

TABLE V
 ELECTRONIC SPECTRA OF $[\text{Au}(\text{dien-H})\text{X}]^+$ COMPLEXES

Complex	$b_1, b_2(\pi^*) \rightarrow 2a_1(\sigma^*)$			$2p_\pi(\text{dien-H}) \rightarrow 2a_1(\sigma^*)$		
	τ_{max} , Å.	ν_{max} , cm.^{-1}	ϵ_{max}	τ_{max} , Å.	ν_{max} , cm.^{-1}	ϵ_{max}
$[\text{Au}(\text{dien-H})\text{Cl}]^{a+}$	2630	38,020	2930	3700	27,030	1900
$[\text{Au}(\text{dien-H})\text{Br}]^{b+}$	2840	35,210	2340	3800	26,320	2180
$[\text{Au}(\text{dien-H})\text{OH}]^{c+}$	Not observed			3500	28,570	1680

^a Equivalent concentrations of $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ and OH^- , with 0.5 M Cl^- . ^b Equivalent concentrations of $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ and OH^- , with 0.5 M Br^- . ^c Complex present in a solution originally containing $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ at pH 11.5.

transfer process, since the stability of $\pi(\text{X})$ is expected to increase in the order $\pi(\text{I}) < \pi(\text{Br}) < \pi(\text{Cl})$.

The charge-transfer assignment is also indicated from a comparison of analogous Pt^{2+} and Au^{3+} complexes. Thus the band for any given X complex shifts to lower energy in going from Pt^{2+} to the better electron acceptor, Au^{3+} . This type of evidence has been used to assign ligand \rightarrow metal charge transfer in PtX_4^{2-} and AuX_4^- complexes.²²

A final observation in favor of the interpretation presented above is that the $[\text{Pt}(\text{dien})\text{OH}]^+$ complex does not show the band at all in the spectral region examined.

The electronic spectra of several $[\text{Au}(\text{dien-H})\text{X}]^+$ complexes are given in Table V. The high-energy band in each case is readily assigned to the $b_2, b_1(\pi^*) \rightarrow 2a_1(\sigma^*)$ transition, since a blue shift is anticipated for $\text{X} \rightarrow \text{Au}$ type charge transfer in going from $[\text{Au}(\text{dien})-$

$\text{X}]^{2+}$ to $[\text{Au}(\text{dien-H})\text{X}]^+$. The new band, at lower energy, is assigned to the transition $2p_\pi(\text{dien-H}) \rightarrow 2a_1(\sigma^*)$, since dien-H has a relatively unstable electron pair in a $2p_\pi$ type orbital.

The fact that $[\text{Au}(\text{dien-H})\text{OH}]^+$ shows *only* the low-energy band due to dien-H \rightarrow Au charge transfer is evidence of the correctness of these assignments.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Polymeric Complexes of Cobalt(III) with Some Mercapto Compounds^{1a}

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Hexanethiol (HShex) and cobalt(II) react with oxygen and sodium hydroxide to form a complex $[\text{Co}(\text{Shex})_3]$. A product of the same composition also is obtained from (HShex), sodium hydroxide, and *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride. These complexes are very similar to the tris-(3-mercaptopropionato)-cobalt(III) and the triscysteinato-cobalt(III) obtained earlier.² It is concluded that these complexes are polymeric and involve only mercaptide-cobalt(III) coordination, with the (Shex) groups acting as bridges between pairs of cobalt(III) atoms (see Fig. 1). Qualitative evidence for the polymeric nature of the complexes is obtained from measurements of viscosity, diffusion, and osmotic pressure. The infrared spectrum of tris-(3-mercaptopropionato)-cobalt(III) indicates that the carboxyl group is not coordinated.

