1970

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Recommended Citation

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71-14,258

SCHOBERT, Harold Harris, 1943-
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Iowa State University, Ph.D., 1970
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THE PREPARATION AND CHARACTERIZATION OF SOME ALKANETHIOLATOOSMIUM COMPOUNDS

by

Harold Harris Schobert

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Ames, Iowa

1970

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INTRODUCTION

During the last decade, trimeric rhenium(III) chloride, together with anionic species derived from it, has been the subject of considerable interest to inorganic chemists. In view of this interest, it is natural to look about for systems which might contain analogs of this well-known rhenium compound.

The elements which adjoin rhenium in the periodic table are tungsten and osmium. Of these two elements, the chemistry of osmium has been explored to a much smaller extent than that of tungsten. Osmium is an intriguing element; lying as it does almost in the center of the 5d transition series, its chemistry is not wholly typical of the better-known earlier elements of the series, nor is it typical of the better-known later elements.

Efforts during the course of this study to synthesize osmium halide and sulfide compounds isoelectronic and isostructural with rhenium(III) chloride were not successful. An investigation of the possibility of employing coordination compounds of osmium with organosulfur ligands as precursors for the synthesis of rhenium analogs led to the discovery that these compounds themselves represented an area of osmium chemistry almost wholly unexplored by the techniques of modern inorganic chemistry.

Coordination compounds of osmium in which the ligand is an organic compound containing one or more sulfur atoms have a central role in the chemistry of osmium. Reagents such as 1-thiocarbamido-3-methylpyrazol-5-one, 2-mercaptobenzimadazole, 5-mercapto-1,3,4-thiadiazolidine-2-thione, and 2-mercaptobenzothiazole are finding wide use in the separation, analysis, and recovery of osmium. In a far different field, the well-known osmium blacks, which are very important reagents in histochemistry, have now been shown (1) to be coordination polymers of osmium in which osmium is coordinated with sulfur atoms in the naturally-occurring compounds present in the stained tissues.

In both these disparate though important areas of osmium chemistry, the ligands involved are very complex in the sense that several possible coordination sites are available and in the sense that the structures of the ligands are frequently quite complicated. As a result of this, it is extremely difficult to make a good interpretation of many of the important properties, such as the absorption spectra, of these complexes.

Despite this fact, no study had ever been undertaken to investigate the synthesis and properties of osmium compounds with chemically simple organosulfur ligands such as the lower alkanethiols. It was the purpose of this investigation to prepare some representative coordination compounds of osmium containing alkanethiolato ligands and to study and interpret some of their fundamental properties, such as the degree of polymerization, magnetic behavior, and absorption spectra.

REVIEW OF PREVIOUS WORK

Zeise (2) discovered the first alkanethiol, ethanethiol, in 1834, and prepared the first metal thiolates. Since that time a host of other alkanethiols have been synthesized or discovered to exist in nature. Many of these thiols have been used to prepare the corresponding metal thiolates. Such compounds have, at one time or another, been prepared for more than thirty metals.

One of the important factors which has influenced the search for and study of metal thiolates has been the broad range of industrial applications of these compounds. Metal thiolates have been manufactured for such diverse purposes as these: antifouling agents in paint (3), decorative materials for glass and ceramic ware (4, 5, 6), fungicides (7), thickeners and stabilizers for lubricants (8, 9), processing agents for elastomers (10), anti-arthritic drugs (11), and as stabilizers in polyvinyl chloride (12).

An unfortunate consequence of the concentration of investigations of metal thiolates in the area of applied chemistry has been that only very few of the many such compounds known have ever been the subjects of a comprehensive characterization study. During the twenty-year period from 1945 to 1965, approximately two-thirds of the articles on M(SR)x compounds appearing in Chemical Abstracts were taken from the patent literature, where characterization is often confined to melting point determinations and solubility studies. Only in recent years, with studies such as those of Abel and Crosse (13) on the hexameric nickel thiolates, Kunchur (14) on the analogous palladium compounds, Hughes and Dintzis (15) on dimeric mercury mercaptalbumins, and Akerstrom (16, 17) on octameric and dodecameric silver thiolates, has much attention been given to securing a deeper understanding of the physical and chemical nature of the many fascinating metal thiolates.

It is not surprising that with the great variety of metal thiolates which have been synthesized so too are the synthetic methods various and many. It is however possible to state without dogmatism that the reaction of a metal chloride or metal oxide with an alkanethiol, either neat or in one of the common organic solvents, at temperatures between ambient and the boiling temperature of the solvent, suffices well for the preparation of a great many of metal thiolates. A few specific examples include the use of mercuric chloride by Petrunkin (18); calcium chloride and barium oxide by Klemchuk and Dexter (12); cuprous chloride by Fox (19), Adams and Ferretti (20), Warner (3), and Wendler, Hoffsommer, and Taub (21); cuprous oxide by Reifschneider and co-workers (22); gold halides by Fitch (4, 5, 6); zinc oxide by Minoura (23), Millikan and Fronczak (8), and Verbanc (10); and zinc chloride by Steiger (24).

The catholicity of the above reaction notwithstanding, variations of this method abound in the literature. That most frequently encountered is the employment of metal compounds other than the chloride or oxide as starting materials. For example, Moore (11) and later Fitch (6) employed potassium tetrahaloaurate(III) compounds for the preparation of gold thiolates. Silver nitrate has been used by Akerstram (16, 17) and Belohradsky and co-workers (25). Radcliffe (26) and Klemchuk and Dexter (12) used cadmium acetate; lead acetate was used by Petrunkin (18). Alkali metal hydroxides are frequently employed for the synthesis of alkali thiolates, one recent study having been carried out by Zelvenskii and co-workers (27). Gilman and Abbott (28) used thallous hydroxide to prepare thallium(I) methanethiolate; in a later study Gilman and his co-workers (29) synthesized uranium(IV) ethanethiolate by starting with uranium(IV) diethylamide. Mehrotra, Gupta, and Sukhani (30, 31) made use of germanium and tin isopropoxides. Neuberg and Grauer (32) synthesized mercury ethanethiolate from mercuric cyanide. Imaizumi (33) reported the preparation of small quantities of nickel ethanethiolate from Raney nickel, while Dittrich (34) has claimed the preparation of cuprous thiolates by reacting copper with the appropriate thiols in the presence of oxygen. Kalal and Mostecky (35) prepared thiolates from sodium hydride, sodium amide, and calcium carbide.

It has also been found possible to employ organosulfur compounds other than thiols for the preparation of metal thiolates. Lechler (36), and, later, von Konek (37) reported the preparation of mercury thiolates by the reaction of mercury with the corresponding dialkyldisulfides. Steiger (38) extended this work to the preparation of the analogous zinc compounds. Abel and Crosse (13) prepared nickel thiolates by reacting nickel salts with dimethyltinbis(alkanethiolates). Nickel and cobalt thiolates were prepared by Siddhanta and Banerjee (39) by the reaction of the metal salts with 2-methyl-2-thiopseudourea. The reaction of mercuric acetate with benzophenone diphenylmercaptole was reported by Mukaiyama and Katsuyama (40) to yield mercuric thiophenolate. Chabrier and Renard (41) reported the preparation of lead methanethiolate from the reaction of lead acetate with the methiodides of morpholine thioamides. Razumovskaya and her co-workers (42) found copper butanethiolate to be one of the products arising from the reaction of copper metal with tributyl trithiophosphite.

Despite the wide interest in the synthesis and applications of metal thiols, the reaction of osmium compounds with organosulfur compounds has received little attention. Perhaps the first mention of such a reaction occurs in the work of Phillips (43, 44) on the chemical properties of gases. Mention is made in his second paper (44) of the reaction of osmium tetroxide with methanethiol. Unfortunately, the only information reported by Phillips on the characterization of the product of this reaction is the terse comment "schwarze Fallüng".

The reaction of osmium tetroxide with organic compounds has been studied from the time of Tennant (45) but no attention was given by the early workers to the nature of the products of these reactions. It was the work of Schultze (46) which introduced the use of osmium tetroxide as a histochemical reagent. The black material resulting from the action of osmium tetroxide staining solutions was called, simply "osmium black". Osmium black was widely regarded to be either finely divided osmium metal or a hydrated form of osmium dioxide; during the early years of this century a vitriolic debate raged in the literature concerning whether the osmium black was in fact the metal or the dioxide.

Following the invention of the electron microscope, osmium tetroxide quickly attained the premier position as a fixative, particularly for ultrathin sections. It was found (47) that in these thin sections, of roughly 100 to 300Å thickness, the osmium black had the most important role in contrast formation. In fact, in the very thinnest sections it is only the osmium which can be seen. Consequently it became of great importance to know what structures in the tissues were represented by the deposits of osmium black.

This in turn depended upon the reaction of osmium tetroxide with the various functional groups present in the biological substances.

Some of the first studies were carried out by Bahr (47, 48). He investigated the reaction of osmium tetroxide with many functional groups, of which the -SH group was one. Bahr reported that the sulfhydryl group (as, for example, in compounds such as thioglucollic acid and glutathione) reacted immediately with osmium tetroxide. Indeed, the sulfhydryl group reacted faster than any of the other functional groups which Bahr investigated. Bahr still regarded the reduction product of osmium tetroxide to be a lower oxide or the metal.

Later, Hanker and his co-workers (1, 49, 50) began to investigate the nature of osmiophilic reagents. In their early investigations (49, 50), Bahr's findings (47, 48) that thiols reduced osmium tetroxide more readily than any alternative functional group were substantiated. However it was still believed that the osmium black was probably the hydrated dioxide.

During one of the investigations (50) it was observed that the reaction product, that is, the osmium "black", actually exhibited different colors depending upon the nature of the organic reactant. At first this was believed to be due to the presence of different oxidation states of osmium. It was later found (1) that the "osmium black" was not a single, discreet chemical entity but rather that a whole family of osmium blacks existed. These were found to be coordination polymers of osmium which differed in the nature of the ligand.

The polymeric osmium compounds arising from the reaction of osmium tetroxide with naturally occurring compounds containing thiol functional groups proved to be highly insoluble materials. This fact prevented much characterization work from being carried out. Consequently Hanker and his group synthesized some analogs to use as model compounds.

The Hanker group found (1) that the reaction of osmium tetroxide with 3-mercapto-1,2-propanediol leads to the formation of osmium tetrakis(1,2-propanediol-3-thiolate), which was found to be a tetramer. Using different concentrations of reagents it was found possible to synthesize a pentamer of the same $Os(SCH_2CHOH\ CH_2OH)_4$ unit. While other workers (51) had suspected that osmium might form polymers, this work of Hanker represented the first characterization study of polymeric osmium compounds of this type (that is, coordination compounds other than the well-known polymeric carbonyl compounds of osmium).

It remained until the investigation reported here for coordination polymers of osmium with even simpler ligands to be studied.

EXPERIMENTAL

Materials

Osmium metal was obtained as a powder from Englehard Industries, Inc. A sample from the batches received was treated with hydrogen at 500°C for five hours; after this treatment no weight loss was observed and the material was regarded to be free of oxygen.

Chlorine gas was obtained in lecture bottles from The Matheson Co. It was purified by bubbling through concentrated sulfuric acid or by freezing and outgassing under vacuum.

Oxygen and hydrogen gases were obtained in standard laboratory cylinders. A check for moisture was made by passing a portion of the gas from each new cylinder through a six-inch column of indicating Drierite.

Thionyl chloride and thionyl bromide were obtained as reagent grade chemicals from the Matheson, Coleman, and Bell Co. They were vacuum distilled prior to use.

Methanethiol was obtained from Eastman Organic Chemicals. Ethanethiol was obtained from Eastman Organic Chemicals and from the Matheson, Coleman and Bell Co. Butanethiol was obtained from the Matheson, Coleman and Bell Co. and from the Aldrich Chemical Co. Toluene-3,4-dithiol was obtained from the Matheson, Coleman, and Bell Co. Dodecylbenzyl mercaptan was a gift of Evans Chemetics, Inc. These reagents were frozen and outgassed prior to use. Methanethiol and ethanethiol were also vacuum distilled.

Organic solvents such as carbon tetrachloride, tetrahydrofuran, and similar materials were obtained as reagent grade chemicals from local stocks. For use as solvents in syntheses these solvents were outgassed and vacuum distilled. For general laboratory purposes they were used without special purification.

All other compounds were employed as reagent grade chemicals with no special purification.

Synthesis

Hexakis(ethanethiolato)diosmium, $Os_2(SC_2H_5)_6$. A solution of osmium tetroxide in carbon tetrachloride (2 gm. OsO_4 per 40 ml.) was treated with 30 ml. neat ethanethiol. The solution was allowed to stand at room temperature in a stoppered flask for one day. The carbon tetrachloride and excess ethanethiol were then removed by vacuum distillation. The solid residue was treated with successive 20 ml. portions of tetrahydrofuran until no more dissolved; the portions of tetrahydrofuran were combined and the solvent was removed by vacuum distillation. The product was obtained as a brown powder. Yield 42%. Anal: Calcd. for $Os_2(SC_2H_5)_6$: Os, 50.9; S, 25.7; C, 19.3; H, 4.1. Found: Os, 51.8; S, 24.6; C, 23.5; H, 4.8; S/Os=2.82.

Osmium bis(ethanethiolate), $Os(SC_2H_5)_2$. This compound was found in the same reaction as hexakis (ethanethiolato) diosmium. It was separated from $Os_2(SC_2H_5)_6$ by virtue of its insolubility in tetrahydrofuran. The product was obtained as a black powder. Yield 58%. Anal: Calcd. for $Os(SC_2H_5)_2$: Os, 61.0; S, 20.5; C, 15.4; H, 3.2. Found: Os, 59.2; S, 20.3; C, 17.6; H, 4.6; S/Os=2.04.

Osmium dioxide, OsO_2. A solution of 1.5 grams osmium tetrachloride in approximately 75 ml. distilled water was refluxed for four hours and was then allowed to stand overnight. The osmium dioxide was collected as black crystals by filtering the solution. Yield 97%. Anal. Calcd. for OsO_2: Os, 85.6. Found: Os, 84.2.

Osmium disulfide, OsS_2. Two grams of osmium metal and a large molar excess of sulfur were placed in a cylindrical Vycor tube, which was then evacuated and sealed. The tube was heated in a 450/800° gradient, positioned such that the osmium is at the end heated to 800°. The tube was heated in this manner for four hours. The product was formed as a brownish-black powder at the hot end. It was purified by heating to 400° under dynamic vacuum for two hours to ensure that all the excess sulfur was removed. Yield 100%. Anal. Calcd. for OsS_2: Os, 74.8; S, 25.2. Found: Os, 74.8; S, 25.2; S/Os=2.00.

Osmium tetrabromide, $OsBr_4$. One gram of osmium tetroxide was dissolved in 20 ml. of carbon tetrachloride and approximately 25 ml. of thionyl bromide was added. The solution was allowed to stand at room temperature for one week. The solvent and excess thionyl bromide were removed by vacuum distillation. The black solid obtained was heated to 150° under dynamic vacuum for six hours. The product finally was recrystallized from tetrahydrofuran. It was still contaminated with some thionyl bromide. Yield approximately 90%. Anal. Calcd. for $OsBr_4$: Os, 37.2; Br, 62.8. Found: Os, 32.5; Br, 64.8; Br/Os=4.7 (N.b.: Calcd. for $OsBr_4 \cdot 0.35\ SOBr_2$: Os, 32.8; Br, 64.6.)

Osmium tetrachloride, $OsCl_4$. Three procedures were employed. A.) Five grams of osmium metal were placed in the central compartment (C) of the apparatus shown in Figure 1. Chlorine was distilled into compartment A and outgassed. The tube was sealed and placed in a furnace where compartment C and the major portions of compartments B and D were heated to 500°. The chlorine was distilled back and forth by surrounding compartments A and E alternately with a slush bath of a mixture of 80% isopropanol-20% water. The reaction was allowed to proceed for 37 days, during which time the osmium tetrachloride collected in the cooler portions of the tube. Yield 70%. Anal. Calcd. for $OsCl_4$: Os, 57.2; Cl, 42.8. Found: Os, 57.2; Cl, 42.8; Cl/Os=4.00. B.) One gram of osmium dioxide was refluxed with 35 ml. thionyl chloride for one week in conventional laboratory apparatus. The

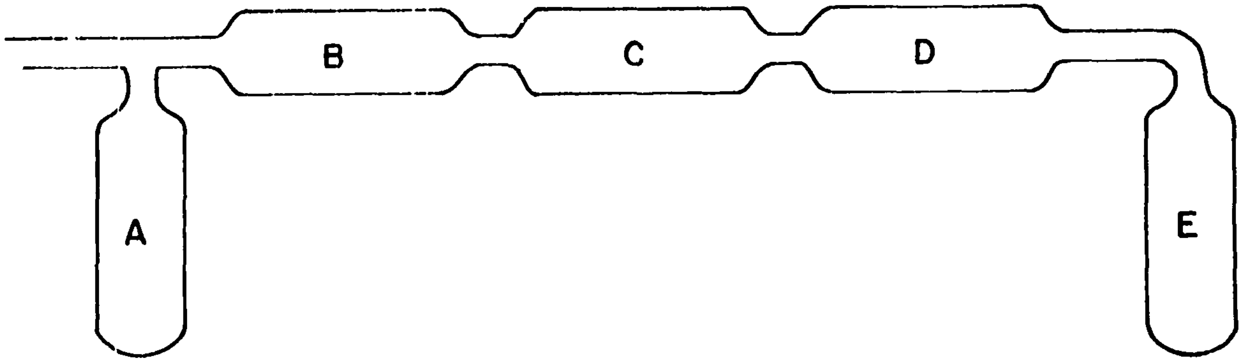

Figure 1. Apparatus for the high-temperature preparation of osmium tetrachloride

solution was filtered through a glass frit. The filtrate was evaporated to dryness by vacuum distillation of the thionyl chloride. Yield approximately 65%. C.) Osmium tetroxide was dissolved in a large excess of thionyl chloride (approximately 30 ml. $SOCl_2$ per gram of OsO_4). This solution was refluxed for three days, or, alternatively, allowed to stand at room temperature for one week. At the end of this time the excess thionyl chloride was removed by vacuum distillation. The product was a brownish-black, extremely hygroscopic solid, $OsCl_4 \cdot SOCl_2$ (Anal. Calcd. for $OsCl_4 \cdot SOCl_2$: Os, 42.1; Cl, 47.2. Found: Os, 41.8; Cl, 46.8; Cl/Os=6.) Heat treatment of this solid at 150° under dynamic vacuum for six to eight hours (until the product became free-flowing) yielded osmium tetrachloride as a black powder. Yield 95%. Anal. Calcd. for $OsCl_4$: Os, 57.2; Cl, 42.8. Found: Os, 57.1; Cl, 42.9; Cl/Os=4.00.

Osmium tetroxide, OsO_4. Apparatus corresponding to that shown in Figure 2 was assembled. One to three grams of osmium metal were weighed into a porcelain combustion boat, which was introduced into the tube in the furnace. The gas washing bottle was filled about half full with a 5% (by weight) solution of thiourea in 2N sulfuric acid. The U-trap was immersed in a dry ice-acetone bath. Oxygen gas was passed through the apparatus at a rate of approximately one bubble every two seconds, the rate being decreased in the

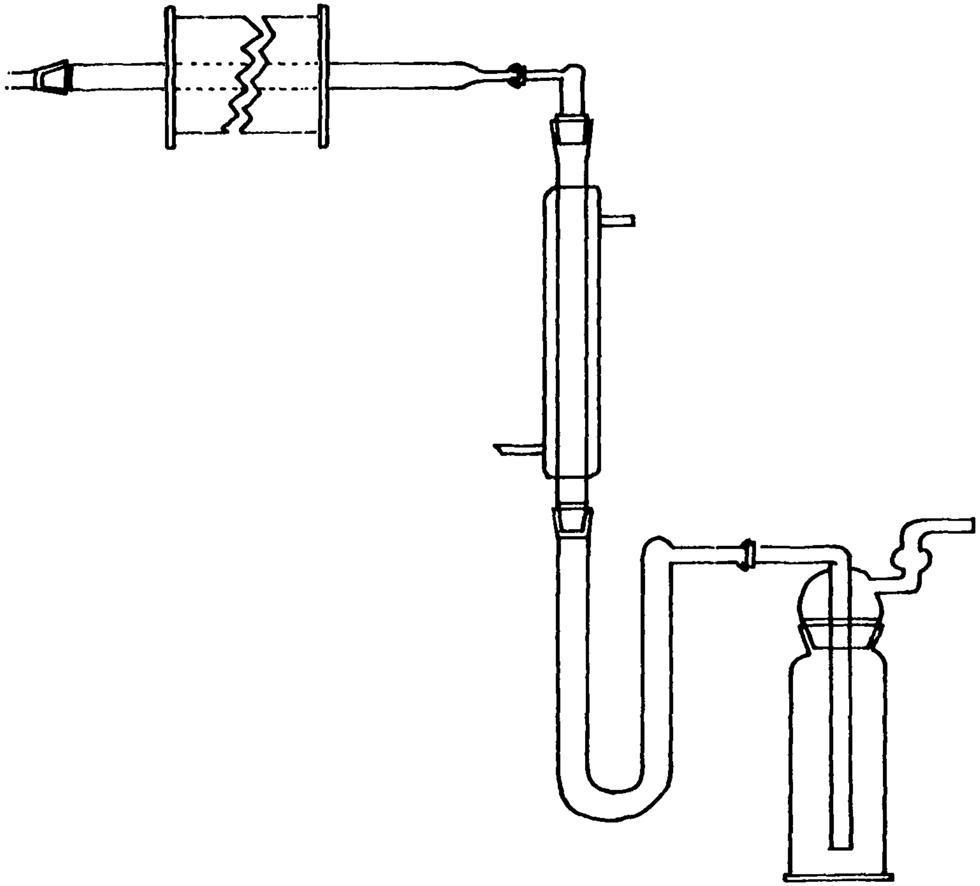

Figure 2. Apparatus for the preparation of osmium tetroxide

event of formation of a bright red color due to hexakis(thiourea)osmium(III) in the washing bottle. The metal was heated to 450-525° for six hours, during which time the product collected in the cooled portions of the apparatus. The yield of this experiment was never determined accurately because the product was almost always immediately used in a subsequent experiment to minimize the hazards of handling this extremely dangerous material.

