C6'
C33
C2
C122
C123
Si12
Si1
C11
Si111
C121
C113
C112
C111

The bond distances and angles in TTCH are listed in Table 1. Anisotropic thermal vibration is indicated in Figure 4 by the ellipsoids which are drawn to a scale such that the atomic centers are found within them 50% of the time. Root-mean-square amplitudes of thermal vibration along the principal axes 1-3 of the ellipsoids are presented in Table 2. There are 23 crystallographically independent Si-C(sp^3) bonds in TTCH all of which should be chemically equivalent. However, a rather large scatter is observed in these Si-C bond lengths (1.81 - 1.97 Å). Such a range is not uncommon in organosilicon compounds[3,15] and, in the case of the methyl-carbon to silicon distances, can be attributed to the large amplitudes of thermal motion and methyl-methyl group steric interactions. The ring-carbon atoms to silicon atom distances are in much better agreement (1.86 - 1.91 Å) with exception of the Si_6-C_6 distance of 1.97(2)Å which is apparently lengthened due to steric interactions with the adjacent trisilane moiety. In addition, the inability to silyate the last ring-carbon atom can be attributed to this effect in agreement with mechanisms proposed by Harrell[11] and Weyenberg and Toporger.[16] The mean Si-Si distance is 2.35 ± 0.01 Å which is in agreement with the value of 2.3517 ± 0.0001 Å in metallic silicon.[17] With respect to the approximate plane of the ring, the four trimethylsilyl groups are bonded δ, α, β, β, to ring carbons C_3, C_4, C_5,

Table 1. Distances (Å) and angles (deg) with standard deviations in parentheses

Bond	Value	Angle	Value	Angle	Value
		Non-methyl bond distances and angles			
Si_1-Si_{11}	2.335(7)	Si_{11}-Si_1-Si_{12}	111.6(0.2)	Si_4-C_4-C_3	105.4(0.9)
Si_1-Si_{12}	2.361(8)	Si_{11}-Si_1-C_1	115.6(0.5)	Si_4-C_4-C_5	117.3(0.9)
Si_1-C_1	1.884(17)	Si_{12}-Si_1-C_1	105.7(0.5)	C_3-C_4-C_5	110.6(1.2)
Si_3-C_3	1.912(19)	Si_1-C_1-C_2	116.5(1.0)	Si_5-C_5-C_4	119.1(0.9)
Si_4-C_4	1.856(17)	Si_1-C_1-C_6	120.7(1.0)	Si_5-C_5-C_6	113.2(0.9)
Si_5-C_5	1.893(17)	C_6-C_1-C_2	120.4(1.3)	C_5-C_5-C_6	113.9(1.6)
Si_6-C_6	1.971(18)	C_1-C_2-C_3	125.4(1.3)	Si_6-C_6-C_5	118.4(0.9)
C_1-C_2	1.325(22)	Si_3-C_3-C_4	117.7(1.0)	Si_6-C_6-C_1	110.3(0.9)
C_2-C_3	1.544(24)	Si_3-C_3-C_2	107.3(1.0)	C_5-C_6-C_1	110.1(1.2)
C_3-C_4	1.635(24)	C_2-C_3-C_4	115.1(1.2)		
C_4-C_5	1.569(23)				
C_5-C_6	1.577(23)				
C_6-C_1	1.504(24)				

Table 1. (Continued)

Bond	Value	Bond	Value	Bond	Value
		Bond distances involving methyl groups			
Si_1-C_{11}	1.908(23)	Si_4-C_{43}	1.857(23)	Si_6-C_{63}	1.911(25)
Si_3-C_{31}	1.903(23)	Si_5-C_{51}	1.899(23)	Si_{11}-C_{111}	1.873(35)
Si_3-C_{32}	1.824(27)	Si_5-C_{52}	1.878(25)	Si_{11}-C_{112}	1.882(39)
Si_3-C_{33}	1.840(24)	Si_5-C_{53}	1.971(24)	Si_{11}-C_{113}	1.811(33)
Si_4-C_{41}	1.878(25)	Si_6-C_{61}	1.889(24)	Si_{12}-C_{121}	1.873(27)
Si_4-C_{42}	1.895(24)	Si_6-C_{62}	1.814(24)	Si_{12}-C_{122}	1.871(23)
				Si_{12}-C_{123}	1.906(23)

Table 1. (Continued)

Angle	Value	Angle	Value	Angle	Value
		Bond angles involving methyl groups			
C_{11}-Si_1-C_1	112.0(0.9)	C_{41}-Si_4-C_{43}	103.6(1.0)	C_{62}-Si_6-C_{63}	109.3(1.0)
C_{11}-Si_1-Si_{11}	107.7(0.7)	C_{42}-Si_4-C_{43}	105.4(1.0)	Si_1-Si_{12}-C_{121}	111.7(0.8)
C_{11}-Si_1-S_{12}	106.8(0.7)	C_5-Si_5-C_{51}	115.3(0.9)	Si_1-Si_{12}-C_{122}	110.6(0.7)
C_3-Si_3-C_{31}	112.1(0.9)	C_5-Si_5-C_{52}	113.6(0.9)	Si_1-Si_{12}-C_{123}	107.9(0.7)
C_3-Si_3-C_{32}	107.9(1.0)	C_5-Si_5-C_{53}	111.2(0.9)	C_{121}-Si_{12}-C_{122}	109.7(1.1)
C_3-Si_3-C_{33}	112.4(0.9)	C_{51}-Si_5-C_{52}	107.7(1.0)	C_{122}-Si_{12}-C_{123}	107.8(1.0)
C_{31}-Si_3-C_{32}	111.0(1.1)	C_{51}-Si_5-C_{53}	107.6(1.0)	C_{121}-Si_{12}-C_{123}	109.0(1.1)
C_{31}-Si_3-C_{33}	107.2(1.0)	C_{52}-Si_5-C_{53}	100.3(1.0)	Si_1-Si_{11}-C_{111}	109.9(1.1)
C_{32}-Si_3-C_{33}	106.1(1.0)	C_6-Si_6-C_{61}	110.4(0.9)	Si_1-Si_{11}-C_{112}	108.8(1.2)
C_4-Si_4-C_{41}	110.6(0.9)	C_6-Si_6-C_{62}	117.9(0.9)	Si_1-Si_{11}-C_{113}	111.9(1.0)
C_4-Si_4-C_{42}	109.5(0.9)	C_6-Si_6-C_{63}	109.3(0.9)	C_{111}-Si_{11}-C_{112}	112.1(1.6)
C_4-Si_4-C_{43}	113.3(0.9)	C_{61}-Si_6-C_{62}	105.3(1.0)	C_{111}-Si_{11}-C_{113}	110.3(1.5)
C_{41}-Si_4-C_{42}	114.5(1.1)	C_{61}-Si_6-C_{63}	103.7(1.0)	C_{112}-Si_{11}-C_{113}	103.7(1.6)

Table 2. Root-mean-square amplitude of vibration (angstroms x 10^3)

Atom	Min.	Med.	Max.	Atom	Min.	Med.	Max.
Si_1	200	252	282	C_{33}	250	280	406
Si_{11}	207	280	362	C_{41}	277	330	382
Si_{12}	235	250	291	C_{42}	160	335	450
Si_3	238	255	310	C_{43}	237	331	344
Si_4	216	259	302	C_{51}	191	337	399
Si_5	216	265	327	C_{52}	200	340	445
Si_6	218	262	310	C_{53}	238	310	426
C_1	178	190	297	C_{61}	260	311	386
C_2	94	261	289	C_{62}	227	308	348
C_3	200	259	312	C_{63}	204	324	461
C_4	178	198	301	C_{111}	229	390	637
C_5	188	231	252	C_{112}	218	393	703
C_6	155	246	328	C_{113}	300	377	535
C_{11}	240	292	401	C_{121}	285	347	402
C_{31}	241	293	407	C_{122}	248	293	383
C_{32}	256	359	421	C_{123}	281	288	386

and C_6, respectively. The torsion angles about the three $C(sp^3)$-$C(sp^3)$ bonds within the cyclohexene ring are listed in Table 3. Methyl groups on adjacent silyl groups are meshed as follows: C_{11} is between C_{61} and C_{63}; C_{51}, between C_{62} and C_{63}; C_{52}, between C_{41} and C_{42}; and C_{43}, between C_{31} and C_{32}. In this way intramolecular nonbonded repulsions are minimized. TTCH is obviously a racemate as is required by the presence of improper symmetry elements in the space group. The molecular packing is apparently governed entirely by steric factors because there exists no possibility for hydrogen bonding. The shortest intermolecular distances were 3.86 Å between C_{11} and C_{122} (molecule at $\bar{x}$, $\bar{y}$, 1/2 + z) and 3.88 Å between C_{53} and C_{113} (molecule at $\bar{x}$, $\bar{y}$, 1/2 + z).

Table 3. Torsion angles

Bond	Torsion angle (degrees)
C_3 - C_4	84.8
C_4 - C_5	59.3
C_5 - C_6	69.5

STRUCTURE OF cis-DICHLOROBIS(DIMETHYLPHENYLPHOSPHINE)PALLADIUM(II)

Introduction

It has been observed that square planar complexes of the type PdX_2Y_2, where X is a halide, very often adopt the trans configuration.[18] In fact, only recently have any cis complexes of this type been characterized. The cis, chloro complexes usually form pale yellow or colorless crystals while crystals of the trans complexes are more decidedly yellow.[19] However, a recent far-infrared study[20] by R. Keiter of $PdCl_2(P(CH_3)_2C_6H_5)_2$ which forms distinctly yellow crystals, indicated that this compound unlike $PdI_2(P(CH_3)_2C_6H_5)_2$[21] was probably not trans but no configuration could be assigned from the spectra. Therefore we undertook a crystal structure investigation to determine if the complex is square-planar and, if so, which isomer is present.

Experimental

A sample of this compound was kindly supplied by R. Keiter and the yellow crystals were used without further purification. Inspection of the crystals showed them to be square plates with sharply-defined faces. Weissenberg and precession photographs indicated a tetragonal space group with systematic extinctions of the type $00l, l = 2n + 1$; $hk0$, $h + k = 2n + 1$. These conditions indicate the space

group to be $P4_2/n$. In addition, systematically weak reflections of the type $\underline{h} + \underline{k} = 2\underline{n} + 1$ and $\underline{l} = 2\underline{n} + 1$ for general $\underline{hkl}$ reflections were observed.

The unit cell dimensions were determined by least-squares fit of 13 independent reflections whose 2θ values were determined from Weissenberg photographs calibrated with Al powder lines. The values obtained were $\underline{a} = \underline{b} = 9.324 \pm 0.004$ Å and $\underline{c} = 21.485 \pm 0.004$ Å. The measured density was 1.61 g/cc obtained by flotation techniques in a solution of diiodomethane and 1-bromopropane The calculated density with four molecules per unit cell ($V_c = 1868$ Å^3) is 1.62 g/cc.

A crystal of approximate dimensions 0.2 x 0.2 x 0.1 mm was selected for use in data collection. The crystal was mounted such that the (110) axis would be coincident with the phi axis of the diffractometer. Data were collected at room temperature using a Hilger-Watts four circle diffractometer equipped with a scintillation counter employing Zr-filtered Mo-Kα ($\lambda = 0.7107$ Å) radiation. All data within a 2θ sphere of 60 deg ($\sin\theta/\lambda = 0.70$) were measured using a θ-2θ coupled scan with a five deg take-off angle. Stationary-counter measurements of the background were made at the beginning and the end of each scan. The scan range was over 50 steps of 0.01 deg, one step per 0.4096 sec, and was increased by 1 step per deg increase in 2θ to insure complete integration over the entire peak. The length of the back-

ground measurement was adjusted accordingly. No appreciable decrease in the intensities of three standard reflections which were measured periodically throughout the data taking period was observed.

The measured intensities were corrected for background, Lorentz and polarization effects, and for adsorption[7] (μ = 14.2 cm^{-1}); minimum and maximum transmission factors were 0.67 and 0.87, respectively. The standard deviations were assigned to the intensities according to the following formula:

$$\sigma(I) = (C_t + C_b + (0.05\ C_t)^2 + (0.10\ C_b)^2 + (0.05\ C_n)^2)^{1/2}$$

where C_t, C_b, C_n and A are the total counts, background counts, net counts, and the absorption factor. The quadratic terms correspond to the estimated systematic errors in the intensity, background and absorption correction of 5, 10 and 5% respectively. The standard deviations in the structural amplitudes were obtained by the method of finite differences[5],

$$\sigma(\underline{F}_o) = ((I + \sigma(I))^{1/2} - I^{1/2})/(Lp)^{1/2}$$

where Lp is the Lorentz-polarization factor. Of the 2877 measured reflections, 850 were found to have values of F_o less than 2.0 x $\sigma(F_o)$. These reflections were considered

to be unobserved and were not included in the refinement.

Solution and Refinement of the Structure

Since the space group $P4_2/n$ has eightfold general positions, it was necessary to place the palladium atoms in special positions. From a consideration of the systematically weak reflections of the type $\underline{l} = 2\underline{n} + 1$, the palladiums were placed in the fourfold special position denoted by the Wycoff symbol 'e'; that is on the twofold axis perpendicular to the ab plane. Analysis of the Patterson map confirmed this supposition and allowed ready determination of the z-coordinate of the palladium. Three possible sets of chlorine and phosphorus positions were present due to pseudo mirroring. The correct set was determined by trial and error. These atoms gave a value of the discrepancy factor, $\underline{R} = \Sigma||\underline{F_o}| - |\underline{F_c}||/\Sigma|\underline{F_o}|$, of 28% for a structure factor calculation with the heavy atoms alone. The remaining carbon atoms were located from a three-dimensional electron density map. The structure was refined isotropically to an R = 15.4% using a modified version of ORFLS[6,8,22] and unit weights. At this point weights were changed to those based on individual statistics of the reflection ($w = 1/\sigma(\underline{F_o})^2$). The ring hydrogen atoms were added in calculated positions assuming 1.0 Å for the C-H distance. No attempt was made to refine hydrogen positions. A final statistical analysis of the $\underline{F_o}$ and $\underline{F_c}$ values indicated a dependence on the scattering angle. The

relative weights were adjusted to remove this dependence. An additional 134 reflections were removed from the refinement because they failed to fulfill one of the following criteria:

$$||\underline{F}_o| - |\underline{F}_c|| < 10 \times \sigma(\underline{F}_o) \ , \ |\frac{\underline{F}_o}{\underline{F}_c}| < 5.0 \text{ or } |\frac{\underline{F}_c}{\underline{F}_o}| < 5.0.$$

The structure was refined anisotropically to a final R = 8.8% and a final weighted discrepancy index, $R = (\Sigma w(\underline{F}_o - \underline{F}_c)^2)^{1/2}/(\Sigma w \underline{F}_o^2)^{1/2}$, of 7.9%. Convergence was assumed when no parameter shift was greater than 0.1 of that parameter's estimated-standard deviation. A final difference electron density map showed no residual electron density above 1.4 $e^-/\text{Å}^3$.

In Figure 5 are the final values of the positional and thermal parameters and their respective estimated standard deviations.[23] Estimated standard deviations were derived from the inverse matrix. In Table 4 are given the root-mean-square amplitudes of vibration while in Figure 6 are listed the values of the observed and calculated structure factors on an absolute scale. The configuration of the molecule along with the numbering scheme used is shown in Figure 7.[11] Selected intramolecular distances and angles are given in Table 5 (see also Figure 8).

Figure 5. Fractional atomic coordinates and thermal parameters (estimated standard deviation are given in parentheses right adjusted to the least significant figure of the preceding number. β's are times 10^4 and have the form $\exp[-(\beta_{11}\underline{h}^2 + \beta_{22}\underline{k}^2 + \beta_{33}\underline{l}^2 + \beta_{12}\underline{hk} + \beta_{13}\underline{hl} + \beta_{23}\underline{kl})]$.)

ATOM		X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PD		0.75000	0.25000	0.25309(3)	69(1)	79(1)	12(0)	-1(1)	0	0
P		0.8863(2)	0.3716(2)	0.3222(1)	66(2)	74(2)	16(0)	-12(2)	2(1)	-2(1)
CL		0.8977(2)	0.3462(2)	0.1742(1)	151(3)	145(3)	17(0)	-26(2)	17(1)	2(1)
C	1	0.8162(7)	0.4163(7)	0.3973(3)	79(8)	79(8)	17(2)	-21(7)	0(3)	-5(3)
C	2	0.702(1)	0.511(1)	0.4011(4)	122(12)	164(14)	25(2)	6(10)	3(4)	-10(5)
C	3	0.650(1)	0.556(1)	0.4583(6)	159(15)	186(16)	35(3)	27(12)	22(6)	-21(6)
C	4	0.712(1)	0.513(1)	0.5114(5)	185(18)	287(23)	20(2)	-67(17)	19(6)	-38(6)
C	5	0.823(1)	0.417(1)	0.5103(4)	212(18)	239(20)	15(2)	-87(16)	-13(5)	11(5)
C	6	0.8759(9)	0.3678(9)	0.4527(4)	113(11)	165(13)	18(2)	-43(10)	-11(4)	6(4)
C	7	0.933(1)	0.5498(9)	0.2942(4)	187(15)	107(11)	22(2)	-75(10)	4(5)	7(4)
C	8	0.4411(8)	0.2143(9)	0.3340(4)	74(9)	170(14)	37(3)	35(9)	17(4)	16(5)
H	2	0.655	0.544	0.360	5.0					
H	3	0.570	0.631	0.463	5.0					
H	4	0.668	0.550	0.552	5.0					
H	5	0.872	0.382	0.550	5.0					
H	6	0.964	0.301	0.453	5.0					

Table 4. Root-mean-square amplitude of vibration ($\mathring{A} \times 10^3$)

Atom	Min.	Intermed.	Max.
Pd	169	174	187
P	158	185	199
Cl	175	245	284
C_1	157	196	215
C_2	224	240	279
C_3	202	296	324
C_4	176	259	397
C_5	179	246	376
C_6	180	215	294
C_7	158	234	320
C_8	160	251	325

Figure 6. Observed and calculated structure amplitudes (in electrons x 10) for $PdCl_2(P(CH_3)_2C_6H_5)_2$

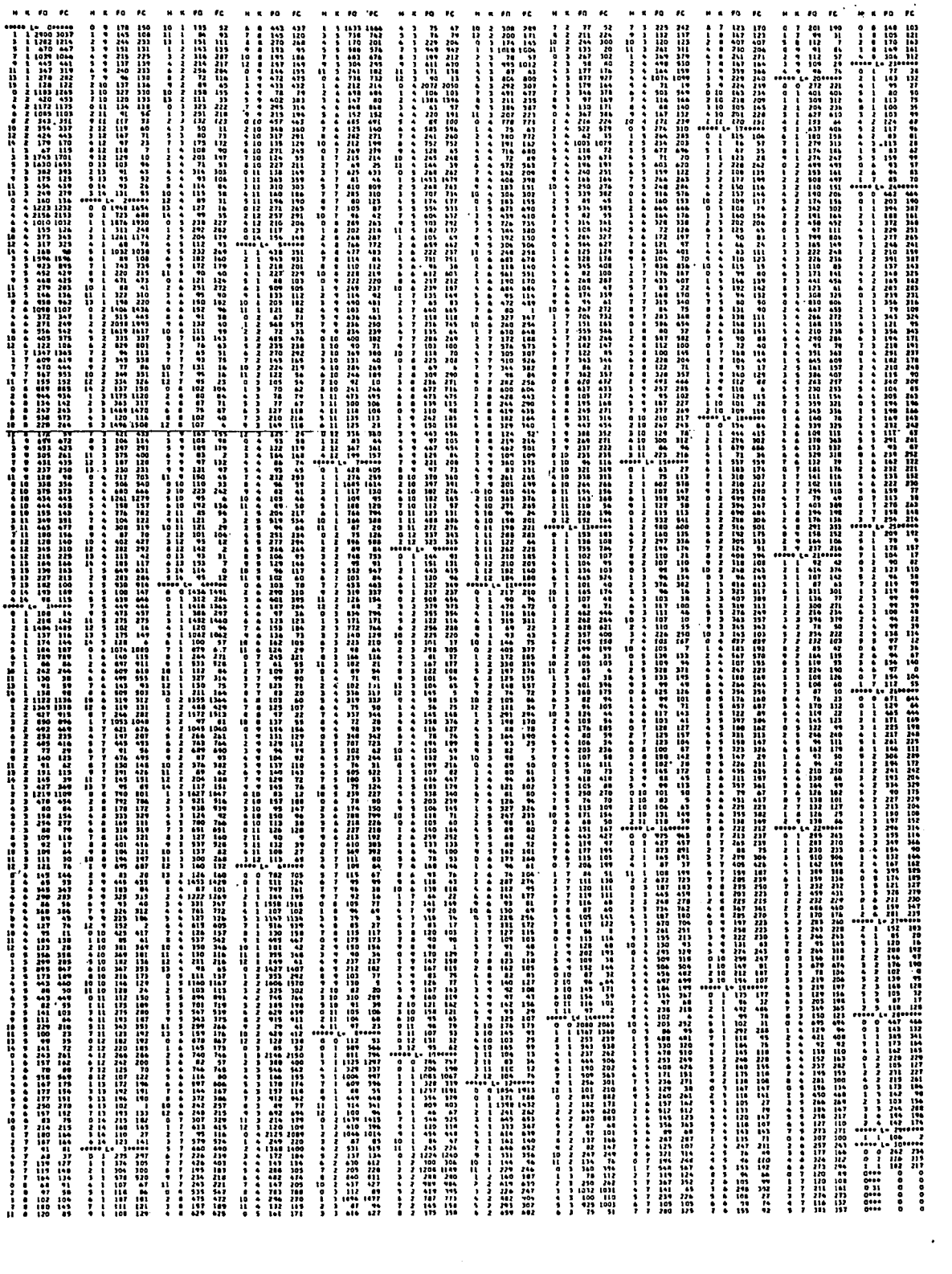


Figure 7. A perspective drawing of cis-dichlorobis(dimethylphenylphosphine) palladium(II). Anisotropic thermal vibration is indicated by 50% probability ellipsoids