Two triscysteinatocobalt(III) complexes were first prepared by Schubert³ and further studied by Gorin, *et al.*² One complex was obtained at high pH and dissolved in water to give green solutions; the other complex was obtained at lower pH and was very insoluble in water, but could be dissolved in base to give cherry-red solutions. It has been established that nitrogen and sulfur atoms serve as donors in the green complex. The red triscysteinato complex has a visible and ultra-

violet spectrum very similar to that of the complex formed from 3-mercaptopropionic acid, and it seemed reasonable to postulate that these complexes contain chelate rings involving the oxygen and sulfur atoms.²

This conclusion could not be regarded as certain, however, and it therefore seemed worthwhile to investigate a ligand containing the mercapto group only. This paper will describe a complex formed from cobalt(III) and hexanethiol (henceforth symbolized by $[\text{HShex}]$) and some of its properties.

Experimental

Materials.—(HShex), obtained from the Eastman Kodak Company, Rochester 3, N. Y., c ystaine hydrochloride hydrate (B

(1) (a) Supported in part by Grant G-5966 from the National Science Foundation. (b) National Science Foundation Cooperative Fellow, 1960–1962; Dow Chemical Corporation Summer Fellow, 1952. (c) To whom inquiries should be sent.

(2) G. Gorin, J. E. Spessard, G. A. Wessler, and J. P. Oliver, *J. Am. Chem. Soc.*, **81**, 3193 (1959).

(3) M. P. Schubert, *ibid.*, **55**, 3336 (1933), and preceding papers.

Grade) from the California Corporation for Biochemical Research, Los Angeles, Calif., and 3-mercaptopropionic acid from Evans Chemetics, New York, N. Y., were used without further purification. *trans*-Dichlorobis-(ethylenediamine)-cobalt(III) chloride and tris-(acetylacetonato)-cobalt(III) were prepared as described in the literature.⁴ Potassium (ethylenedinitrilo)-tetraacetatocobalt(III) dihydrate was prepared according to the direction of Dwyer, Gyarfás, and Mellor.⁵ All other chemicals were of analytical reagent grade.

Spectral Measurements.—All visible and ultraviolet spectral measurements were done with a Beckman Model DU spectrophotometer and 10-mm. Pyrex or silica cells. In all cases, pure solvent was used as the reference solution. The molar absorptivity coefficients of the complexes were calculated on the basis of the empirical formula. Infrared absorption spectra were measured with a Beckman Model IR-7 infrared spectrophotometer. Solid samples (0.2–0.5 mg.) were ground with 200 mg. of dry potassium bromide and the resulting mixtures were pressed into transparent disks. Very thorough, vigorous grinding was required to disperse the complexes properly in the potassium bromide.

Preparation of [Co(Shex)₃] from Cobalt(II) Chloride.—In 300 ml. of denatured ethanol were dissolved 5.1 g. (4.3×10^{-2} mole) of hexanethiol and 3.85 g. (1.4×10^{-2} mole) of cobalt(II) chloride hexahydrate; 1.8 g. (4.5×10^{-2} mole) of sodium hydroxide in 200 ml. of ethanol was then added slowly and air was bubbled through the solution for 3 hr. A voluminous reddish brown precipitate formed. After standing overnight, the mixture was passed through a medium-porosity fritted-glass filter funnel; the residue was washed with alcohol and dried at 50° and 10 mm. pressure. Yields were 85–95% based on the amount of cobalt taken. The dried complex was dissolved in the minimum amount of chloroform, reprecipitated by filtering into an equal volume of ethanol, washed with ethanol, and dried for 4 hr. at 50° and 10 mm. The dry product had a metallic green sheen. *Anal.* Calcd. for [Co(Shex)₃]: C, 52.68; Co, 14.36. Found: C, 51.24; Co, 14.89.

If no base was added, only a small amount of gummy, red precipitate formed. If the experiment was done in the absence of air only a green solution resulted; on exposure to air, a fine red precipitate was rapidly deposited.