Osmium tris(butanethiolate), $Os(SC_4H_9)_3$. A solution of one gram of osmium tetroxide in approximately 30 ml. carbon tetrachloride was treated with a large excess of butanethiol (approximately 25-30 ml.) This mixture was allowed to stand for two days at room temperature. The excess liquid was removed by vacuum distillation. The residue was a brown, greasy solid. This was heated to 200° for 12 hours while being subjected to a dynamic vacuum, giving a black, free-flowing powder. Yield 95% Anal. Calcd. for $Os(SC_4H_9)_3$: Os, 41.6; S, 21.4; C, 31.5; H, 5.9. Found: Os, 43.1; S, 21.4; C, 34.6; H, 5.3; S/Os=2.77.

Pentadeca-, hexadeca(butanethiolato)tetraosmium, $[Os(SC_4H_9)_{3.75-4.00}]_4$. One gram of osmium tetrachloride was dissolved in approximately 25-30 ml. of butanethiol. The solution was refluxed for two days, or, alternatively, was allowed to stand at room temperature for six or seven days. At the end of this time the excess liquid phase was removed by vacuum distillation. The solid material obtained was recrystallized several times from tetrahydrofuran until it no longer exhibited a greasy appearance. Yield (of mixture) 98%. Anal.: Calcd. for $Os_4(SC_4H_9)_{15}$: Os, 36.3; S, 22.9; C, 34.4; H, 6.4; for $Os_4(SC_5H_9)_{16}$: Os, 34.6, S, 23.4; C, 35.2; H, 6.6. Found (typical prep.): Os, 34.9; S, 23.3; C, 32.1, H, 5.6. S/Os=3.96.

Pentadeca-, hexadeca(ethanethiolato)tetraosmium, $[Os(SC_2H_5)_{3.75-4.00}]_4$. One to 1.5 grams of osmium tetrachloride was dissolved in a large excess (ca. 35 ml.) of neat ethanethiol. The solution was allowed to stand in a stoppered flask at room temperature for four to seven days. The product was recovered by removing the excess liquid by vacuum distillation. The product was recrystallized from tetrahydrofuran. Yield (of mixture) 100%. Anal.: Calcd. for $Os_4(SC_2H_5)_{15}$: Os, 45.3; S, 28.4; C, 21.5; H, 4.5; for $Os_4(SC_2H_5)_{16}$: Os, 43.8; S, 29.5; C, 22.1; H, 4.6. Found (typical prep.): Os, 45.6; S, 28.9; C, 20.2; H, 4.4. S/Os=3.76.

Pentadeca-, hexadeca(methanethiolate)tetraosmium. $[Os(SCH_3)_{3.75-4.00}]_4$. One gram of osmium tetrachloride was placed in a container made from a 6 to 8 inch piece of 15 mm Pyrex tubing. This tube was connected to the vacuum line and methanethiol was distilled in until the tube was half to two-thirds full. The methanethiol was frozen and outgassed and the tube was sealed. The system was allowed to warm up to room temperature and was allowed to stand for four to eight days. At the end of this time, the seal was broken and the excess methanethiolate was allowed to evaporate in the hood. The solid product was subjected to a dynamic vacuum for about two hours to insure that all methanethiol had in fact been removed. Yield (of mixture) 99%. Anal.: Calcd. for $Os_4(SCH_3)_{15}$: Os, 51.8; S, 32.8; C, 12.2; H, 3.2; for $Os_4(SCH_3)_{16}$: Os, 50.3; S, 34.0; C, 12.7; H, 3.2. Found (typical prep.): Os, 52.4; S, 34.4; C, 12.5; H, 2.8. S/Os=3.87.

Sodium ethanethiolate, $NaSC_2H_5$. Ethanethiol was slowly added to small pieces of sodium kept under an inert solvent (e.g., tetrahydrofuran). The reaction mixture was kept cool to avoid an obstreperous reaction. The product formed as a white precipitate recoverable by filtration. Excess unreacted sodium was removed by the "Pasteur method" (52); that is to say, by picking it out with fine tweezers. Yield 100%.

Analytical Procedures

Osmium. Two procedures were employed. The colorimetric analysis was used for the determination of osmium in the alkanethiolates, while the hydrogen reduction method was used for all other compounds. A.) Analysis by hydrogen reduction. A Pyrex tube fitted with ground joints at both ends was used for the reduction reaction. To one end was attached a gas washing bottle filled half full of distilled water. A sample of about 100-250 mg. was weighed accurately into a porcelain combustion boat, which was then introduced into the tube, placed so that it would be well inside the furnace. An adapter allowing connection to the hydrogen tank was attached to the free end. Hydrogen was passed through the apparatus, at a rate of about one bubble per second, for ten minutes. Then the furnace was turned on and heated to 450-500°. This temperature (and the hydrogen stream) were maintained for five hours. After this period of heating, the boat containing the sample was allowed to cool slowly in an atmosphere of hydrogen. Once cool, the boat, now containing osmium metal, was weighed accurately. Calculation of percentage of osmium was done by obvious means. The solution in the gas washing bottle was retained for halide or sulfide analysis. B.) Colorimetric Analysis. The apparatus used was a fairly common distillation apparatus: a round bottom boiling flask; a distilling head having a thistle-type addition funnel and drip tube in the side arm; and a condenser with outlet tube drawn to a smooth taper. It was of all-glass construction; the joints were lubricated by means of concentrated perchloric acid. A sample of 25-75 mg. was weighed accurately and transferred to the boiling flask.

The receiving vessel (a large test tube or small Erlenmeyer flask) was filled approximately two-thirds full of carbon tetrachloride. Thirty milliliters of an equivolumnar mixture of concentrated nitric and perchloric acids was added to the boiling flask. The resulting solution was boiled vigorously until all color due to the sample was destroyed; boiling was continued for an additional forty-five minutes beyond this point. Then the carbon tetrachloride in the receiving vessel was separated, after vigorous shaking, from the aqueous material which had distilled. The aqueous phase was extracted with another portion of carbon tetrachloride and was then discarded. The carbon tetrachloride portions were combined and shaken in a separatory funnel with successive 20 ml. aliquots of a 5% (by weight) solution of thiourea in 2N sulfuric acid until one of the aqueous aliquots did not take on a pink color (three or four such aliquots usually being required). The thiourea solution aliquots were combined and diluted to 100 ml. in a suitable volumetric flask. Two 5 ml. aliquots of this solution were in turn each diluted to 50 ml. in volumetric flasks. The absorbance of the resulting solutions was measured in 1 cm. cells at 480 and 540 mμ with a Beckman model DU spectrophotometer. The amount of osmium in the sample was read from a calibration curve, prepared by employing osmium disulfide as a standard. The calibration curves are given in Figure 3.

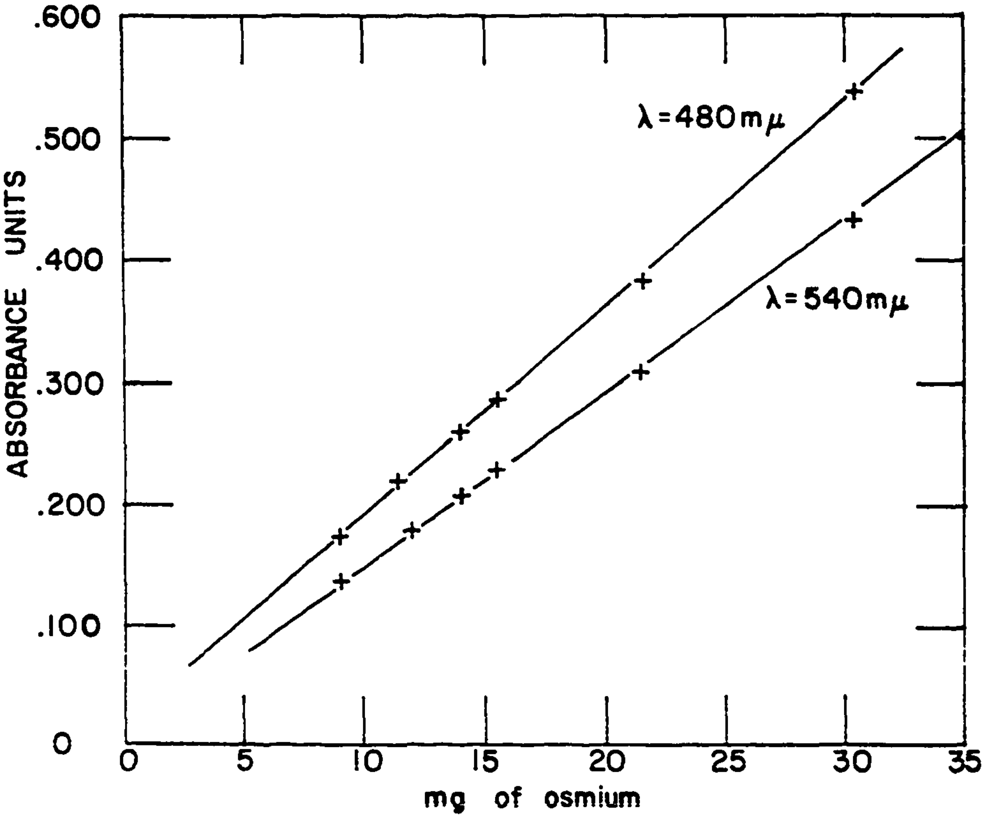

Figure 3. Calibration curves for the colorimetric determination of osmium

The solution remaining in the boiling flask was retained for sulfur analysis.

Carbon and hydrogen. Carbon and hydrogen analyses were performed by Mr. John Richard of the Analytical Services Group of the Ames Laboratory.

Halogen. Two procedures were employed. Chlorine was determined by the Volhard method and by potentiometric titration. Bromine was determined only by the former technique. Both methods are very well known and are widely discussed in the literature (53, 54) and hardly need discussion here. The potentiometric titration was performed using a silver wire and a glass electrode pair, with a Beckman model G pH meter used as a potentiometer.

Sulfur. The sulfur content of compounds analyzed by hydrogen reduction was determined by potentiometric titration as described previously. The sulfur content of the alkanethiolato-compounds was determined by a volumetric procedure. The residue in the boiling flask (from the colorimetric determination of osmium) was transferred to a 250 ml. Erlenmeyer flask. The solution was neutralized by cautious addition of solid sodium hydroxide; it was kept cool during this process by swirling the flask under a stream of water. Phenolphthalian was employed as an indicator. When the solution had been neutralized, the red color of the phenolphthalien was destroyed by the careful dropwise addition of 0.001 N nitric acid. The solution was diluted with an equal volume of 95% ethanol. Then a measured quantity (2 to 5 ml.) of standard barium chloride solution was added. The solution was titrated to the reappearance of the phenolphthalien color with standard sodium carbonate. Calculation of the amount of sulfur present was done by straight-forward back-titration methods. Reagent grade sodium sulfate was employed as a standard for determination of the normality of the barium chloride; reagent grade sodium carbonate was taken as a primary standard.

Oxidation State Determination

A small quantity of the sample to be measured (about 10-25 mg.) was placed in a 25 ml. volumetric flask, together with an approximately equal amount of lithium chloride. To this mixture, 3 ml. of acetic anhydride was added and the system was allowed to stand overnight. Then a drop of concentrated sulfuric acid was added and the solution was diluted up to the 25 ml. volume with ethanol. This new solution was allowed to stand for one day. The spectrum was then measured on a Cary model 14 spectrophotometer. To establish extinction coefficients for Os(IV) and Os(III) in this medium, a sample of osmium tetrachloride was used. Carrying the osmium tetrachloride through this procedure provided extinction coefficients for Os(IV); subsequent reduction of the osmium tetrachloride with ferrous ammonium sulfate and redetermination of the spectrum provided extinction coefficients for Os(III).

Calculation of the quantities of Os(IV) and Os(III) was carried out by solution of the following pair of simultaneous equations:

$$A_{275} = \varepsilon_{275}^{(+4)}C^{(+4)} + \varepsilon_{275}^{(+3)}C^{(+3)}$$

$$A_{335} = \varepsilon_{335}^{(+4)}C^{(+4)} + \varepsilon_{335}^{(+3)}C^{(+3)}$$

The absorbances, A_i, were measured in the experiment, and the extinction coefficients, ε_i, were known in advance. The concentrations, C, were then readily found.

Physical Measurements

Electronic spectra. The electronic spectra were measured in the region 200-1000 mμ with a Beckman model DU and a Cary model 14 spectrophotometer. Solvents employed were acetone, chloroform, dichloromethane, dimethyl sulfoxide, ethanol, and tetrahydrofuran.

Electron spin resonance spectra. The electron spin resonance spectra were recorded by Mr. William Antholine. The instrumentation employed consisted of a Strand spectrometer with standard Varian cavity and Magnion power supply and magnet. A homemade NMR probe was used for marking the field. The microwave frequency was 9.151 gHz. Diphenylpicrylhydrazine (DPPH) was employed as internal standard. The spectra were measured at 77°K.

Magnetic susceptibilities. The magnetic susceptibilities were measured by the Faraday method over the temperature range 77 to 300°K. The apparatus used consisted of a Cahn model RG electrobalance housed in an evacuable chamber and a Varian electromagnet capable of obtaining field strengths of up to approximately 11,000 gauss. The apparatus and its operation have been discussed in detail by Converse (55).

Mass spectra. Mass spectrometric measurements were made by Miss Willa Jones. An Atlas model CH-4 spectrometer with a type TL-4 source was employed. An accelerator voltage of 3000 volts was employed. Samples were used as solids using a vacuum lock inlet system.

Molecular weights. The molecular weights were determined by the well-known Rast camphor method (56, 57). A sample of approximately 25 mg. was weighed accurately in a small test tube. Approximately 250 mg. of camphor was also weighed accurately in the tube. An oil bath heated to 185°C was kept ready at hand. The test tube with sample and camphor was plunged about half way into the bath. As soon as the camphor had melted, the resulting solution was swirled for about 30 seconds. The tube was then withdrawn. Once cool, the solid solution was transferred to a small porcelain dish and finely ground. A portion of this powder was placed in a melting point capillary. An approximately equal amount of pure camphor was placed in a second such tube. The open ends of both capillaries were sealed shut and both tubes were then attached, by means of a rubber band cut from a piece of gum rubber tubing, to a Philadelphia thermometer which had been preset to a range of 173-178°C. The thermometer and attached capillaries were placed in an oil bath which was heated slowly by means of an electric hot plate. The melting point of the solid solution was taken as the temperature at which the last trace of solid phase disappeared. The melting point of the camphor was also noted. The experiment was repeated until three successive determinations gave the same melting point lowering. Knowing the molality of the solid solution and the freezing point depression constant for camphor, 39.7 deg-gm./mole, calculation of the molecular weight is straightforward.

Proton magnetic resonance. The proton magnetic resonance spectra were measured on Varian model A-60 and Hitachi Perkin-Elmer model R20B nuclear magnetic resonance spectrometers by Mrs. Susan Helzer, Mr. N. S. Morales, and Mr. Thomas Lyttle. A frequency of 60 MHz was used. Chloroform, deuterochloroform, and dichloromethane were used as solvents; the internal standard was tetramethylsilane.

Vibration spectra. The infrared spectra were measured by Miss Evelyn Conrad and Mr. Clifton Hill in the region of

4000 to 35 cm^{-1}. Mineral oil ("Nujol") mulls were used with sodium chloride plates in the 4000-600 cm^{-1} region and with polyethylene windows in the 600-35 cm^{-1} region. The instruments employed were Beckman models IR-7 and IR-11 spectrophotometers.

Recovery of Osmium

Economic prudence demanded that the osmium metal used in this study be recovered and recycled. In any vigorous research program in osmium chemistry, such recovery becomes a veritable work of Penelope.

A variety of procedures were employed, the ultimate goal being to obtain a fresh supply of osmium metal or osmium tetroxide. The comprehensive scheme was first to recover osmium compounds from solution, then to reduce these to osmium metal, and finally to oxidize the metal to the tetroxide.

Osmium compounds were recovered from solution by the obvious process of evaporating the solvent. In the case of aqueous solutions the pH was always adjusted to make the solution basic and thus to prevent inadvertent volatilization of osmium tetroxide. A special recovery procedure, discussed below, was used for solutions of the hexakis(thiourea)osmium (III) complex.

Reduction was effected by two processes. One was essentially the same as the hydrogen reduction analysis discussed previously. The only differences were the use of several combustion boats filled with material, and the employment of a 5% solution of thiourea in 2N sulfuric acid in the gas washing bottle to serve as a trap in the unlikely event that any osmium tetroxide would be volatilized.

The second method was a zinc reduction. A Vycor-glass tube closed at one end (in effect, a giant test tube) was constructed with dimensions sufficient to fill a cylindrical tube furnace. A quantity of dry residues was weighed roughly, and an equal rough weight of zinc granules was mixed intimately. This mixture was placed in the Vycor tube. The furnace having been preheated to 650°C, the tube was introduced into the furnace and the reaction was allowed to proceed for four hours. After cooling, the material in the tube was pulverized and transferred to a beaker, where it was treated with successive portions of boiling hydrochloric acid until the liquid phase was no longer colored and it appeared the volume of solid was no longer diminished by each treatment. The solid remaining was dried and subsequently converted to osmium tetroxide.

A reduction step was found to be essential. Attempts to convert residues directly to osmium tetroxide, without prior reduction, using hot oxygen, a nitric-perchloric acid mixture, acidic potassium permanganate solution, or 30%

hydrogen peroxide solution, always led to violent explosions.

Conversion of the reduced residues to osmium tetroxide was carried out in a manner similar to that employed for the regular laboratory synthesis of osmium tetroxide. The only difference was that several combustion boats of material were used in each run. The material remaining in the combustion boats at the end of the reaction was discarded.

Recovery of osmium from the solutions of the hexakis (thiourea)osmium(III) complex arising from the colorimetric analysis for osmium was complicated by the high dilution of these solutions, causing evaporation to be a very inefficient process. Accordingly, the following procedure was used for the recovery of osmium from these solutions. Approximately 100-150 ml of the thiourea complex solution was placed in a 400 ml. beaker. A 30% solution of hydrogen peroxide was added with vigorous stirring until the red color had been completely destroyed. Once the solution had cooled (the reaction being markedly exothermic), it was transferred to a separatory funnel and shaken with five 20 ml. portions of carbon tetrachloride. Each extraction was carried out by shaking the funnel at least 1000 times. The carbon tetrachloride phases are combined, providing a convenient solution of osmium tetroxide for subsequent experimentation. A test to be sure that all the osmium tetroxide had been extracted was performed by shaking a small amount of the final 20 ml.

portion of carbon tetrachloride with a few milliliters of a 5% thiourea solution; failure of the aqueous phase to turn red indicated completion of the extraction.

Laboratory Safety

Osmium tetroxide is one of the most toxic non-radioactive inorganic substances known. It is far more toxic than such better-known poisons as hydrogen sulfide and hydrogen cyanide (58). Exposure to osmium tetroxide vapor can lead to blindness (59); injection of osmium tetroxide into the lungs of experimental animals causes instant death (60, 61). Accordingly, osmium tetroxide was handled only with extreme caution and only when necessary. In almost all cases, osmium tetroxide was employed in a reaction immediately after its synthesis, and in fact, the solution of the tetroxide in carbon tetrachloride or thionyl chloride was prepared in the same trap in which the tetroxide was condensed during its synthesis. On the few occasions when it was necessary to store the substance, it was transferred to an ampoule and sealed. The obvious precautions of always working in a hood and never heating osmium or its compounds or bringing them into contact with oxidizing agents (except of course when it was desired to prepare the tetroxide) were strictly observed.

The alkanethiols are fairly efficient poisons in their own right, causing cardiovascular disorders (62) and death by respiratory failure (63, 64). As in the better-known case of hydrogen sulfide, the odor of the thiols makes them readily detectable in air at concentrations far below the danger level. For example, Blinova (62) has determined the partial lethal concentration (that is, Loit's index) of ethanethiol in air to be 15 mg./liter, while Reid (65) and others (66) have stated that this substance is detectable by its odor at concentrations in air of one part in 50,000,000,000. The odor thus provides a very effective warning system, and detection of such odor makes it possible to institute precautions. The compounds were of course always handled in the hood or in an efficient vacuum system.

RESULTS AND DISCUSSION

The $[Os(SR)_{3.75-4.00}]_4$ Compounds

Preparation and properties

Mixtures of compounds of the general formulas $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ are formed in the reaction of osmium tetrachloride with alkanethiols, according to the equations below:

$$8\ OsCl_4 + 32\ RSH \rightarrow 2\ Os_4(SR)_{15} + 32\ HCl + R_2S_2$$

$$4\ OsCl_4 + 16\ RSH \rightarrow Os_4(SR)_{16} + 16\ HCl\ .$$

The reactions seem to be complete in about three or four days at room temperature. No attempt was made to determine the minimum length of time necessary for the reaction. The reaction proceeds equally well whether carried out in neat alkanethiol or in a suitable solvent such as ethanol or dichloromethane; it proceeds equally well whether carried out at room temperature or under reflux conditions. No correlation was ever observed between reaction time and the S/Os ratio of the product; reaction times of two to eight days were most commonly employed; S/Os ratios of 3.73 to 4.03 were observed in the products with no discernible relationships or trends.

When it occurs that a particular reaction of interest leads to a mixture of products, it is a natural step to investigate methods of resolving the mixture into its constituent compounds. A number of the traditional separation methods of synthetic chemistry were applied to this case. In general, the methods employed were those of recrystallization, chromatography, and fractional sublimation.

Recrystallization is such a common and widely used technique that it needs no special discussion here. It is amply covered in standard laboratory manuals (56, 57). The solvents employed were those which usually come under the general catch-all of "common laboratory solvents" and were, most frequently, acetone, benzene, chloroform, dichloromethane, ethanol, and tetrahydrofuran, or mixtures of these compounds. Analysis of both fractions revealed no purification nor sensibly discernible trend of separation.

Chromatography is similarly a sufficiently well-known procedure to require no explanatory comment. Two methods were used exclusively, column chromatography and ascending paper strip chromatography.