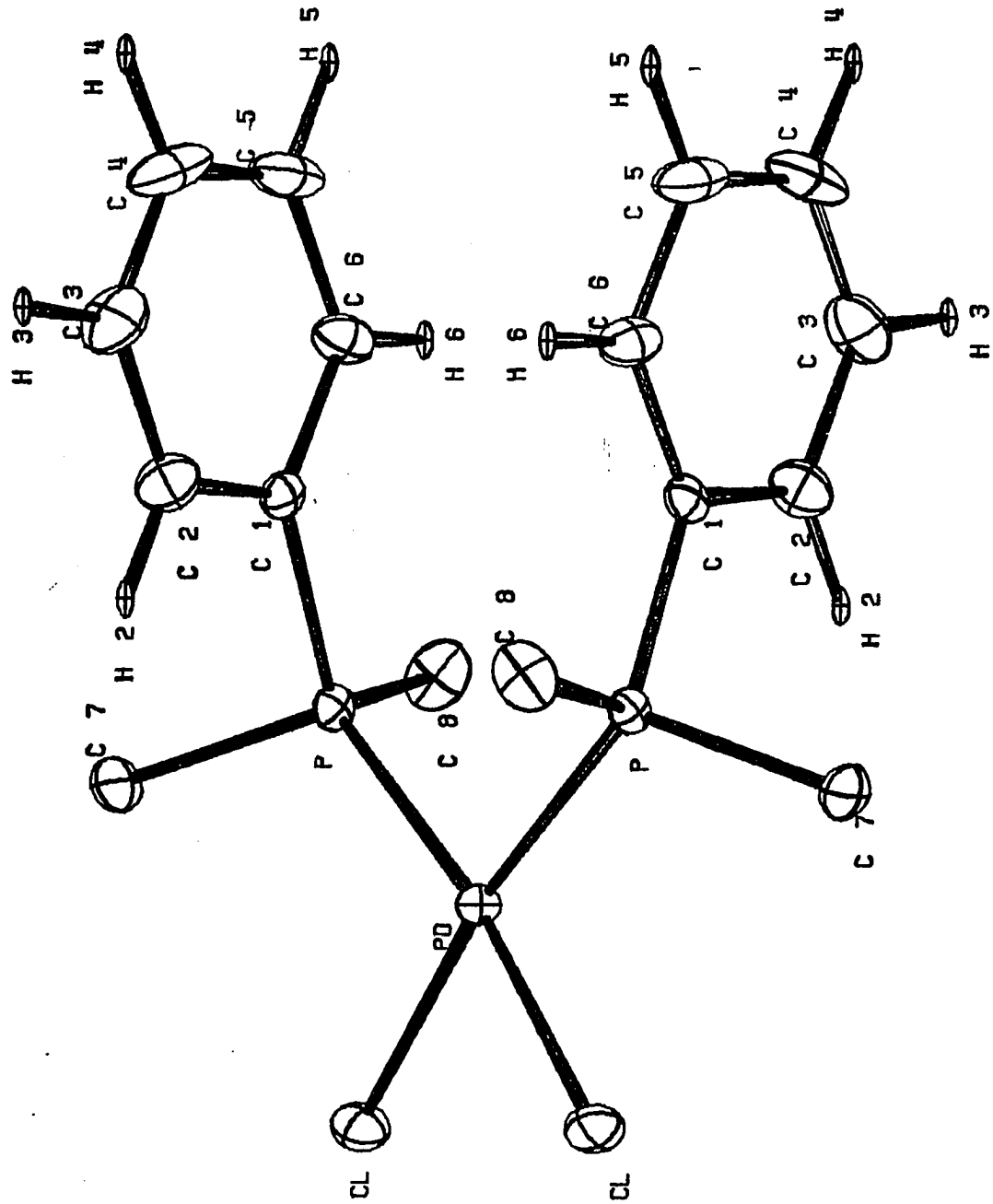
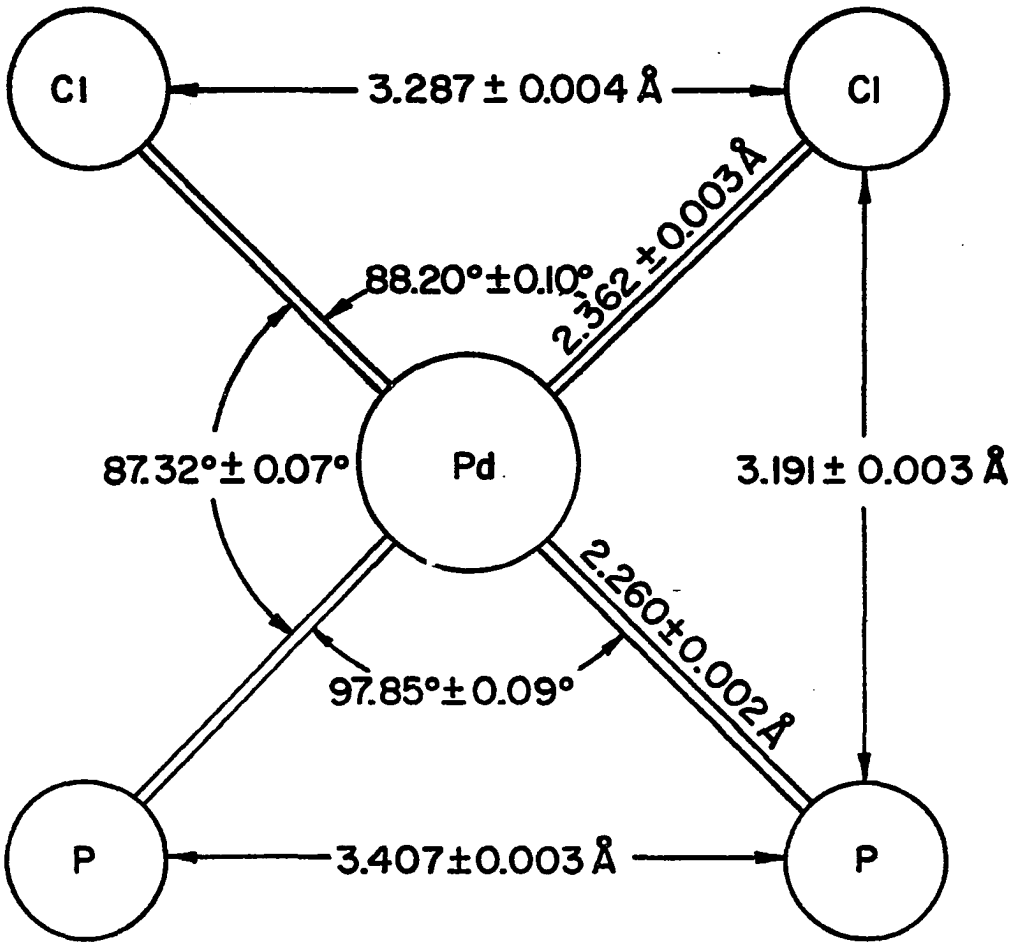

H 4
H 5
C 4
C 5
H 3
C 3
C 6
H 6
C 2
C 1
H 2
C 7
C 8
P
PD
CL
CL
H 5
H 4
C 5
C 4
H 6
C 6
C 3
H 3
C 1
C 2
C 8
H 2
P
C 7

Table 5. Selected distances (Å) and angles (deg) with standard deviations in parentheses

Bond	Value	Angle	Value	Angle	Value
P-Cl	3.191(3)	Cl-Pd-Cl'	88.2(1)	P-C_1-C_2	118.8(6)
P-P'	3.407(3)	Cl-Pd-P	87.32(7)	P-C_1-C_6	123.4(5)
Cl-Cl'	3.287(4)	P-Pd-P'	97.85(9)	P-C_1-C_4	174.6(5)
P-C_1	1.791(7)	Pd-P-C_1	120.2(2)	C_6-C_1-C_2	117.7(7)
P-C_7	1.819(7)	Pd-P-C_7	112.0(3)	C_1-C_2-C_3	121.0(8)
P-C_8	1.815(8)	Pd-P-C_8	111.7(3)	C_2-C_3-C_4	120.6(9)
C_1-C_2	1.38(1)	C_1-P-C_7	100.0(3)	C_3-C_4-C_5	120.6(9)
C_2-C_3	1.39(1)	C_1-P-C_8	107.4(4)	C_4-C_5-C_6	119.4(8)
C_3-C_4	1.34(2)	C_7-P-C_8	103.8(6)	C_5-C_6-C_1	120.6(8)
C_4-C_5	1.37(2)				
C_5-C_6	1.41(2)				
C_6-C_1	1.39(1)				

Figure 8. The arrangement of palladium and its four neighbors along with cogent distances and angles


Cl
3.287 ± 0.004 Å
Cl
2.362 ± 0.003 Å
88.20° ± 0.10°
87.32° ± 0.07°
Pd
3.191 ± 0.003 Å
2.260 ± 0.002 Å
97.85° ± 0.09°
P
3.407 ± 0.003 Å
P

Description of the Structure

The complex is best described as approximately cis, square-planar. However there are slight, but significant distortions since the ∠ Cl-Pd-Cl' ("'" denotes atom at $\bar{x}$, $\bar{y}$, $\bar{z}$) has closed two deg and the ∠ P-Pd-P' has opened some eight deg from their theoretical value of 90 deg. The Cl's are +0.13 Å and -0.13 Å from the least-squares plane defined by the palladium and its four nearest neighbors while the P's are ±0.12 Å from the plane. This is best viewed as a tetragonal distortion of 4.3 deg. The dihedral angle between the planes defined by the two phosphorus atoms and the palladium, and the two chlorine atoms and the palladium is 171.3 ± 0.1 deg. The equations of the two planes in the form ax + by + cz - d = 0 are (a = -0.66, b = 0.746, c = 0.00, d = -2.92) and (a = -0.546, b = 0.838, c = 0.00, d = -1.86), respectively.

The six carbon atoms in the phenyl ring showed no significant deviations from the best least-squares plane (a = 0.642, b = 0.766, c = -0.025, d = 7.64). The largest deviation from the plane was 0.02 Å by C_4 which is not statistically significant. The angles within the ring are all within three e.s.d.'s of the normal value of 120 deg. The ring bond distances also agree well with the expected value[24] of 1.41 Å with the exception of the C_3-C_4 distance which is slightly short.

Discussion

The apparent deviations in this complex from the ideal square-planar configuration can be primarily attributed to overcrowding caused by the bulky phosphorus ligands cis to each other. The phenyl rings of the different phosphorus ligands on the same palladium interact sterically with one another. This accounts for the fact that the P-Pd-P' angle is 98 deg and the Pd-P-C_1 angle is found to be 120 deg since in this way steric interactions can be reduced. However, the two rings still approach each other within 3.2 Å, (C_6-C'_6); somewhat less than the sum of the van der Waals radii.[24] This interaction could also easily explain the slight screwing of the phenyl rings as indicated by the ∠ P-C_1-C_4 of 174.6 deg. In order to accommodate the bulky phosphorus ligands, the chlorine atoms are forced closer together as shown by the ∠ Cl-Pd-Cl' of 88.2 deg. The Cl-Cl' distance of 3.287 Å is still greater than the distance of 2.88 Å which is the sum of the van der Waals radii of two chlorine atoms bonded to a common atom.[25] The slight tetragonal distortion may also be attributed to this overcrowding.

The agreement between the three nonequivalent P-C distances is good. The two phosphorus-methyl distances (1.819, 1.815 Å) are similar while the phosphorus-ring distance (1.791 Å) is just slightly shorter as would be expected from the slightly smaller covalent radii for the

ring carbon. The C-C distances are within 3σ of their normal values and the Pd-Pd distance of 6.6 Å is so great that any interaction is precluded despite an apparent alignment of the atoms.

The Pd-P bond in this compound (2.260 ± 0.003 Å) is significantly shorter than that found by Bailey and Mason[21] of 2.333 ± 0.007 Å in the trans-iodo complex, while the Cl-Pd bond (2.362 ± 0.003 Å) is significantly longer than that found by Bennett, Cotton and Weaver[26] of 2.290 ± 0.002 Å in $PdCl_2(DMSO)_2$. The predicted values from the sum of the covalent radii are 2.38 Å and 2.28 Å for the Pd-P and Pd-Cl distances, respectively. Our results generally agree with those expected from a strong "trans-effect".[27] That is, the bond trans to a strongly "trans-direction" ligand such as phosphorus is weaker and therefore longer than a bond trans to the somewhat less "trans-directing" chlorine. As has already been noted by Messmer, Amma and Ibers,[28] these distances may be sensitive to the substituents on the phosphorus as well as variations in the halide used. However, it would be expected that as long as the ligands are similar with respect to their "trans-directing" ability, the effect on either the M-Cl or M-P distance would be the same whether M is Pd or Pt. In Table 6 are listed a number of M-Cl and M-P bond lengths involving ligands of similar "trans-directing" ability.[29] As would be expected from the different covalent radii and electro-negativities of palladium and platinum,

Table 6. Selected metal-phosphorus and metal chloride bond lengths

Pd trans			
Bond	Distance (Å)	Compound	Ref.
Pd-P	2.333 ± 0.007	$PdI_2(P(CH_3)_2C_6H_5)_2$	21
Pd-Cl	2.287 ± 0.002	$PdCl_2(DMSO)_2$	26
Pd cis			
Bond	Distance (Å)	Compound	Ref.
Pd-P	2.260 ± 0.003	$PdCl_2(P(CH_3)_2C_6H_5)_2$	this work
Pd-Cl	2.362 ± 0.003	"	"
Δ trans to cis Pd			
Bond	Δ (Å)		
Pd-P	- 0.073		
Pd-Cl	+ 0.075		

Pt trans

Bond	Distance (Å)	Compound	Ref.
Pt-P	2.315 ± 0.004	Pt $P(C_2H_5)_3{}_2Br$	28
Pt-Cl	2.294 ± 0.009	Pt $P(C_2H_5)_3{}_2Cl_2$	28

Pt cis

Bond	Distance (Å)	Compound	Ref.
Pt-P	2.247 ± 0.008	$PtCl_2(P(CH_2)_3)_2$	29
Pt-Cl	2.376 ± 0.009	"	

Δ trans to cis Pt

Bond	Δ (Å)
Pt-P	- 0.068
Pt-Cl	+ 0.082

the M-Cl and M-P distances are somewhat different. However, the changes in the bond distances are identical within 1 e.s.d. in going from the trans to the cis configuration.

STRUCTURE OF NITRILOTRIACETODIAQUOPRASEODYMIUM(III)-MONOHYDRATE

Introduction

The complexes formed by the reaction of the trivalent lanthanons with nitrilotriacetate (NTA) in aqueous solution have been studied for some time.[30] The crystalline complexes formed by precipitation from saturated solution have been found to form one of several hydrates depending upon the temperature at which recrystallization is carried out and the rare earth used. Our preliminary study of the series of complexes formed at 25° C indicates that the series is divided into three crystallographically distinct groups: (1) the La-Ce group, (2) the Pr-Tb (Pm?) group and (3) the Dy-Lu group. Crystals of the first group are so poorly formed that they could not be characterized. Crystals of the second group belong to the space group Pbca with $\underline{a}$ = 13.21 ± 0.01, $\underline{b}$ = 29.98 ± 0.01 and $\underline{c}$ = 8.132 ± 0.006 Å. Those of the third group are in space group $Pca2_1$ with $\underline{a}$ = 21.535 ± 0.013 Å, $\underline{b}$ = 9.02 ± 0.004 Å, $\underline{c}$ = 12.186 ± 0.007 Å.

This division into groups also coincides with observed changes in hydration number across the series from 5 to 3 to 4.[31] The break between groups at Tb occurs near a sudden change in thermodynamic properties of these as well as other lanthanon (III) complexes.[32] Coordination numbers ranging from 6 to 12 have been observed in various com-

plexes.[33-36] The smaller coordination numbers are usually associated with the heavier rare earths while coordination numbers of 9 or greater are not uncommon for the light rare earths. We therefore undertook a three-dimensional X-ray structural study of Pr(NTA) $3H_2O$ in order to determine its coordination. In the next chapter the structure of Dy(NTA) $4H_2O$ is described.

Experimental

Well formed, rectangular prismatic crystals of the Pr·NTA·$3H_2O$ complex M.W. = 383.1 g), were kindly supplied by J. E. Powell of this Laboratory. Preliminary Weissenberg and precession photographs indicated orthorhombic symmetry. Systematic absences were observed for 0kl, $\underline{k}$ odd; $\underline{h}0\underline{l}$, $\underline{l}$ odd; $\underline{hk}0$, $\underline{h}$ odd and are consistent with space group Pbca (D_{2h}^{15}). Accurate unit cell parameters were obtained from a least-squares fit of 16 independent reflections whose 2θ values were obtained from Weissenberg photographs calibrated with Al powder using CuKα radiation (λ = 1.54051 Å). The unit cell parameters and their standard deviations calculated from the inverse matrix are $\underline{a}$ = 13.21 ± 0.01, $\underline{b}$ = 20.98 ± 0.01, $\underline{c}$ = 8.132 ± 0.006 Å and $\underline{V}$ = 2254 $Å^3$. The density determined by flotation techniques in a diiodomethane-1-bromopropane mixture is 2.24 g/cc, while the calculated density with Z = 8 is 2.26 g/cc.

A crystal having approximate dimensions 0.07 x 0.05 x

0.26 mm was mounted so that its long axis (100) was coincident with the phi axis of the diffractometer. A General Electric, XRD-6, X-ray diffractometer equipped with single crystal orienter and scintillation counter was used with Zr-filtered, MoKα radiation (λ = 0.71 7 Å) in the moving-crystal-moving-counter mode (θ.2θ coupled) to measure the intensities. A 40 sec scan covering 1.36° in 2θ was employed with a take-off angle of 2°. Since the background was seen to be a function of θ only, individual reflections were obtained from a plot of 2θ vs. background. One crystallographic independent octant of data was collected within a 2θ sphere of 45° ($\sin\theta/\lambda$ = 0.538). No appreciable decrease in the intensities of three independent reflections which were remeasured periodically throughout the data taking period was observed.

The measured intensities were also corrected for Lorentz and polarization effects and for absorption[7] with minimum and maximum transmission factors of 0.74 and 0.76 (μ = 43.2 cm^{-1}). The standard deviations were assigned to the intensities according to the formula:

$$\sigma(I) = (C_t + C_b + (0.05 \times C_t)^2 + (0.10 \times C_b)^2 + (0.05 \times C_n)^2)^{1/2} \times A$$

where C_t, C_b, C_n and A are the total count, background count, net count and absorption factor, respectively. The quadratic

terms correspond to estimated systematic errors of 5, 10, and 5% in the total count, background count, and net count, respectively. The standard deviations of the structure amplitudes ($\sigma(\underline{F})$) were obtained by the method of finite differences.[5] Of the 1494 measured reflections, 368 had a value of $\underline{F}_o < 2\,\sigma(\underline{F})$. They were considered to be unobserved and were not included in the refinement.

Solution of the Structure

The structure was solved by normal heavy atom techniques. The heavy atom was readily located in the Patterson map and the light atoms were found in a series of structure factor-electron density map calculations. Scattering factors used were those of Cromer and Waber[37] for the praseodymium(III) atom corrected for anomalous scattering[22] and those of Hanson *et al.*[8] for the light atoms. All atoms were refined[6] isotropically to a value of the discrepancy indicator ($R = \Sigma\Delta/\Sigma|\underline{F}_o|$ where $\Delta = ||F_o| - |F_c||$) of 0.13. At this point weights were introduced based on the individual statistics of the reflections ($\underline{w} = 1/\sigma^2(\underline{F})$). These weights were later adjusted slightly to remove a dependence of $\underline{w}\,\Delta^2$ on $|\underline{F}_o|$. In addition, 15 reflections with values of $\Delta > 6.0 \times \sigma(\underline{F})$ were excluded from the refinement. The large isotropic temperature factor of O_{W3} suggested occupational disorder. However, refinement of the occupational parameter yielded a value near unity. An attempt was then made to refine all

atoms anisotropically but was aborted when no physically meaningful results were obtained. With only the Pr^{3+} anisotropic final values of $\underline{R}$ and the weighted discrepancy index, $\underline{R}_w$ ($\underline{R}_w = \Sigma \underline{w} \Delta^2 / \Sigma \underline{w} F_o^2)^{1/2}$), of 0.085 and 0.080 were obtained. The final difference electron density map contained no residual density greater than 0.8 $e^-/\mathring{A}^2$ and confirmed that all nonhydrogen atoms had been located. In Table 7 are listed the final atomic positional parameters and temperature factor coefficients along with their estimated standard deviation (esd) as derived from the inverse matrix.[23] For praseodymium, the maximum, intermediate and minimum root-mean-square amplitudes of vibration are 0.145, 0.144 and 0.135. The magnitudes of the observed and calculated structure factors are shown in Figure 9.

Results and Discussion

The configuration of the NTA ligand around the Pr^{3+} is shown in Figure 10.[11] There are six carboxylic oxygens (O_c), two waters (O_w) and one nitrogen coordinated to the metal atom. Relevant distances and angles are given in Table 8. There are no discrete molecular units in the complex. One bridge is formed by O_{21} by which two different adjacent metal atoms are coordinated. In addition, O_{22} and O_{31} coordinate to metal atoms other than the one to which the remainder of the NTA ligand is coordinated. Two oxygen atoms O_{w3} and O_{12} are not coordinated to any metal atom.

Table 7. Fractional atomic coordinates and thermal parameters[a,b]

Atom	X	Y	Z	B_{iso} ($Å^2$)
N	0.330(1)	0.1444(8)	0.021(2)	2.0(3)
O_{11}	0.137(1)	0.1719(8)	0.117(2)	2.4(3)
O_{12}	0.158(1)	0.2753(8)	0.073(2)	3.3(3)
C_{11}	0.307(2)	0.211(1)	0.073(3)	2.3(4)
C_{12}	0.190(2)	0.220(1)	0.089(3)	2.5(4)
O_{21}	0.283(1)	0.0271(6)	-0.105(2)	1.8(3)
O_{22}	0.328(1)	0.0551(7)	-0.352(2)	3.1(3)
C_{21}	0.307(2)	0.137(1)	-0.154(3)	2.7(4)
C_{22}	0.307(1)	0.0691(9)	-0.204(2)	1.4(3)
O_{31}	0.541(1)	0.0544(7)	0.201(2)	2.6(3)
O_{32}	0.377(1)	0.0410(6)	0.219(2)	2.2(3)
C_{32}	0.452(2)	0.072(1)	0.171(3)	2.8(4)
C_{31}	0.441(2)	0.130(1)	0.055(3)	2.6(5)
O_{W1}	0.252(1)	0.1286(7)	0.409(2)	2.7(3)

[a]Estimated standard deviations are given in parentheses right adjusted to the least significant figure of the preceding number.