Preparation of [Co(Shex)₃] from *trans*-Dichlorobis-(ethylenediamine)-cobalt(III) Chloride.—A solution of *trans*-[Co(en)₂Cl₂]Cl, 7 g. (2.45×10^{-2} mole), in 25 ml. of distilled water was mixed with 50 ml. of denatured ethanol, and the mixture was added slowly with stirring to 16.5 g. (14.7×10^{-2} mole) of hexanethiol in 15 ml. of 10 *M* sodium hydroxide. A reddish brown precipitate formed immediately. The precipitate was allowed to stand overnight in contact with the mother liquor, which then was filtered through Whatman No. 42 filter paper in a Büchner funnel. The complex was washed with 300 ml. of ethanol followed by 50 ml. of ether and then air-dried. The yield of the metallic green complex was 95–100% based on the cobalt taken. *Anal.* Calcd. for [Co(Shex)₃]: C, 52.68; Co, 14.36. Found: C, 52.73; Co, 14.43.

The reaction could be carried out in the absence of oxygen.

The complex could be prepared from hexaamminecobalt(III) chloride by the same method.

Preparation of H₃[Co(SCH₂CH₂COO)₃] and its Potassium Salt.²—To a thick slurry of 12.3 g. of sodium acetate in a small amount of water were added 3 g. of 3-mercaptopropionic acid and then 10 ml. of 1 *M* cobalt(II) chloride (molar ratios of acetate: acid:cobalt are 15:3:1). A fleeting green color which likely was due to the cobalt(II) complex could be observed. A reddish brown precipitate quickly formed and the resulting thick slurry was allowed to stand exposed to the air for 12 hr. with occasional stirring; then the precipitate was filtered through paper in a Büchner funnel and pressed as dry as possible.

This product was dissolved in several ml. of 0.1 *M* sodium hydroxide and the solution was filtered; concentrated hydrochloric acid was then added until the solution was distinctly acid and the precipitate had re-formed. It was separated by filtration, washed with water until free of acid, and then washed with a few ml. of alcohol and dried, first in air and then *in vacuo* at 80° for 4 hr. Yields were 75–80% based on the cobalt taken. *Anal.* Calcd. for H₃[Co(SCH₂CH₂COO)₃]: C, 28.88; H, 4.04. Found: C, 28.70; H, 4.28.

The potassium salt was prepared by dissolving 0.5 g. of H₃[Co(SCH₂CH₂COO)₃] in 50 ml. of 0.1 *M* potassium hydroxide, filtering, and adding 15 ml. of ethanol with stirring. The precipitate so formed was filtered and washed successively with 20% alcohol, 50% alcohol, and ether. It was dried at 50° in a vacuum oven.

Properties of [Co(Shex)₃].—The complex was insoluble (<0.02 g./l.) in water, 15 *M* ammonium hydroxide, 12 *M* hydrochloric acid, 16 *M* sulfuric acid, dioxane, dimethylformamide, dimethyl sulfoxide, acetonitrile, ethyl acetate, and dichloroacetic acid; very slightly soluble (0.02–0.1 g./l.) in carbon tetrachloride, benzene, bromobenzene, acetic acid, and diethylamine; and moderately soluble in chloroform (see Discussion). Mechanical shaking was utilized in preparing chloroform solutions, as the process of dissolution was very slow.

When heated on a metal block, the complex gave evidence of decomposition (smoking) around 160–170°, and, at 200°, crumbled to a gray powder. When placed in a flame, the complex evolved a gas and burned with a smoky flame; a gray powder remained after ignition.

Viscosity Measurements.—Viscosity determinations were done in a specially constructed Ostwald viscometer at 24.8°. The flow time of pure solvent, T_0 , was about 100 sec. Flow times were measured for at least three different concentrations. The specific viscosity was calculated from the equation $\eta_s = (T_s - T_0)/T_0$, where T_s is the flow time of the solution; the intrinsic viscosity, η_i , was obtained by extrapolating the values of η_s/c vs. c to $c = 0$.