Two supports were employed for the column chromatography experiments. The first was neutral alumina, which proved totally worthless. The mixture could be loaded onto the column, in solution, but it remained in a narrow band at the very top and could not be eluted with any solvent or mixture of solvents. Cellulose was found to be a more tractable support. In this case the mixture could be eluted from the column, but it always travelled down the column in a single band no matter what solvent or mixture of solvents was employed. The best that can be said is that after the mixture had been run through the same column material a dozen or so times, the normally white cellulose took on a very light tan color.

The paper strip chromatography was carried out in stoppered test tubes so that the strip would be in equilibrium with the solvent vapor. As in the case of column chromatography, the solvents listed above (and most of the possible binary mixtures of these solvents) were employed. No separation was ever observed.

The sublimation studies were carried out primarily to learn whether these compounds would be suitable subjects for a mass spectrographic study. However, it would also have been of great interest to find that the $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ could be separated on the basis of a difference in volatility. No separation - indeed, no volatility - was observed.

The compounds of interest are obtained by removing the excess liquid phase via vacuum distillation at the end of the reaction. They are recovered as brownish-black amorphous powders, soluble in and able to be "recrystallized" from a variety of common organic laboratory solvents.

The compounds are inert toward air; once purified, they evince no odor of the parent thiol even if allowed to stand in open air for several weeks. (This behavior is in marked contrast to that of sodium ethanethiolate, which begins to smell strongly of ethanethiol a short time after being exposed to air.) The compounds resist decomposition by alkali, withstanding boiling in 1M sodium hydroxide for a day. Hydrochloric acid very slowly converts the compounds to the hexachloroosmates. Oxidizing acids destroy these compounds in a few minutes.

These substances are nonvolatile even at pressures of a few microns and temperatures of 350-400°C. Above these temperatures, the compounds undergo thermal decomposition, yielding tarry products.

The results of the analyses for osmium, sulfur, carbon, and hydrogen have been given previously. Little reliance can be placed on the carbon and hydrogen analyses. It was found (67) that, because of the considerable difficulties encountered in trying to remove osmium tetroxide from the combustion train, the carbon and hydrogen results are accurate only to about two or three percentage points. Thus these results indicate that no gross errors have been made in determining the S/Os ratio to be approximately 4, but they are of no use in differentiating between $Os(SR)_{3.75}$ and $Os(SR)_4$.

Of the remaining two elements, it was found that osmium could be determined with good precision, while the sulfur determinations were occasionally less precise. Provided that sufficient time is allowed for all osmium tetroxide to distill from the oxidizing mixture and that sufficient care is taken to extract all osmium tetroxide from the carbon tetrachloride into the thiourea solution, the osmium analysis is essentially foolproof. The sulfur analysis was occasionally complicated by the fact that the sample solution would irreversibly turn yellow on neutralization. Superimposition of the phenolphthalien color change on the yellow color of the solution meant that it was necessary to observe a yellow-to-orange color change, a far more difficult task than the usual colorless-to-red change occurring at the end point. In addition, errors could arise in the sulfur analysis if all excess thiol or disulfide were not removed. At any rate all the S/Os ratios observed during the course of the project fell in the range 3.69-4.13; all but three of these were in the narrower range 3.73-4.03.

The molecular weights, determined by the Rast method, show remarkably good agreement with the calculated molecular weights for tetramers, $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ (tetramers, it will be noticed, are the first possible "whole number" compounds for materials of empirical formula $Os(SR)_{3.75}$), and excellent correlation between the observed molecular weights and the molecular weights calculated for a mixture of $Os_4(SR)_{15}$ and $Os(SR)_{16}$ having the composition demanded by the observed S/Os ratio. In Table 1, below, are shown molecular weight data obtained for the methane-, ethane-, and butane-homologs. Given in the table are the S/Os ratios for the exact samples used for the determinations, the calculated molecular weights of the pure $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ species, the calculated molecular weight of the mixture described by the S/Os ratio, the observed molecular weight, and the error (determined as the difference between the observed molecular weight and the calculated molecular weight of the mixture, divided by the latter quantity).

The results of the oxidation state determination do indicate that some reduction of osmium(IV) occurs during the reaction of osmium tetrachloride with alkanethiols. In a pure compound of the $Os_4(SR)_{15}$ formula (that is, S/Os=3.75) it can be seen that three osmium atoms must be of oxidation state 4+ and one of oxidation state 3+. In other words, the ratio [Os(IV)]/[Os(III)] must be 3.

Table 1. Molecular weight data for the $[Os(SR)_{3.75-4.00}]$ compounds

R	S/Os	Calculated M.W. of $Os_4(SR)_{15}$	Calculated M.W. of $Os_4(SR)_{16}$	Calculated M.W. of mixture	M.W. observed	error
CH_3-	3.87	1465	1512	1488	1515	1.8%
C_2H_5-	3.76	1675	1736	1678	1705	1.6%
C_4H_9-	3.96	2095	2184	2173	2254	3.7%

The spectra of pure hexachloroosmate(III) and hexachloroosmate(IV) are shown, after Jorgensen (68), in Figure 4 with solid and dashed lines respectively. It is at once apparent that the sharp peak at 35,000 cm^{-1} (ca. 275 mμ) in the spectrum of $OsCl_6^{-3}$ occurs in a region where one expects very low absorbance from $OsCl_6^{-2}$. Consequently one can compare the absorbance in the 25-30,000 cm^{-1} region with that at 35,000 cm^{-1} and obtain a good estimate of the relative quantities of Os(IV) and Os(III) present.

The extinction coefficients were measured as described previously. Measurements were made at 335 mμ and 275 mμ, wavelengths at which Os(IV) and Os(III) respectively display absorption maxima. Results are given in Table 2.

Table 2. Extinction coefficients, liters/mole-cm

	λ	
ION	275 mμ	335 mμ
$OsCl_6^{-3}$	2300	155
$OsCl_6^{-2}$	200	6900

Use of the extinction coefficients given above and observed absorption data provides a determination of Os(IV)/Os(III) in these compounds. Experiments were carried out with samples of $Os(SCH_3)_{3.79}$ and $Os(SC_2H_5)_{3.76}$. In the former case it was found that Os(IV)/Os(III)=2.91, while the

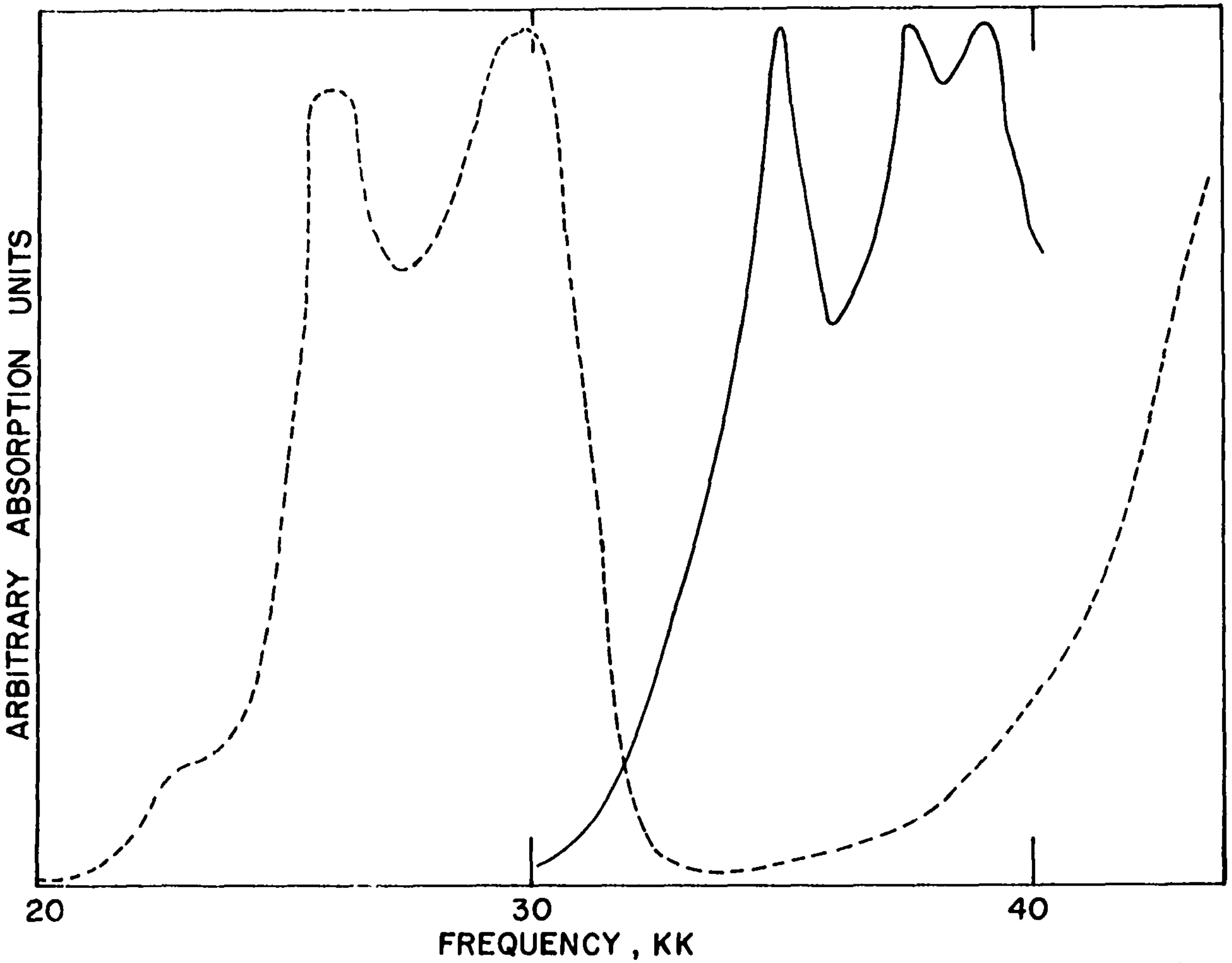

Figure 4. The electronic spectra of $OsCl_6^{-2}$ (dashed line) and $OsCl_6^{-3}$ (solid line)

value of this ratio for the latter material was found to be 3.05 (it will be recalled that pure $Os(SR)_{3.75}$ should show a value of 3.00). In the particular case of the ethane-homolog the correlation between the observed 4+/3+ ratio and the composition of the mixture as indicated by the S/Os ratio is striking since the theoretical prediction for a mixture composed of 96% $Os_4(SR)_{15}$ and 4% $Os_4(SR)_{16}$ is 3.04. It must certainly be pointed out that this correlation is not nearly as good in the case of the methane-homolog, but certainly the value obtained for the 4+/3+ ratio, is, to use the popular scientific colloquialism, in the right ballpark.

Additional evidence for the reduction of some osmium(IV) during the reaction of osmium tetrachloride with alkanethiols, specifically ethanethiol, is the identification of traces of the oxidation product, diethyl disulfide, remaining in the solid. Diethyl disulfide has a normal boiling point of 153° and it is difficult to remove this material completely under dynamic vacuum without resorting to the use of elevated temperatures. The infrared spectrum of a sample of the product of the reaction of osmium tetrachloride with ethanethiol taken before "recrystallization" shows two weak peaks characteristic of traces of diethyl disulfide: a peak at 530 cm^{-1} assignable (69) to the S-S stretch, and another peak at 775 cm^{-1} the assignment of which is not given in the literature but which appears as a strong peak in the spectrum of diethyl disulfide.

Infrared Spectra

The infrared spectra observed for the $Os_4(SR)_{15}$-$Os_4(SR)_{16}$ mixtures are shown in Figures 5 and 6. The spectra shown in these figures are of the normal and far infrared regions respectively. No noticeable variation could be seen for spectra run on two different mixtures of the same R but different S/Os ratio. Assignments are given below. The references given in the following tables are to actual spectral assignments for the uncomplexed ligands or to compilations of assignments for characteristic "fingerprint" vibrations. Unreferenced assignments were made by the author. Peaks labelled with the letter N are those arising from the "Nujol" mineral oil used to make the mulls. These peaks are not included in the table of assignments.

There is little corroboration in the literature for the assignment of Os-S stretching frequencies. In the main this appears due to the general lack of characterization work done on thiolato complexes, a point touched on earlier. It is interesting to note, however, that Brown, Glass, and Kumar (70) assign a peak at 490 cm^{-1} to a Cr-S stretch in $Cr(SR)_3$ ($R=CH_3$- and C_2H_5-).

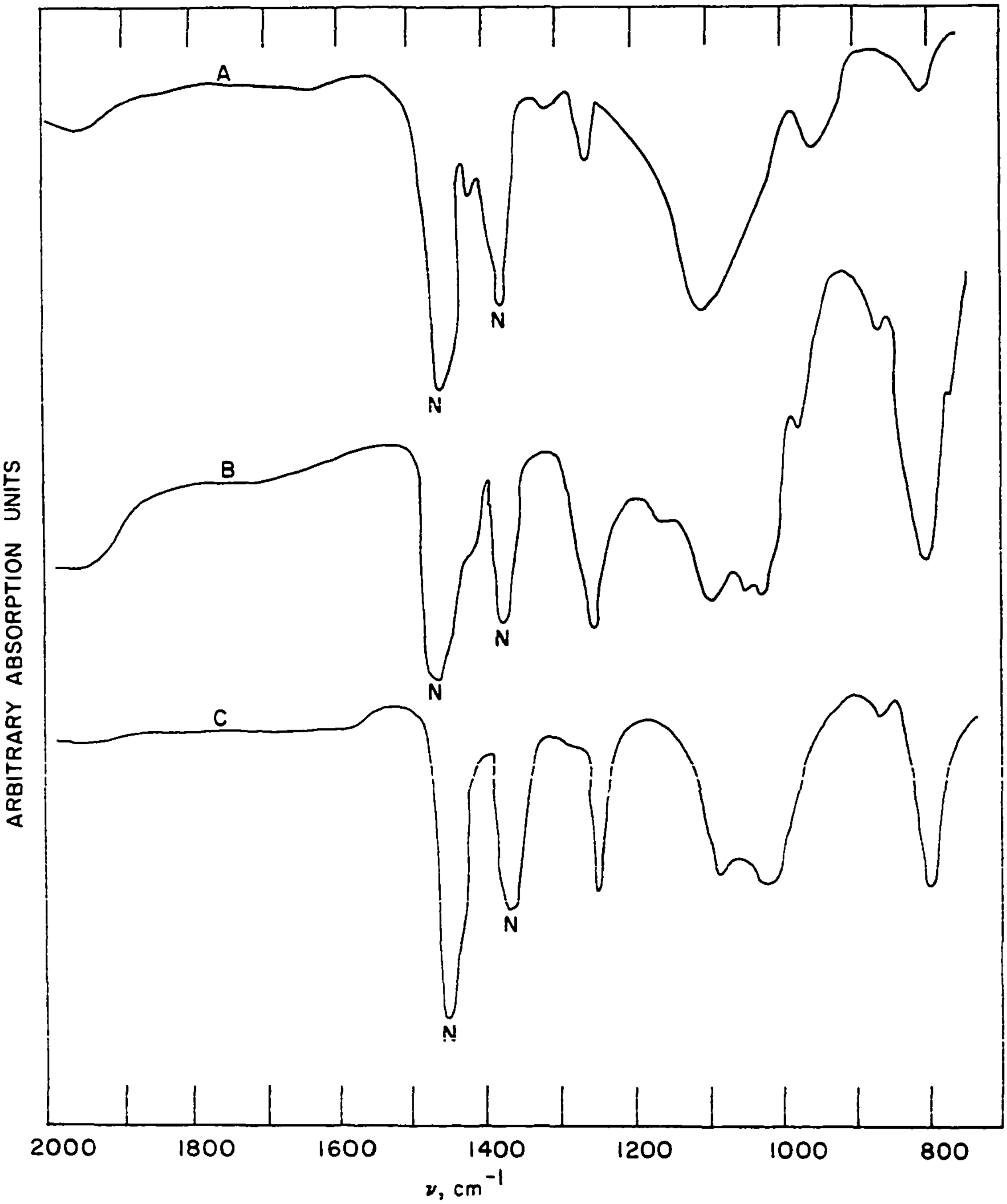

Figure 5. The infrared spectra of $[Os(SCH_3)_x]_4$ (A), $[Os(SC_2H_5)_x]_4$ (B), and $[Os(SC_4H_9)_x]_4$ (C) from 2000-800 cm^{-1}

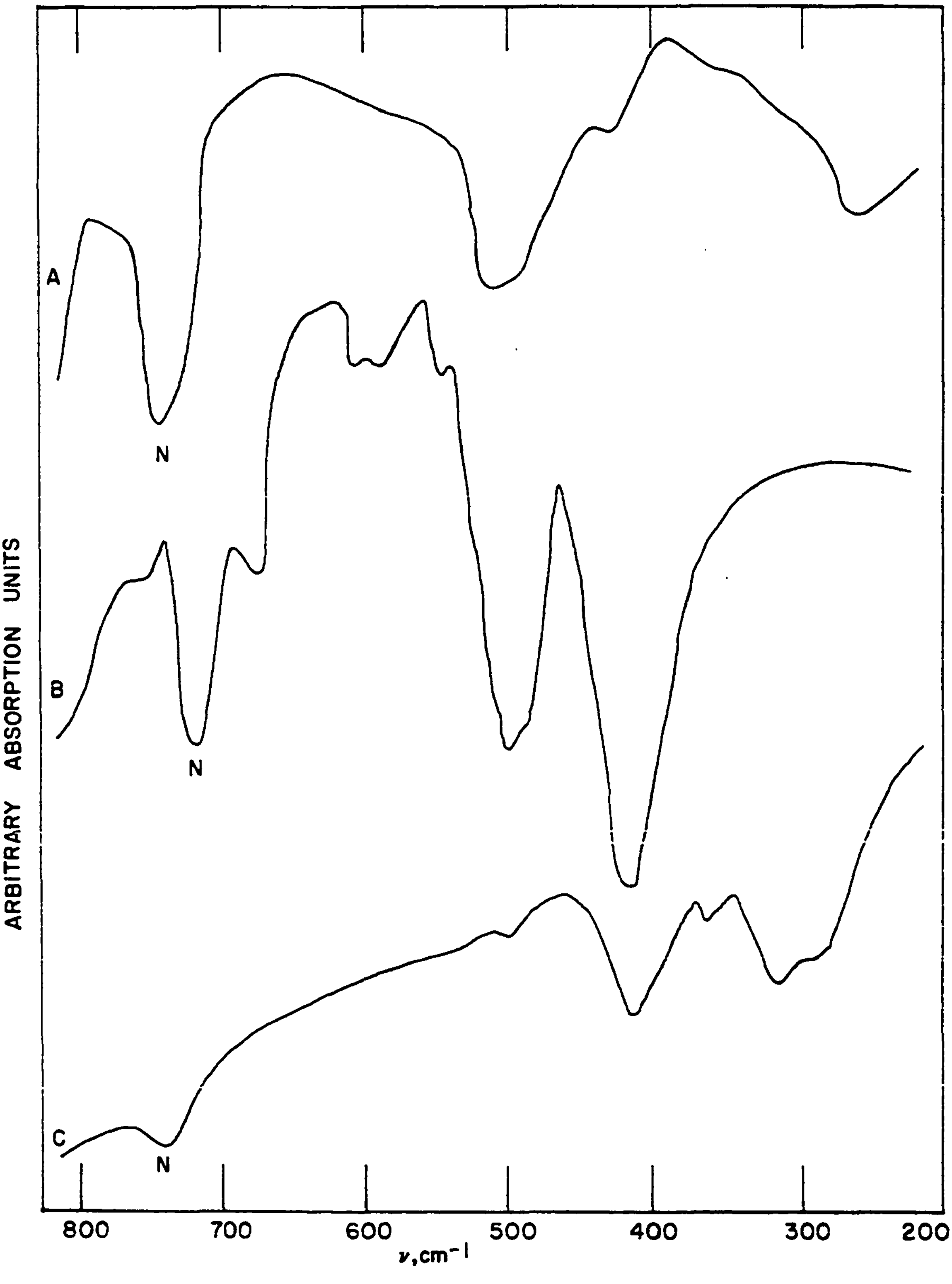

Figure 6. The infrared spectra of $[Os(SCH_3)_x]_4$ (A), $[Os(SC_2H_5)_x]_4$ (B), and $[Os(SC_4H_9)_x]_4$ (C) from 800-200 cm^{-1}

Table 3. Infrared assignments for $[Os(SCH_3)_x]_4$

Band	Assignment	Reference
1415	$-CH_3$ deformation	71
1305	$-CH_3$ sym. bend	72
1260	-CH wag	72
1105	$-CH_3$ rock	71
950	$-CH_3$ rock	72
805	$-CH_3$ wag + rock	71
500	Os-S stretch	
412	Os-S stretch	
250	S-Os-S bend	
70	ligand torsion mode	73

Table 4. Infrared assignments for $[Os(SC_2H_5)_x]_4$

Band	Assignment	Reference
1265	$-CH_2-$ wag	72
1110	$-CH_2-$ twist	71
1050	$-CH_3$ rock	72
1030	$-CH_2-$ rock	71
980	C-C stretch	72
870	C-C stretch	71
805	$-CH_3$ wag + rock	71
775	$(C_2H_5)_2S_2$ mode	69
660	C-S stretch	72
575	C-S stretch	72

Table 4 (Continued)

Band	Assignment	Reference
530	$(C_2H_5)_2S_2$ mode	69
485	Os-S stretch	
400	Os-S stretch	

Table 5. Infrared assignments for $[Os(SC_4H_9)_x]_4$

Band	Assignment	Reference
1260	$-CH_2-$ wag	71
1100 w	$-CH_3$ bond	71
1025 w	$-CH_2-$ wag	71
910 w	C-C stretch	71
870 w	C-C stretch	71
805	$-CH_3$ wag + rock	71
740 w	-C-H rock	71
700 w	C-S stretch	72
485 w	Os-S stretch	
400	Os-S stretch	
300 w	S-Os-S bend	
280 w	S-Os-S bend	

Magnetic Susceptibilities

The magnetic susceptibilities were measured from liquid nitrogen to room temperatures. The raw data obtained were treated by the procedure outlined in detail by Converse (55). In essence, data were processed on an IBM 360 computer according to the well-known Honda-Owen (74) equation:

$$\frac{\Delta f}{\Delta F} = m\chi_g + c\sigma(1/\Delta H)$$

in which f is the force on the substance, m is its mass, χ_g the gram susceptibility, F the magnet force constant H(dH/dz), c the concentration of ferromagnetic impurity, and σ the saturation magnetization of that impurity. A set of five $\Delta f/\Delta F$ values was plotted, by least squares fitting, against $1/\Delta H$. A correction was made for the susceptibility of the sample container, which in this work was a screw-capped vial of diamagnetic Teflon. After this correction was made, the gram susceptibility was calculated from the intercept, at $1/\Delta H=0$, of the Honda-Owen plot. All this was done in the computer; the output provided the following information: the temperature at which the data were taken, the reciprocal temperature, the gram susceptibility χ_g, the molar susceptibility χ_M, the uncertainty in χ_M, and the slope and intercept of the Honda-Owen plot for each data set.