[b]Anisotropic temperature factors are given for Pr only. They are times 10^5 and have the form

$$\exp[-(\underline{\beta}_{11}\,\underline{h}^2 + \underline{\beta}_{22}\,\underline{k}^2 + \underline{\beta}_{33}\,\underline{l}^2 + \underline{\beta}_{12}\,\underline{hk} + \underline{\beta}_{13}\,\underline{hl} + \underline{\beta}_{23}\,\underline{kl})].$$

Table 7. (Continued)

Atom	X	Y	Z	B_{iso} ($Å^2$)
O_{W2}	0.076(1)	0.0576(8)	-0.075(2)	3.0(3)
O_{W3}	0.508(2)	0.299(1)	0.183(3)	7.2(5)
Pr	0.19901(8)	0.06427(5)	0.16546(13)	

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
234(7)	83(3)	619(19)	6(4)	-1(13)	-8(8)

Figure 9. Observed and calculated structure factors (in electrons times 10) for $Pr{\cdot}N(C_2H_2O_2)_3{\cdot}3H_2O$

H	K	FO	FC
*****	L=	0	*****
2	0	4360	4683
4	0	1257	1133
6	0	2179	2119
8	0	2958	3087
10	0	2185	2103
12	0	1636	1601
2	1	1015	1038
4	1	986	1031
6	1	523	551
8	1	418	255
12	1	324	300
14	1	400	450
0	2	3876	3638
2	2	2070	1971
4	2	897	841
6	2	388	230
8	2	1890	1872
10	2	1715	1568
12	2	1418	1319
14	2	553	231
2	3	676	560
4	3	1921	1711
6	3	2872	2730
8	3	1770	1744
10	3	297	78
12	3	1155	1096
14	3	1319	1295
2	4	339	248
4	4	552	355
6	4	607	422
10	4	377	249
2	5	2277	2147
4	5	2309	2296
6	5	3401	3338
8	5	1183	1069
10	5	629	682
12	5	1068	1068
0	6	3392	3354
2	6	1935	1861
6	6	860	764
8	6	2398	2268
10	6	1734	1645
12	6	1107	1015
2	7	600	508
4	7	375	144
6	7	1136	963
10	7	423	124
12	7	440	251
0	8	4900	4910
2	8	1974	1744
4	8	579	478
6	8	1452	1412
8	8	2261	2295
10	8	2236	2186
12	8	1516	1558
2	9	1980	1754
4	9	1789	1772
6	9	1332	1286
8	9	786	765
10	9	303	119
12	9	602	381
0	10	4043	3636
2	10	2022	1768
6	10	726	552
8	10	1471	1535
10	10	1059	972
12	10	859	792
2	11	2114	1989
4	11	2370	2307
6	11	2453	2316
8	11	1623	1529
10	11	234	198
12	11	923	757
4	12	498	233
6	12	345	139
8	12	281	108
12	12	422	205
2	13	960	1002
4	13	1571	1507
6	13	2223	2089
8	13	1231	1196
0	14	2751	2879
2	14	1991	1882
4	14	809	851
6	14	986	968
8	14	2117	2062
10	14	1519	1458
2	15	656	452
4	15	375	305
6	15	781	823
8	15	344	279
10	15	269	13
0	16	2746	2569
2	16	1517	1464
4	16	889	864
6	16	460	391
8	16	1732	1630
10	16	1358	1329
4	17	895	977
6	17	644	557
8	17	714	641
0	18	1656	1413
6	18	622	519
8	18	708	853
2	19	1690	1628
4	19	2027	1968
6	19	1479	1361
2	20	872	669
4	20	393	228
6	20	395	25
2	21	801	851
4	21	839	911
0	22	1501	1295
2	22	1201	1122
*****	L=	1	*****
1	1	402	360
2	1	2107	2212
3	1	1219	1318
4	1	3694	4018
5	1	1009	1018
6	1	3050	3287
8	1	974	1096
9	1	457	269
1	10	296	196
1	11	540	567
2	10	1180	1124
3	10	471	447
4	10	573	566
6	10	651	732
8	10	1222	1250
9	10	286	363
10	10	1172	1168
0	11	262	384
2	11	978	982
3	11	310	289
2	11	211	171
3	11	307	107
4	11	692	739
6	11	1086	1193
7	11	470	487
8	11	261	207
0	11	303	199
1	11	236	167
2	11	282	247
0	12	2578	2518
1	12	1380	1327
2	12	1690	1580
3	12	215	536
4	12	1200	1163
6	12	1438	1429
9	12	1261	1311
1	4	1666	1612
2	4	1003	1001
3	4	820	876
4	4	1302	1375
2	13	846	868
3	13	377	425
4	13	1102	1206
5	13	549	556
6	13	789	760
7	13	698	669
8	13	609	627
9	13	295	355
0	14	1377	1426
1	14	594	508
2	14	1037	1046
4	14	698	520
7	14	378	480
8	14	630	718
9	14	664	707
10	14	562	683
11	14	326	359
0	15	404	295
2	15	1323	1328
3	15	858	909
4	15	2021	2100
5	15	1020	1057
6	15	1651	1603
7	15	821	794
8	15	740	819
9	15	386	396
0	16	1264	1254
1	16	485	484
2	16	316	318
4	16	278	159
7	16	422	511
8	16	372	386
2	17	574	521
3	7	1516	1492
4	7	2602	2817
5	7	1603	1683
6	7	2401	2471
7	7	1267	1370
8	7	978	1019
10	7	283	231
11	7	528	594
12	7	1045	1068
13	7	536	578
14	8	301	115
1	8	532	436
2	8	795	779
3	8	387	290
4	8	545	529
5	8	409	384
8	8	582	657
9	8	322	282
10	8	376	377
1	9	1039	988
2	9	2042	1927
3	9	1819	1757
4	9	2598	2539
5	9	1061	1075
6	9	2083	2229
7	9	833	808
8	9	416	578
9	9	403	851
1	9	974	1096
2	9	457	269
1	10	1273	1209
1	11	1463	1463
2	10	1451	1463
3	10	471	447
4	10	573	566
0	10	2327	2234
1	10	1273	1209
1	11	540	567
2	10	1451	1463
3	10	471	447
4	10	573	566
6	10	651	732
8	10	1222	1250
9	10	286	363
10	10	1172	1168
0	11	262	384
2	11	978	982
3	11	310	289
2	11	211	171
3	11	307	107
4	11	692	739
6	11	1086	1193
7	11	470	487
8	11	261	207
0	11	303	199
1	11	236	167
2	11	282	247
0	12	2578	2518
1	12	1380	1327
2	12	1690	1580
3	12	215	536
4	12	1200	1163
6	12	1438	1429
9	12	1261	1311
1	4	1666	1612
2	4	1003	1001
3	4	820	876
4	4	1302	1375
2	13	846	868
3	13	377	425
4	13	1102	1206
5	13	549	556
6	13	789	760
7	13	698	669
8	13	609	627
9	13	295	355
0	14	1377	1426
1	14	594	508
2	14	1037	1046
4	14	698	520
7	14	378	480
8	14	630	718
9	14	664	707
10	14	562	683
11	14	326	359
0	15	404	295
2	15	1323	1328
3	15	858	909
4	15	2021	2100
5	15	1020	1057
6	15	1651	1603
7	15	821	794
8	15	740	819
9	15	386	396
0	16	1264	1254
1	16	485	484
2	16	316	318
4	16	278	159
7	16	422	511
8	16	372	386
2	17	574	521
2	17	1106	1161
3	17	1191	1192
4	17	1384	1492
5	17	983	979
6	17	1202	1243
7	17	624	709
8	17	430	429
0	18	1415	1383
1	18	765	685
3	18	398	248
4	18	587	590
6	18	370	321
7	18	425	481
8	18	891	888
2	19	232	181
6	19	344	269
7	19	477	285
0	20	1479	1508
1	20	753	899
2	20	1186	1214
3	20	520	517
4	20	482	545
5	20	249	39
6	20	405	511
1	21	321	170
2	21	564	612
3	21	580	470
4	21	887	961
5	21	425	412
0	22	543	526
2	22	547	319
3	22	427	249
*****	L=	2	*****
0	0	2010	1906
1	0	3388	3753
3	0	541	534
4	0	954	967
5	0	570	716
6	0	1728	1838
0	1	679	735
7	0	2074	2211
8	0	800	756
9	0	1856	1893
0	10	1217	1251
1	10	1507	1475
4	10	196	128
5	10	464	508
6	10	334	307
7	10	853	794
8	10	607	554
9	10	895	875
10	10	642	611
11	10	852	791
12	10	946	665
0	2	2774	2682
1	2	994	1022
2	2	1510	1524
3	2	1140	1107
4	2	341	218
5	11	1943	2076
7	2	902	795
8	2	899	930
9	2	1186	1204
10	2	601	613
11	11	617	612
12	11	932	450
0	12	280	248
1	12	366	484
2	12	411	438
3	12	1314	1240
4	12	388	263
5	12	345	375
8	12	382	423
1	13	247	79
2	13	627	602
3	13	1452	1494
7	5	968	1006
2	20	249	207
3	20	955	929
4	13	808	811
5	13	1677	1792
6	13	930	985
7	13	1074	1179
8	13	322	250
11	13	559	634
0	14	676	687
1	14	1772	1782
2	14	592	675
3	14	1443	1338
4	14	613	573
7	14	1155	1146
8	14	487	677
9	14	1297	1338
10	14	695	715
6	15	310	401
0	16	1358	1315
1	16	1550	1586
13	5	1087	991
2	16	1111	1032
3	16	1032	1073
4	16	375	366
6	16	589	662
7	16	968	970
8	16	907	920
9	16	1302	1312
2	17	500	522
3	17	932	907
4	17	576	510
5	17	1003	1030
7	17	739	780
8	17	268	210
0	18	618	608
1	18	1542	1445
2	18	323	426
3	18	905	886
5	18	363	334
7	18	524	595
8	18	428	388
1	19	490	615
2	19	430	397
3	19	1699	1587
4	19	452	622
5	19	1625	1538
6	19	699	579
7	19	872	856
1	20	519	238
2	20	474	39
3	20	1360	1263
4	20	589	494
5	11	760	762
7	11	361	448
11	11	391	339
1	12	2271	2219
2	12	485	537
3	12	1453	1515
4	12	352	345
7	12	1133	1188
9	12	1784	1860
11	12	1507	1547
1	13	402	347
2	13	407	306
3	13	1192	1231
5	13	937	1011
7	13	573	693
0	14	290	69
1	14	1035	1096
2	14	633	529
3	14	918	867
4	14	418	336
7	14	541	556
9	14	929	1031
1	15	644	656
2	15	349	413
3	15	1701	1700
5	15	1708	1944
6	15	231	129
7	15	1323	1309
9	15	544	476
0	16	491	425
1	16	545	350
2	16	300	392
3	16	519	449
3	17	1510	1554
5	17	1327	1474
7	17	1013	1055
0	18	419	248
1	18	1644	1661
3	18	866	933
7	18	947	1016
2	19	2270	106
4	12	388	263
2	5	357	315
5	19	1270	1301
0	20	343	122
1	20	1556	1534
2	20	249	207
3	20	955	929
6	13	1678	1792
6	19	1519	1368
7	19	1074	1179
6	20	1078	1108
6	6	502	547
7	6	735	802
9	6	1313	1251
6	15	315	509
6	16	1166	1104
7	6	667	646
2	7	327	385
3	7	2477	2525
4	7	243	39
7	7	2691	2807
7	7	1582	1686
9	7	747	760
7	7	837	820
12	7	369	37
0	8	457	581
1	8	243	254
2	8	468	262
3	8	352	69
4	8	379	328
5	8	239	99
7	8	415	511
2	2	952	1069
3	2	954	859
4	2	550	662
5	2	401	422
7	2	981	1016
8	2	884	893
0	2	1294	1335
2	2	582	721
4	2	876	902
5	2	455	325
7	2	1539	1553
9	2	1359	1398
11	2	1191	1114
2	11	242	306
3	11	716	729
4	11	1337	1264
5	11	760	762
7	11	361	448
11	11	391	339
1	12	2271	2219
2	12	485	537
3	12	1453	1515
4	12	352	345
7	12	1133	1188
9	12	1784	1860
11	12	1507	1547
1	13	402	347
2	13	407	306
3	13	1192	1231
5	13	937	1011
7	13	573	693
0	14	290	69
1	14	1035	1096
2	14	633	529
3	14	918	867
4	14	418	336
7	14	541	556
9	14	929	1031
1	15	644	656
2	15	349	413
3	15	1701	1700
5	15	1708	1944
6	15	231	129
7	15	1323	1309
9	15	544	476
0	16	491	425
1	16	545	350
2	16	300	392
3	16	519	449
3	17	1510	1554
5	17	1327	1474
7	17	1013	1055
0	18	419	248
1	18	1644	1661
3	18	866	933
7	18	947	1016
2	19	2270	106
4	12	388	263
2	5	357	315
5	19	1270	1301
0	20	343	122
1	20	1556	1534
2	20	249	207
3	20	955	929
6	13	1678	1792
6	19	1519	1368
7	19	1074	1179
6	20	1078	1108
6	6	502	547
7	6	735	802
9	6	1313	1251
6	15	315	509
6	16	1166	1104
7	6	667	646
2	7	327	385
3	7	2477	2525
4	7	243	39
7	7	2691	2807
7	7	1582	1686
9	7	747	760
7	7	837	820
2	1	823	874
3	1	929	931
4	1	709	734
5	1	699	817
7	1	1021	1089
8	11	894	879
9	11	923	958
0	2	1028	999
1	2	2839	2778
2	2	952	1069
3	2	954	859
4	2	550	662
5	2	401	422
7	2	981	1016
8	2	884	893
0	2	1294	1335
2	2	582	721
4	2	876	902
5	2	455	325
7	2	1539	1553
9	2	1359	1398
11	2	1191	1114
2	11	242	306
3	11	716	729
4	11	1337	1264
5	11	760	762
7	11	361	448
11	11	391	339
1	12	2271	2219
2	12	485	537
3	12	1453	1515
4	12	352	345
7	12	1133	1188
9	12	1784	1860
11	12	1507	1547
1	13	402	347
2	13	407	306
3	13	1192	1231
5	13	937	1011
7	13	573	693
0	14	290	69
1	14	1035	1096
2	14	633	529
3	14	918	867
4	14	418	336
7	14	541	556
9	14	929	1031
1	15	644	656
2	15	349	413
3	15	1701	1700
5	15	1708	1944
6	15	231	129
7	15	1323	1309
9	15	544	476
0	16	491	425
1	16	545	350
2	16	300	392
3	16	519	449
3	17	1510	1554
5	17	1327	1474
7	17	1013	1055
0	18	419	248
1	18	1644	1661
3	18	866	933
7	18	947	1016
2	19	2270	106
4	12	388	263
2	5	357	315
5	19	1270	1301
0	20	343	122
1	20	1556	1534
2	20	249	207
3	20	955	929
6	13	1678	1792
6	19	1519	1368
7	19	1074	1179
6	20	1078	1108
6	6	502	547
7	6	735	802
9	6	1313	1251
6	15	315	509
6	16	1166	1104
7	6	667	646
2	7	327	385
3	7	2477	2525
4	7	243	39
7	7	2691	2807
7	7	1582	1686
9	7	747	760
7	7	837	820
3	11	1791	1785
4	11	1331	1353
5	11	1869	1905
6	11	968	1067
7	11	1231	1320
8	11	894	879
9	11	923	958
0	2	1028	999
1	2	2839	2778
2	2	952	1069
3	2	954	859
4	2	550	662
5	2	401	422
7	2	981	1016
8	2	884	893
0	2	1294	1335
2	2	582	721
4	2	876	902
5	2	455	325
7	2	1539	1553
9	2	1359	1398
11	2	1191	1114
2	11	242	306
3	11	716	729
4	11	1337	1264
5	11	760	762
7	11	361	448
11	11	391	339
1	12	2271	2219
2	12	485	537
3	12	1453	1515
4	12	352	345
7	12	1133	1188
9	12	1784	1860
11	12	1507	1547
1	13	402	347
2	13	407	306
3	13	1192	1231
5	13	937	1011
7	13	573	693
0	14	290	69
1	14	1035	1096
2	14	633	529
3	14	918	867
4	14	418	336
7	14	541	556
9	14	929	1031
1	15	644	656
2	15	349	413
3	15	1701	1700
5	15	1708	1944
6	15	231	129
7	15	1323	1309
9	15	544	476
0	16	491	425
1	16	545	350
2	16	300	392
3	16	519	449
3	17	1510	1554
5	17	1327	1474
7	17	1013	1055
0	18	419	248
1	18	1644	1661
3	18	866	933
7	18	947	1016
2	19	2270	106
4	12	388	263
2	5	357	315
5	19	1270	1301
0	20	343	122
1	20	1556	1534
2	20	249	207
3	20	955	929
6	13	1678	1792
6	19	1519	1368
7	19	1074	1179
6	20	1078	1108
6	6	502	547
7	6	735	802
9	6	1313	1251
6	15	315	509
6	16	1166	1104
7	6	667	646
2	7	327	385
3	7	2477	2525
4	7	243	39
7	7	2691	2807
7	7	1582	1686
9	7	747	760
7	7	837	820
5	5	528	427
6	5	858	768
6	5	870	901
6	5	466	484
8	2	1224	1248
2	6	1694	1675
4	6	1015	1073
1	6	352	419
2	5	1186	1210
3	5	318	60
4	3	1922	2084
3	3	1559	1618
8	3	834	906
4	3	1120	1061
2	5	581	591
5	5	780	850
2	4	308	314
4	4	269	347
8	5	340	388
6	7	1448	1473
3	5	410	300
2	6	968	964
4	5	2034	2067
6	5	1528	1608
2	6	885	920
5	8	350	198
6	8	295	184
2	7	1190	1179
4	7	1334	1428
5	7	1212	1219
6	7	1136	1226
7	6	316	553
0	6	1096	1003
6	8	282	9
2	9	672	784
3	9	728	781
4	9	1225	1183
0	12	1456	1379
1	12	829	803
2	12	917	828
3	12	482	490
2	13	324	331
*****	L=	9	*****
0	0	1224	1062
1	0	1786	1634
2	0	470	405
3	0	970	953
6	10	540	663
8	10	1049	1026
1	4	450	203
5	1	550	448
0	2	582	518
1	2	1357	1321
2	2	311	229
3	2	721	693
2	2	262	102
5	2	307	42
1	3	303	507
2	3	551	445
3	3	1097	1083
4	3	648	611
5	3	1115	1129
1	4	322	220
3	4	250	23
4	4	286	124
5	4	328	39
1	5	501	524
2	5	574	595
3	5	985	932
4	5	403	487
0	6	897	886
1	6	1222	1067
2	6	599	478
3	6	473	499
1	7	380	227
0	8	851	827
1	A	1513	1342
2	8	561	498
3	8	790	696

Figure 10. The perspective drawing of nitrilotriacetate-triaquopraseodymium III-monohydrate. (The numbering in the NTA ligand is such that the left number indicates the acetate group to which the atom belongs. In the case of the carbon atoms the right number indicates its position relative to the nitrogen and in the case of the oxygen atoms, is solely for uniqueness. The primes indicate atoms related to those of the coordinate list by symmetry operations which are described elsewhere)

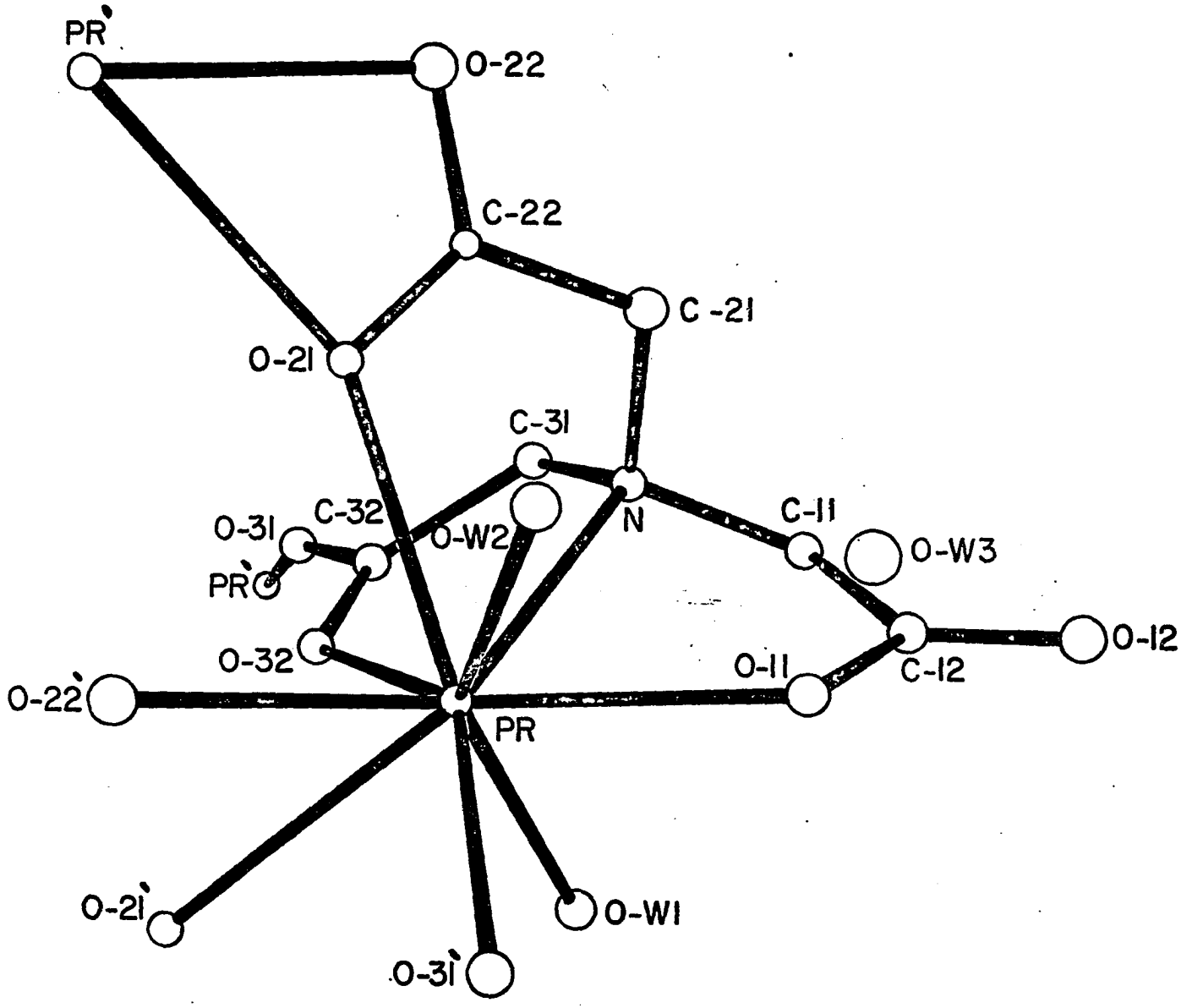

PR'
O-22
C-22
C-21
O-21
C-31
O-31
C-32
O-W2
N
C-11
O-W3
PR'
O-32
O-12
O-11
C-12
O-22'
PR
O-21'
O-W1
O-31'

Table 8. Selected distances (Å) and angles (deg) with associated standard errors as calculated from the parameters in Table 7[a]

Distances

$Pr-O_{11}$	2·43(1)	$N-C_{11}$	1·48(2)	$C_{22}-O_{22}$	1·27(2)
$Pr-O_{21}$	2·59(1)	$N-C_{21}$	1·49(3)	$C_{32}-O_{31}$	1·25(2)
$Pr-O^{1}_{21}$	2·69(1)	$N-C_{31}$	1·53(3)	$C_{32}-O_{32}$	1·25(2)
$Pr-O^{1}_{22}$	2·53(1)	$C_{11}-C_{22}$	1·57(3)	$O_{12}-O^{2}_{w3}$	2·85(3)
$Pr-O^{2}_{31}$	2·37(1)	$C_{21}-C_{22}$	1·47(3)	$O^{3}_{12}-O^{2}_{w3}$	2·72(2)
$Pr-O_{32}$	2·44(1)	$C_{31}-C_{32}$	1·55(3)	$O_{21}-O_{w2}$	2·82(2)
$Pr-O_{w1}$	2·50(1)	$C_{12}-O_{11}$	1·25(2)	$O_{32}-O^{1}_{w2}$	2·73(2)
$Pr-O_{w2}$	2·54(1)	$C_{12}-O_{22}$	1·24(2)	$O_{21}-O_{22}$	2·18(2)
Pr-N	2·68(2)	$C_{22}-O_{21}$	1·24(2)	$O_{11}-O_{12}$	2·21(2)
				$O_{31}-O_{32}$	2·19(2)

[a]Superscripts indicate symmetry operations which relate the atom to the original coordinates: 1) 1/2 − x, $\bar{y}$, 1/2 + z; 2) -1/2 + x, y, 1/2 - z; 3) x, 1/2 - y, 1/2 + z; 4) 1/2 - x, $\bar{y}$, -1/2 + z; 5) 1/2 + x, y, 1/2 - z.