The susceptibility of any substance can be represented by a series of terms as follows:

$$\chi_M = \chi_P + \chi_D + \chi_{TIP}$$

in which χ_P is the paramagnetic contribution, χ_D is the diamagnetic contribution arising from the atomic cores, and χ_{TIP} is a residual temperature independent paramagnetism. The diamagnetic contribution may be assessed if the value of the molar diamagnetic susceptibilities of the component atoms is known. These may be calculated by the method of Pascal (75); however, extensive compilations of these values are now available in the literature (74, 76, 77, 78, 79). Values of the diamagnetic susceptibilities of osmium, carbon, and hydrogen were taken from the data given by Selwood (74). A value for the diamagnetic susceptibility of sulfur was taken from the work of Francois (80) who actually measured the magnetic susceptibilities of pure alkanethiols and was consequently able to obtain an accurate value for the diamagnetic susceptibility of sulfur.

Having taken the diamagnetic contribution into account, one is left with a corrected molar susceptibility, χ_M^{CORR}. These values were then plotted against 1/T by least squares techniques. The plot being linear, the slope of the line gave the Curie constant C (from the Curie relation χ_M=C/T). From this, the magnetic moment of the compound was calculated from the equation

$$\mu = \frac{3kC}{N\beta^2}$$

where k is Boltzmann's constant, N is Avogadro's number, and β is the Bohr magneton. The intercept of this plot gave an estimate of χ_{TIP}.

A plot was also made (again by least squares techniques) of $1/\chi$ vs. T. For a compound exactly obeying the Curie Law, the line should intersect the axes at the origin. Many compounds do not show this behavior. The intercept of the plot with the T axis provided a value of the Weiss constant, θ, which is a measure of the deviation from Curie behavior.

It is valid to question whether the equation

$$\chi = C/T$$

or the equation

$$\chi = C/(T-\theta)$$

is the more accurate representation of the magnetic data. The values of θ determined during this study all were found to have standard deviations which were 20-35% of the value of θ itself. Furthermore, no correlation could be found between the values of θ and the magnetic moments, S/Os ratios, or nature of the alkyl group. Thus it is regarded that the θ values do not have fundamental significance but rather arise from indeterminate errors in the experiments. Accordingly, the data are presented in terms of the simple

Curie equation rather than the Curie-Weiss equation.

In Tables 6, 7, and 8 below are given some of the susceptibility data obtained for $[Os(SR)_x]_4$ compounds. With this, values of the Curie constant C, the magnetic moment μ, the diamagnetic susceptibility χ_D, the temperature independent susceptibility χ_{TIP}, and the Weiss constant θ are also given. Graphs of χ vs 1/T are given in Figures 7, 8, and 9 for the methane-, ethane-, and butane-homologs respectively. Graphs of $1/\chi$ vs. T are not shown since no special significance is attached to θ.

Table 6a. Temperature variation of corrected molar susceptibility of $[Os(SCH_3)_{3.79}]_4$

Temp., °K	χ_M^{CORR}, emu/mole
77	4200×10^{-6}
115	2984×10^{-6}
123	2673×10^{-6}
146	2424×10^{-6}
159	2127×10^{-6}
169	1991×10^{-6}
192	1844×10^{-6}
207	1766×10^{-6}
295	1348×10^{-6}

Table 6b. Magnetic constants for $[Os(SCH_3)_{3.79}]_4$

Term	Value
C	301×10^{-3} emu/mole °K
μ	1.55 B.M.
χ_D	-625×10^{-6} emu/mole
χ_{TIP}	412×10^{-6} emu/mole
θ	-32.7 °K

Table 7a. Temperature variation of corrected molar susceptibility of $[Os(SC_2H_5)_{3.98}]_4$

Temp, °K	χ_M^{CORR}, emu/mole
77	1080×10^{-6}
122	716×10^{-6}
126	676×10^{-6}
153	639×10^{-6}
200	550×10^{-6}
226	431×10^{-6}
242	401×10^{-6}
295	259×10^{-6}

Table 7b. Magnetic constants for $[Os(SC_2H_5)_{3.98}]_4$

Term	Value
C	80.2×10^{-3} emu/mole °K
μ	0.80 B.M.
χ_D	-799×10^{-6} emu/mole
χ_{TIP}	60×10^{-6} emu/mole
θ	-20.2 °K

Table 8a. Temperature variation of corrected molar susceptibility of $[Os(SC_4H_9)_{3.96}]_4$

Temp., °K	χ_M^{CORR}, emu/mole
78	1681×10^{-6}
136	1096×10^{-6}
146	1041×10^{-6}
189	971×10^{-6}
201	806×10^{-6}
295	626×10^{-6}

Table 8b. Magnetic constants for $[Os(SC_4H_9)_{3.96}]_4$

Term	Value
C	108×10^{-3} emu/mole °K
μ	0.93 B.M.
χ_D	-1024×10^{-6} emu/mole
χ_{TIP}	270×10^{-6} emu/mole
θ	-53.7 °K

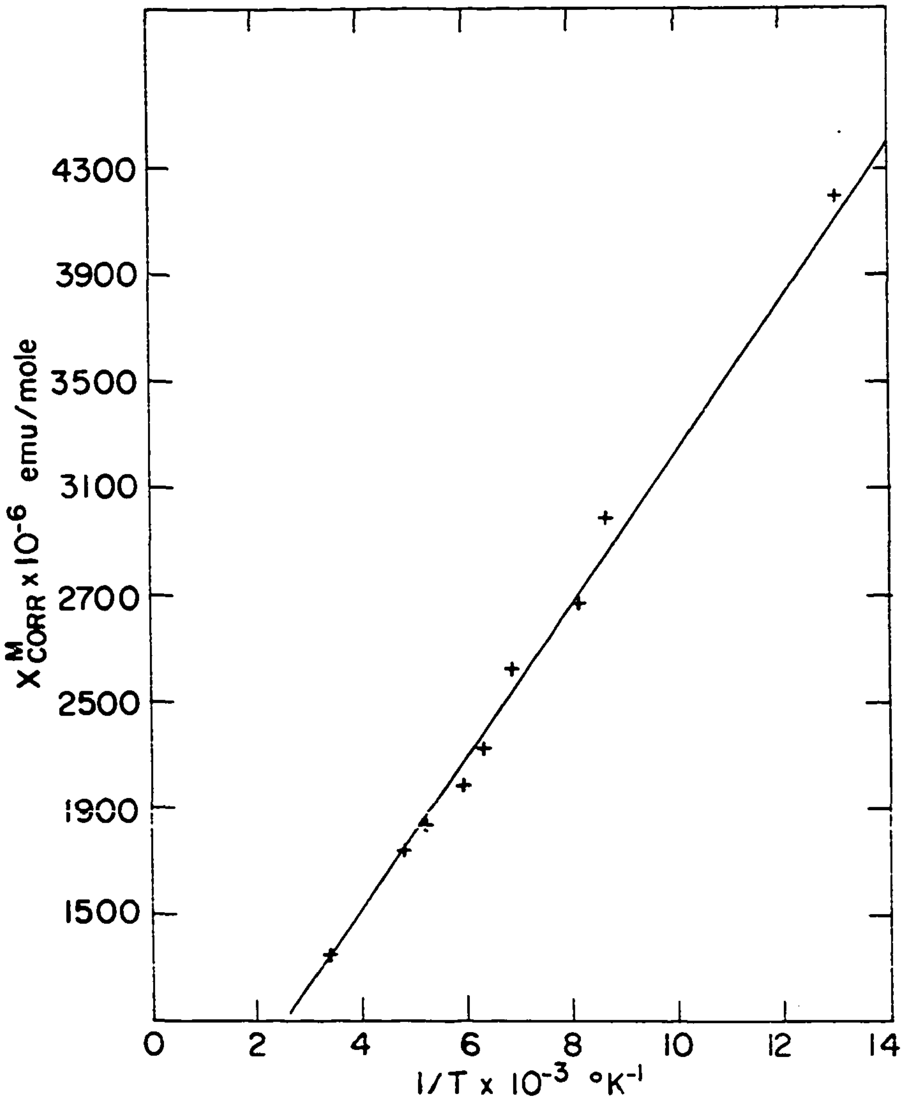

Figure 7. χ^{CORR} vs 1/T for $[Os(SCH_3)_{3.79}]_4$

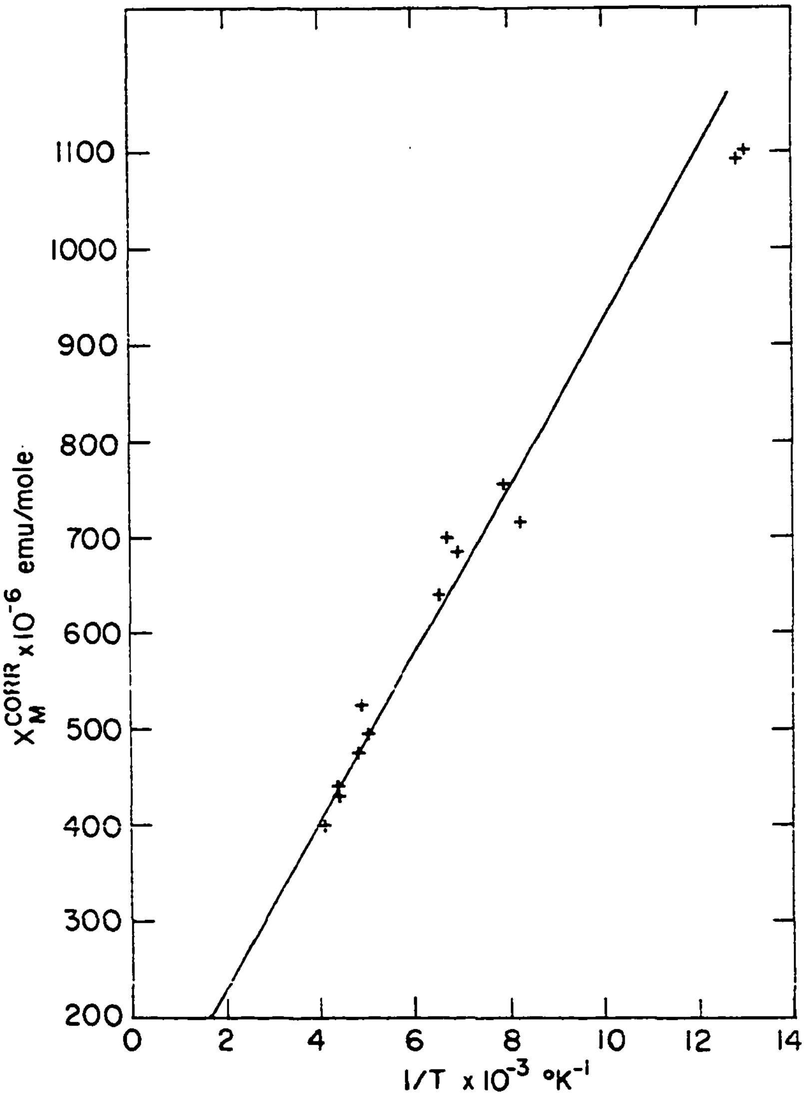

Figure 8. χ^{CORR} vs 1/T for $[Os(SC_2H_5)_{3.98}]_4$

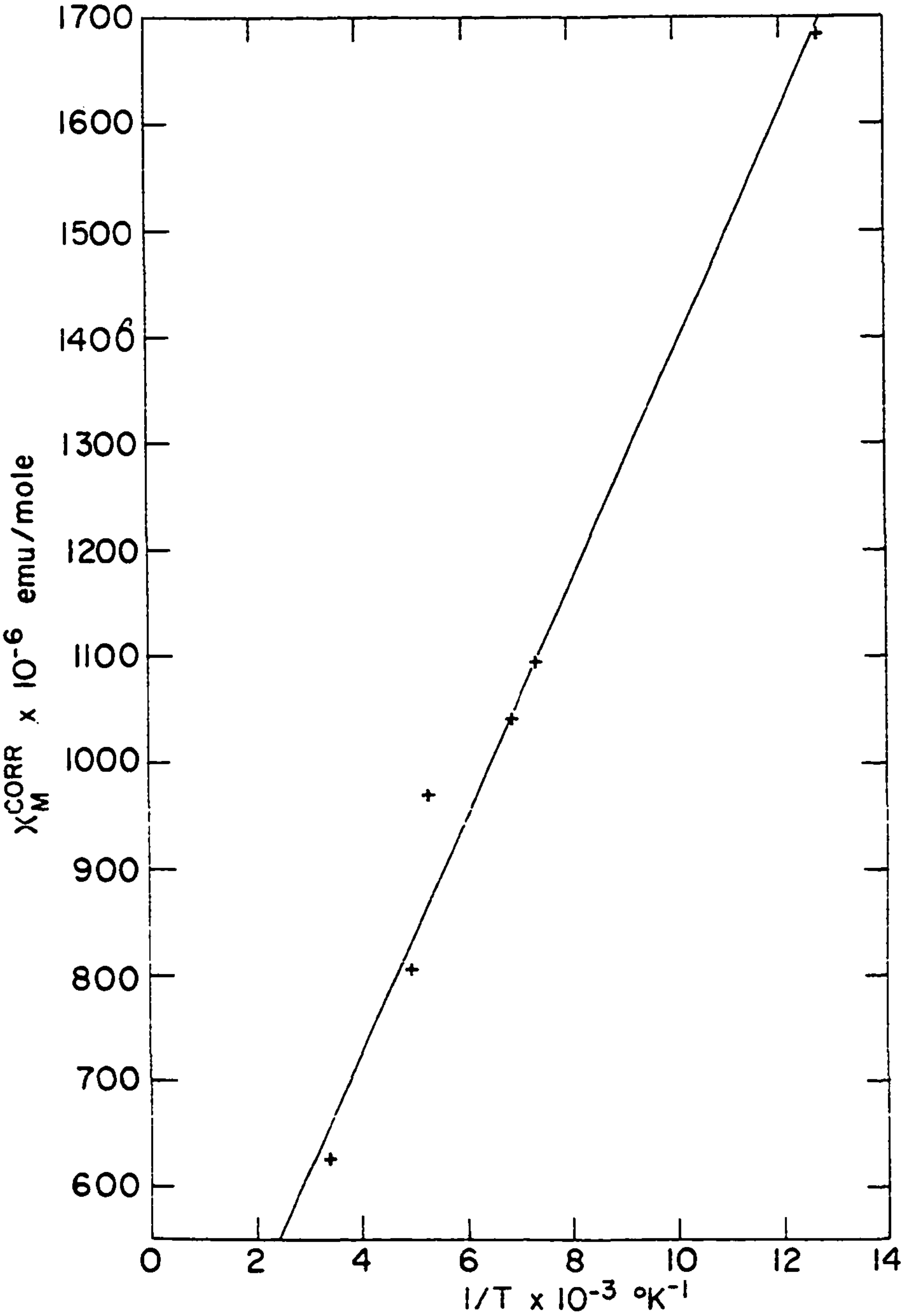

Figure 9. χ^{CORR} vs 1/T for $[Os(SC_4H_9)_{3.96}]_4$

Electron Spin Resonance

Electron spin resonance spectra were measured by Mr. William Antholine for the methane- and ethanethiolato derivatives. Measurements were made at 77°K. Diphenylpicrylhydrazine was used as an internal standard. The spectra are shown in Figures 10 and 11 respectively. From the spectra it was possible to calculate values of the Lande g factor, the so-called spectroscopic splitting factor. This may be obtained from the equation

$$g = \frac{h\nu}{\beta_e H}$$

where ν is the microwave frequency, β_e the Bohr magneton, H the magnetic field, and h of course is Planck's constant. The field H is determined by means of the equation

$$H = \frac{h\nu}{g_H \beta_N}$$

where ν is the frequency obtained with the NMR probe, g_H the g-value of the proton, and β_N the nuclear magneton. For $[Os(SCH_3)_{3.79}]_4$ a g-value of 2.054 was calculated. The spectrum of $[Os(SC_2H_5)_{3.98}]_4$ showed a marked asymmetry; two g-values were estimated, as ca. 2.15 and 2.06; owing to the peculiar shape of the spectrum, more exact values could not be readily obtained.

The fine structure in the spectrum of $[Os(SCH_3)_{3.79}]_4$ is regarded as being due to a trace of ruthenium as an

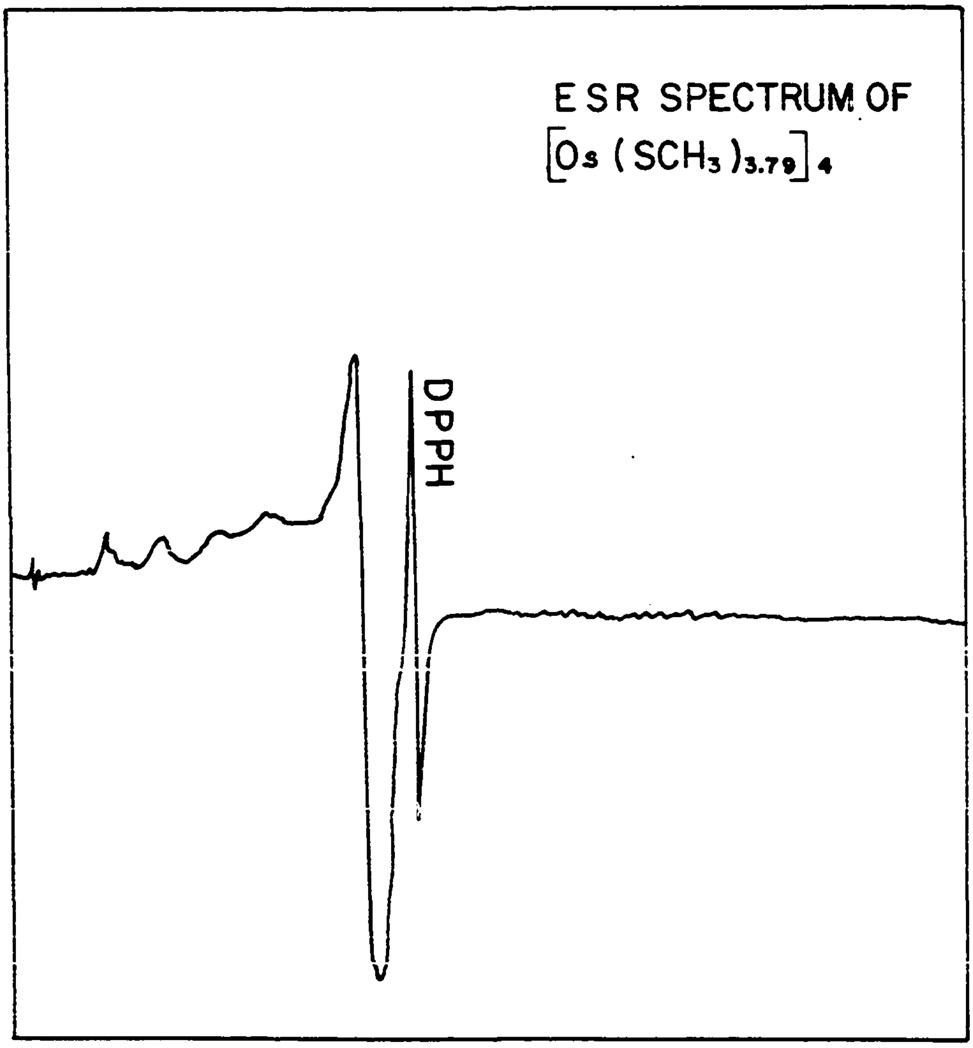

Figure 10. ESR spectrum of $[Os(SCH_3)_{3.79}]_4$

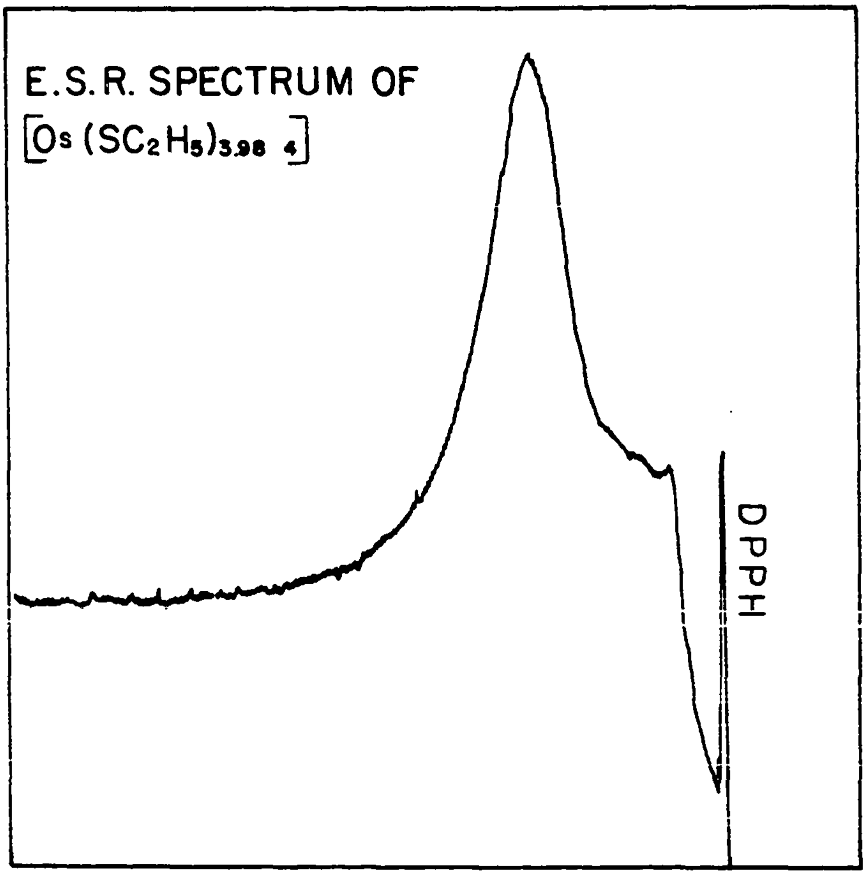

Figure 11. ESR spectrum of $[Os(SC_2H_5)_{3.98}]_4$

impurity. The major isotopes of ruthenium have a nuclear spin I=5/2, which should give rise to a six-line spectrum. The two lines not observed may lie under the signal arising from the compound.

Electronic Spectra

The electronic spectra of $[Os(SR)_x]_4$ compounds are shown in Figure 12 for the methane-(x=3.79), ethane-(x=3.98), and butanethiolato (x=3.96) homologs.

The spectra which are shown here were measured in tetrahydrofuran solution. Spectra run in other solvents are similar except that the peaks are shifted about ± 5 mμ (comparing compounds with the same ligand in different solvents); of course, the ultraviolet cut-off is different for different solvents. Unfortunately the peaks in the visible and near ultraviolet appear only as shoulders, being swamped by the very large peak which occurs farther out in the ultraviolet. In Table 9 a comparison is given of the positions of the peaks in the electronic spectra with respect to the different ligands.

Table 9. Summary of electronic spectral data for $[Os(SR)_x]_4$

Ligand	CH_3S-	C_2H_5S-	C_4H_9S-
Peak positions	-[a]	230	255
m_μ	275	320	330
	360	430	450

[a] The actual position of this peak was beyond the cut-off limit of all solvents used.

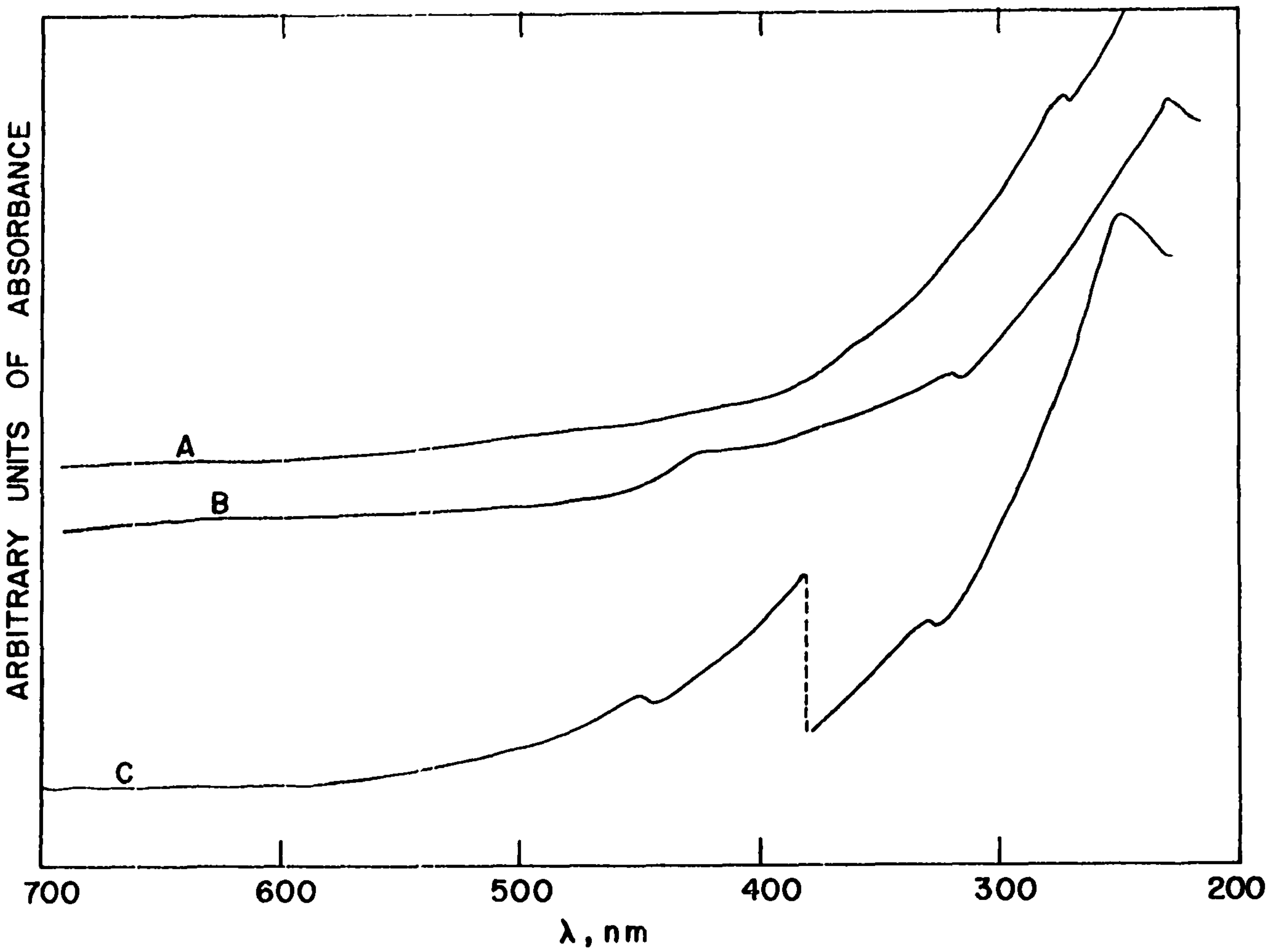

Figure 12. The electronic spectra of $[Os(SCH_3)_x]_4$ (A), $[Os(SC_2H_5)_x]_4$ (B), and $[Os(SC_4H_9)_x]_4$ (C)

It is also worth pointing out that changing the S/Os ratio shifted the peaks by about 15 mμ, as can be seen from some data given in Table 10 below ($R=C_2H_5$).

Table 10. Spectral data for $[Os(SC_2H_5)_x]_4$

S/Os	3.78	3.98
peak positions	–[a]	240
mμ	305	320
	420	430

[a] Beyond THF cut-off.

Mass Spectrometry

The mass spectra of $[Os(SCH_3)_{3.79}]_4$ and $[Os(SC_2H_5)_{3.98}]_4$ were attempted but provided little information. The highest peak observed occurred at approximately 205 a.m.u. Below approximately 100 a.m.u. a veritable forest of peaks occurred, arising from fragmentation of the ligands.

Interpretation and discussion of results

The investigation of the nature of the products formed in the reaction of osmium tetrachloride with alkanethiols was severely hampered by two serious experimental difficulties, namely, the amorphous nature of the materials and the intractability of the mixture with respect to resolution.

The amorphous nature of the products was confirmed on numerous occasions with samples displaying S/Os ratios running through the whole range of possible values. Powder pattern studies, carried out on a Gunier-deWulff camera with exposure times of up to 24 hours, produced no diffraction patterns. Some small comfort can be had from the fact that Hanker (1) reported the similar $[Os(SCH_2CHOHCH_2OH)_4]_4$ compounds to be likewise amorphous.

In some respects the amorphous nature of the materials represented a more serious consequence than their inability to be resolved into the constituent pure compounds, for in principle at least one can obtain structural information from x-ray diffraction studies on mixed crystals. The unfortunate consequence is of course that it is not possible to carry out a traditional single crystal structure determination and therefore it is not possible to make an unequivocal statement regarding the structure of the molecule. It thus becomes necessary to deal with model structures which, it would be hoped, should at least be able to account for the salient features of the molecule.

It can, however, also be mentioned that all hope for structural information need not be abandoned. Work is currently in progress (81) on methods for locating heavy atoms in amorphous powders by analysis of diffuse x-ray scattering; at the time of writing some tentative results have been reported, which will be discussed in their due course.

The problem of unresolvable mixtures also throws formidable difficulties in the way of understanding a chemical reaction. Nevertheless, the very fact of unresolvability must in itself convey some information to the chemist, and too must, in lieu of any more substantial foundation stones, serve as a base of sorts upon which to build.

Two points are worthy of discussion at this juncture. First, the experimental evidence based on sulfur and osmium analyses seems to clearly indicate that a mixture is formed. To reiterate some facts discussed earlier, the S/Os ratio of the solid material recovered from the reaction of osmium tetrachloride with alkanethiols varies from, generally, about 3.75 to about 4.00 with no correlation between the observed S/Os ratio and the variables of reaction time, reaction temperature, presence of an inert solvent, or nature of the alkanethiol. It is of course valid to question the reliability of the analyses on which this conclusion is based; indeed this is a question which must be raised. It is felt that the osmium analyses offer good precision and good accuracy, a fact which can be substantiated by repeated analyses of osmium(II) disulfide, a substance easily prepared in high purity and one susceptible to analysis by other time-tested procedures. Sulfur analyses are not quite in the same first-rate category, being on rare occasion beset by experimental difficulties previously discussed. Nevertheless, when sulfur was calculated as thiolate, RS^-, material balances (i.e., %Os + %SR^-) almost invariably totalled better than 95%.

The second point is that experimental evidence also seems clear that a partial reduction of Os(IV) to Os(III) does take place. The oxidation product, the alkyl disulfide, has been identified by infrared spectroscopy. Similarly the reduction product - Os(III) - has been identified by its conversion to the well-known $OsCl_6^{-3}$ and subsequent spectroscopic identification of this material. It is important to state, in this connection, that Os(IV) is not reduced under the conditions of the oxidation state determination experiment; for example, a sample of $OsCl_4$ carried through the procedure is converted quantitatively to $OsCl_6^{-2}$, with no observable trace of $OsCl_6^{-3}$ formed. Furthermore, it was observed that the spectra obtained in the oxidation state determination did not change with time (once the chloro-osmates had formed and the excess acetic anhydride had reacted with the ethanol). This indicates that the organo-sulfur compound formed, $CH_3COSC_2H_5$, does not react with $OsCl_6^{-2}$ to reduce this species to $OsCl_6^{-3}$. Since, in the reaction of osmium tetrachloride with the thiols, reduction does in fact take place to some extent, it can then no longer be that the simple formula of the product formed is $Os(SR)_{4.00}$.

On the basis of the foregoing two questions, questions which are intimately connected, present themselves. Why does the reaction give a mixture of products? Why does some reduction of Os(IV) occur?

The second is perhaps the easier to answer. The alkanethiols are moderately good reducing agents, reducing, for example, iodine to iodide. Similarly, osmium(IV) is a good oxidizing agent, the potential for its reduction to Os(III) in halide media being about 0.85 volts (82). It is not surprising that an oxidation-reduction reaction would occur between Os(IV) and SR^-. What is surprising is that the extent of reduction (that is to say, the percentage of the Os(IV) getting reduced) varies uncontrollably from reaction to reaction. Furthermore, no relation is seen between the S/Os ratio in the product and the reducing strength of the thiols. Of the simple alkanethiols, the reducing strength falls off directly with the acidity (83), so that methanethiol is the best reducing agent of the three thiols used in this study, and butanethiol is the poorest. While in the comparatively few reactions done in this study it did turn out that the S/Os ratios ratios for $R=CH_3^-$ and $C_2H_5^-$ were most usually clustered around 3.8 and those for $R=C_4H_9^-$ were usually over 3.9, nevertheless the number of reactions run certainly does not provide a statistically significant sample and S/Os values near 4 were observed for the first two ligands also.

Thus reduction of Os(IV) to Os(III) does occur to some extent, but does not occur reproducibly, nor does it occur quantitatively in the sense of leading to pure $Os(SR)_{3.75}$ or $Os(SR)_3$, for that matter. The consequence of this is that a mixture of products is formed. It is necessary then to speculate on why this should be so; that is, it is necessary to return to the first question posed above and ask why the reaction gives a mixture of products.

In general the course of a reaction is governed by two considerations: that of equilibrium (or thermodynamics) and that of kinetics.

A consideration of the disparate conditions under which the reaction of osmium tetrachloride with the alkanethiols was carried out seems to indicate that equilibrium considerations are not paramount in this reaction. The procedure for synthesis of the methanethiolato-compounds was that of a sealed tube in which the reaction proceeded under an atmosphere of methanethiol, together with the hydrogen chloride generated during the reaction. Observed S/Os ratios varied over the whole possible range.

The ethanethiolato-compounds were prepared in loosely stoppered flasks containing an atmosphere of air, ethanethiol vapor, and hydrogen chloride. In this case however, in contrast to that above, the stopper could "pop" in the event of excessive pressure build-up (as with a safety valve on a steam boiler) and allow some of the C_2H_5SH and HCl vapor to escape. A reaction was also carried out under reflux conditions, in which case of course the hydrogen chloride escaped through the condenser. Again, observed S/Os ratios varied over the whole possible range.

The same remarks are pertinent to the reactions carried out with butanethiol, except in this case the reflux procedure was the more common one. In the room temperature reactions the partial pressure of butanethiol in the atmosphere over the reaction mixture would be far less than the partial pressure of the thiol in the corresponding ethanethiol reaction, since the latter is by far the more volatile of the two. For the third time, observed S/Os ratios showed considerable variation.

More fruitful speculation can be obtained from kinetic and mechanistic considerations. The number of possible intermediates is enormous because of the two processes, which, it may be assumed, are going on simultaneously. These two processes are the replacement of Cl^- ligands by RS^- ligands, and the joining of monomeric osmium units into polynuclear ones. Thus there are five possible compounds of the type $OsCl_w(SR)_x$, and nine of the type $Os_2Cl_y(SR)_z$, not taking account of the possible isomers of the compounds of a given value of, say, y and z. It seems reasonable that not all of the plethora of intermediates would react at the same rate, nor would all be equally susceptible to reduction. No evidence was ever obtained for the presence of Cl^- in the final products, so that all of the possible intermediates must ultimately lose all chloride. However, somewhere during the process, some set of intermediates must appear which differ in their oxidizing ability toward thiols.

This is not to claim that all possible intermediates must be formed. Indeed it seems more likely that only a few intermediates of each stage of polymerization form. These must be sufficiently similar so that each individual species of the group forms in slightly differing amounts in each reaction without however markedly affecting the overall course of the reaction; yet at the same time they must be just sufficiently different so that one (or a few) is more readily reduced than the others.

A second indication that the intermediates in the reaction are few in number and that apparently the same group of intermediates form in every reaction is that no isomers were detected. That is, not only could the mixture not be resolved into its constituent pure compounds, but also no evidence was ever obtained from the solubility or chromatographic studies to support the possibility of the existence of isomers of either $Os_4(SR)_{15}$ or $Os_4(SR)_{16}$. Yet certainly molecules as complex as these - with four metal atoms and fifteen or sixteen ligands - offer at least the opportunity for isomerization to take place, and it would seem that if such isomerization were to occur, at least some of the possible isomeric structures would be sufficiently different to be capable of resolution by recrystallization or chromatographic techniques.

The fact that the mixture of $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ is incapable of being resolved by standard techniques seems to be a clear indication that the structures of the two pure components must be extremely similar, so that, for example, they exhibit the same solubility behavior and essentially the same infrared spectra. It then becomes necessary to examine the principal lines of experimental investigation to see what can be said about these materials on the basis of those experiments. In this study, strong emphasis was placed on magnetic (susceptibility and resonance) and spectral (ultraviolet, visible, and infrared) work. Some additional evidence was obtained from mass spectrometric and x-ray techniques. The information obtained from these experiments will be discussed in subsequent paragraphs.

Before turning to that discussion, however, it is necessary to dispose of one other question. It has been argued in the material presented above that the structures of $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ must be very similar. Given that, it is relevant to question whether or not they are not only very similar but rather are in fact the same, that is, whether or not the compounds are $Os_4(SR)_{16}$ and $Os_4(SR)_{15}(HSR)$. The answer to this question, as based on the experimental evidence at hand, is clearly negative. First, no evidence was found in any of the infrared spectra of these compounds for the existence of a S-H bond. In the free ligands, ethanethiol for example, the C-S-H bending mode occurs at a frequency of 870 cm^{-1} (72), while the S-H stretching frequencies usually occur in the vicinity of 2550 cm^{-1} (84). Even allowing for some shift of these values upon coordination of the free thiol to the open coordination site on the $Os_4(SR)_{15}$ molecule, no bands could be found which could be assigned to a S-H bond. Second, if a thiol were coordinated sufficiently strongly (as thiol, not thiolate) to resist displacement by a solvent molecule during attempts at recrystallization, then the sulfur from this thiol molecule should show up in the sulfur analysis. Put in other terms, this means that the S/Os ratio observed should always be 16/4 (i.e., 4). Such is not the case. On the basis of these points the existence of $Os_4(SR)_{15}(HSR)$ seems very improbable.

It now becomes appropriate to examine the experimental evidence obtained for the product mixtures obtained in typical runs of the reaction. Most of the data discussed below was obtained for preparations of $[Os(SCH_3)_{3.79}]_4$, $[Os(SC_2H_5)_{3.98}]_4$, $[Os(SC_4H_9)_{3.96}]_4$. The S/Os ratios of the samples used here were selected mainly by chance. Once the synthetic and analytical procedures had been worked out, a large (ca. 1.5 grams) scale preparation was carried out using each different ligand, so as to have sufficient stock on hand for a series of experiments without having the bother of stopping characterization work every few weeks and going back through the series of synthetic steps. Unless specifically mentioned as being otherwise, the data discussed in the following paragraphs will be that obtained from a study of these specific materials.

The observed magnetic moments of these are difficult to interpret for several reasons. First, since a quantity of pure $Os_4(SR)_{15}$ or pure $Os_4(SR)_{16}$ was never obtained for magnetic work, the moments of these pure materials remain unknown. Second, because the magnetic behavior of the heavy transition metals, osmium being no exception, is extremely complicated, and because the coordination symmetry about the osmium atoms is not known, it is virtually impossible to predict what the moments of these materials should be. The most concrete statement which can be made is that $Os_4(SR)_{15}$, with an "extra" electron, so to speak, must be paramagnetic.

The single Os(III) atom in $Os_4(SR)_{15}$ had a d^5 electron configuration, while the Os(IV) atoms in that compound and in $Os_4(SR)_{16}$ have d^4 configuration. The important question to be resolved is the extent to which the four d electrons of Os(IV) and the remaining four (after the odd electron has been considered) of Os(III) contribute to the observed magnetic moment. If the four d electron spins are paired by some mechanism, they contribute only to the diamagnetism of the compound. Thus the moment of $Os_4(SR)_{16}$ would be expected to be zero, while the moment of $Os_4(SR)_{15}$ would result from the single unpaired electron, and should come close to 1.73 B.M.

This seems to be the case in this situation. It is necessary to interject a digression concerning the calculation of the magnetic moments of mixtures. It can be shown (74, 85) that the magnetic moment of a mixture of two substances can be found from

$$\mu^2{}_a = \frac{M_a}{M_1}\ a(\mu_1{}^2) + \frac{M_a}{M_2}\ (1-a)\ (\mu_2{}^2)$$

where μ_a is the moment of the mixture, a the mole fraction of component 1, M_a the molecular weight of the mixture, M_1 and M_2 the molecular weights of components 1 and 2, and μ_1 and μ_2 the moments of components 1 and 2. In the particular situation under discussion, one of the components ($Os_4(SR)_{16}$) is assumed to be diamagnetic so that $\mu_2=0$. Furthermore, to an excellent first approximation, $M_1=M_2=M_a$.

Thus one can immediately write that

$$\mu_a^2 = a(\mu_1^2).$$

The problem which arises at this point is the selection of a value for the magnetic moment of $Os_4(SR)_{15}$. The "spin-only" moment for a single unpaired electron is 1.73 B.M. However in the case of these heavy transition metal ions one cannot neglect a consideration of spin-orbit coupling interactions. The real question which needs to be answered then is to find the extent to which spin-orbit coupling changes the moment from the spin-only value. It is known (86) that in the case of Os(III) with a single electron "hole" in the t_{2g} levels the spin-orbit coupling constant is so large that the moment is raised slightly from the spin-only value of 1.73 B.M. to a value ranging up to about 1.90 B.M. This, however, is for the case of an octahedral complex, and it seems likely that, whatever its structure, $Os_4(SR)_{15}$ has no osmium atoms in a perfect octahedral environment. Consequently a compromise position was adopted and the magnetic moments of a mixture of $Os_4(SR)_{15}$ and $Os_4(SR)_{16}$ were calculated first assuming μ=1.73 and second, μ=1.90 for the former compound, and μ=0 for the latter. Graphs of the moment of the mixture plotted against composition, expressed as the S/Os ratio, are shown in Figure 13.