Table 8. (Continued)

Angles around Pr

O_{11}-Pr-O^2_{31}	82·0(5)	O^2_{31}-Pr-O_{21}	138·1(4)	O_{w2}-Pr-O^1_{22}	79·1(5)
O_{11}-Pr-O_{w1}	73·9(4)	O^2_{31}-Pr-O^1_{22}	79·3(5)	O_{w2}-Pr-O^1_{21}	123·4(4)
O_{11}-Pr-O_{w2}	73·3(5)	O^2_{31}-Pr-O^1_{21}	72·3(4)	N-Pr-O_{32}	65·3(5)
O_{11}-Pr-N	64·1(5)	O_{w1}-Pr-O_{w2}	145·0(5)	N-Pr-O_{21}	62.6(5)
O_{11}-Pr-O_{32}	122·5(5)	O_{w1}-Pr-N	80·0(5)	N-Pr-O^1_{22}	133·3(5)
O_{11}-Pr-O_{21}	106·6(4)	O_{w1}-Pr-O_{32}	72·2(4)	N-Pr-O^1_{21}	134·0(4)
O_{11}-Pr-O^1_{22}	149·4(5)	O_{w1}-Pr-O_{21}	135·8(4)	O_{32}-Pr-O_{21}	71·3(4)
O_{11}-Pr-O^1_{21}	143·6(4)	O_{w1}-Pr-O^1_{22}	128·2(5)	O_{32}-Pr-O^1_{22}	87·1(4)
O^2_{31}-Pr-O_{w1}	86·1(5)	O_{w1}-Pr-O^1_{21}	79·0(4)	O_{32}-Pr-O^1_{21}	69.4(4)
O^2_{31}-Pr-O_{w2}	77·6(5)	O_{w2}-Pr-N	96·3(5)	O_{21}-Pr-O^1_{21}	109·8(1)
O^2_{31}-Pr-N	145·7(5)	O_{w2}-Pr-N	137·8(5)	O_{21}-Pr-O^1_{22}	73·4(4)
O^2_{31}-Pr-O_{32}	138·7(4)	O_{w2}-Pr-O_{21}	66·7(4)	O_{21}-Pr-O_{22}	49·2(4)

Table 8. (Continued)

		Angles in NTA ligand			
C_{11}-N-C_{21}	110(2)	N-C_{31}-C_{32}	111(2)	C_{21}-C_{22}-O_{22}	119(2)
C_{11}-N-C_{31}	109(2)	C_{11}-C_{12}-O_{11}	118(2)	O_{21}-C_{22}-O_{22}	120(2)
C_{21}-N-C_{31}	110(2)	C_{11}-C_{12}-O_{22}	117(2)	C_{31}-C_{32}-O_{31}	116(2)
N-C_{11}-C_{12}	110(2)	O_{11}-C_{12}-O_{22}	126(2)	C_{31}-C_{32}-O_{32}	122(2)
N-C_{21}-C_{22}	112(2)	O_{21}-C_{22}-O_{21}	120(2)	O_{31}-C_{32}-O_{32}	122(2)
		Angles involving NTA and Pr			
C_{12}-O_{11}-Pr	126(1)	C_{22}-O_{22}-Pr^4	98(1)	C_4-N-Pr	110(1)
C_{22}-O_{21}-Pr	117(1)	C_{31}-O_{31}-Pr^2	153(1)	C_{21}-N-Pr	103(1)
C_{22}-O_{21}-Pr^4	92(1)	C_{31}-O_{32}-Pr	128(1)	C_{31}-N-Pr	115(1)

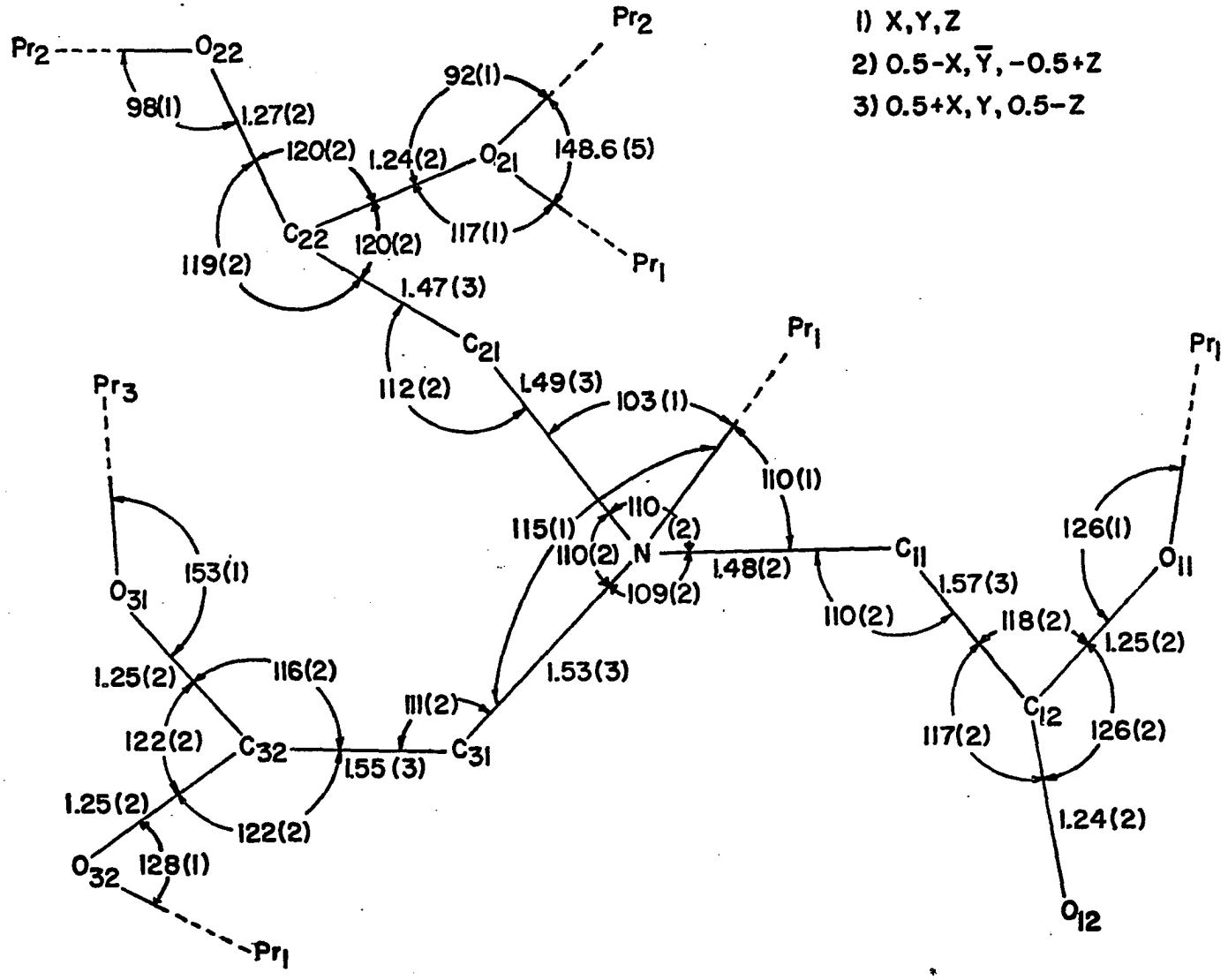
Thus two of the six O_c's in each NTA molecule are coordinated to the same metal atom as the nitrogen, two are coordinated to adjacent metal atoms, one is simultaneously coordinated to two adjacent metal atoms and the last is uncoordinated.

The average for the six independent terminal carbon to carboxylic oxygen bond distances is 1.25 ± 0.02 Å. This is in excellent agreement with the expected value for the C-O distance in a carboxylate ion.[38,39] Moreover, none of the C-O distances vary from this value by more than one esd which indicates the acid is completely deprotonated and that the O_{12}-C_{12} bond (1.24 ± 0.02 Å) has no significantly greater double bond character than the rest. The three acetate groups are planar to within 0.1 Å, while the angles around the carboxylate carbons are 120° ± 3° with the exception of the O_{11}-C_{12}-O_{12} angle which is slightly larger (126 ± 2°). This increase in angle can be attributed to steric strain in the unsymmetric environment caused by single coordination of this carboxylate group. The angles around the nitrogen are essentially tetrahedral with the "lone pair" directed approximately towards the metal atom (see Figure 11).

There are four short O_w-O_c distances ranging from 2.72 to 2.85 Å which are suggestive of possible hydrogen bond formation. The large thermal parameters of O_{w3} suggests that it is involved in only a weak hydrogen bond.

The arrangement of the atoms in the coordination sphere

Figure 11. The conformation of the NTA ligand (bond distances (Å) and angles (deg) are shown along with their estimated errors right adjusted to the least significant figure of the preceding number. The subscripts of the Pr atoms indicate their relation to the Pr in the coordinate list)

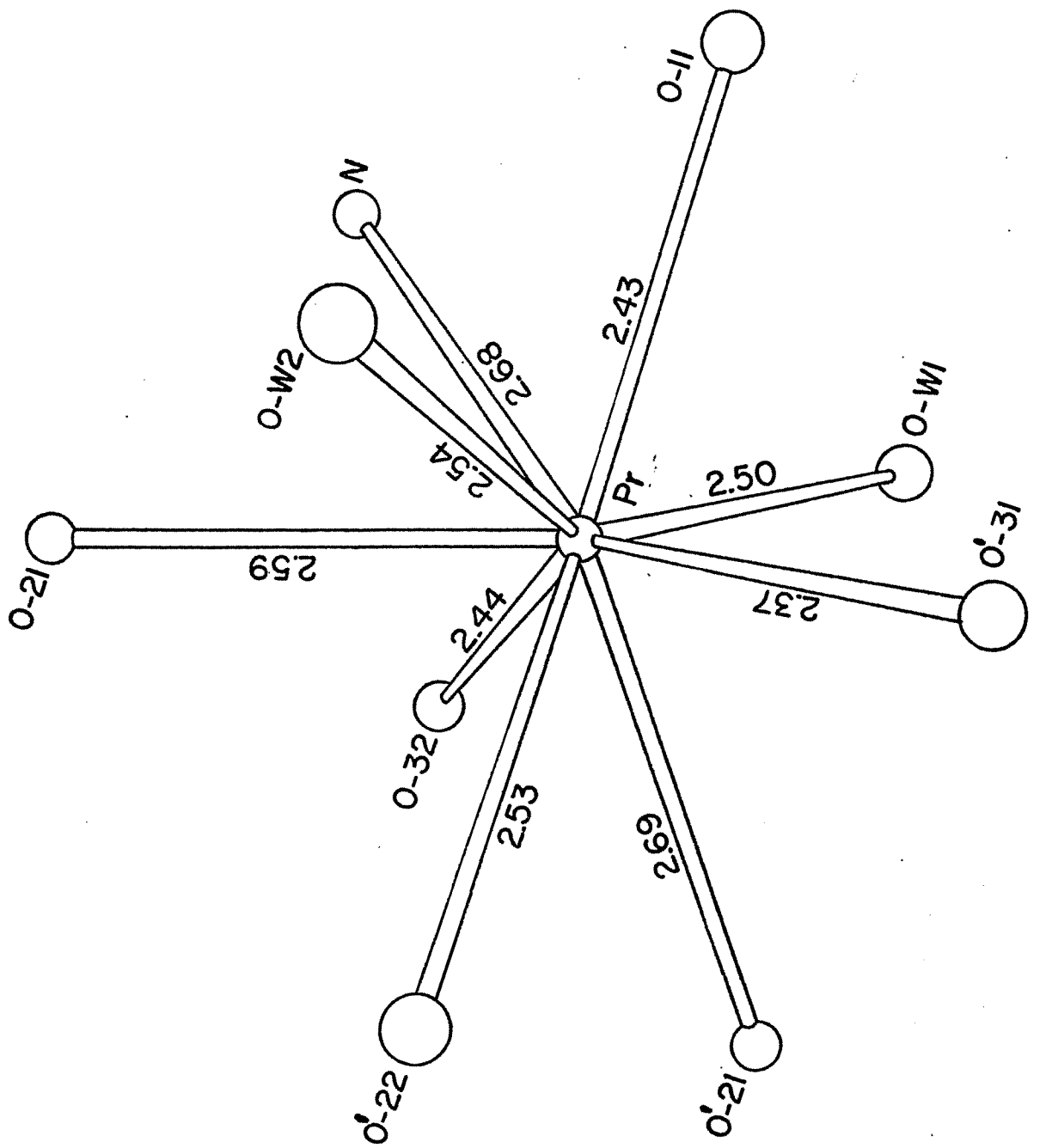

1) X,Y,Z
2) 0.5-X, $\bar{Y}$, -0.5+Z
3) 0.5+X, Y, 0.5-Z
Pr2
O22
98(1)
1.27(2)
120(2)
1.24(2)
O21
92(1)
148.6(5)
117(1)
C22
120(2)
119(2)
1.47(3)
C21
112(2)
1.49(3)
103(1)
Pr3
O31
153(1)
1.25(2)
116(2)
122(2)
C32
1.55(3)
C31
111(2)
1.53(3)
1.25(2)
122(2)
O32
128(1)
Pr1
110(1)
115(1)
110(2)
N
109(2)
1.48(2)
C11
110(2)
1.57(3)
118(2)
126(1)
O11
1.25(2)
C12
117(2)
126(2)
1.24(2)
O12

is shown in Figure 12. The average Pr-O_c distance is 2.47 ± 0.02 Å while the average Pr-O_w distance is 2.52 ± 0.02 Å.

The Pr-O_{21} distances have been excluded from this calculation since they are significantly longer than the other Pr-O_c distances due to the different coordination mode exhibited by O_{21}. The Pr-N distance is 2.68 ± 0.02 Å. The average metal-oxygen distance is in reasonable agreement with the value predicted either from the sum of the covalent radii[24] or from the sum of the crystal radii.[40] The Pr-N distance is ~0.1 Å longer than would be expected, indicating weaker coordination. These values are 0.04 to 0.08 Å shorter than those observed by Hoard et al.[41] in the nine coordinate La.EDTA complex (2.51 Å, 2.58 Å, 2.76 Å for the average La-O_c, La-O_w and La-N distances). This general shortening is consistent with a decrease in the rare earth ionic radius from 1.15 Å to 1.09 Å. In fact, assuming the average oxygen-metal-oxygen angle remains constant (72 to 74°), a continued decrease in the metal-oxygen bond distance of 0.10 Å to 0.14 Å would cause significant oxygen-oxygen steric interactions. This would occur at Dy^{3+} (0.99 Å) or Ho^{3+} (0.97 Å) and a change in coordination number from 9 to 8 would be expected.

The arrangement of atoms around the Pr^{3+} can be described equally well in any of three ways: (1) as a distorted, tri-capped trigonal prism, (2) as a capped square anti-prism or (3) as in the description by Hoard et al. of

Figure 12. A perspective drawing of the Pr coordination. (The orientation is the same as in Figure 11. The primes indicate atoms related to those in the coordinates list: (1) O'_{21}:1/2 - x, $\bar{y}$, 1/2 + z, (2) O'_{22}:1/2 - x, $\bar{y}$, 1/2 + z and (3) O'_{31}:-1/2 + x, y, 1/2 - z)


O-11
2.43
N
2.68
O-W2
2.54
Pr
2.50
O-W1
O'-31
2.37
O-21
2.59
2.44
O-32
2.53
2.69
O'-22
O'-21

the La·EDTA complex.

The tri-capped, trigonal prism arrangement has been observed for many nona-coordinate structures and have been described in some detail in a review by Muetterties and Wright.[42] Typical of these are the anhydrous, rare earth tri-chlorides.[43] Referring to Figure 12, the three rectangular faces of the trigonal prism are as follows: O'_{22}-O_{32}-N-O_{w2}-O'_{22}, O_{w2}-N-O_{w1}-O'_{31}-O_{w2}, and O'_{31}-O_{w1}-O'_{32}-O'_{22}-O'_{31}. The two triangular faces of the prism are described by O'_{22}-O_{w2}-O'_{31}-O'_{22} and O_{32}-N-O_{w1}-O_{32}. The atoms O_{21}, O'_{21} and O_{11} occupy the capping positions.

The capped square anti-prism is observed somewhat less frequently than is the tri-capped trigonal prism;[42] however, the square anti-prism is a very common arrangement for octa-coordination. In Figure 12, the rectangular faces of the square anti-prism are defined by O'_{22}, O_{32}, O_{w1}, O'_{31}, O'_{22} and O_{21}, N, O_{11}, O_{w2}, O_{21}. The atom in the capping position (O'_{21}) shows a significant distortion towards O'_{22}.

The description favored by Hoard *et al.*[41] for the nona-coordinate La·EDTA complex, due to the large distortions from any regular geometric figure, is a one, five, three arrangement where one atom (O'_{31}) is located 1.9 ± 0.2 Å below a plane of five atoms, O'_{21}, O'_{22}, O_{w2}, O_{11}, O_{w1}. The equation of this plane along with selected distances from the plane are given in Table 9. The average O-Pr-O angle in

Table 9. Selected distances to and equations of the planes

Atom	Distance from plane (Å)	Atom	Distance from plane (Å)
		Plane 1	
O_{22}	0.22	O_{31}	1.90
O_{21}	0.23	Pr	0.46
O_{w1}	0.14	N	2.54
O_{11}	0.06	O_{21}	2.47
O_{w2}	0.05	O_{32}	2.31
Equation:			
$(0.881)x + (0.005)y - (0.474)z - 1.229 = 0$			
		Plane 2	
O_{21}	0.0	O_{22}	2.10
O_{32}	0.0	O_{21}	2.44
N	0.0	O_{w1}	2.23
O_{31}	4.31	O_{11}	2.66
Pr	1.97	O_{w2}	2.61
Equation:			
$(0.907)x - (0.052)y - (0.418)z - 3.720 = 0$			

the plane is 71° while the average O-O distance is 2.97 Å. The most significant distortions from these averages occur in the O'_{22}-Pr-O'_{21} angle of 49.2° and O'_{21}-O'_{22} distance of 2.18 ± 0.02 Å. This appears to be a result of both carboxylate oxygens being in the same acid moiety. The Pr^{3+} is located 0.5 Å above the approximate center of this plane away from the O'_{31}. In the La·EDTA complex, the distance from the similar plane to La^{3+} is 0.6 Å; some increase being expected due to the longer oxygen-La^{3+} distances.

At a distance of 2.0 Å from the Pr^{3+} and opposite the first plane is a second plane of three atoms: O_{21}, N, O_{32}. The equation of this plane and some selected distances from the plane are given in Table 9. The two planes are within 9° of being parallel.

In complexes such as ceric ammonium nitrate[44] considerable distortion of the N-O bonds and O-N-O angles have been observed and have been attributed to the presence of metal-oxygen covalent bonding. However, in the $La{\cdot}EDTA^-$ complex the bonding has been described as primarily electrostatic in nature. In the title compound no systematic distortions in C-O distances or O-C-O angles are observed. This, coupled with the wide range in Pr-O-C angles (92° to 153°), would imply primarily electrostatic bonding effects.

STRUCTURE OF NITRILOTRIACETODIAQUODYSPROSIUM(III)-DIHYDRATE

Introduction

The diversity in types of coordination found in the rare-earth complexes is large (45-49). In an endeavor to determine the effect of changing metal-ion size on coordination, we have investigated the structures of the lanthanon (III)-nitrilotriacetate (NTA) complexes from Pr-Lu. The series is broken into two groups--the Pr group and the Dy group. In the previous chapter the structure of the Pr group has been discussed. In this chapter the structure of the Dy NTA complex will be discussed and comparisons made to the Pr structure.

Experimental

Well formed rectangular-prismatic crystals of Dy·NTA·$4H_2O$ (M.W. = 422.7 g) were supplied by J. E. Powell and were used without additional purification. Weissenberg and precession photographs indicated an orthorombic space group with systematic extinctions of the type 0$k$$l$, l odd and h0l, h odd. These conditions indicate the space group to be either $Pca2_1$ or Pcam (No. 57-Pbcm). In addition the 0k0, k odd reflections were unobserved. However, there are no special positions in $Pca2_1$ or Pcam which can account for this type of extinction. The light lanthanon(III) NTA com-

plexes crystallize in space Pbca, and $Pca2_1$ can be obtained from Pbca by removal of the center of symmetry, interchanging the a and b axes, and translation of the origin to the 2_1. In addition, the 0k0 extinction condition suggests that the y, 1/2 + y relationship has been retained from Pbca. Therefore, it was decided to initially assume $Pca2_1$ as the space group, which was later justified by successful refinement in this space group.

The unit cell dimensions were determined by least-squares fit of 29 independent reflections whose 2θ values were obtained from Weissenberg photographs calibrated with Al powder lines at 25° C using Cu-Kα radiation (λ = 1.5405 Å). The values obtained along with the estimated errors are: a = 21.535 ± 0.013 Å, b = 9.028 ± 0.004 Å, c = 12.186 ± 0.007 Å and V_c = 2369 A^3. The measured density was 2.3 g/cc while the calculated density with eight molecules per unit cell is 2.4 g/cc.

A crystal with approximate dimensions 0.12 x 0.12 x 0.26 mm was selected for use in data collection. The crystal was mounted along its long axis with the (001) axis coincident with the phi axis of the diffractometer. Data were collected at room temperature using a Hilger-Watts, four circle diffractometer equipped with a scintillation counter employing Zr-filtered Mo-Kα (λ = 0.7107 A) radiation. All data in one octant within a 2θ sphere of 60° ($\sin\theta/\lambda$ =

0.70) were measured using a θ-2θ coupled scan with a 5° take-off angle. Stationary counter measurements of the background were made at the beginning and the end of each scan. The scan range was over 50 steps of 0.01°, one step per 0.4096 sec., increased by 1 step per deg in 2θ to insure complete integration over the entire peak. The length of the background measurements were adjusted accordingly. No appreciable decrease in the intensities of three standard reflections which were remeasured periodically throughout the data taking period was observed.

The measured intensities were corrected for Lorentz and polarization effects and for absorption[8] with minimum and maximum transmission factors of 0.43 and 0.47 (μ = 65.5 cm^{-1}). The standard deviations were assigned to the intensities according to the following formula:

$$\sigma(I) = (C_t + C_b + (0.03 \times C_t)^2 + (0.06 \times C_b)^2 + (0.06 \times C_n)^2)^{1/2} \times A$$

where C_t, C_b, C_n and A represent the total count, background count, net count and the absorption factor, respectively. The quadratic terms correspond to the estimated systematic errors in the intensity, background, and absorption correction of 3, 6, and 6% respectively. The standard deviations in the structural amplitudes were obtained by the method of finite differences,[5] $\sigma(\underline{F}) = ((I + (\underline{I}))^{1/2} - \underline{I}^{1/2})/(\underline{L_p})^{1/2}$, where

L_p is the Lorentz-polarization factor. Of the 3407 measured reflections, 375 had values of $\underline{F}$ less than $\sigma(F)$ and were considered to be unobserved. They were not used in the refinement.

Solution of the Structure

The structure was determined using a combination of heavy atom and superposition[50] techniques. Since the space group $Pca2_1$ has only four general positions, two independent molecules must be present in the unit cell. From the Patterson map the two heavy atom positions were readily located. However, due to the placement of the heavy atoms at almost exactly 0 and 1/2 in y, the phasing was such that two sets of light atoms appeared in the electron density maps which were related by mirroring at 0 and 1/2 in the y direction. Because of the large number of light atoms and their small individual contributions to the scattering, it was very difficult to consistently select atoms in the same image. Therefore, a superposition procedure was used starting with a known heavy atom vector. This superposition enabled us to locate single heavy atom-light atom vectors around the heavy atoms. A second superposition eliminated a number of the pseudo peaks. Using vectors from this second superposition, two more superpositions were carried out. The resultant map had, in addition to the peaks corresponding to the heavy atoms, seven peaks which appeared at chemically reasonable

positions for oxygen atoms. By successive electron density map-structure factor calculations, the remaining light atoms positions were determined. In the process, it was found that all but one of the original seven light atoms were correct. Scattering factors used were those of Cromer and Waber[37] for dysprosium^{3+} corrected for anomalous scattering[22] and those of Hanson et al.[8] for the light atoms.

All atoms were refined[6] isotropically with unit weights resulting in a value for the discrepancy factor, $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ of 0.089. Weights were then introduced based on the individual statistics of the reflections ($w = 1/\sigma^2(F)$). In addition, 65 reflections were removed from the refinement since they did not fulfill the requirement $||F_o| - |F_c|| < 9 \times \sigma(F)$. The refinement was continued with anisotropic temperature factors for the dysprosium atoms to an R of 0.057 and of the weighted discrepancy factor $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ of 0.082. In order to further refine the structure, it was necessary to use a variation of a block diagonal procedure. In successive cycles, the parameters of one and then the other of the independent molecules were allowed to vary with all temperature factors anisotropic. This procedure seemed appropriate since the correlation matrix in the isotropic refinement had indicated that the interaction between atoms in nonequivalent molecules were small. In addition, in two final cycles of refinement,

first all positional parameters, and then all temperature factors were allowed to vary to minimize as much as possible any dependence of the parameters on intermolecular correlations. In these two final cycles no parameter shift was greater than 0.5 of the associated estimated standard deviation (esd). Final values of $\underline{R}$ and $\underline{R}_w$ were 0.050 and 0.070. A final difference electron density map showed no residual electron density greater than 0.5 $e^-/\text{Å}^3$.