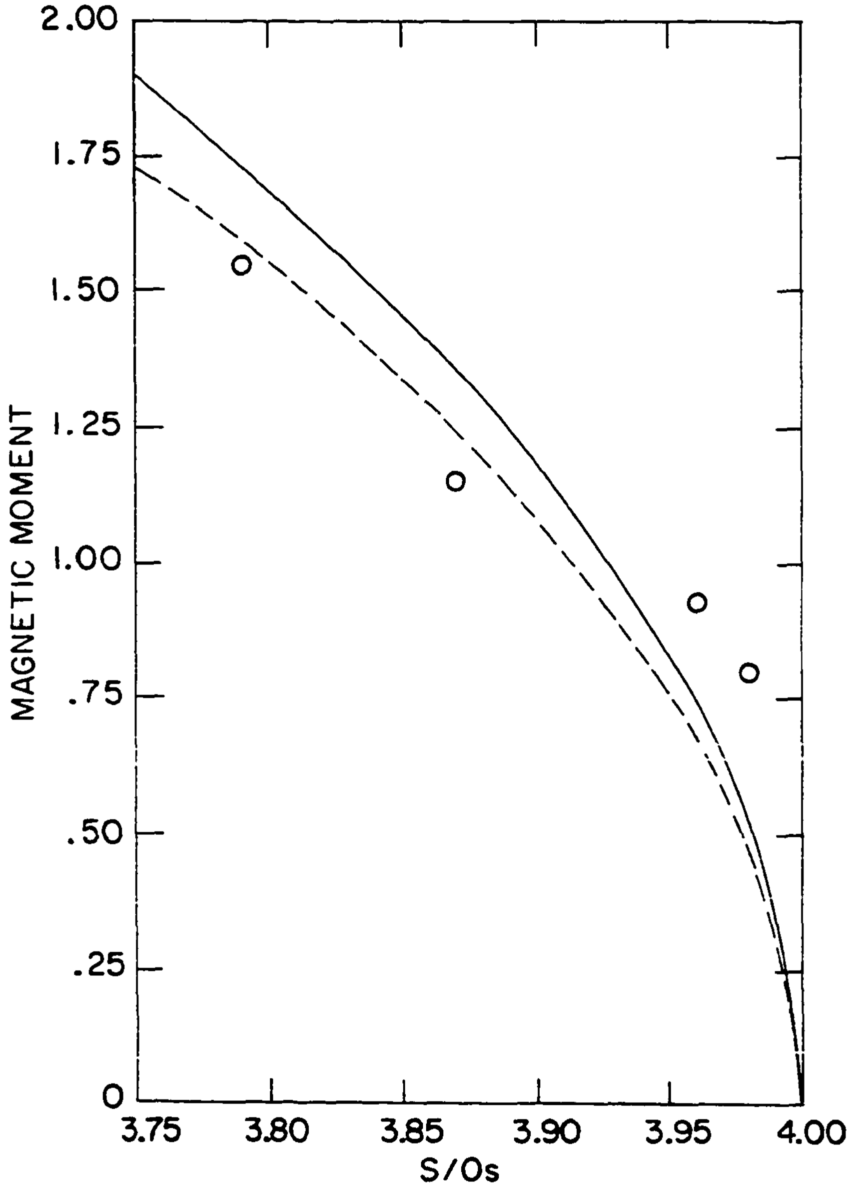

Figure 13. Magnetic moment as a function of S/OS ratio in $[Os(SR_x]_4$ compounds. Solid line represents $\mu=1.9$ for $[Os(SR)_{3.75}]_4$; dashed line represents $\mu=1.73$. Experimental points denoted by O

The case of μ=1.90 B.M. is shown with a solid line; that of μ=1.73 B.M., by a dashed line. Observed magnetic data for $[Os(SCH_3)_{3.79}]_4$, $[Os(SC_2H_5)_{3.87}]_4$, $[Os(SC_4H_9)_{3.96}]_4$ and $[Os(SC_2H_5)_{3.98}]_4$ are also included, denoted by "bullseyes". The trend of the experimental points is unmistakable. Unfortunately, however, it is not clear from the data which, if either, curve is the better representation. An approximate line-of-sight straight line through the experimental points seems to indicate that the moment of $Os_4(SR)_{15}$ is close to 1.73 B.M., but there is so much scatter in the data that little importance can be attached to this observation. Since the values of g for the compounds as observed from electron spin resonance are close to the free electron value of g, this also seems to indicate that the moment of $Os_4(SR)_{15}$ does not differ by a great extent from the spin-only value.

On the basis of this experimental evidence, then, it can be concluded that $Os_4(SR)_{16}$ is diamagnetic and that $Os_4(SR)_{15}$ is paramagnetic with a moment close to the spin-only value for a single unpaired electron. That being the case, it is necessary to inquire about the mechanism whereby the other d electrons are paired up. (In the case of a strong field octahedral complex with four d electrons in the t_{2g} orbitals one would expect two unpaired electrons, giving rise to paramagnetic behavior.) Several mechanisms come to mind. One is the participation of these electrons in direct osmium-osmium bonding. A second is the destruction of the degeneracy of the t_{2g} orbitals by lowering the symmetry about the osmium atom. To cite an extreme case, changing the coordination from six to five and the geometry from octahedral to trigonal bypyramidal would alter the ordering of metal d orbitals in a way such that a doubly degenerate set would lie lowest and hence accommodate the four d electrons with no unpaired spins. This is a topic which will be returned to at a later time when a model structure is proposed and discussed in light of the experimental evidence.

The infrared spectra have been presented previously. A consideration of the metal-ligand bands in the far infrared indicates that there are at least two peaks assignable to Os-S vibrations. Attempts at resolving these peaks were not successful. It would seem that there are however at least two different kinds of Os-S bonds, presumably involving terminal and bridging sulfur atoms. It is also noteworthy that the relative intensities of the two peaks change in a regular manner on changing the nature of the alkyl group (cf. Figure 6), so that for $R=CH_3$ the high frequency peak is by far the more intense, but with $R=C_4H_9$ it is the low frequency peak which is now the more intense. If more detailed structural information is forthcoming it should be possible to relate these observations to the structure of the molecule.

The electronic spectra, unfortunately, provide very little information. A very large peak can be seen forming well out in the ultraviolet, at a wavelength of less than 200 mμ. The actual "hump" of the peak could not be observed under the experimental conditions observed here. It is regarded, however, that the extinction coefficient of this absorption must be at least 15,000. This is a strong indication that the peak must be due to charge transfer.

The other peaks can be seen only as shoulders, slightly jutting out from the mammoth charge transfer peak. In the $R=CH_3$ material (S/Os=3.79) they occur at 275 mμ and 360 mμ. Both peaks appear to have extinction coefficients of over 1000. The most reasonable interpretation seems to be that the peaks observed are sulfur to osmium charge-transfer bands.

The mass spectrometric evidence indicates the absence of strong Os-Os bonds. If such bonds did exist in the molecule it would be expected that the Os_n fragments would appear in the mass spectrum. The highest mass peak appears at about 207. It is tempting to assign this to Os-O (190+16) which in fact it probably is, for it was reported (87) that air was inadvertently admitted while the sample was being heated. A mass peak also appears at about 190 (Os).

X-ray diffuse scattering studies from a sample of $[Os(SC_2H_5)_{3.76}]_4$ indicate (81) heavy atom distances of approximately 2.5, 3.5, and 4.9Å. Given the absence of Os-Os bonds indicated by the mass spectral results, the distance of 2.5Å seems reasonable for an Os-S distance. (cf. the sum of Os radius, 1.35Å, and S covalent bond radius, 1.0Å). The reported distance of 3.5Å can be assigned to an Os-Os distance. If a scale model is constructed with non-bonded Os atoms joined by two sulfur bridges (sulfur being trigonally bound to two Os and one C atom) having Os-S distances of about 2.4Å, it turns out that the Os-Os distance is in fact 3.5Å, assuming <Os-S-Os to be 100°. Using the same model it appears that one can obtain Os-Os distances of 4.9Å between alternate Os atoms in a bent chain of Os atoms with S bridges. This distance, however, is highly dependent on bond angles and steric effects which cannot be precisely evaluated on the basis of the scanty x-ray evidence so far accumulated.

It is regarded that a linear structure, that is to say, one with a linear array of osmium atoms, may be more reasonable than an alternative arrangement of osmium atoms if the thiolate compounds prepared in this study are analogous to the osmium blacks. The reaction of osmium atoms with thiol functional groups spaced along the chain of a naturally occurring molecule may be much more facile if the osmium atoms can coordinate along the chain, rather than requiring the organic molecule to wrap itself in a ball about a small cluster of osmium atoms.

The amorphous character of these materials would appear to be due to the difficulty of packing into a crystal lattice molecules with such a large number of alkyl groups flapping about all over the periphery. The requirements for forcing the alkyl groups into at least a semi-rigid configuration for packing into a lattice do not appear to be compensated by the slight gain from having the molecules in a regular lattice arrangement in the solid.

Hexakis(ethanethiolato)diosmium

Preparation and properties

Hexakis(ethanethiolato)diosmium is one of the products formed in the reaction of osmium tetroxide with ethanethiol in carbon tetrachloride. One possible equation for this reaction is

$$3OsO_4 + 24C_2H_5SH \rightarrow Os(SC_2H_5)_2 + Os_2(SC_2H_5)_6 + 12H_2O$$
$$+ 8(C_2H_5)_2S_2 \, .$$

This equation is advanced only on tentative grounds, since the exact nature of the oxidation product of the thiol was not determined. In any event, the reaction seems to be complete in a matter of a few minutes. The reaction is vigorous and noticeably exothermic.

The compounds $Os(SC_2H_5)_2$ and $Os_2(SC_2H_5)_6$ are recovered at the end of the reaction by removing the excess liquid phase via vacuum distillation. The mixture of the two osmium-containing products is readily separated by extracting the hexakis(ethanethiolato)diosmium into tetrahydrofuran. Removal of the tetrahydrofuran by vacuum distillation yields the hexakis(ethanethiolato)diosmium as a brown, amorphous powder.

The chemical reactivity of hexakis(ethanethiolato)-diosmium remains little explored. The compound is inert toward air and water, in contrast to sodium ethanethiolate. Hydrochloric acid converts the compound to hexachloroosmate(III). Like all other osmium compounds, hexakis-(ethanethiolato)diosmium reacts with oxidizing acids, being converted to osmium tetroxide. It is nonvolatile in high vacuum at temperatures up to 100°C.

The results of the elemental analyses indicate the empirical formula to be $Os(SC_2H_5)_3$. An experimental value of the molecular weight, determined by the Rast camphor method is 727, which compares well with a calculated value of 746 for the formulation $Os_2(SC_2H_5)_6$. An oxidation state determination indicates that only Os(III) is present in the compound (the spectrum of hexachloroosmate(III) has been given previously, in Figure 4).

An investigation of this compound by x-ray methods indicated it to be amorphous. Samples of what were thought to be crystals were examined by rotation, oscillation, and Weissenburg photography with both copper and molybdenum radiation with exposure times of up to 15 hours, with no pattern being observed. Similarly, the compound gave no powder pattern when examined with a Gunier-deWulff camera. From an analysis of the small angle diffuse scattering, it was indicated (88) that the short range order in the compound must be less than 100Å. It was interesting to observe that the diffraction photographs obtained for hexakis-(ethanethiolato)diosmium bear a remarkable similarity to diffraction photographs published by Gunier (89) for lampblack.

Infrared spectra The infrared spectra observed for hexakis(ethanethiolato)diosmium are shown in Figures 14a and 14b for the normal and far i.r. regions respectively. Assignments are given below in Table 11. The presence of a trace of unreacted ethanethiol is indicated by the weak band at 860 cm^{-1}, assignable to the C-S-H bending mode.

Magnetic susceptibility The magnetic susceptibility was measured from liquid nitrogen to room temperatures by the Faraday method; data treatment has been discussed previously. The variation of the susceptibility with temperature is shown in Table 12. Over the temperature range 117-298°K the corrected molar susceptibility is

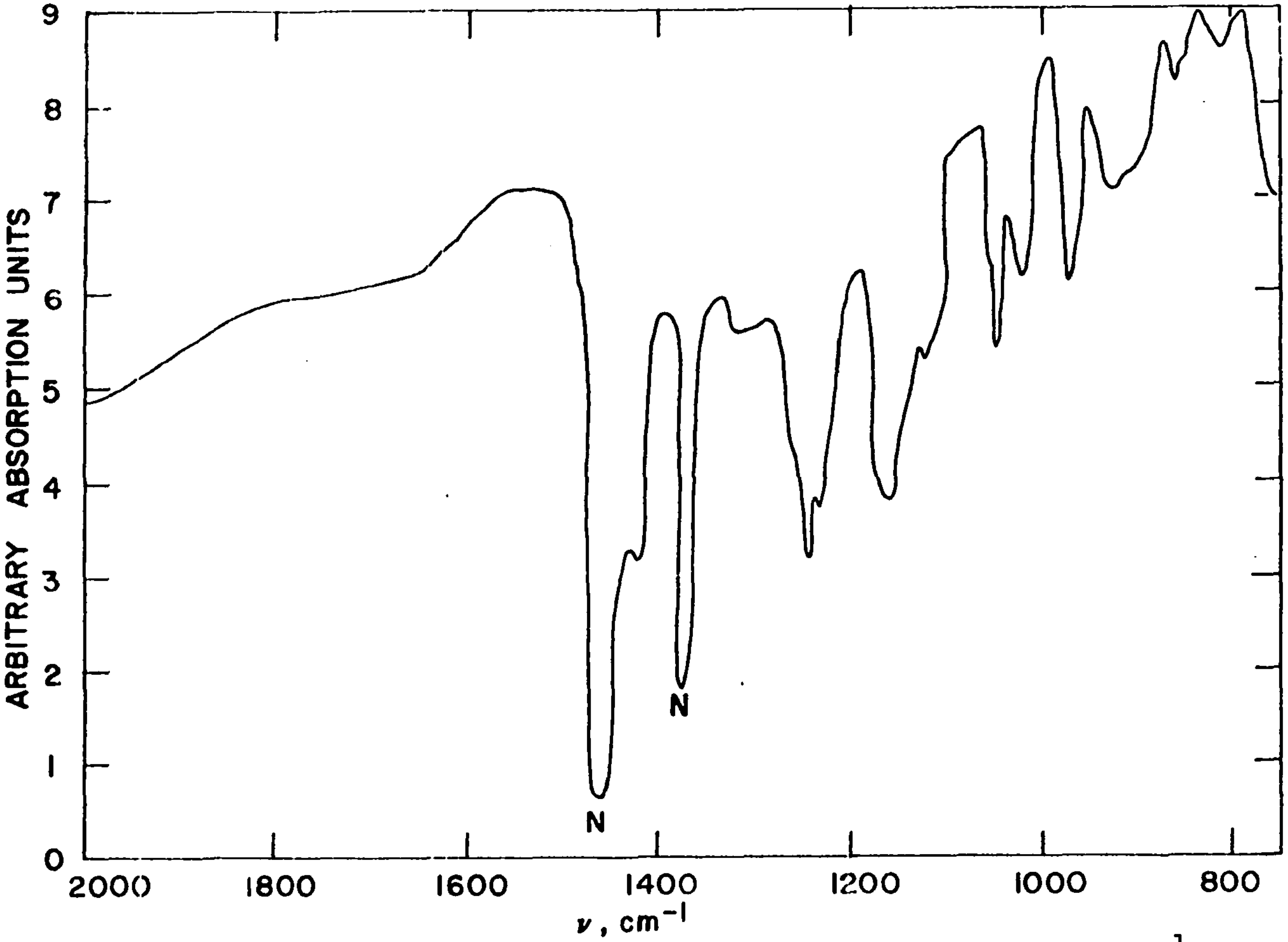

Figure 14a. The infrared spectrum of $Os_2(SC_2H_5)_6$ from 2000 to 800 cm^{-1}

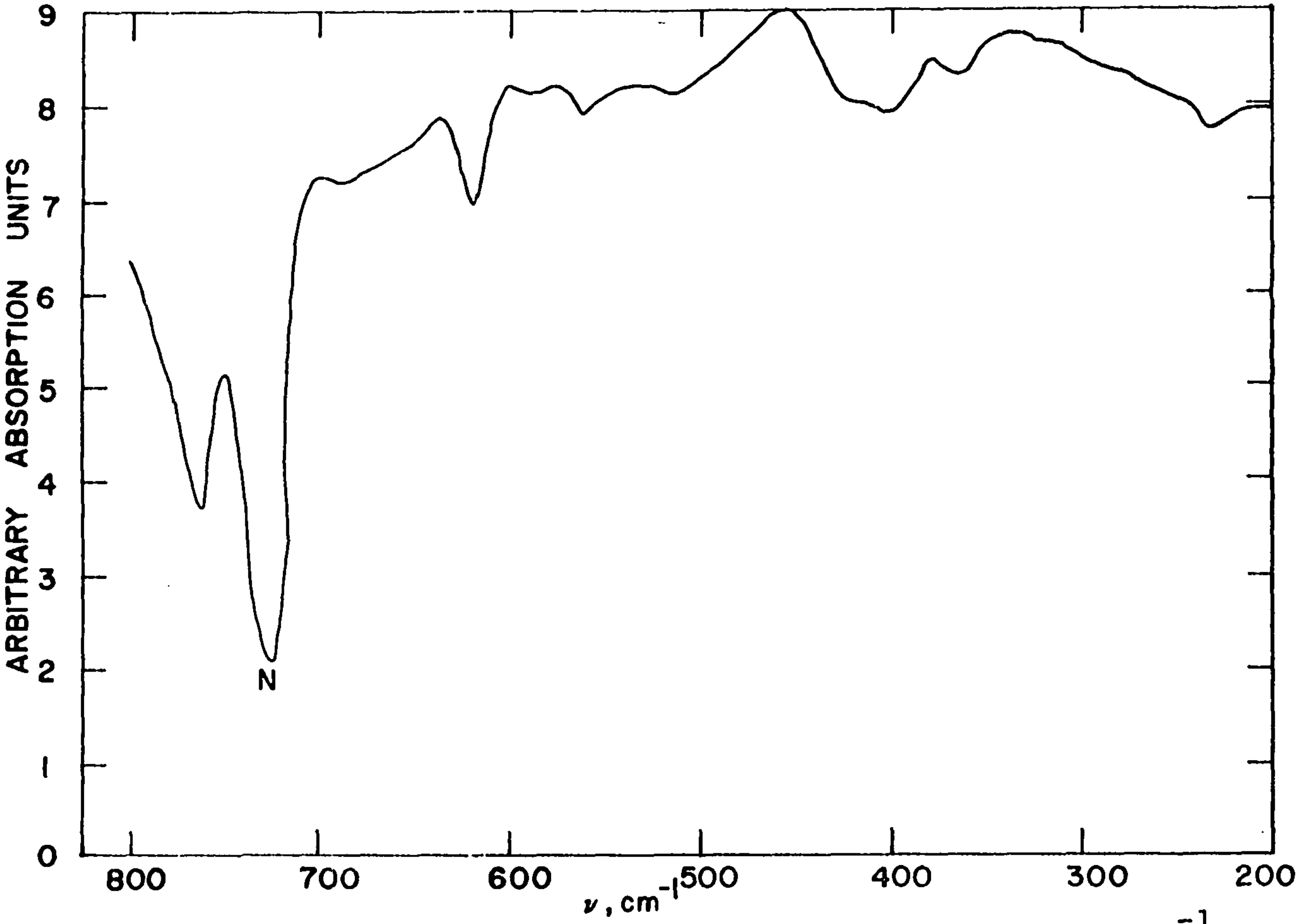

Figure 14b. The infrared spectrum of $Os_2(SC_2H_5)_6$ from 800 to 200 cm^{-1}

Table 11. Infrared assignments for hexakis(ethanethiolato)-diosmium

Band	Assignment	Reference
1300 w	$-CH_3$ sym. bend	72
1245	$-CH_2-$ wag	72
1155	$-CH_2-$ rock	71
1120 w	$-CH_2-$ wag	71
1045	$-CH_3$ rock	72
1020 w	$-CH_2-$ wag	71
970	C-C stretch	72
930 w	C-C stretch	71
860 w	C-S-H bend	72
810 w	$-CH_3$ wag + rock	71
765	$-CH_2-$ rock	72
610	C-S stretch	72
555	Ligand skeletal mode	71
400	Os-S stretch	

Table 12. Temperature variation of corrected molar susceptibility of hexakis(ethanethiolato)diosmium

Temp., °K	χ_m^{CORR}, emu/mole
77	263×10^{-6}
117	112×10^{-6}
133	120×10^{-6}
140	139×10^{-6}
152	111×10^{-6}

Table 12 (Continued)

Temp., °K	χ_m^{CORR}, emu/mole
192	99×10^{-6}
196	94×10^{-6}
206	103×10^{-6}
246	78×10^{-6}
255	91×10^{-6}
278	102×10^{-6}
298	76×10^{-6}

relatively constant, having an average value of 103×10^{-6} emu/mole, with a standard deviation (90) of 16×10^{-6} emu/mole. The scatter in these points is regarded as being due to the considerable experimental difficulties encountered in handling the compound in the susceptibility apparatus. The compound and the teflon container readily acquired a static charge on the slightest handling and consequently the container would frequently lodge against the walls of the apparatus, from which it could be freed only with considerable work. The marked rise in χ_m^{CORR} at liquid nitrogen temperature is regarded to be due to the presence of an impurity which becomes strongly magnetic at low temperatures. There is more uncertainty in the slope and intercept of the Honda-Owen plots for the data sets taken at these temperatures than for most of the other data sets.

Essentially, then, hexakis(ethanethiolato)diosmium is diamagnetic from 117-300°K, with $\chi_m^{300} = -237 \times 10^{-6}$ emu/mole. The diamagnetic contribution calculated from values given by Selwood (74) and Francois (80) is -313×10^{-6} emu/mole. When χ_D is subtracted from χ_m, one obtains the χ_{TIP} of 103×10^{-6} emu/mole.

Electronic spectrum The electronic spectrum of hexakis(ethanethiolato)diosmium is shown in Figure 15. The spectrum shown here was run in tetrahydrofuran. The essential features can be seen to be a strong peak at 250 mμ with shoulders at 275, 330, and 425 mμ.

Nuclear magnetic resonance spectrum Since hexakis-(ethanethiolato)diosmium is diamagnetic, it becomes possible to observe nuclear magnetic resonance without the annoying line broadening or large contact shifts observed with paramagnetic substances. The nuclear magnetic resonance spectrum of a chloroform solution of hexakis(ethanethiolato)diosmium is shown in Figure 16. The multiplet centered at $\delta=1.4$ is assigned to the resonance of methyl protons. It consists of a triplet normally expected for the methyl protons together with an additional, spurious peak arising as a spinning side band from the tetramethylsilane signal. (It is regarded to be a spinning side band since, if it arose from an alkyl moiety present as an impurity one would expect to see other

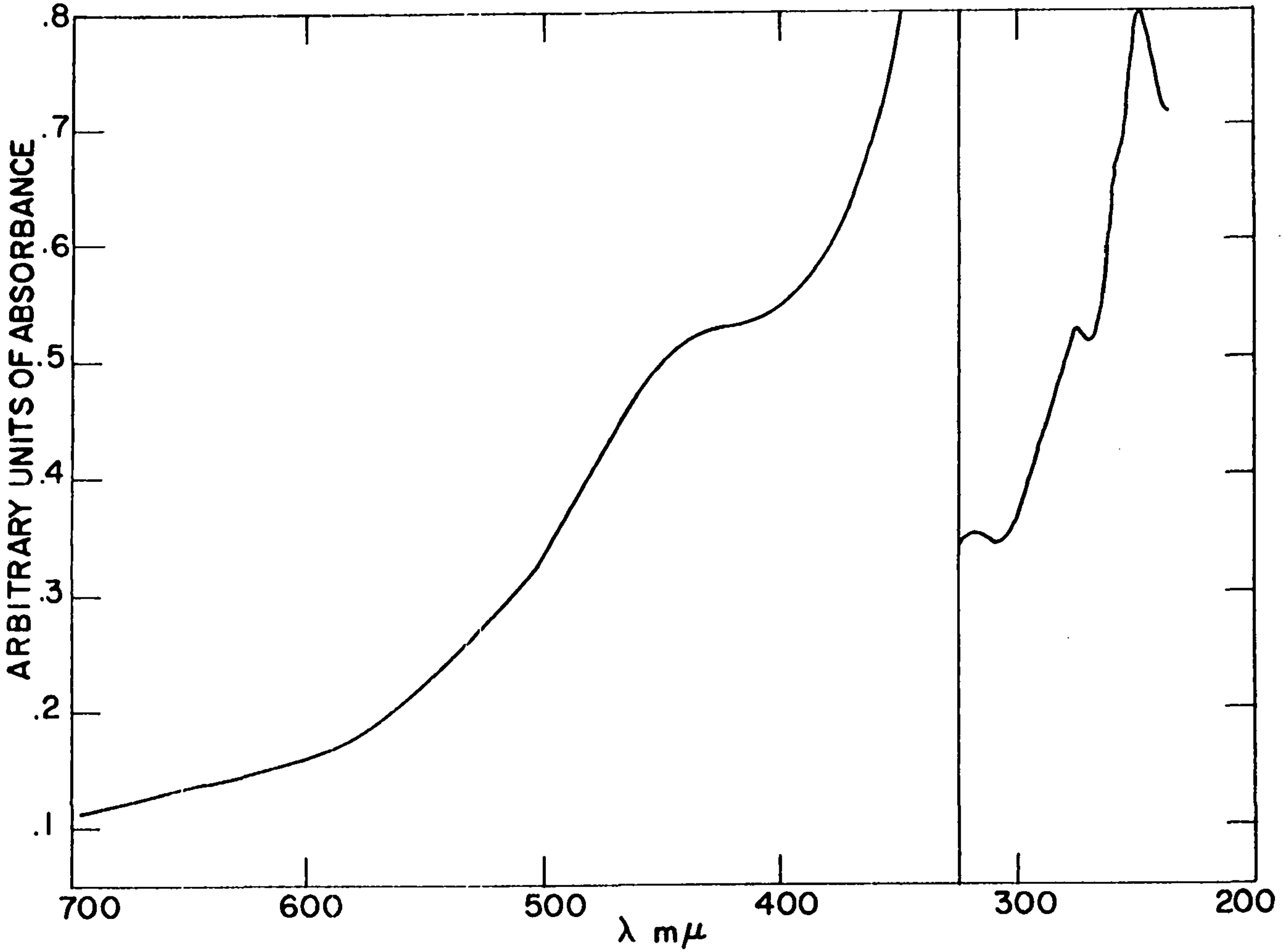

Figure 15. The electronic spectrum of $Os_2(SC_2H_5)_6$

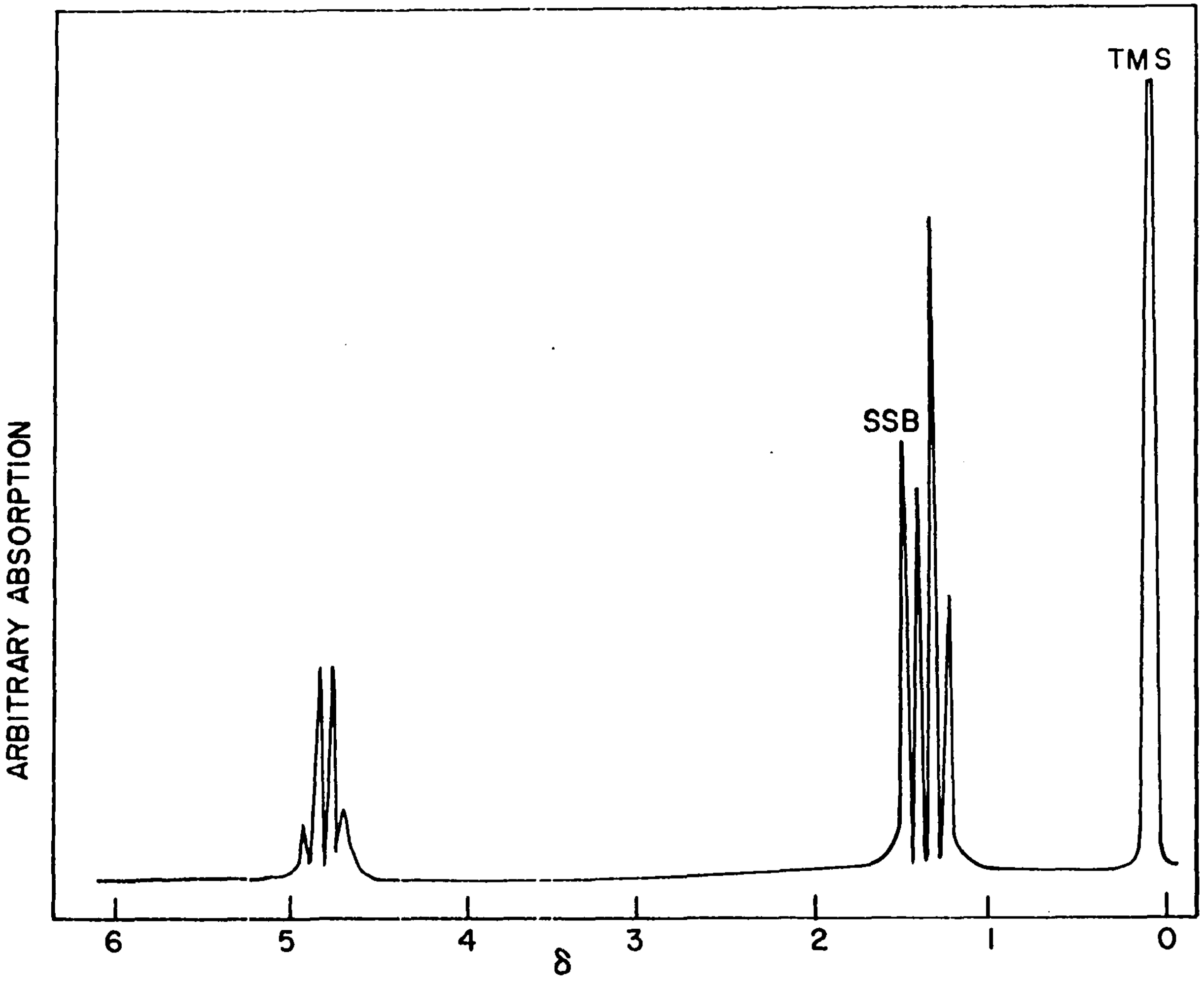

Figure 16. The proton magnetic resonance spectrum of $Os_2(SC_2H_5)_6$

resonances from that moiety with approximately similar intensity; these do not appear.) The quartet at $\delta=4.8$ is assigned to the resonance arising from the methylene protons. Deleting the spurious side band gives an integrated intensity ratio of 2:3 for the methylene and methyl protons.

It seems apparent from this spectrum that all of the ethanethiolato- ligands are chemically equivalent. This result limits the number of possible structures for the molecule. It is perhaps an unusual result in that it would seem to indicate that there are no bridging groups helping to hold the dimer together.

Interpretation and discussion of results

To summarize the important experimental findings, hexakis(ethanethiolato)diosmium is a diamagnetic, amorphous compound containing only a single type of ethanethiolato- ligand. Oxidation state evidence indicates that the osmium atoms are present as Os(III).

It must be recalled that Os(III) is a d^5 ion, which implies that if the osmium atoms were not in interaction, one would expect the compound to be a moderately strong paramagnet, having two unpaired electrons per molecule. The fact that the compound is diamagnetic indicates that the spins of these two electrons must be coupled.

Since it appears from the infrared and nuclear magnetic resonance data that only a single type of ligand is present, it is most reasonable to presume that the mechanism which accounts for this interaction is a direct osmium-osmium bond. Thus each osmium atom has about it three terminal ethanethiolato-ligands and one other osmium atom (or, more specifically, an $Os(SC_2H_5)_3$ group bonded to it through the osmium atom) arrayed in, presumably, a tetrahedral-like structure. The shape is then, in effect, an hourglass type.

The molecular structure has an unusually low coordination number for Os(III). This may be in part due to strong multiple bonding between the osmium atoms, causing a very short Os-Os distance. Another factor to take into consideration is the possibility of weak intermolecular interactions between the osmium atoms and the sulfur atoms on ligands belonging to other $Os_2(SC_2H_5)_6$ units. These interactions would have to be sufficiently weak so as to be easily overcome when the molecule is dissolved in molten camphor. That being the case, it is not unreasonable to expect these intermolecular interactions to be too weak and too easily disrupted to enforce long-range ordering in the solid, thus accounting for the amorphous character of this substance.

The Intractable Compounds

While it can certainly be said that all six compounds prepared during this study were, in one respect or another, intractable, osmium bis(ethanethiolate) and osmium tris(butanethiolate) were especially difficult. There is little doubt that these compounds must be different chemically; however, they are discussed together here because very little fruitful information was accumulated concerning these compounds.

Osmium bis(ethanethiolate)

Preparation and properties Osmium bis(ethanethiolate) is one of the compounds arising from the reaction of ethanethiol with osmium tetroxide in carbon tetrachloride solution. Its most salient characteristic is its insolubility in every common laboratory solvent (the range of solvents tried ran, in terms of polarity, from carbon tetrachloride and cyclohexane all the way to water). This at least does provide an excellent way to separate osmium bis(ethanethiolate) from the other osmium compound formed in the reaction, osmium tris(ethanethiolate), because the latter does dissolve in a number of common solvents, such as, for example, chloroform and tetrahydrofuran.

It is worth noting in passing that a compound of the same empirical formula and same insolubility is found, at least sometimes, in the reaction of osmium tetrachloride with sodium ethanethiolate in ethanol. This reaction is, however, not reproducible.

Osmium bis(ethanethiolate) is inert toward water and aqueous bases. It is inert toward most acids except the oxidizing acids, which convert it to tetroxide. The compound is nonvolatile.

This compound is completely insoluble in molten camphor. As a result, it is not possible to carry out a molecular weight determination by the Rast method. Of course, all other molecular weight techniques in which the compound to be measured must be in solution are also impossible.

The oxidation state determination was also not unequivocal. Osmium bis(ethanethiolate) did react with acetic anhydride and lithium chloride upon long standing at room temperature. The resulting solution was green, which is typical of osmium(IV) in solution. The spectrum did not correspond with the known spectrum of hexachloroosmate(IV). Indeed, it corresponded with no known spectrum.

The infrared spectrum of osmium bis(ethanethiolate) is shown in Figures 17a and b, for the normal and far regions respectively. In Table 13 below are given the assignments of the observed peaks.

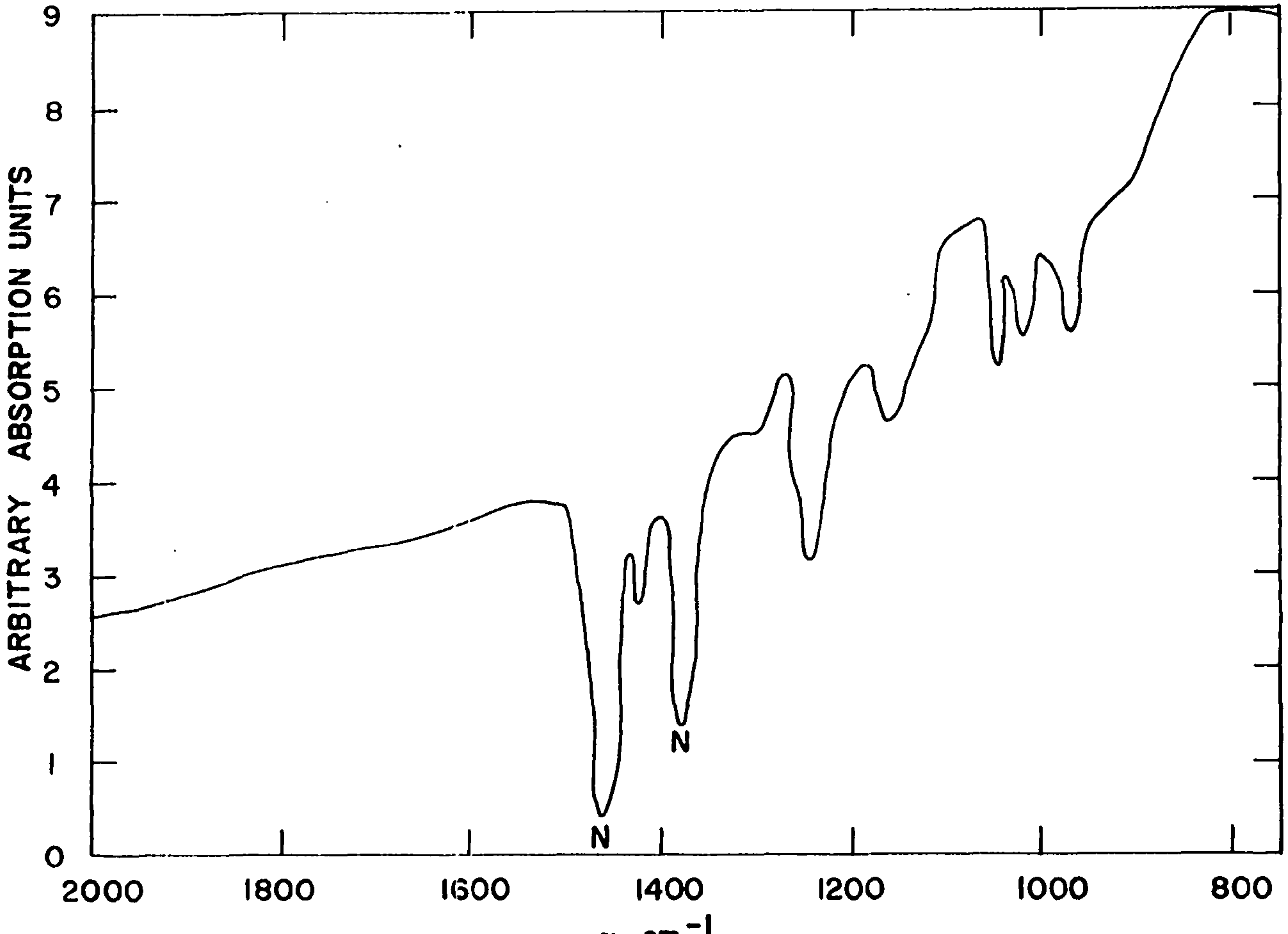

Figure 17a. The infrared spectrum of $Os(SC_2H_5)_2$ from 2000 to 800 cm^{-1}

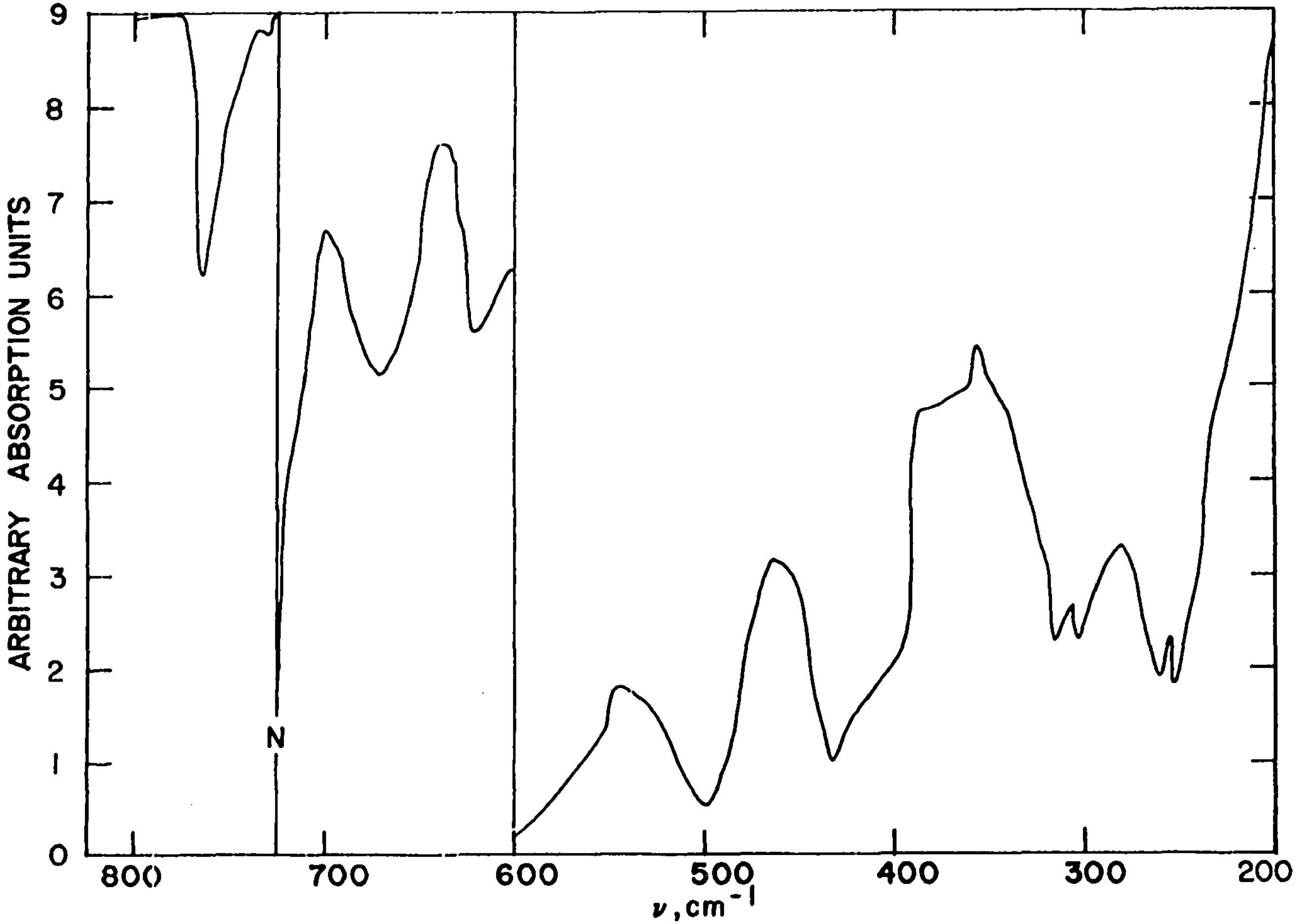

Figure 17b. The infrared spectrum of $Os(SC_2H_5)_2$ from 800 to 200 cm^{-1}

Table 13. Infrared assignments for osmium bis(ethanethiolate)

Band, cm^{-1}	Assignment	Reference
1425 w	$-CH_3$ deformation	71
1300 sh	$-CH_2-$ twist	72
1245	$-CH_2-$ wag	72
1160 w	$-CH_2-$ rock	71
1045 w	$-CH_3$ rock	72
1020 w	$-CH_3$ rock	72
970 w	C-C stretch	72
765	$-CH_2-$ rock	72
675	C-S stretch	72
617	C-S stretch	72
500	Os-S stretch	
425	Os-S stretch	
310 w	S-Os-S bend	
260 w	S-Os-S bend	
205	ligand torsion modes	73
190	ligand torsion modes	73

The magnetic susceptibility calculations were carried out in the manner described previously. The graph of χ vs. 1/T is given in Figure 18. The data is summarized in Table 14 below.

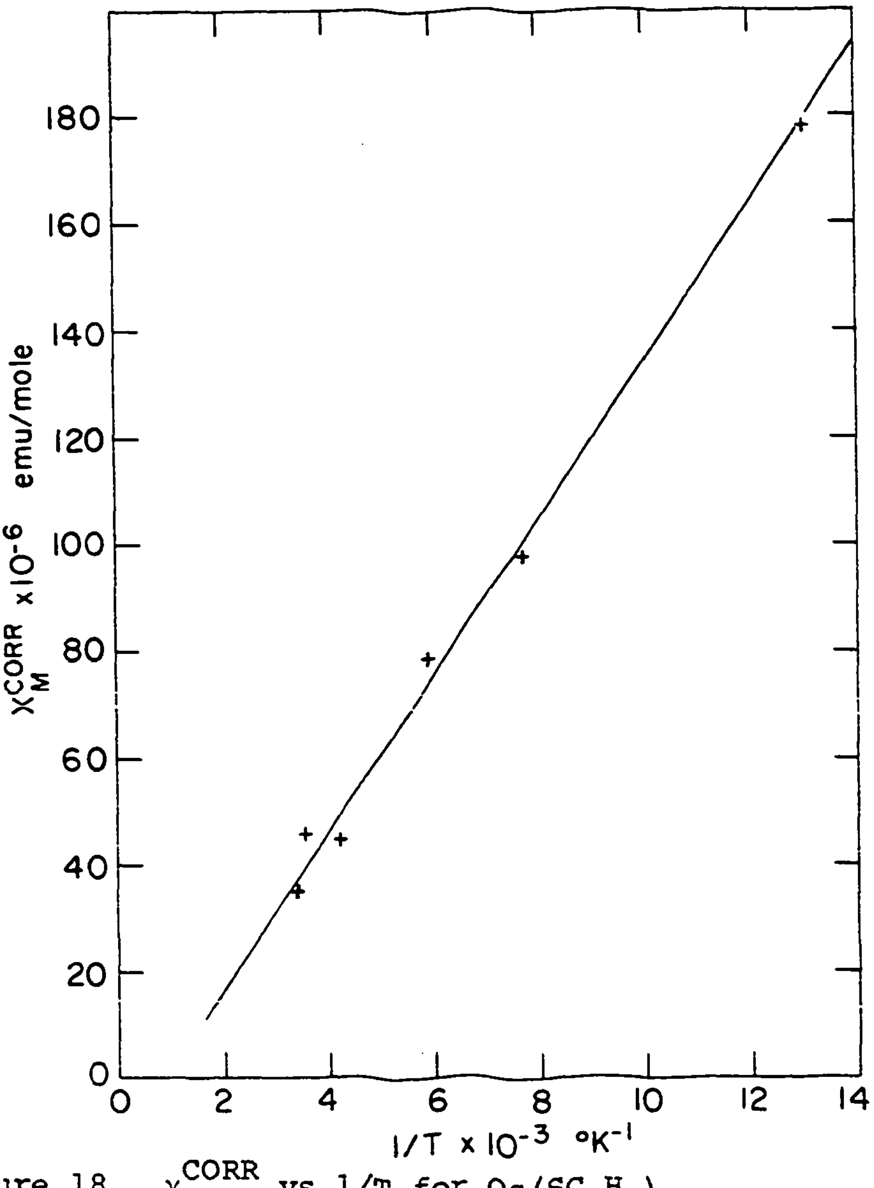

Figure 18. χ^{CORR} vs 1/T for $Os(SC_2H_5)_2$

Table 14a. Temperature variation of corrected molar susceptibility of osmium bis(ethanethiolate)

Temp., °K	χ_m^{CORR}, emu/mole
77	178×10^{-6}
130	98×10^{-6}
170	78×10^{-6}
235	45×10^{-6}
280	46×10^{-6}
298	35×10^{-6}

Table 14b. Magnetic constants of osmium bis(ethanethiolate)

Term	Value
C	14.6×10^{3} emu/mole °K
μ	0.35 B.M.
χ_D.	-125×10^{-6} emu/mole
Θ	+35°K

As a result of the insolubility of osmium bis(ethanethiolate), it was not possible to obtain electronic spectra in solution. For the same reason, it was not possible to obtain nuclear magnetic resonance spectra.