An attempt was made to determine the absolute configuration of the molecules. One image, the positional parameters of which are listed in Table 10, gave a value of $\underline{R}$ 0.1 lower than the other image, which suggests the former to be the correct configuration. A larger difference was not observed due to the approximate centrosymmetric relationship between the two independent molecules. The independence of the two molecules is indicated by the fact that only 8 out of a possible 108 correlations between terms related by the approximate centering had values greater than 0.1 and no term exceeded 0.36.

Previous experience on the trisilane structure using a 9 x 9 block diagonal procedure indicated that the method may lead to an underestimate of the esd's by 0.20. This is probably a maximum value for the esd's in Table 10 since much larger blocks were used. In Table 11 are listed the root-mean-square amplitudes of vibration while in Figure 13

Table 10. Atom positions and anisotropic temperature factors[a]

Atom	x	y	z	β_{11}
Dy1	61202(2)	-130(5)	0	60(1)
Dy2	19555(2)	49940(5)	18663(5)	60(1)
O1E1	415(5)	3745(11)	-1868(9)	20(3)
O1E2	166(7)	52(11)	-3300(8)	26(3)
O1D1	889(4)	-2259(9)	748(8)	17(2)
O1D2	1080(4)	-4690(8)	625(8)	14(2)
O1U1	470(4)	456(11)	-203(10)	11(2)
O1U2	-1416(5)	-545(14)	-88(13)	9(2)
C1E1	-43(6)	-205(14)	-2033(11)	17(3)
C1E2	68(6)	-440(15)	-2454(12)	10(3)
C1D1	363(7)	-3673(14)	-628(15)	18(3)
C1D2	810(5)	-3540(12)	363(9)	6(2)
C1U1	-574(6)	-2241(14)	-325(15)	16(3)
C1U2	-847(6)	-636(14)	-181(12)	12(3)
O2E1	2269(5)	5158(8)	3748(8)	15(2)
O2E2	2702(4)	4106(10)	5198(7)	17(2)
O2D1	1450(3)	2723(7)	1796(8)	7(2)
O2D2	1491(5)	496(11)	1067(9)	15(2)
O2U1	3019(3)	5570(10)	1850(10)	7(2)

[a]Heavy atom parameters are times 10^5 while light atom parameters are times 10^4.

β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
380(7)	242(4)	17(2)	-17(2)	-37(4)
421(8)	229(4)	16(2)	-13(2)	-52(4)
85(11)	36(7)	-5(5)	-5(4)	20(8)
169(19)	13(6)	-15(5)	-12(3)	26(8)
68(11)	45(7)	6(4)	-14(33)	-12(7)
28(8)	41(6)	7(3)	-9(3)	-5(6)
79(11)	69(8)	-3(4)	-3(3)	-32(9)
127(15)	135(15)	-1(5)	7(5)	-10(14)
64(15)	50(10)	4(6)	-10(5)	-8(10)
86(15)	39(9)	9(5)	2(4)	-1(11)
74(16)	82(15)	22(6)	-17(6)	-7(13)
55(12)	29(7)	3(4)	-3(4)	-9(8)
52(16)	74(13)	-8(5)	3(5)	-14(12)
59(14)	66(10)	49(5)	6(4)	22(11)
73(11)	26(6)	8(3)	-1(3)	-3(6)
101(13)	29(6)	-1(4)	-4(3)	-23(8)
30(8)	61(7)	1(3)	-1(3)	3(6)
78(10)	57(8)	-10(4)	-17(4)	-10(8)
54(10)	72(8)	12(3)	-9(3)	-5(9)

Table 10. (Continued)

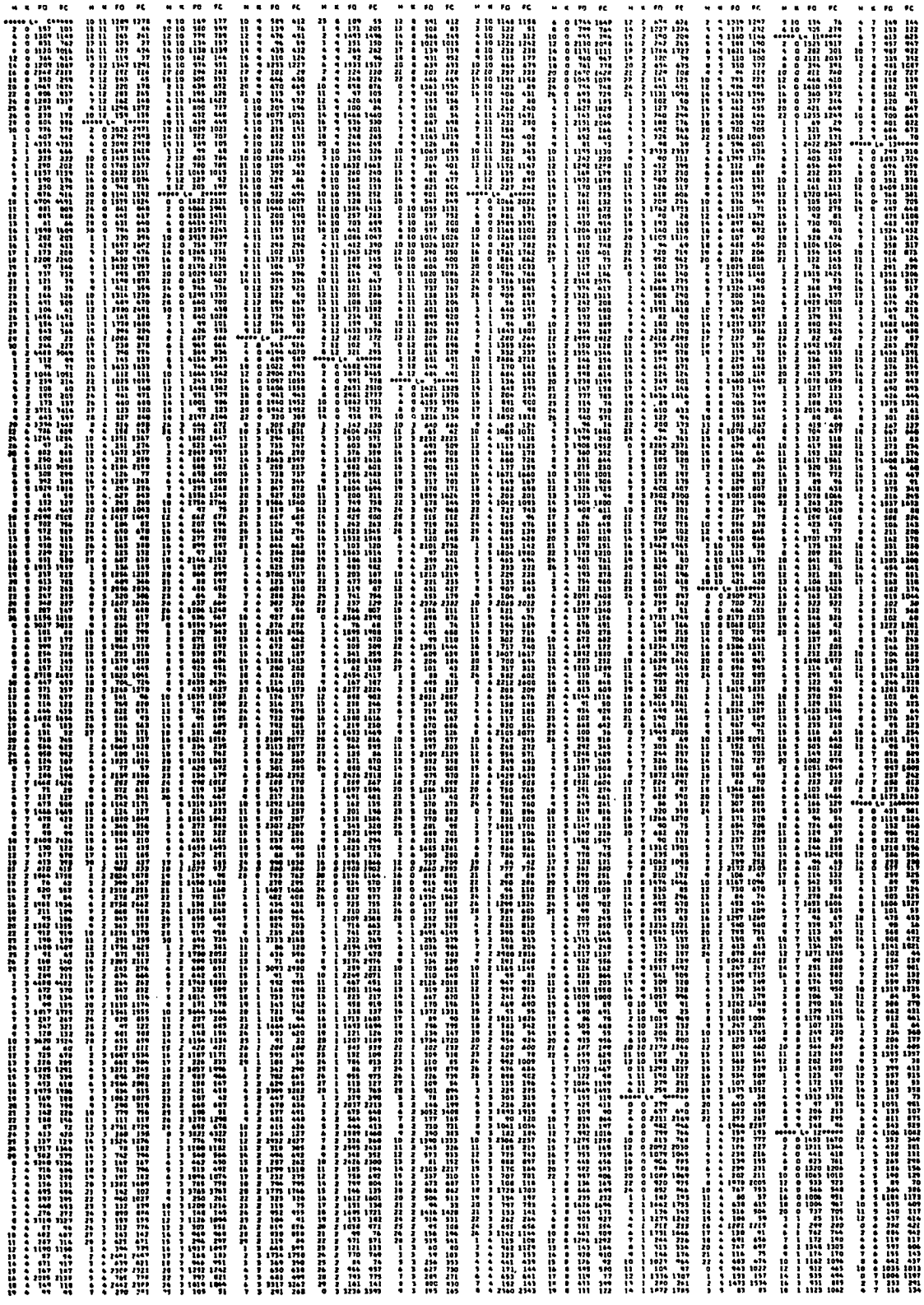
Atom	x	y	z	β_{11}
O2U2	3997(5)	4988(9)	1811(14)	9(2)
C2E1	2547(6)	2603(13)	3616(11)	13(3)
C2E2	2500(6)	4218(14)	4244(12)	5(2)
C2D1	2402(5)	1415(10)	1905(12)	6(2)
C2D2	1719(5)	1611(13)	1568(9)	9(2)
C2U1	3294(6)	3056(11)	2814(12)	13(3)
C2U2	3444(6)	4659(12)	1941(10)	17(3)
OW11	1501(4)	-633(14)	-1046(10)	8(2)
OW12	634(4)	2596(9)	-232(9)	21(2)
OW21	1100(4)	5684(12)	2951(8)	11(2)
OW22	2041(4)	7570(9)	1705(11)	13(2)
OW13	-2352(5)	1721(12)	-386(14)	14(3)
OW14	-1547(6)	1463(12)	1925(13)	44(4)
OW23	4907(4)	3347(11)	2705(11)	14(2)
OW24	4108(7)	6634(14)	-36(11)	57(6)
N1	41(4)	-2228(9)	-871(8)	14(2)
N2	2625(4)	2764(9)	2460(7)	5(2)

β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
124(15)	97(11)	-13(4)	-9(5)	5(11)
77(15)	45(10)	-5(5)	-10(4)	29(11)
115(17)	38(9)	-7(6)	-7(4)	-2(11)
42(11)	60(10)	-2(4)	-14(4)	-5(10)
64(13)	17(7)	5(5)	-6(3)	-16(8)
28(11)	60(11)	2(4)	5(4)	8(9)
56(12)	12(6)	-1(4)	-4(4)	2(8)
202(18)	66(9)	1(5)	8(3)	-23(12)
41(10)	76(8)	-1(4)	-27(4)	5(8)
161(16)	38(7)	31(5)	-2(3)	-10(9)
46(10)	114(12)	-1(4)	-10(4)	8(10)
169(18)	141(15)	22(6)	-8(5)	58(15)
79(14)	103(12)	12(6)	5(7)	18(12)
96(13)	98(10)	-1(4)	-5(4)	22(10)
136(19)	71(13)	-41(8)	-1(7)	-7(12)
29(10)	29(7)	1(4)	-4(3)	-4(7)
6(10)	21(6)	-9(3)	4(3)	-21(7)

Table 11. Root-mean-square thermal displacement (Å)

Atom	Min.	Med.	Max.	Atom	Min.	Med.	Max.
Dy1	0.118	0.121	0.144	Dy2	0.115	0.120	0.145
N1	0.115	0.138	0.188	N2	0.078	0.114	0.179
C1E1	0.136	0.179	0.226	C2E1	0.124	0.161	0.230
C1E2	0.130	0.175	0.200	C2E2	0.095	0.181	0.215
O1E1	0.142	0.190	0.241	O2E1	0.141	0.157	0.202
O1E2	0.083	0.229	0.281	O2E2	0.129	0.204	0.220
C1D1	0.091	0.203	0.288	C2D1	0.068	0.136	0.226
C1D2	0.102	0.114	0.179	C2D2	0.091	0.133	0.185
O1D1	0.133	0.174	0.232	O2D1	0.113	0.122	0.212
O1D2	0.104	0.145	0.211	O2D2	0.121	0.173	0.258
C1U1	0.134	0.195	0.240	C2U1	0.105	0.166	0.220
C1U2	0.132	0.165	0.217	C2U2	0.101	0.154	0.195
O1U1	0.133	0.174	0.237	O2U1	0.133	0.153	0.227
O1U2	0.143	0.226	0.325	O2U2	0.130	0.187	0.303
OW11	0.115	0.201	0.309	OW21	0.108	0.170	0.280
OW12	0.130	0.139	0.279	OW21	0.143	0.170	02.96
OW13	0.155	0.252	0.353	OW23	0.177	0.192	0.276
OW14	0.177	0.274	0.319	OW24	0.209	0.236	0.377

Figure 13. Observed and calculated structure factors for $Dy(N(C_2H_2O_2)_3)4H_2O$ in electrons x 10



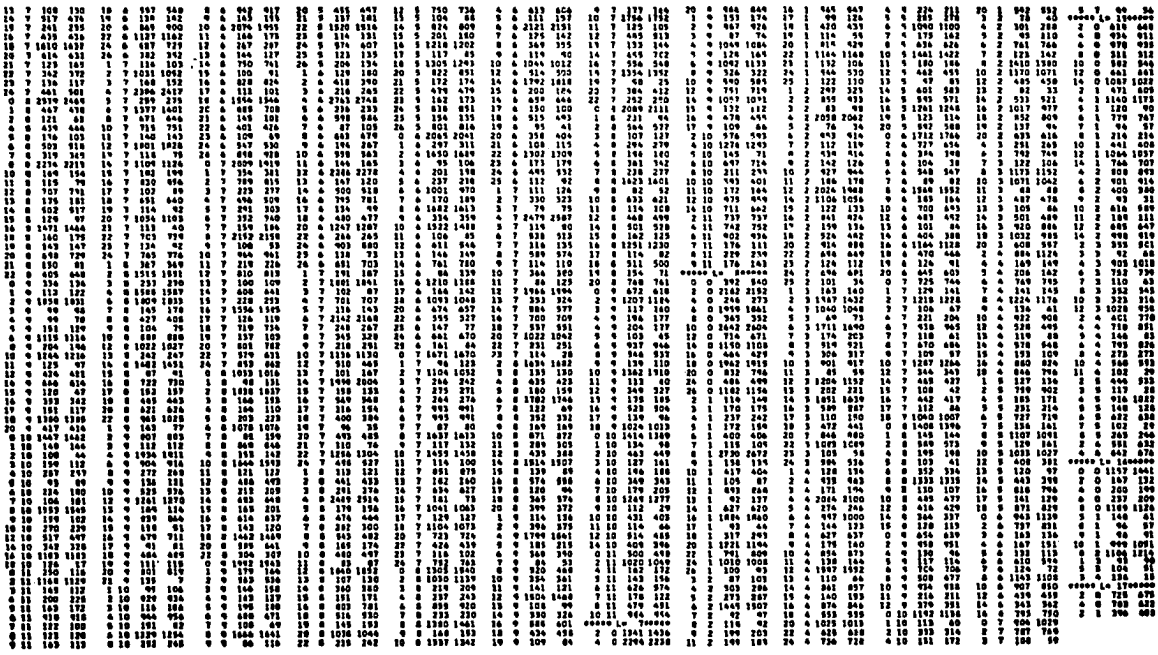


Figure 13. (Continued)

are listed the values of the observed and calculated structure factors. Selected intramolecular distances, both corrected and uncorrected for thermal motion, and angles are given in Table 12. Their estimated errors[23] were determined from the inverse matrix obtained when only the positional parameters were allowed to vary.

Discussion

The thermal parameters of the atoms in the NTA ligand exhibit a general increase as the distance from the nitrogen increases. Therefore, a correction for thermal motion using a riding model[51] seemed appropriate and was applied to the intraligand distances. Corrections using both a riding model and an independent atom model were made to the metal-oxygen distances.

The molecular configurations of the two independent Dy. $NTA \cdot 4H_2O$ molecules are shown in Figure 14. The two ligands exhibit similar metal coordinations. The three acetate groups in each independent ligand can be placed in one of three categories dependent upon the acetate-oxygen atom (O_a)-metal atom coordination. For a given ligand, one O_a atom in each of the three acetate groups, along with the nitrogen atom, coordinate to the same metal atom. Of the remaining three O_a atoms in each ligand, one is coordinated to an adjacent, symmetry-equivalent dysprosium atom (E type), one is coordinated to an adjacent, nonequivalent metal atom

Table 12. Selected interatomic distances (Å) and angles (deg)[a]

Atoms	Uncorr.	Riding	Independent
	Metal-light atom distances		
Dy1-O1E1	2.342(10)	2.354	2.368
Dy1-O1E2	2.283(10)	2.304	2.317
Dy1-O1D1	2.303(9)	2.311	2.326
Dy1-O2D2	2.345(9)	2.350	2.373
Dy1-O1U1	2.376(9)	2.385	2.400
Dy1-OW11	2.371(9)	2.392	2.406
Dy1-OW12	2.373(8)	2.386	2.400
Dy1-N1	2.575(9)	2.578	2.592
Dy2-O2E1	2.394(9)	2.401	2.414
Dy2-O2E2	2.307(8)	2.319	2.333
Dy2-O2D1	2.323(7)	2.329	2.343
Dy2-O1D2	2.438(9)	2.453	2.434
Dy2-O2U1	2.348(7)	2.356	2.371
Dy2-OW21	2.352(9)	2.366	2.380
Dy2-OW22	2.341(8)	2.359	2.372
Dy2-N2	2.580(8)	2.580	2.592

[a]Standard deviations are given in parentheses right justified to the last significant figure of the preceding number.

Table 12. (Continued)

Atoms	Uncorr.	Riding	Atoms	Uncorr.	Riding
		Intraligand distances			
C1E2-O1E1	1.27(2)	1.28	C2E2-O2E1	1.22(1)	1.22
C1E2-O1E2	1.20(2)	1.23	C2E2-O2E2	1.24(1)	1.25
C1E2-C1E1	1.56(2)	1.56	C2E2-C2E1	1.58(2)	1.58
C1D2-O1D1	1.26(1)	1.27	C2D2-O2D1	1.19(1)	1.20
C1D2-O1D2	1.23(1)	1.24	C2D2-O2D2	1.28(1)	1.30
C1D2-C1D1	1.51(1)	1.53	C2D2-C2D1	1.53(1)	1.53
C1U2-O1U1	1.28(2)	1.29	C2U2-O2U1	1.24(1)	1.25
C1U2-O1U2	1.23(1)	1.27	C2U2-O2U2	1.24(2)	1.27
C1U2-C1U1	1.57(2)	1.57	C2U2-C2U1	1.50(1)	1.50
N1-C1E1	1.44(2)	1.44	N2-C2E1	1.43(2)	1.44
N1-C1D1	1.51(1)	1.53	N2-C2D1	1.47(1)	1.48
N1-C1U1	1.48(2)	1.50	N2-C2U1	1.50(1)	1.51

Atoms	Angles	Atoms	Angles
	Intraligand angles		
O2E1-C2E2-O2E2	128(1)	O1E1-C1E2-O1E2	124(1)
O2E1-C2E2-C2E1	117(1)	O1E1-C1E2-C1E1	119(1)
O2E2-C2E2-C2E1	115(1)	O1E2-C1E2-C1E1	116(1)
C2E2-C2E1-N2	113(1)	C1E2-C1E1-N1	114(1)
O2D1-C2D2-O2D2	126(1)	O1D1-C1D2-O1D2	128(1)
O2D1-C2D2-C2D1	120.0(9)	O1D1-C1D2-C1D1	116(1)
O2D2-C2D2-C2D1	113.9(9)	O1D2-C1D2-C1D1	115(1)

Table 12. (Continued)

Atoms	Angles	Atoms	Angles
	Intraligand angles cont.		
C2D2-C2D1-N2	109.9(8)	C1D2-C1D1-N1	112(1)
O2U1-C2U2-O2U2	123(1)	O1U1-C1U2-O1U2	126(1)
O2U1-C2U2-C2U1	120(1)	O1U1-C1U2-C1U1	118(1)
O2U2-C2U2-C2U1	117(1)	O1U2-C1U2-C1U1	116(1)
C2U2-C2U1-N2	114.6(9)	C1U2-C1U1-N1	112(1)
C2E1-N2-C2D1	109.3(9)	C1E1-N1-C1D1	110(1)
C2E1-N2-C2U1	110.6(9)	C1E1-N1-C1U1	109(1)
C2D1-N2-C2U1	110.8(8)	C1D1-N1-C1U1	108(1)
	Angles involving a metal atom		
N2-Dy2-OW21	119.1(3)	OW11-Dy1-O1U1	141.1(4)
O2D1-Dy2-O2E1	102.8(3)	N1-Dy1-O1E1	68.2(3)
O2E2-Dy2-OW22	104.2(4)	O2D2-Dy1-O1E2	80.3(4)
O2U1-Dy2-O1D2	136.4(4)	O1D1-Dy1-OW12	156.3(3)
N2-Dy2-O1D2	134.3(2)	O2D2-Dy1-O1E1	130.9(3)
O2D1-Dy2-O2E2	79.1(3)	OW11-Dy1-OW12	98.8(4)
O2E1-Dy2-OW22	89.8(4)	N1-Dy1-O1E2	101.2(3)
OW21-Dy2-O2U1	135.2(4)	O1D1-Dy1-O1U1	116.9(3)
O2E2-Dy2-O2E1	140.9(3)	O1U1-Dy1-O1E1	72.3(4)
OW22-Dy2-O2D1	155.5(3)	O1D1-Dy1-O2D2	75.1(3)
N2-Dy2-O2U1	68.3(3)	OW12-Dy1-N1	137.1(3)
OW21-Dy2-O1D2	73.2(3)	O1E2-Dy1-OW11	146.4(4)

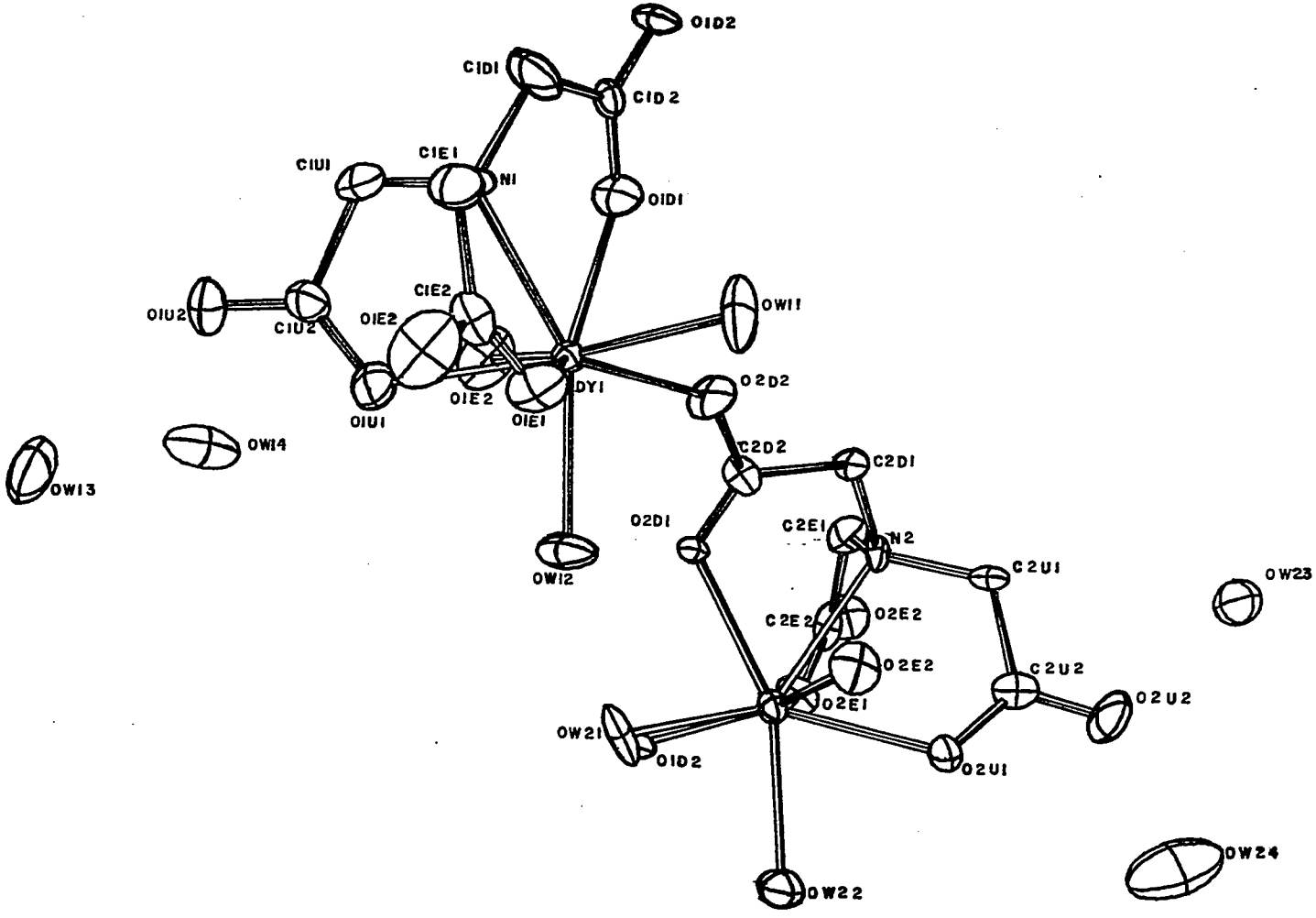
Table 12. (Continued)

Atoms	Angles	Atoms	Angles
	Angles involving a metal atom cont.		
C2U2-O2U1-Dy2	125.0(8)	C1U2-O1U1-Dy1	118.9(9)
C2E2-O2E1-Dy2	123.0(8)	C1E2-O1E1-Dy1	124.5(8)
C2E2-O2E2-Dy2[b]	159(1)	C1E2-O1E2-Dy2[b]	164(1)
C2D2-O2D2-Dy2	121.5(7)	C1E2-O1D1-Dy1	128.7(7)
C2D2-O2D1-Dy1	134.0(8)	C1D2-O1D2-Dy2[b]	128.7(7)

Atoms	Distance	Atoms	Distance
	Additional interatomic distances		
O1E1-O1E2	2.18(1)	OW13-O1U2	2.89(2)
O2E1-O2E2	2.24(1)	OW14-OW11	2.59(2)
O1D1-O1D2	2.23(1)	OW14-O1U2	3.06(2)
O2D1-O2D2	2.21(1)	OW23-O2U2	2.69(2)
O1U1-O1U2	2.20(1)	OW23-OW12	2.85(1)
O2U1-O2U2	2.17(1)	OW24-O2U2	2.71(2)
OW13-OW11	2.78(2)	OW23-OW21	2.64(2)

[b]For an explanation of symmetry related positions see Figures 15 and 16.

Figure 14. Configuration of the two independent molecules. (The two metal atoms are numbered for uniqueness. The nitrogen atoms have the same number as the metal to which they are coordinated which is also the left-most number for the remaining atoms in the ligand. The letters specify the type of metal-oxygen coordination (see text), while the right-most number indicates a skeletal position for the carbon atoms. In the case of the oxygen atoms, a one in the right-most position indicates coordination to the same metal atoms as the nitrogen atom while a two indicates a different interaction)


O1D2
C1D1
C1D2
C1E1
C1U1
NI
O1D1
C1E2
O1U2
C1U2
O1E2
OW11
O1E2
DY1
O2D2
O1U1
O1E1
OW14
OW13
C2D2
C2D1
O2D1
C2E1
N2
C2U1
OW12
OW23
C2E2
O2E2
O2E2
C2U2
O2U2
O2E1
OW21
O1D2
O2U1
OW22
OW24

(D type), and one is not coordinated to any metal atom (U type). Schematic drawings of the two independent NTA ligands are shown in Figures 15 and 16. The acetate groups are all planar to within 0.03 Å; the O_a-C-O_a angles average 126° (123-128°) while the O_a-C-C angles average 117° (114-120°). The average carbon-oxygen (1.26 Å), carbon-carbon (1.55 Å) and carbon-nitrogen (1.48 Å) bond distances, corrected for thermal motion are all within 0.01 Å of the expected values.[39]

The variation in C-C and C-N bond distances does not appear to be significant. The systematically large O_a-C-O_a angles are apparently the result of intermolecular steric interactions and intracarboxylate oxygen-oxygen repulsions.[25] Also, the wide range in metal-oxygen and C-O_a distances probably is a result of a combination of steric and electrostatic effects. There does not appear to be any correlation between lengthenings and shortenings of C-O distances in a manner which would suggest covalent effects. In addition, the C-O_a distance for the two uncoordinated oxygens are 0.01 Å longer than the average; a shortening of this bond would be expected in the presence of covalent bonding.[44]

Five acetate oxygen atoms, two water molecules and one nitrogen atom are in the coordination sphere of each metal atom. These coordinating atoms reside at the corners of a distorted dodecahedron with triangular faces with approximate

Figure 15. Schematic drawing of NTA ligand one

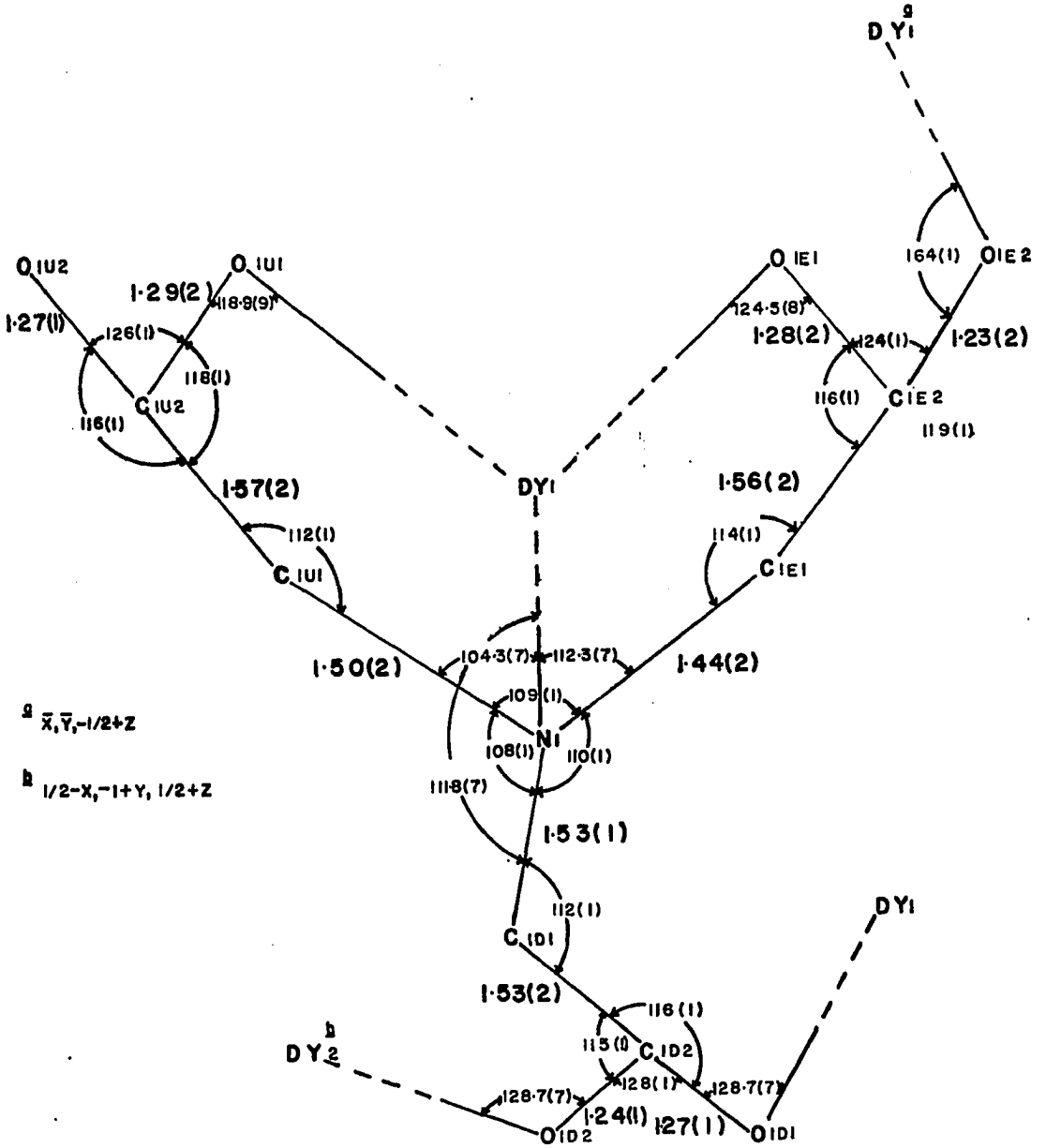
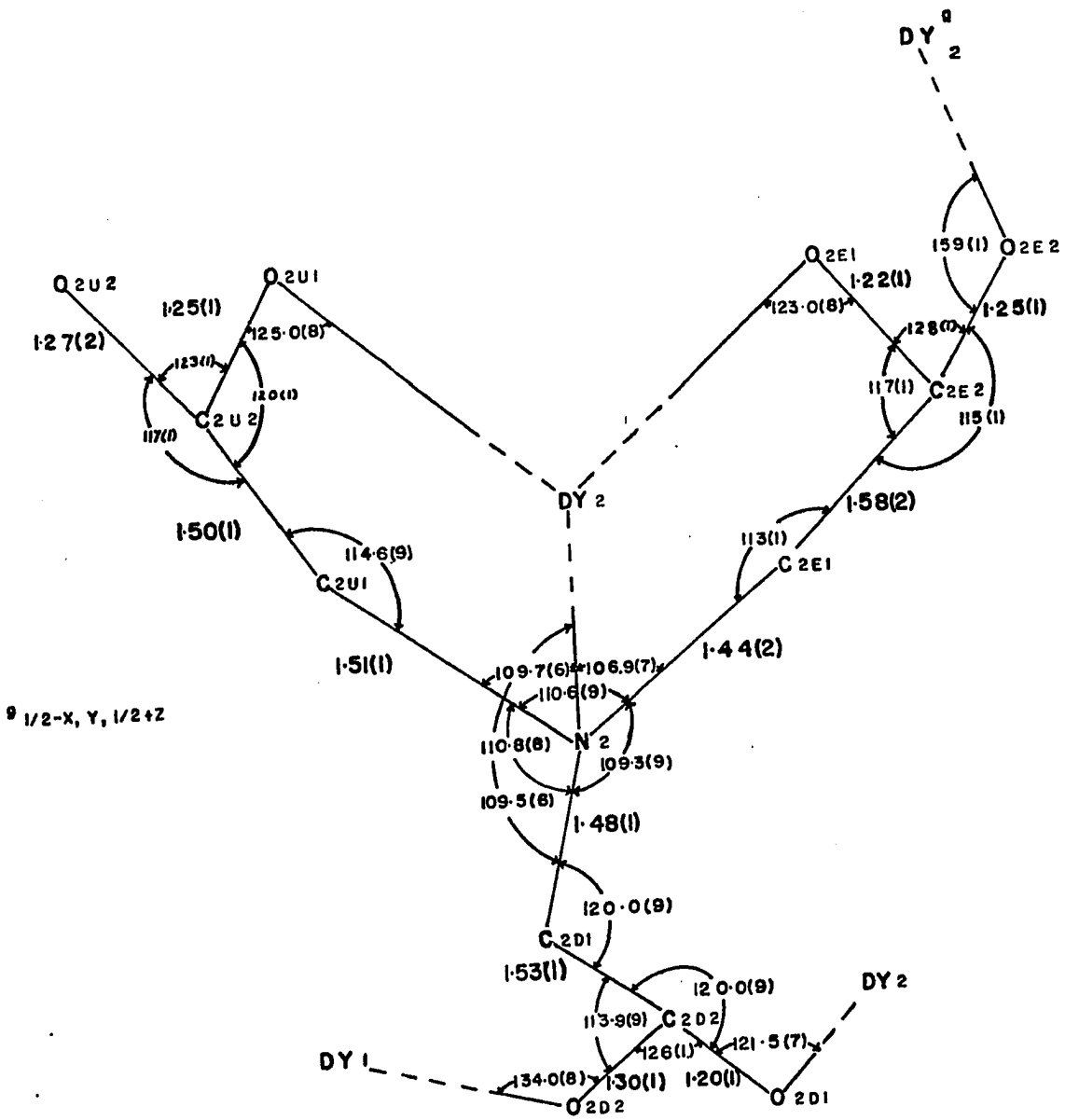

O1U2
O1U1
1·29(2)
118·9(9)
1·27(1)
126(1)
118(1)
C1U2
116(1)
1·57(2)
112(1)
C1U1
1·50(2)
DY1
O1E1
124·5(8)
1·28(2)
164(1)
O1E2
1·23(2)
124(1)
116(1)
C1E2
119(1)
1·56(2)
114(1)
C1E1
1·44(2)
104·3(7)
112·3(7)
109(1)
Ni
108(1)
110(1)
111·8(7)
1·53(1)
112(1)
C1D1
1·53(2)
DY1
116(1)
115(1)
C1D2
128(1)
128·7(7)
128·7(7)
1·24(1)
1·27(1)
O1D2
O1D1
DY2
a x̄, ȳ, -1/2+z
b 1/2-x, -1+y, 1/2+z

Figure 16. Schematic drawing of NTA ligand two


DY 2 a
O 2E 2
159(1)
O 2E 1
1·22(1)
1·25(1)
123·0(8)
126(1)
O 2U 2
O 2U 1
1·25(1)
125·0(8)
1·27(2)
123(1)
120(1)
C 2E 2
117(1)
115(1)
C 2U 2
117(1)
DY 2
1·58(2)
1·50(1)
113(1)
114·6(9)
C 2E 1
C 2U 1
1·44(2)
1·51(1)
109·7(6)
106·9(7)
110·6(9)
a 1/2-X, Y, 1/2+Z
110·8(8)
N 2
109·3(9)
109·5(6)
1·48(1)
120·0(9)
C 2D1
1·53(1)
120·0(9)
DY 2
113·9(9)
C 2D2
126(1)
121·5(7)
DY 1
134·0(8)
1·30(1)
1·20(1)
O 2D2
O 2D1

D_{2d} symmetry. A projection down one of the two folds in molecule one and a projection showing the fourfold inversion axis in molecule two are given in Figures 17 and 18. The good agreement, in most cases, between symmetry equivalent distances (see Table 13) illustrates the approximate D_{2d} symmetry. The nona-coordinate, capped, square antiprism found in the $Pr \cdot NTA \cdot 3H_2O$ can be converted to the octa-coordinate dodecahedron by removal of the atom in the capping position and relatively minor changes in angles. The NTA ligand in the Pr complex would then be hexadentate as it is in the title compound with no doubly coordinated oxygen atom.

The coordination can also be described as a distorted one-five-two complex similar to the one-five-three description given by Hoard *et al.*[41] for the La·EDTA complex. The distortions are much greater in this case than for the dodecahedron and we prefer the latter.

The average Dy-O_a, Dy-N and Dy-O_w distances, uncorrected for thermal motion are 2.346, 2.578, and 2.359 Å. This corresponds to a decrease of approximately 0.1 Å compared to the corresponding praseodymium distances for the M-O_a and M-N bonds. This is in good agreement with the decrease in the ionic radius.[40] The Dy-O_w distances average approximately 0.06 Å shorter than expected. However, there are a large number of O_w-O distances which are in the range typical of

Figure 17. Coordination of Dy_1 (viewed down a pseudo, twofold axis)

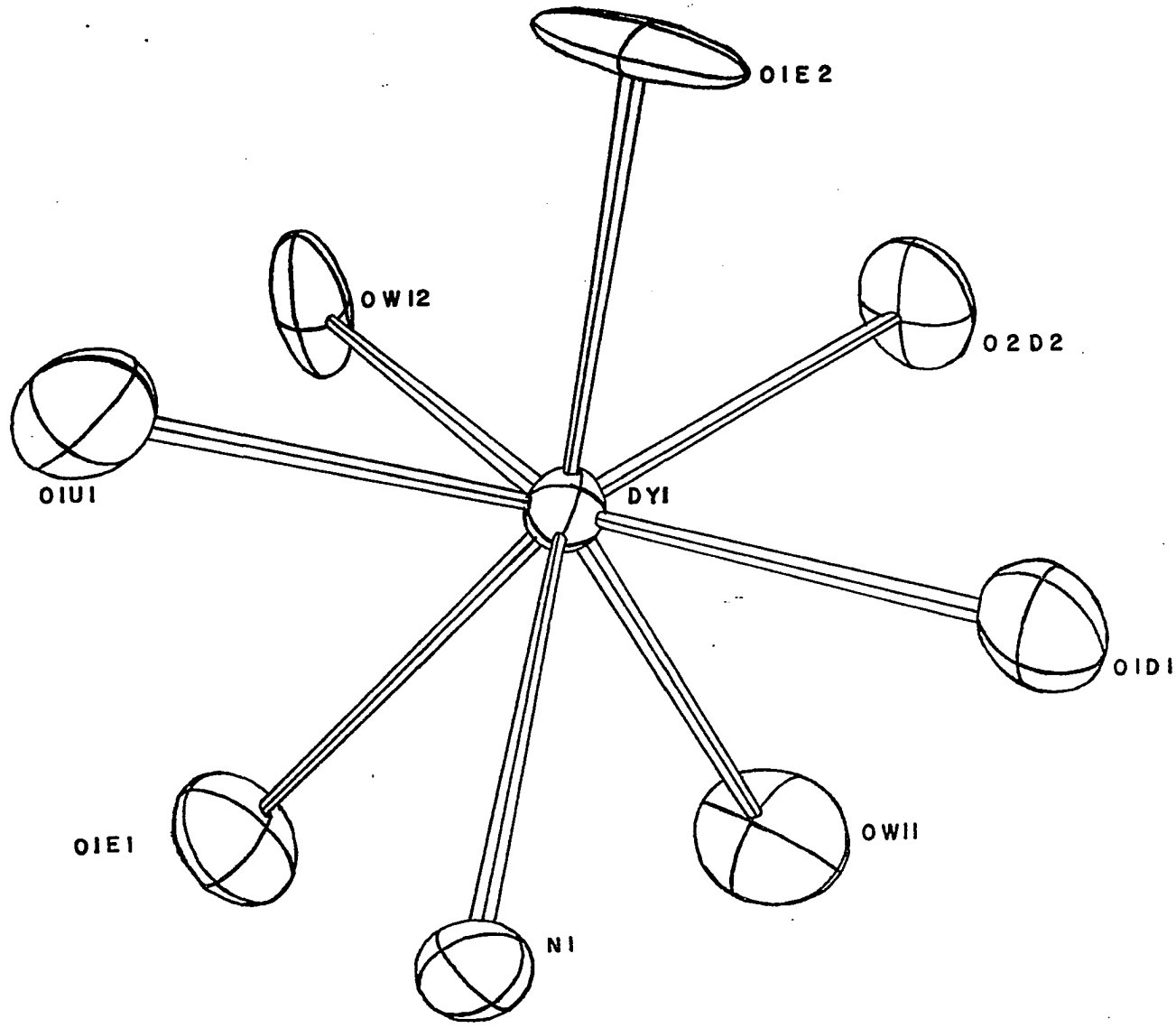

O1E2
OW12
O2D2
O1U1
DY1
O1D1
O1E1
OW11
N1

Figure 18. Coordination of Dy_2 (viewed perpendicular to a pseudo, $\bar{4}$ axis)

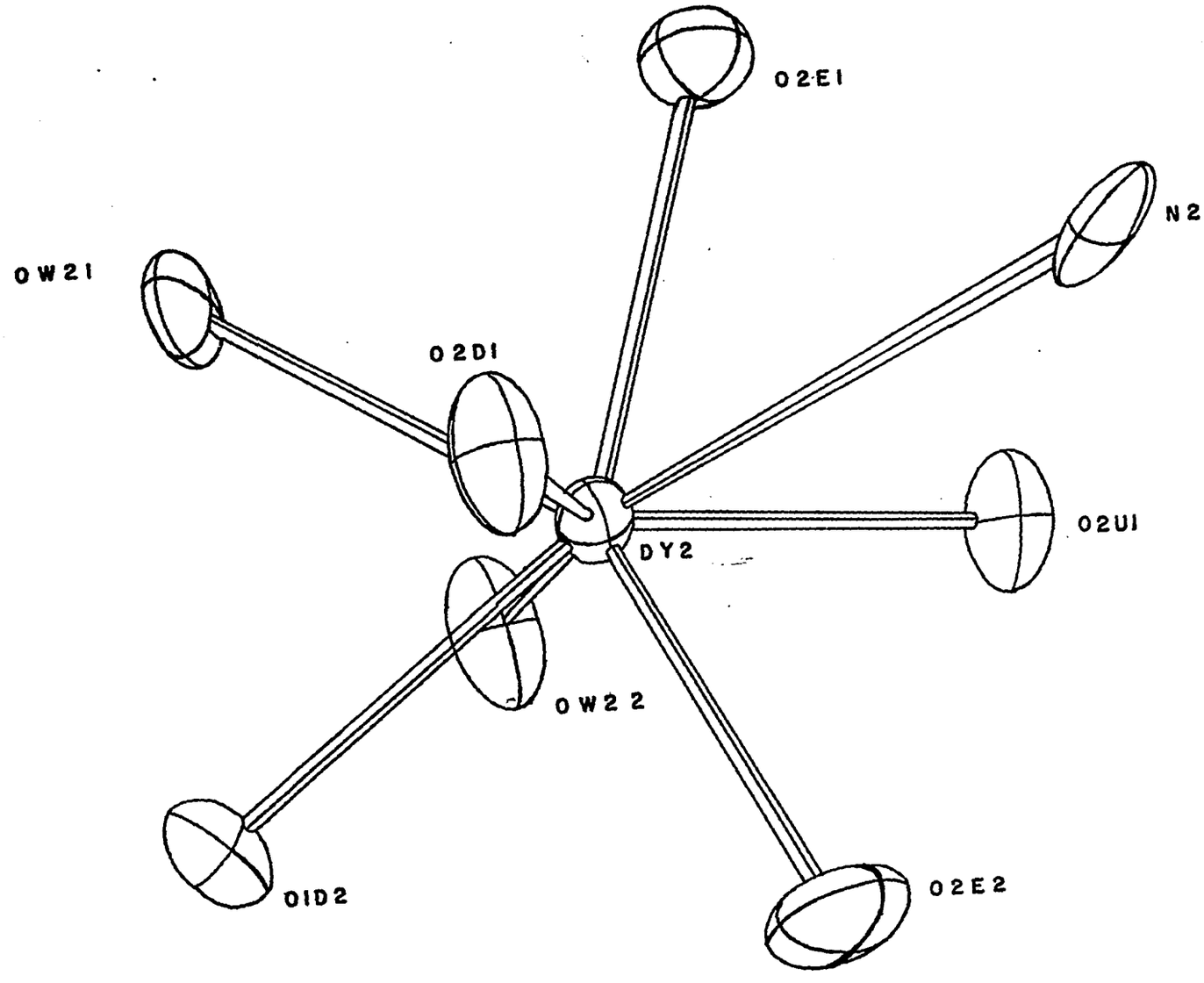

O2E1
N2
OW21
O2D1
O2U1
DY2
OW22
O1D2
O2E2

Table 13. Atoms and distances[a] related by pseudo-symmetry

Atoms related by a twofold

Molecule 1		Molecule 2	
N1-O1E1	O2D2-O1E1	N2-OW21	OW21-O2U1
OW11-O1U1	OW11-OW12	O1D2-O2U1	O2D1-O2E2
O2D2-O1E2	N1-O1E2	O2D1-O2E1	N2-O1D2
O1D1-OW12	O1D1-O1U1	O2E2-OW22	O2E1-OW22

Atoms related by $\bar{4}$

O1U1-O1D1-O1E1-O2D2	O2E2-OW22-O2E1-O2D1
OW12-O1E2-N1-OW11	N2-OW21-O2U1-O1D2

Equivalent distances related by pseudo-symmetry

Molecule 1			Molecule 2		
Atoms	Dist.	Ave.	Atoms	Dist.	Ave.
O1E1-O1U1	2.78		O1D2-OW21	2.85	
		2.80			2.81
O1D1-O2D2	2.83		O2U1-N2	2.77	
O1E1-N1	2.77		O1D2-O2D1	2.85	
O1D1-O1E2	2.85		OW21-OW22	3.05	
O1U1-OW12	3.06		N2-O2E1	2.78	
O2D2-OW11	2.78		O2E2-O2U1	2.87	
		2.88			2.97
O1E1-OW12	2.87		O1D2-OW22	3.19	
O1E1-N1	2.77		OW21-O2D1	3.11	

[a]Average standard deviation in distances is 0.02 Å.