Interpretation of results In light of the perverse resistance of osmium bis(ethanethiolate) to dissolution, little can be said about this compound. The magnetic moment is peculiar to say the least. It is interesting to note that Cabrera and Duperier (91) some years ago reported a value of 0.35 B.M. for the magnetic moment of what they regarded to be osmium dichloride. In light of more recent investigations by Schäfer and Huneke (92) and by Bell and co-workers (93) it seems certain that $OsCl_2$ does not exist. Since Cabrera and Duperier did not supply details of the source of their experimental materials, it is difficult to know of which osmium compound they actually measured the moment.

The oxidation state data is also ambiguous. One would predict an oxidation state of +2 from the empirical formula. A solution of osmium(II) might be expected to oxidize when standing for long periods of time in air.

It seems reasonable that osmium bis(ethanethiolate) is polymeric to some extent. A monomeric unit of formula $Os(SC_2H_5)_2$ would have a ridiculously low coordination number for a heavy transition metal; one might expect the compound to not be so stubbornly insoluble.

In their article on the bonding of metal cluster compounds, **Haas and Cotton** (94) discuss the possibility of the existence of an $Os_6X_8^{+4}$ cluster containing Os(II). It is obvious that the empirical formula of $[Os_6(SC_2H_5)_8](SC_2H_5)_4$ is in fact $Os(SC_2H_5)_2$. Perhaps some future x-ray studies may reveal that $[Os_6(SC_2H_5)_8](SC_2H_5)_4$ is not an unreasonable formulation.

Osmium tris(butanethiolate)

Preparation and properties Osmium tris(butanethiolate) arises from the reaction of osmium tetroxide with butanethiol in carbon tetrachloride. The product recovered from this reaction is a gummy, brownish-black solid. If this material is heat treated for several hours at 200°C under dynamic vacuum, the result is the formation of the jet black, free-flowing powder having the empirical formula $Os(SC_4H_9)_3$.

In its behavior $Os(SC_4H_9)_3$ resembles $Os(SC_2H_5)_2$ much more than it does $Os(SC_2H_5)_3$. That is, osmium tris(butanethiolate) is not soluble in any common laboratory solvent. Like osmium bis(ethanethiolate), this compound is inert toward air and water, and is nonvolatile. Oxidizing acids convert the compound to the tetroxide. Hydrochloric acid slowly reacts with osmium tris(butanethiolate) over a period of several weeks, yielding a reddish-orange solution. The color is typical of Os(III) in solution but the solution does not display the $OsCl_6^{-3}$ spectrum. The insolubility renders molecular weight, electronic spectrum, and nuclear magnetic resonance spectrum determinations impossible.

The infrared spectrum of osmium tris(butanethiolate) is shown in Figures 20a and 20b for the normal and far regions respectively. Assignments are given below in Table 15.

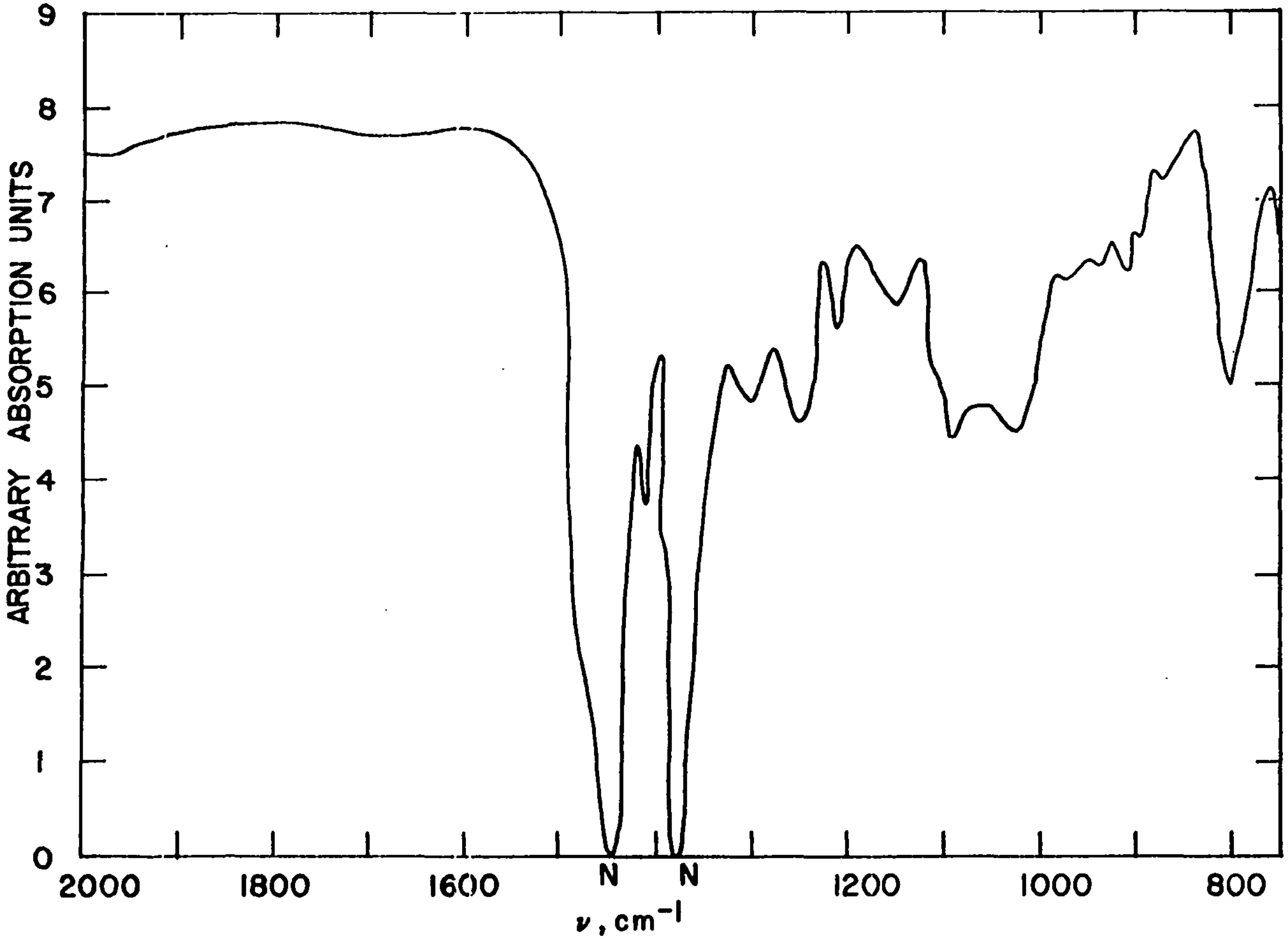

Figure 20a. The infrared spectrum of $Os(SC_4H_9)_3$ from 2000-800 cm^{-1}

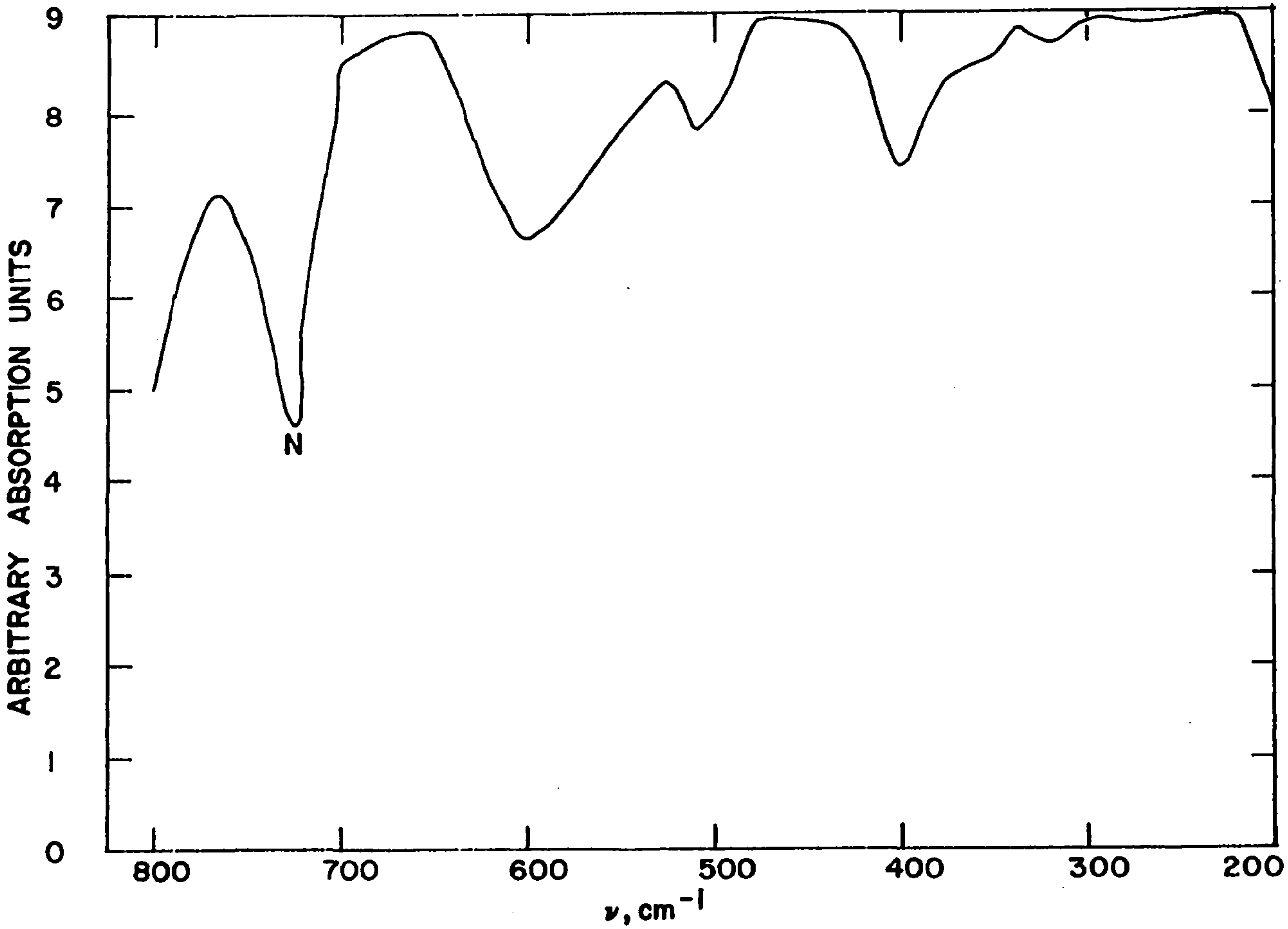

Figure 20b. The infrared spectrum of $Os(SC_4H_9)_3$ from 800 to 200 cm^{-1}

Table 15. Infrared assignments for osmium tris(butanethiolate)

Band	Assignment	Reference
2710 w		
2650 w	S-H stretch	84
1415	$-CH_3$ deformation	71
1300 w	$-CH_2-$ twist	71
1257	$-CH_2-$ wag	71
1212 w	S=O stretch	84
1160	$-CH_2-$ rock	71
1095 w	$-CH_3$ rock	71
1020 w	$-CH_2-$ wag	71
970	C-C stretch	71
935	C-H bend	71
908	C-C stretch	71
870 w	C-S-H bend	72
800	CH_3 wag + rock	71
663	C-S stretch	72
600	C-C-C bending	72
510	C-C-C skeletal mode	72
400	Os-S stretch	
195	ligand torsion modes	73
160	ligand torsion modes	73
85	ligand torsion modes	73

It can be seen that there is a trace of unreacted thiol present (peaks at 2710 and 870 cm^{-1}) and a trace of a sulfenic acid (S=O peak at 1212 cm^{-1}) which apparently arises from the oxidation of butanethiol by osmium tetroxide.

The magnetic data is given in Table 16 below. Like hexakis(ethanethiolato)diosmium, osmium tris(butanethiolate) is diamagnetic, having $\chi_m = -193 \times 10^{-6}$ emu/mole at room temperature. The diamagnetic correction, χ_D, is -282×10^{-6} emu/mole, leaving a residual χ_{TIP} of $+87 \times 10^{-6}$ emu/mole on the temperature range 113-295°K (the standard deviation in χ_{TIP} on this range is 8×10^{-6} emu/mole).

Table 16. Temperature variation of corrected molar susceptibility of osmium tris(butanethiolate)

Temp., °K	χ_m^{CORR}, emu/mole
81	115×10^{-6}
83	110×10^{-6}
84	116×10^{-6}
113	87×10^{-6}
114	90×10^{-6}
128	103×10^{-6}
135	94×10^{-6}
138	94×10^{-6}
140	89×10^{-6}
153	92×10^{-6}
167	97×10^{-6}

Table 16 (Continued)

Temp., °K	χ_m^{CORR}, emu/mole
190	92×10^{-6}
193	80×10^{-6}
195	87×10^{-6}
200	87×10^{-6}
203	88×10^{-6}
207	72×10^{-6}
264	79×10^{-6}
265	75×10^{-6}
268	77×10^{-6}
271	85×10^{-6}
274	78×10^{-6}
295	89×10^{-6}

Interpretation of results Despite the same empirical formulas, $Os(SR)_3$, and despite having similar magnetic behavior, osmium tris(butanethiolate) and hexakis(ethanethiolato)diosmium must be otherwise very different. To be sure, one always expects some variation in the properties of compound on changing one ligand to another; nevertheless, these variations are usually small (it is instructive to compare the pair $Os_4(SC_2H_5)_{15,16}$-$Os_4(SC_4H_9)_{15,16}$ with the pair $[Os(SC_2H_5)_3]_2$-$[Os(SC_4H_9)_3]_n$). Certainly then it is not at all reasonable to presume that the compounds have the same structure. If this compound is in fact a compound of osmium (III), as evidence suggests, then the diamagnetism of the compounds indicates that it must be a polymer with osmium-osmium interactions to couple the electron spins; furthermore, it seems that the degree of polymerization n must be an even number, to provide an even number of electrons in the compound. It is hoped that a future experimenter in this area will be able to obtain single crystals of these materials for an x-ray study.

SUGGESTIONS FOR FUTURE WORK

Despite its having been discovered nearly two centuries ago, osmium remains an element the chemistry of which has scarcely been explored. It is impossible to read widely in the literature pertaining to the chemistry of this element without uncovering many questions which still need to be answered. One interested in the chemistry of osmium could fill many pages outlining potential research projects. The points discussed below are restricted to some interesting ideas which arose during the course of this investigation.

The most frustrating problem encountered was that of the inability to prepare pure $[Os(SR)_{3.75}]_4$ or $[Os(SR)_{4.00}]_4$, and the correlated problem of resolving the mixture of products obtained in the synthetic reactions investigated. Since all of the classical separation methods failed, perhaps the most fruitful route to these compounds might be the variation in some way of the synthetic procedure. For instance, the mixture might be reacted further with RSH for reduction to pure $[Os(SR)_{3.75}]_4$, or it might perhaps be reacted with R_2S_2 for oxidation to pure $[Os(SR)_4]_4$.

It was of course a major disappointment to find that the compounds of prime interest were amorphous. This consequently prevented a definitive determination of the molecular structure by x-ray single crystal diffraction studies. It would therefore be of considerable value to investigate methods by which these materials might be prepared in a crystalline state. Hopefully if pure $[Os(SR)_{3.75}]_4$ or $[Os(SR)_{4.00}]_4$ were prepared, it could be induced to crystallize. It is hoped too that the studies of diffuse scattering of x-rays from the powdered samples will continue to bear fruit.

Hanker (1) has also described compounds of the type $Os_5(SR)_{20}$, that is, pentamers of the $Os(SR)_4$ unit. It would be worthwhile to consider the nature and mechanism of the polymerization of these compounds, the possibility of preparing other "n-mers" of the types $[Os(SR)_4]_n$ and $[Os(SR)_{3.75}]_n$, and the possibilities of interconversion of these various "n-mers".

Certainly the reaction of osmium tetroxide with thiols is one which needs a great deal more study. An obvious question to ask is why aqueous solutions of osmium tetroxide give $Os(SR)_4$ type compounds, while solutions of that reagent in carbon tetrochloride give at least two different $Os(SR)_3$ compounds and one $Os(SR)_2$ compound. The reactions which have been carried out have been essentially uncontrolled, in that an excess of thiol is added to the tetroxide and the reaction occurs almost instantaneously. More careful attention needs to be given to the stoichiometric proportions of the reactants and to the rate of mixing. Some painstaking work will be needed to unravel the complex details of this reaction.

Another area of investigation worthy of a second look is the reaction of osmium halides with alkali thiolates, such as, for example, sodium ethanethiolate. A few such reactions were tried during the course of this investigation, but this study was abandoned when it appeared that the products were not reproducible. The use of alkali metal thiolates is a potentially valuable synthetic procedure since, the thiolates being solids, it is quite easy to control exactly the stoichiometry of the reaction. Should it be possible to obtain reproducible results with this method, it is conceivable that a number of very interesting families of compounds could be prepared, including such examples as $OsX_x(SR)_y$, $Os(SR)_x(SR')_y$, and $M_xOs(SR)_yX_z$. One might well expect at least the first two such families to be polymeric.

It is also of interest to consider the use of other thiols as ligands. Propanethiol is a trivial example. One can consider the possibilities of using more complicated alkyl moieties than the simple straight-chain groups of having other functional groups present in the molecules or of using multidentate thiols.

Standing then on the first patches of plowed ground carved out by the Hanker group and by this author, one can visualize the possibilities of oxidation-reduction equilibria of the type $Os(SR)_{3.5} \rightleftarrows Os(SR)_{3.75} \rightleftarrows Os(SR)_4$;

the use of ligands of greater complexity than the simple lower normal alkanethiols; the interconversion of polymers such as $Os_4(SR)_{16} \leftrightarrow Os_5(SR)_{20}$; and the formation of mixed-ligand compounds containing both thiols and other ligands, or mixtures of thiols, seeing thereby almost limitless horizons in the field of the chemistry of thiolatoosmium compounds.

Perhaps in the long range the most promising discovery in this investigation has been the elucidation of a very slick and convenient method for the preparation of anhydrous osmium tetrachloride and tetrabromide. It has been well demonstrated that anhydrous metal halides are extremely versatile starting materials for a wide range of chemical investigations including such general areas as coordination chemistry, solid state chemistry, and the chemistry of polynuclear metal compounds. The thionyl halide reaction represents a method for preparing the anhydrous osmium halides which is vastly superior to the previously employed procedure of direct combination of the elements. It is hoped the availability of a relatively fast and easy route to the osmium halides will attract workers interested in exploring some facet of osmium chemistry but who have heretofore shied away from the difficult synthesis of the necessary starting material.

Finally it is hoped that some of the recovery procedures employed in this study will prove useful to future workers. It is felt that the metallothermic reduction of residues would be much superior to the classic hydrogen reduction, particularly for handling large quantities of residues, if some tinkering were done to find the exact conditions giving maximum efficiency.

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ACKNOWLEDGMENTS

The author would like to express his appreciation to Dr. Robert McCarley for his guidance, suggestions, and advice during the course of this project.

The author also gratefully acknowledges the support and encouragement of his wife Linda, without which this project might never have been completed.

Special thanks are due to Mr. John Greiner for his unselfish assistance with the operation of the Faraday balance and many interesting discussions on magnetic phenomena.

Special thanks are also due to Mr. Don Bailey for his assistance with x-ray procedures and computational problems.

For determination of the infrared spectra thanks are owed to Miss Evelyn Conrad and especially to Mr. Clifton Hill for his patience and perseverance in working with these hideously intractable compounds.

The author would also like to acknowledge the assistance of Mr. Richard Clark for neutron activation analyses; Mrs. Susan Helzer, Mr. N. S. Morales, and Mr. Thomas Lyttle for the determination of nuclear magnetic resonance spectra; Miss Willa Jones for the determination of mass spectra; and Mr. John Richard for the determination of carbon and hydrogen and assistance with molecular weight determinations.

Commendation is certainly due to the author's friends and fellow graduate students on the third floor of the Research

Building who endured occasional accidental introduction of noisome mercaptan vapors into the atmosphere with tolerance and good humor.

A great deal is owed to the author's good friend and colleague, the late John F. Culp, for his inspiration, encouragement, and suggestions during the early stages of this project. It is regretted that he did not have a sufficiently long life to see this project come to fruition.

Some kind of appreciation is due to the author's cronies, Mr. Frank Eshelman and Mr. Denzil Stacy, for their encouragement, and especially for their inordinate zeal to cooperate with, participate in, and discuss innumerable experiments in the exterior ballistics of small projectiles.

The author certainly wishes to acknowledge the past and present members of Physical and Inorganic Group X, for their assistance, comments, and suggestions regarding this project.

Finally, for providing companionship on many a long night with cantankerous apparatus and especially for providing a respite and occasional surcease from the worries of a difficult research project, the author would like to thank the following individuals: Mr. Sherlock Holmes and Dr. John H. Watson, Messrs. Nero Wolfe and Archie Goodwin, Dr. Clark Savage, Jr., Mr. Lew Archer, Lt. Luis Mendoza, Lt. Charles

Chan, "G-8", and Mr. Lamont Cranston, who knows what evil lurks in the hearts of men.

Valete et plaudite!