Table 13. (Continued)

Atoms	Dist.	Ave.	Atoms	Dist.	Ave.
O1D1-OW11	2.95		N2-O2E2	3.09	
O2D2-O1E2	2.98		O2U1-O2E1	2.85	
N1-O1E2	3.76		O2D1-O2E1	3.69	
OW11-OW12	3.60		O2D1-O2E2	2.95	
		3.57			3.41
N1-OW11	3.47		OW22-O2E1	3.34	
OW12-O1E2	3.44		OW22-O2E2	3.67	
O1E1-OW11	2.70		O1D2-O2E2	2.89	
O1U1-O1E2	2.72		OW21-O2E1	2.94	
		2.80			2.77
O1D1-N1	2.69		N2-O2D1	2.67	
O2D2-OW12	3.08		O2U1-OW22	2.78	

hydrogen bonding (Tables 12 and 13) and such hydrogen bonding might be expected to increase the metal-O_w interactions on electrostatic grounds.

THE QUADRUPLE PRODUCT

Introduction

The basis for the method to be described below as well as for any of the so called "direct methods" is the Sayre[52] squared equation

$$V \times S \times \underline{F}_{\vec{h}} = \sum_{k} \underline{F}_{\vec{k}} \underline{F}_{\vec{h}-\vec{k}} \qquad (1)$$

where V is the volume of the unit cell and S is a function to correct for a difference in peak-shape between $\underline{F}_{\vec{h}}$ and $\underline{F}_{\vec{h}}$. This function is a direct result of the self-convolution of the structure factor, $\underline{F}_{\vec{h}}$.[53] It is apparent for centrosymmetric space groups, where phases are limited to integral values ($\pm$ 1), that in order for $\underline{F}_{\vec{h}}$ to be large, the values within the summation must tend strongly towards terms with the same sign. Therefore, for most terms in Equation 1,

$$s(\underline{F}_{\vec{h}}) = s(\underline{F}_{\vec{k}})s(\underline{F}_{\vec{h}-\vec{k}}) \qquad (2)$$

where s represents "the sign of". The larger the values of $\underline{F}_{\vec{h}}$, $\underline{F}_{\vec{k}}$, and $\underline{F}_{\vec{h}-\vec{k}}$, the more probable that (2) will hold. A more useful measure of a particular reflections "largeness" is its $\underline{E}$ value.[54] This is simply the value of $\underline{F}$ corrected for $\sin\theta/\lambda$ fall-off in the scattering power

$$\underline{E}^2_{\vec{h}} = \underline{F}^2_{\vec{h}} / \underline{\epsilon} \sum_{j}^{N} f_j^2 \qquad (3)$$

where f_j is the scattering factor, $\underline{\varepsilon}$ is a term which is introduced to correct for symmetry, and $\underline{F}_{\vec{h}}$ is corrected for thermal motion. The use of $\underline{E}_{\vec{h}}$ instead of $\underline{F}_{\vec{h}}$ makes possible meaningful size comparisons between reflections at different values of θ. When the size of a particular reflection is expressed in terms of $\underline{E}_{\vec{h}}$'s, then the probability that (2) will hold is given by[55]

$$P_{(+)} = 1/2 + 1/2 \tanh \rho_3/\rho_2^{3/2} |\underline{E}_{\vec{h}}\underline{E}_{\vec{k}}\underline{E}_{\vec{h}-\vec{k}}| \qquad (4)$$

where $\rho_q = \sum_i^N n_i^q$ and $n_i = f_i / \sum_j^N f_j$. If there are multiple relations which yield $\underline{E}_{\vec{h}}$, then

$$P_{(+)} = 1/2 + 1/2 \tanh \sum_k \rho_3/\rho_2^{3/2} |\underline{E}_{\vec{h}}\underline{E}_{\vec{k}}\underline{E}_{\vec{h}-\vec{k}}| \qquad (5)$$

The normal manner in which the signs of the various reflections are determined in a centrosymmetric structure is to use a "symbolic addition procedure".[56-59] In this procedure initial signs are given to a few reflections (three or less) with larger values of $\underline{E}$ to fix the origin and additional algebraic symbols are given to a few other reflections as needed. By the application of Equation (2), additional signs may be determined. Failure in this method usually is a result of either poor data, difficulty in choosing a good starting set, or few type (2) relationships with high probability. The last case is especially important in triclinic systems because of the low symmetry. In the method

described below, an attempt was made to develop additional phase relationships between the various reflections. In this manner, the dependency of the solution upon the choice of a good starting set can be eliminated and the problems caused by only a few type (2) relationships may be reduced.

Description of the Method

When $\underline{E}_{\vec{h}}$ is large, all the individual signs of the terms in Equation (1) are equated; this results in a series of equations of the type

$$s(\underline{E}_{\vec{k}})s(\underline{E}_{\vec{h}-\vec{k}}) = s(\underline{E}_{\vec{k}'})s(\underline{E}_{\vec{h}-\vec{k}'}) \qquad (6)$$

for all possible values of $\vec{k}$ and $\vec{k}'$, $\vec{k} \neq \vec{k}'$. The probability that these equations hold is just the product of the probabilities that each individual relation of the type (2) holds. Upon rearrangement of (6)

$$s(\underline{E}_{\vec{k}})s(\underline{E}_{\vec{h}-\vec{k}})s(\underline{E}_{\vec{k}'})s(\underline{E}_{\vec{h}-\vec{k}'}) = +1 \qquad (7)$$

is obtained. This relationship we have chosen to call the quadruple product. In every centrosymmetric structure there will be at least one set, and sometimes several sets, depending upon the amount of symmetry present, of $\vec{h}$, $\vec{k}$, $\vec{k}'$ values where two of the unknowns can be eliminated from Equation (7). For example, two sets of $\underline{E}$'s which satisfy Equation (2) for a value of $\vec{h}$ = 1, 3, 3 are $\underline{E}_{111}\cdot\underline{E}_{022}$ and

$\underline{E}_{\bar{1}\bar{1}\bar{1}} \cdot \underline{E}_{244}$. These two sets would then give rise to the quadruple product

$$s(\underline{E}_{111}) \cdot s(\underline{E}_{022}) \cdot s(\underline{E}_{\bar{1}\bar{1}\bar{1}}) \cdot s(\underline{E}_{244}) = +1 \qquad (8)$$

For a centrosymmetric structure $E_{111} = E_{\bar{1}\bar{1}\bar{1}}$ and

$$s(E_{\bar{1}\bar{1}\bar{1}}) \cdot s(E_{111}) = +1 \qquad (9)$$

Upon substitution of Equation (9) into Equation (8)

$$s(\underline{E}_{022}) \cdot s(\underline{E}_{244}) \cdot (+1) = +1 \qquad (10)$$

is obtained, or, upon rearrangement

$$s(\underline{E}_{022}) = s(\underline{E}_{244}) \qquad (11)$$

The probability that the relationship given by Equation (11) holds is the same as that of the parent quadruple relation holding.

As soon as the relationship between two $\underline{E}_{\vec{h}}$'s is known with high probability (~ 0.95), then this relation can be fed back into the sign determining process and the number of quadruple products, from which two unknowns can be eliminated, rapidly increases. The probability that these new relationships will hold is just equal to the product of the probabilities that the quadruple product holds and the relation between the two $\underline{E}_{\vec{h}}$'s, which are eliminated, is valid. Since this new probability is the product of four numbers all less

than one, it is apparent that a single relationship may well have a probability which is small ($<< 0.95$). However, as the number of relationships between $\underline{E}_{\vec{h}}$'s increases, so will the number of multiple indications of a particular relationship between two $\underline{E}$'s. For two indications, the probability that an indication is correct is

$$P_{(c)} = P_1 \times P_2/(1 - P_1 - P_2 + 2P_1 \times P_2) \qquad (12)$$

where P_1 and P_2 are the probabilities of the individual relationships being valid. In general, for n indications the probability can be expressed as

$$P_{(c)} = \prod_{i=1}^{n} P_i/(\prod_{i=1}^{n}(1 - P_i) + \prod_{i=1}^{n}(P_i)) \qquad (13)$$

It is apparent that with only a few indications of moderate probability (~ 0.8), Equation (13) will rapidly approach unity.

A particular reflection may be placed in any one of eight parity groups: eee, eeo, eoe, oee, eoo, oeo, ooe, and ooo where e indicates even and o indicates an odd index. The parties are seen to form a group with respect to multiplication (Table 14). It is readily seen that, in order to satisfy Equation (2) for a given parity of $\vec{h}$, $\underline{E}$'s of appropriate parity must be used. For example, if $\vec{h}$ has parity eoe, there will be four combinations of two E's which will yield this parity (oeo, ooo; eee, eoe; ooe, oee;

Table 14. Parity group multiplication table

	eee	eeo	eoe	oee	ooe	oeo	eoo	ooo
eee	eee	eeo	eoe	oee	ooe	oeo	eoo	ooo
eeo	eeo	eee	eoo	oeo	ooo	oee	eoe	ooe
eoe	eoe	eoo	eee	ooe	oee	ooo	eeo	oeo
oee	oee	oeo	ooe	eee	eoe	eeo	ooo	eoo
ooe	ooe	ooo	oee	eoe	eee	eoo	oeo	eeo
oeo	oeo	oee	ooo	eeo	eoo	eee	ooe	eoe
eoo	eoo	eoe	eeo	ooo	oeo	ooe	eee	oee
ooo	ooo	ooe	oeo	eoo	eeo	eoe	oee	eee

eeo, eoo). In addition, if two of the three parity groups are specified then, obviously, the parity of the third term is determined. This is important since it dictates that only terms of like parity may be related through Equation (11) before the origin is defined.

When relationships within the various parity groups are known, the origin may be specified. Using the known intra-parity relationships, absolute signs may be assigned to the E's in the parity groups of the origin defining E's. Since there are now many new relationships between E's in the different parity groups, there will be many additional quadruple products where two of the unknowns, now of dif-

ferent parity classes, may be eliminated.

Absolute signs may be determined for the remaining parity groups by two different procedures. The first procedure is to make use of type (2) relationships. When two $E_{\vec{h}}$'s have known absolute signs and the third $E_{\vec{h}}$ is of a parity class for which absolute signs are not known, the absolute signs of the third parity group can be obtained. For example, the necessary relationships needed to relate relative signs of the undetermined parity groups to those of the three parity groups eee, oee, eoe are shown in Table 15.

Table 15. Parities which relate relative signs

	$\vec{h}$	$\vec{k}$	$\vec{h}-\vec{k}$
Cycle 1	ooe	oee	eoe
	oeo	oee	eeo
	eoo	eoe	eeo
	eee	oee	oee
	eee	ooe	ooe
	eee	eoe	eoe
Cycle 2	ooo	eeo	ooe

In order to determine the ooo parity group, it would be necessary to recycle using relative signs generated in the first cycle. The probability that these new signs are

correct would be the probability that Equation (2) holds, times the probability that the relationship between the two known $\underline{E}_{\vec{h}}$'s, as determined from the quadruple product, is valid. Only relationships of very high probability (~ 0.99) need be used in this process since there will be numerous indications for the absolute signs of each of the unknown groups and these probabilities will rapidly approach certainty by the use of equations similar to (13).

The second procedure, which can be used to determine the absolute signs of the unknown parity classes, utilizes the absolute signs of the eee-type reflections which can be determined before the origin is defined. When two $\underline{E}$'s with the same parity are involved in a type 2 relation, the parity of the third $\underline{E}$ must be eee. If the $\underline{E}$'s are of the same parity, their relative signs will be known and Equation (2) can be uniquely solved for the absolute sign of the eee-$\underline{E}$. There are usually a number of these types of relations for every eee-$\underline{E}$ and the associated probabilities will approach certainty by the use of equations similar to (13). After the origin is defined, there are a number of quadruple products which involve two $\underline{E}_{\vec{h}}$'s of a parity class with known absolute signs, an $\underline{E}_{\vec{h}}$ of eee parity with known absolute sign, and one $\underline{E}_{\vec{h}}$ from an unknown parity group. The absolute sign for this $\underline{E}_{\vec{h}}$ is then uniquely determined. The types of parities needed to relate the absolute signs of the undeter-

mined parity groups to the three parity groups eeo, eoe, oee by the use of the quadruple product and known signs for the eee-$\underline{E}$'s are shown in Table 16. The quadruple products are, of course, formed with $\vec{k}$ and $\vec{h}$-$\vec{k}$ terms. It is also seen in

Table 16. Types of parities needed to relate undetermine signs

$\vec{h}$	$\vec{k}$	$\vec{h}$-$\vec{k}$	$\vec{h}$	$\vec{k}$	$\vec{h}$-$\vec{k}$	$\vec{h}$	$\vec{k}$	$\vec{h}$-$\vec{k}$
	oee	oeo		oee	ooe		oee	eee
eeo	eoe	eoo	eoe	eoe	eee	oee	eoe	ooe
	eeo	eee		eeo	eoo		eeo	oeo
	eeo	ooo		eoe	ooo		oee	ooo
ooe	eoe	oee	oeo	oee	eeo	eoo	eoe	eeo
	oee	eoe		eeo	oee		eeo	eoe

Table 16 that the absolute signs of one of the parity groups (in this case the ooo type) is determined directly from the origin defining parity groups.

In practice a mixture of the two methods described above is used. The second method is routinely used in an automated procedure since it is easier to program and, in addition, it leads to new relationships between $\underline{E}_{\vec{h}}$'s which are not found through symmetry alone. The first procedure is used only if

the automated procedure fails. This only occurs when there are a small number of $\underline{E}$'s in a particular parity group or when small sub-groups form where a few of the $\underline{E}$'s have no interrelations with the bulk of the $\underline{E}$'s in a particular parity group. In these cases the (2)-type relationships may be used to find the unknown signs.

Application of the Method

To facilitate the application of this method two programs, Quads and Relate have been written. The calculation of the quadruple products is carried out by the use of the program Quads. A listing of this Fortron IV program is supplied in Appendix A. Input to this program is a tape containing all relations of the type (2). The actual sign determination process is carried out using Relate. Relate is a PL-1 program written for the 360-65 system. It uses 22K words of high speed core with some dynamic allocation of arrays plus an additional 50K words of slow core. A listing of this program can be found in Appendix B.

Relate searches through the entire list of quadruple products for relationships where the relative signs of two of the four members are known. The remaining two members are then given the appropriate relative sign and the probability is stored, or if there is already some indication known between these $\underline{E}_{\vec{h}}$'s, a new probability is calculated. At the end of each cycle, the probabilities are searched for values

exceeding a cut-off value (~ 0.95). These relationships are then output along with their associated probabilities. This list of related $\underline{E}_{\vec{h}}$'s is then searched for relationships of the type $a = \pm b$ and $b = \pm c$. Then a is set equal to c with the appropriate relative sign. Finally, the list of relationships of type (2) involving eee reflections is searched for cases where two of the three unknowns may be eliminated. If the cumulated probability exceeds a given cut-off value (~ 0.99), the $\underline{E}_{\vec{h}}$, where h is eee, is given the appropriate absolute sign. Then if any of the type (2) relations which contain this $s(\underline{E}_{\vec{h}})$ are not known, the remaining two members are given the appropriate relative sign and probabilities. The program then recycles using these newly determined relations. Whenever most of the relations for the various parity groups are known, the origin is defined by assigning absolute signs to appropriate reflections. The program then recycles through the type (2) relations and determines the signs of the remaining groups. It also continues to cycle through the quadruples since in so doing the signs of some previously undetermined $\underline{E}_{\vec{h}}$'s may be found.

The method has been tested on the structure of $Cs_3Sb_2Cl_9$ which crystallizes in the space group Pnma (No. 62) with Z = 4. This structure was previously solved by W. Pflaum using normal direct methods. Values of the $\underline{E}$'s were calculated using a scale factor of 0.20 and an overall thermal parameter

of 2.65 determined by the method of Hackert.[60] The relations of type (2) were calculated[8] for $\underline{E}_{\vec{h}}$'s above 1.5. The value of $\rho_3/\rho_2^{3/2}$ used in calculating the probabilities was 0.143. Due to the limited core size of 50K words, only the 196 $\underline{E}_{\vec{h}}$'s above 2.28 were used in the calculation of some 62,560 quadruple products. In Relate, quadruple products were accepted only if their probability exceeded 0.80. A relationship between two $\underline{E}_{\vec{h}}$'s had to exceed a probability of 0.95 before it was accepted. Before signs were accepted for groups of reflections or for eee type reflections, the associated probability had to exceed 0.99. After three cycles through Relate, absolute signs were given appropriate members of the oee, ooe and eoo parity groups. In this case, all signs of the remaining groups were obtained automatically. Of the 196 inputs $\underline{E}_{\vec{h}}$'s, 194 were successfully assigned signs. Of these 194 signs, all were correct. From an E-map using these signs the positions of the Cs and Sb atoms were readily located. In Table 17 are listed the hkl values, and the signed $\underline{E}_{\vec{h}}$ values.

Table 17. Signed E values as determined by Relate(h,k,l,E)

0	0	6	-3.00	4	2	10	2.96	8	4	2	-2.50	15	1	14	2.56
0	0	12	5.07	4	2	14	2.47	8	4	4	3.65	15	2	2	3.34
0	0	18	-3.10	4	4	4	3.15	8	4	8	3.24	15	2	4	2.28
0	1	3	2.28	4	4	8	2.87	8	4	16	2.33	15	2	10	-3.20
0	1	9	-2.80	4	6	2	3.09	8	5	1	-2.40	15	2	14	3.51
0	1	15	2.49	4	6	10	2.62	8	6	2	3.23	15	3	14	-2.40
0	2	0	-2.90	4	8	4	2.66	8	6	10	2.90	15	4	4	-2.90
0	2	6	4.15	4	8	8	2.69	8	6	14	2.59	15	4	8	2.85
0	2	12	-2.70	4	10	2	2.44	8	8	4	2.76	15	6	10	-2.50
0	2	18	3.73	5	0	11	2.48	8	8	8	2.82	16	0	4	3.35
0	3	3	-2.60	5	0	16	-2.40	8	10	2	2.61	16	0	8	2.91
0	3	9	2.37	5	0	17	-4.40	9	0	8	-2.30	16	2	2	3.15
0	3	15	-2.30	5	1	14	2.85	9	0	13	-2.70	16	2	10	2.43
0	4	0	4.69	5	2	11	-2.40	9	1	10	2.28	16	4	4	2.58
0	4	6	-2.50	5	2	17	3.17	9	1	16	-3.00	17	0	11	2.87
0	4	12	3.74	5	3	14	-2.70	9	2	13	2.36	17	0	8	-2.40
0	5	3	2.65	5	5	14	2.77	9	3	16	3.02	17	2	11	-2.80
0	5	9	-2.50	5	6	11	-2.40	10	0	8	-2.30	17	4	11	2.31
0	6	0	-2.70	5	8	11	2.55	10	0	16	-3.10	18	0	0	-2.30
0	6	6	3.93	6	0	0	-2.40	10	2	14	-2.30	18	0	12	-3.60
0	7	3	-2.70	6	0	12	-3.70	12	0	0	4.25	18	2	6	-3.00
0	8	0	3.91	6	2	6	-3.00	12	0	6	-3.80	19	0	7	2.67
0	8	6	-2.50	6	4	12	-2.40	12	0	12	5.84	19	1	10	3.23
0	8	12	3.57	7	0	4	2.90	12	1	3	3.73	19	3	4	2.23
0	9	3	2.63	7	0	8	-2.80	12	1	9	-3.20	19	3	10	-2.60
0	9	9	-2.80	7	0	14	2.44	12	2	0	-2.50	20	0	2	-2.50
0	10	0	-2.40	7	0	16	3.27	12	2	6	5.80	20	0	4	3.59
0	10	6	3.85	7	1	17	2.40	12	2	12	-2.90	20	0	8	3.14
3	0	4	-3.40	7	2	2	-2.60	12	3	3	-3.40	20	1	1	-2.50
3	0	8	5.04	7	2	10	2.59	12	3	9	2.74	20	1	5	-2.40
3	0	13	-2.50	7	2	16	-2.30	12	4	0	3.47	20	2	2	3.12
3	0	14	-2.40	7	4	4	2.40	12	4	6	-3.00	20	2	10	2.75
3	0	16	-2.90	7	4	16	2.72	12	4	12	4.45	20	4	4	2.73
3	1	16	-2.50	8	0	2	-2.80	12	5	2	2.78	20	4	8	2.53
3	2	2	3.19	8	0	4	4.22	12	5	9	-2.80	21	0	9	-2.40
3	2	10	-2.60	8	0	8	4.19	12	6	6	4.24	22	0	6	-3.20
3	2	14	3.05	8	0	10	-2.30	12	7	3	-2.40	22	1	3	2.77
3	3	16	2.51	8	0	14	-2.60	13	0	13	-3.50	22	1	9	-2.80
3	4	4	-2.70	8	0	16	3.34	13	0	15	2.50	22	2	6	2.49
3	4	8	2.75	8	1	1	-2.80	13	2	13	2.39	22	3	3	-2.40
3	5	16	-2.40	8	1	5	-2.50	13	4	13	-3.00	22	4	6	-2.50
3	6	2	2.60	8	1	7	2.42	15	0	2	-2.30	24	0	2	-2.50
3	6	14	2.36	8	2	2	4.14	15	0	4	-3.60	24	0	4	2.66
3	8	8	2.32	8	2	4	-2.40	15	0	8	3.73	24	1	1	-2.50
4	0	4	3.74	8	2	8	-2.40	15	0	10	2.62	24	1	5	-2.40

Table 17. (Continued)

4	0	8	3.93	8	2	10	3.38	15	0	14	-2.70	24	2	2	2.30
4	0	10	-2.40	8	2	14	3.05	15	1	1	2.30				
4	0	16	2.65	8	3	1	2.57	15	1	7	-2.30				
4	2	2	3.65	8	3	5	2.29	15	1	13	2.50				

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APPENDIX A. A LISTING OF QUADS

```
C     QUADS IS A FORTRAN IV PROGRAM TO CALCULATE THE QUADRUPLE PRODUCTS QUA 0010
C     AND THE ASSOCIATED PROBIBILITIES.........INPUT TO THIS PROGRAM    QUA 0020
C     IS THREE TAPES AND ONE CARD......INFORMATION SUPPLIED ON THE      QUA 0030
C     INPUT TAPE IS THE SAME AS THAT OUTPUT FROM NRC-SAP-2              QUA 0040
C     INFORMATION SUPPLIED BY THE USER ON CARDS IS AS FOLLOWS.......... QUA 0050
C     NTAP-SPECIFIES ON WHICH UNIT THE INPUT TAPE SHOULD BE MOUNTED     QUA 0060
C     IOTAP-SPECIFIES ON WHICH UNIT THE OUTPUT TAPE 1 SHOULD BE MOUNTED QUA 0070
C     NOTAP-SPECIFIES ON WHICH UNIT THE OUTPUT TAPE 2 SHOULD BE MOUNTED QUA 0080
C     AMIN-THE MINUMUN ACCEPTABLE PROBABILITY                           QUA 0090
C     MH-MAXIMUM SERIAL NUMBER TO BE CONSIDERED IN EVEN PARITY SEARCH   QUA 0100
C     MK-MAXIUM SERIAL NUMBER TO BE CONSIDERED                          QUA 0110
C     ML-DUMMY VARIABLE                                                 QUA 0120
C     SIGMA-VALUE OF SIGMA3/SIGMA2 TO THE 3/2 POWER                     QUA 0130
C     FORMAT 3I10,F10.5,3I5,F10.5                                       QUA 0140
C     OUTPUT FROM PROGRAM IS AS FOLLOWS.......HKL VALUES FOR ALL E'S    QUA 0150
C     ALONG WITH AN INDICATOR FOR EEE PARITY                            QUA 0160
C     ALL OF THE QUADRUPLE PRODUCTS                                     QUA 0170
C     THE TOTAL NUMBER OF QUADS CALCULATED                              QUA 0180
C     THE MAGNETIC TAPES CONTAIN THE FOLLOWING INFORMATION.......       QUA 0190
C     TAPE 1 HAS ALL OF THE QUADRUPLE PRODUCTS AND THEIR ASSOCIATED     QUA 0200
C     PROBABILITIES............................                         QUA 0210
C      TAPE 2 CONTAINS ALL THE EEE TRIPLES.........                     QUA 0220
C     BOTH OF THESE TAPES WILL BE NEEDED REPEATEDLY.......              QUA 0230
      DIMENSION N1(200),N2(200),A(200),TITLE(20),NQ(24),NNA(12),NNB(12) QUA 0240
      DIMENSION MMM(401),NNC(12),NND(12),SIGG(12)                       QUA 0250
      IZ=0                                                              QUA 0260
      II=0                                                              QUA 0270
      IN=0                                                              QUA 0280
C     INPUT INFORMATION...........                                      QUA 0290
      READ(1,100)TITLE                                                  QUA 0300
  100 FORMAT(20A4)                                                      QUA 0310
      WRITE(3,101)TITLE                                                 QUA 0320
  101 FORMAT(1H ,20A4//)                                                QUA 0330
      READ(1,102)NTAP,IOTAP,NOTAP,AMIN,MH,MK,ML,SIGMA                   QUA 0340
  102 FORMAT(3I10,F10.5,3I5,F10.4)                                      QUA 0350
      ND=0                                                              QUA 0360
      WRITE(3,1001)NTAP,IOTAP,AMIN                                      QUA 0370
```

```
 1001 FORMAT(1H ,'INPUT TAPE IS',I5,'OUTPUT TAPE IS',I5,'AMIN IS',F10.3)QUA 0380
C     CALCULATE PARITY.....................                            QUA 0390
    8 READ(NTAP)IH,IK,IL                                              QUA 0400
      IF(IH.GE.99)GO TO 93                                            QUA 0410
      II=II+1                                                         QUA 0420
      NH=(IH/2)*2                                                     QUA 0430
      NK=(IK/2)*2                                                     QUA 0440
      NL=(IL/2)*2                                                     QUA 0450
      IF(NH.NE.IH)GO TO 90                                            QUA 0460
      IF(NK.NE.IK)GO TO 90                                            QUA 0470
      IF(NL.NE.IL)GO TO 90                                            QUA 0480
      MMM(II)=1                                                       QUA 0490
      GO TO 91                                                        QUA 0500
   90 MMM(II)=0                                                       QUA 0510
   91 WRITE(3,1003)II,IH,IK,IL,MMM(II)                                QUA 0520
 1003 FORMAT(1H ,I5,5X,4I5)                                           QUA 0530
      GO TO 8                                                         QUA 0540
   93 READ(NTAP)                                                      QUA 0550
      WRITE(3,1004)                                                   QUA 0560
 1004 FORMAT(1H ,'I AM HERE')                                         QUA 0570
    5 I=0                                                             QUA 0580
      IN=0                                                            QUA 0590
    6 READ(NTAP,END=60)NA,NB,ES,PS                                    QUA 0600
C     CALCULATE PROBABILITIES.............                            QUA 0610
      VAL=ABS(ES)                                                     QUA 0620
      ARG=SIGMA*VAL                                                   QUA 0630
      PROB=0.5+0.5*TANH(ARG)                                          QUA 0640
      PROB=PROB*VAL/ES                                                QUA 0650
      IF(NA)20,20,7                                                   QUA 0660
    7 IF(NA.GT.MH)GO TO 6                                             QUA 0670
      IF(NB.GT.MH)GO TO 6                                             QUA 0680
      IZ=IZ+1                                                         QUA 0690
      NNA(IZ)=NA                                                      QUA 0700
      NNB(IZ)=NB                                                      QUA 0710
      SIGG(IZ)=PROB                                                   QUA 0720
      IF(IZ.LT.8)GO TO 23                                             QUA 0730
      WRITE(3,1006)(NNA(N),NNB(N),SIGG(N),N=1,8)                      QUA 0740
```

```
 1006 FORMAT(1H ,8(2I4,F5.3,2X))                                    QUA 0750
      IZ=0                                                          QUA 0760
   23 IN=IN+1                                                       QUA 0770
      IF(IN.GT.100)GO TO 6                                          QUA 0780
      I=I+1                                                         QUA 0790
      N1(I)=NA                                                      QUA 0800
      N2(I)=NB                                                      QUA 0810
      A(I)=PROB                                                     QUA 0820
      GO TO 6                                                       QUA 0830
   20 NB=NB-1                                                       QUA 0840
      IF(NB.GT.MK)GO TO 60                                          QUA 0850
      DO 21 N=1,I                                                   QUA 0860
      IF(MMM(NB).NE.1)GO TO 92                                      QUA 0870
      IF(N1(N).EQ.0)GO TO 92                                        QUA 0880
C     OUTPUT EEE-TRIPLES.....................                      QUA 0890
      WRITE(NOTAP)NB,N1(N),N2(N),A(N)                               QUA 0900
   92 DO 21 K=1,I                                                   QUA 0910
      IF(N.GE.K) GO TO 21                                           QUA 0920
C     CALCULATE QUADRUPLES...........                               QUA 0930
      SIGN=A(N)*A(K)                                                QUA 0940
      ASIGN=ABS(SIGN)                                               QUA 0950
      IF(ASIGN.LT.AMIN)GO TO 21                                     QUA 0960
C     OUTPUT QUADRUPLES...................                          QUA 0970
      WRITE(IOTAP)N1(N),N2(N),N1(K),N2(K),SIGN                      QUA 0980
   24 ND=ND+1                                                       QUA 0990
   22 FORMAT(1H ,4I5,F10.2)                                         QUA 1000
   21 CONTINUE                                                      QUA 1010
      IF(NA)60,5,5                                                  QUA 1020
   60 WRITE(3,999)ND                                                QUA 1030
  999 FORMAT(1H ,'TOTAL NUMBER OF QUADS=',I9)                       QUA 1040
      END                                                           QUA 1050
```

APPENDIX B. A LISTING OF RELATE

```
(SUBRG,STRG):                                                          REL00010
  RELATE: PROC OPTIONS(MAIN);                                          REL00020
/* ***************************************************************** REL00030
   RELATE: A PL-1 PROGRAM TO CALCULATE THE SIGNS OF THE E'S USING THE  REL00040
           QUADRUPLE PRODUCT METHOD.........L.L.MARTIN                 REL00050
                                                                       REL00060
    THIS PROGRAM REQUIRES THE FOLLOWING INPUT INFORMATION:             REL00070
   1) AOFS-THE CUTOFF PROBABILITY-USUALLY THE SAME AS AMIN IN QUADS    REL00080
   2)NOES-THE LARGEST SERIAL NUMBER TO BE CONSIDERED<200               REL00090
   3)NTOTCY-TOTAL NO. OF CYCLES TO BE DONE                             REL00100
   4)ITRIC-1 IF PROCEDURE CROSS IS TO BE AVOIDED-ONLY USED IN          REL00110
  EARLY STAGES OF A TRICLINIC SOLUTION                                 REL00120
   5)NOSI-NO. OF SIGNED E'S TO BE INPUT                                REL00130
   THE FORMAT USED IS F(5,3),4 F(5)                                    REL00140
         THE REMAINDER OF THIS CARD AND ANY OTHER CARDS HAVE           REL00150
       THE SIGNED SERIAL NUMBERS OF THE INPUT E'S                      REL00160
   WITH FORMAT N F(5)                                                  REL00170
   IN ADDITION, THE TWO TAPES WRITTEN IN QUADS ARE NEEDED              REL00180
***************************************************************** */REL00190
   DCL TITLE CHAR(80); DCL IOTAP FILE SEQUENTIAL;                      REL00200
  DCL CARD CHAR(80);                                                   REL00210
   DCL NIN(*)  CTL;                                                    REL00220
   DCL NOES,LA,II,JJ,NTOTCY,NIL,JA,NINA,NINB,NOSI;                     REL00230
   DCL ARRAY(198,198) FLOAT DEC(6) EXTERNAL;                           REL00240
   DCL AEQ,AOFS,CUM,DPROB;                                             REL00250
  DCL  ABEL(7) LABEL;                                                  REL00260
  DCL NCYCLES INITIAL(1);                                              REL00270
    DCL 1 QUAD,2 NA(4) FIXED BINARY(31),2 SIGN;                        REL00280
    DCL KIND;                                                          REL00290
/*   INPUT INFORMATION  */                                             REL00300
     GET EDIT(TITLE)(A(80));                                           REL00310
   PUT EDIT(TITLE)(SKIP, A(80));                                       REL00320
         GET EDIT(AOFS,NOES,NTOTCY,ITRIC,NOSI)(F(5,3),4 F(5));         REL00330
  PUT EDIT('PROB. LIMIT=',AOFS,'NO. OF E S=',NOES,'NO. OF CYCLES=',    REL00340
    NTOTCY,'NO. OF INPUT SIGNS',NOSI)(SKIP,A(12),F(5,3),A(11),F(5),    REL00350
     A(14),F(5),A(19),F(5));                                           REL00360
      ARRAY=0.0;                                                       REL00370
```

```
    ON ENDFILE(IOTAP) GO TO NUEQUAL;                                          REL00380
   IF NOSI=0 THEN GO TO  CYCLE;                                               REL00390
   ALLOCATE  NIN(NOES);                                                       REL00400
    NIN=0;                                                                    REL00410
    DO N=1 TO NOSI; GET EDIT(NIN(N))( F(5)); END;                             REL00420
 CYCLE: IF NCYCLES¬=3 THEN GO TO CYCLE1; IF NOSI=0 THEN GO TO CYCLE1;         REL00430
  DO N=1 TO NOSI; DO J=N TO NOSI;                                             REL00440
        NINA=ABS(NIN(J)); NINB=ABS(NIN(N));                                   REL00450
      ARRAY(NINA,NINB)=((NIN(J)*NIN(N))/(NINA*NINB));                         REL00460
      ARRAY(NINB,NINA)=((NIN(J)*NIN(N))/(NINA*NINB));                         REL00470
    END;                                                                      REL00480
   PUT EDIT(  NIN(N))(SKIP,  F(5));  END;                                     REL00490
  CYCLE1:  DO N=1 TO NOES; ARRAY(N,N)=1.0;    END;                            REL00500
ST: READ FILE(IOTAP) INTO (QUAD);                                             REL00510
/*   START CALCULATION OF THE SIGNS   */                                      REL00520
   DO K=1 TO 4; IF NA(K)>NOES THEN GO TO ST;                                  REL00530
      IF NA(K)=0 THEN GO TO ST; END;                                          REL00540
     DO L=1 TO 3; DO N=2 TO 4;      KIND=0;                                   REL00550
       IF L>= N THEN GO TO CONT;                                              REL00560
    CALL CHECK;                                                               REL00570
       IF KIND=1 THEN GO TO LABLER;                                           REL00580
       ELSE GO TO CONT;                                                       REL00590
LABLER: NIL=(L+2*N)-4;                                                        REL00600
   GO TO ABEL(NIL);                                                           REL00610
   ABEL(1): JA=NA(3); LA=NA(4); GO TO SIGNER;                                 REL00620
   ABEL(3): JA=NA(2); LA=NA(4); GO TO SIGNER;                                 REL00630
   ABEL(4): JA=NA(1); LA=NA(4); GO TO SIGNER;                                 REL00640
   ABEL(5): JA=NA(2); LA=NA(3); GO TO SIGNER;                                 REL00650
   ABEL(6): JA=NA(1); LA=NA(3); GO TO SIGNER;                                 REL00660
   ABEL(7): JA=NA(1); LA=NA(2); GO TO SIGNER;                                 REL00670
   ABEL(2): PUT EDIT(' ERROR IN SEARCH')(SKIP,A(16)); GO TO OUT;              REL00680
SIGNER: IF ARRAY(JA,LA)=0 THEN GO TO ASSIG; BCUM=ABS(ARRAY(JA,LA));           REL00690
     ACUM=ABS(CUM);  IF ARRAY(JA,LA)*CUM<0.0 THEN GO TO DIFFER;               REL00700
    DPROB=1.0-ACUM-BCUM+2.0*ACUM*BCUM;                                        REL00710
   CUM=(CUM*ACUM*BCUM)/(DPROB*ACUM);                                          REL00720
       GO TO ASSIG;                                                           REL00730
 DIFFER: CUM=0;                                                               REL00740
```

```
  ASSIG: ARRAY(JA,LA)=CUM;                                              REL00750
         ARRAY(LA,JA)=CUM;                                              REL00760
 CONT: END; END;  GO TO ST;                                             REL00770
/*  DETEMINATION OF SIGNIFICANCE OF E RELATIONS  */                    REL00780
 NUEQUAL:  DO II=1 TO NOES; DO JJ=1 TO NOES;                            REL00790
           IF II>=JJ THEN GO TO ELOOP;                                  REL00800
                 AEQ=ARRAY(II,JJ); IF ABS(AEQ)>AOFS THEN                REL00810
/*   OUTPUT OF RELATED E'S      */                                      REL00820
           PUT EDIT(' THE SIGN OF',II,'EQUALS THE SIGN',JJ,'***',AEQ,   REL00830
            'PROBS')(SKIP, A(12),F(4),A(15),F(4),A(3),F(8,4), A(5));    REL00840
          ELSE DO; ARRAY(II,JJ)=0.0;  ARRAY(JJ,II)=0.0; END;           REL00850
    ELOOP: END; END;                                                    REL00860
 SKIP3:   NCYCLES=NCYCLES+1;                                            REL00870
    IF ITRIC=1 & NCYCLES< NTOTCY THEN GO TO TRIC;                       REL00880
     CALL PARITY;                                                       REL00890
        IF NCYCLES>NTOTCY THEN GO TO OUT;                               REL00900
     CALL CROSS;                                                        REL00910
  TRIC: CLOSE FILE(IOTAP);                                              REL00920
           PUT EDIT( '  END OF CYCLE',NCYCLES)(SKIP, A(14),F(5));       REL00930
      GO TO CYCLE;                                                      REL00940
/*   CHECK: PROCEDURE FOR CALCULATING PROBABILITIES */                  REL00950
 CHECK: PROC;                                                           REL00960
           CUM=ARRAY(NA(L),NA(N));                                      REL00970
     CUM=CUM*SIGN;                                                      REL00980
           IF ABS(CUM)>0.80 THEN KIND=1;                                REL00990
          RETURN; END CHECK;                                            REL01000
/*   CROSS: PROCEDURE TO RELATE E'S EQUAL TO A COMMON                   REL01010
      E BUT NOT EQUAL TO EACH OTHER    */                              REL01020
 CROSS: PROC;                                                           REL01030
   DCL IA,IB,IC,ID;                                                     REL01040
   DCL AJ,BJ,CJ,DJ,EJ,FJ,GJ;                                           REL01050
   DCL CRS(9); DCL NCR(9),MCR(9); DCL KKK INITIAL(0);                   REL01060
  PUT EDIT('OUTPUT FROM CROSS CHECK IN CYCLE',NCYCLES)(SKIP, A(32)      REL01070
            ,F(3));                                                     REL01080
    DO IA=1 TO NOES; ID=IA+1; DO IB=ID TO NOES;                         REL01090
         AJ=ARRAY(IA,IB); IF ABS(AJ)<AOFS THEN GO TO DONE;              REL01100
     DO IC=1 TO NOES; IF IC=IA|IC=IB THEN GO TO DONEA;                  REL01110
```

```
      BJ=ARRAY(IB,IC); IF ABS(BJ)<AOFS THEN GO TO DONEA;                REL01120
      CJ=ARRAY(IA,IC);                                                 REL01130
     IF ABS(CJ)<0.01 THEN DO; CJ=0.5; GO TO BEGAN;    END;             REL01140
  IF CJ*AJ*BJ <0.0 THEN DO;                  ARRAY(IA,IC)=0.0;         REL01150
        ARRAY(IC,IA)=0.0;  ARRAY(IC,IB)=0.0; ARRAY(IC,IA)=0.0;         REL01160
        ARRAY(IB,IC)=0.0;  ARRAY(IA,IC)=0.0;                           REL01170
    PUT EDIT('INCONSISTENCY INCOUNTERED',IA,IB,IC)(SKIP,A(25),         REL01180
          3 F(5));  GO TO DONEA; END;                                  REL01190
BEGAN:FJ=ABS(AJ*BJ); EJ=ABS(CJ);  GJ=1.0-FJ-EJ+2.0*FJ*EJ;              REL01200
   IF GJ=0.0 THEN PUT EDIT(FJ,EJ,IA,IB,IC)(SKIP,2 F(5,3),3 F(5));      REL01210
      IF FJ>1.01|EJ>1.01 THEN DO; PUT EDIT(' ERROR IN CROSS ',FJ,      REL01220
      IA,IB,IC)(SKIP,A(16),2 F(6,3),3 F(5)); GO TO DONEA; END;         REL01230
   IF FJ<0.01 THEN FJ=1.0;                                             REL01240
     DJ=(FJ*EJ*AJ*BJ)/(GJ*FJ);                                         REL01250
   IF ABS(DJ)>0.98 THEN DO;                                            REL01260
      KKK=KKK+1;                                                       REL01270
            ARRAY(IA,IC)=DJ;                                           REL01280
            ARRAY(IC,IA)=DJ;                                           REL01290
    IF NCYCLES>NTOTCY THEN DO;                                         REL01300
  NCR(KKK)=IA;  MCR(KKK)=IC; CRS(KKK)=DJ;                              REL01310
    IF KKK=9 THEN DO;                                                  REL01320
   PUT EDIT((NCR(IK),'=',MCR(IK),CRS(IK),'**' DO IK=1 TO 9))           REL01330
     (SKIP,9( F(3),A(1),F(3),F(5,3),A(2)));  KKK=0; END; END; END;     REL01340
     DONEA: END;  DONE: END; END; RETURN; END CROSS;                   REL01350
/*   PARITY: PROCEDURE TO DETERMINE ABSOLUTE SIGNS OF EEE TYPE E'S  */ REL01360
  PARITY: PROC;                                                        REL01370
    DCL NOTAP FILE SEQUENTIAL;                                         REL01380
   DCL 1 EVENS,2 NNN(3) FIXED BINARY(31),2 PRD;                        REL01390
   DCL JN INITIAL(0);                                                  REL01400
  DCL INN(300,3); DCL PROD(300);                                       REL01410
  DCL ABCD,DET,ASUM,BOTT;                                              REL01420
   DCL SUM INITIAL(0.0);                                               REL01430
   DCL I INITIAL(1);                                                   REL01440
    DCL  CAR  CHAR(1);                                                 REL01450
     INN(1,1)=99;                                                      REL01460
     ON ENDFILE(NOTAP) GO TO PINK;                                     REL01470
  RED: READ FILE(NOTAP) INTO(EVENS); IF NNN(1)>NOES|NNN(1)=0 THEN      REL01480
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                    GO TO PINK;                                                  REL01490
     IF NCYCLES=NTOTCY THEN PUT EDIT(EVENS)(SKIP,3 F(5),F(5,3));                 REL01500
       DO K=1 TO 3; IF NNN(K)>NOES THEN GO TO RED; END;I=I+1;                    REL01510
     INN(I,1)=NNN(1); INN(I,2)=NNN(2); INN(I,3)=NNN(3); PROD(I)=PRD;             REL01520
SKIP2:IF INN(I,1)¬=INN(I-1,1) THEN GO TO WORK;                                   REL01530
 BLUE: ABCD=ABS(ARRAY(INN(I,2),INN(I,3))*PRD); ASUM=ABS(SUM);                    REL01540
     IF SUM=0.0 THEN GO TO STRIKE; IF ABCD<0.01 THEN GO TO RED;                  REL01550
                    IF SUM*ARRAY(INN(I,2),INN(I,3))*PRD>0.0 THEN                 REL01560
   SUM=(SUM*ASUM*ABCD)/((1.0-ASUM-ABCD+2.0*ASUM*ABCD)*ASUM); ELSE                REL01570
         SUM=0.0; GO TO RED;                                                     REL01580
  STRIKE:SUM=ARRAY(INN(I,2),INN(I,3))*PRD; GO TO RED;                            REL01590
 WORK: IF SUM>0.0 THEN CAR='+'; ELSE CAR='-';                                    REL01600
      PUT EDIT (' THE PROBABILITY THAT',INN(I-1,1),' IS ',CAR,' IS',             REL01610
        SUM)(SKIP,A(21),F(3),A(4),A(1),A(3),F(5,3));                             REL01620
      IF ABS(SUM)<0.99 THEN GO TO SMALL;                                         REL01630
    DO N=1 TO I-1;                                                               REL01640
          DET=ARRAY(INN(N,3),INN(N,2));                                          REL01650
          IF DET=0.0 THEN DO; DET=PROD(N)*SUM;  GO TO EVALU; END;                REL01660
          IF DET*SUM*PROD(N)<0.0 THEN DO; DET=0.0; GO TO EVALU; END;             REL01670
      BOTT=1.0-ABS(PROD(N)*SUM)-ABS(DET)+2.0*PROD(N)*SUM*DET;                    REL01680
        DET=(PROD(N)*DET*SUM*DET)/(BOTT*ABS(DET));                               REL01690
  EVALU:  IF DET> ADFS THEN DO;                                                  REL01700
          ARRAY(INN(N,3),INN(N,2))=DET;                                          REL01710
          ARRAY(INN(N,2),INN(N,3))=DET;    END;                                  REL01720
        PUT EDIT(DET)(SKIP, F(6,3)); END;                                        REL01730
 SMALL: IF JN=1 THEN GO TO COMP;                                                 REL01740
     INN(1,*)=INN(I,*); PROD(1)=PROD(I); I=1; SUM=0.0; GO TO BLUE;               REL01750
 PINK: JN=1; IF I=1 THEN I=2; GO TO WORK;                                        REL01760
     COMP: CLOSE FILE (NOTAP); RETURN; END PARITY;                               REL01770
OUT: END RELATE;                                                                 REL01780
```

APPENDIX C. RESEARCH PROPOSALS

In this appendix are presented a few proposals of additional structure work which are of interest to the author. These are intended to be preliminary in nature and no experimental details will be given.

It would seem unlikely in solution that the bridging NTA oxygen-rare earth bonds would be formed. Instead, these coordination sights would probably be occupied by solvent molecules. The act of crystallization could well involve replacement of these solvent molecules which are then trapped in the forming lattice. It would be of interest to carry out a diffraction study of these complexes in aqueous solution to test this hypothesis. In addition, the large number of apparent hydrogen bonds would make a neutron diffraction study of interest.

Most of the rare earth compounds which have been studied by diffraction techniques have been complexes formed with highly electronegative species such as oxygen or chlorine atoms. To be better able to evaluate the role of covalent bonding, complexes formed with less electronegative ligands, such as urotropin or thiocyanate, could be studied.

Many antibiotics are of moderate molecular weight and are crystalline in nature. Therefore, they would lend well to study by diffraction techniques. In addition, many are well characterized as to their mode of inhibition of bacterial growth. Several antibiotics with similar modes

of inhibition could be selected for structural study to determine what features they have in common. Idealistically, this information could be used in the synthesis of biologically active analogs.