The viscosity was found to depend to some extent on the conditions used in preparing and purifying the samples. A representative sample gave $\eta_s = 1.34, 0.725, \text{ and } 0.617$ at $c = 0.300, 0.173, \text{ and } 0.153$ g./100 ml., respectively, $\eta_i = 3.7$ dl./g.⁻¹; other samples gave values ranging between 3.2 and 3.8.

Similar techniques and a commercial viscometer were employed in determining the viscosity of [Co(SCH₂CH₂COO)₃]⁻³ and [Co(SCH₂CHNH₂COO)₃]⁻³ in solution; $c = 0.82\text{--}0.99$ in 0.1 *M* sodium hydroxide.

Osmometry.—Measurements were made in a Zimm-Meyerson osmometer⁶ fitted with OM osmometer membranes (suitable for use in organic solvents, obtained from the Carl Schleicher and Schuell Company, Keene, N. H.). In a typical experiment, 21 g. of [Co(Shex)₃] was dissolved in 1 l. of chloroform. The osmotic pressure head rose to a maximum height of about 10 cm. in 8 hr., then decreased to nearly zero in a period of about 5 days. In the course of the experiment, the chloroform in the reservoir became slightly pink, and it could be estimated that the amount of leakage was <0.5%.

Diffusion Measurements with Diaphragm Cell.—The cell was made of Teflon and was similar in design to that described by Fuchs and Gorin,⁷ except that the solution and solvent compartments as well as the passage between them were cylindrical, having been made by drilling 1.85-cm. holes into solid Teflon blocks. The compartments were separated by an ultrafine membrane filter, Type UO-Medium (Schleicher and Schuell Company, Keene, N. H.). A 0.5% solution of complex was placed in one compartment and pure solvent in the other; both were stirred. The rate of diffusion was measured by taking small aliquot samples and determining their absorbance.

Tris-(acetylacetonato)-cobalt(III) was taken as the basis for

(4) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946); B. E. Bryant and W. C. Fernelius, *ibid.*, **5**, 188 (1957).

(5) F. P. Dwyer, E. C. Gyarfás, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(6) B. H. Zimm and I. Meyerson, *J. Am. Chem. Soc.*, **68**, 911 (1946).

(7) E. Fuchs and G. Gorin, *Biochem. Biophys. Res. Commun.*, **5**, 196 (1961).

comparison. With this substance, equilibrium, *i.e.*, uniform concentration on both sides of the membrane, was attained in less than 10 hr. With tris-hexanethiolatocobalt(III), less than 2% diffusion occurred in 50 hr.

Dialysis Experiments.—Dialysis bags were made from 5-cm. lengths of cellulose dialysis tubing, 15 mm. in diameter, size 18/32 (Visking Company, Chicago, Ill.). A solution of the complex was placed in the bag and this was suspended in a 100-ml. graduated cylinder containing 50 ml. of water. The solution outside the bag was stirred magnetically and the absorbance of small aliquot portions was determined at appropriate intervals.

With potassium (ethylenedinitrilo)-tetraacetatocobalt(III) in water, the concentration inside and outside the bag became equal in about 8 hr.; the same result was obtained when the complex was dissolved in 0.05 *M* sodium hydroxide (in this medium, some decomposition of the complex took place, with consequent alteration of the spectrum). With $[\text{Co}(\text{SCH}_2\text{CH}_2\text{COO})_3]^{-3}$ or $[\text{Co}(\text{SCH}_2\text{CHNH}_2\text{COO})_3]^{-3}$ in 0.1 *M* sodium hydroxide less than 5% diffusion took place in the same time.

Analysis of Complexes.—The sample was weighed in a porcelain crucible, heated carefully, without igniting the gases evolved, until converted to a dull gray powder, and then heated in a muffle furnace at 750–800° for about 4 hr. The residue was dissolved by heating with about 3 ml. of concentrated hydrochloric acid; dissolution was slow, and the hydrochloric acid was replenished as needed. The blue solution finally obtained was diluted with water, neutralized with ammonium hydroxide, and cobalt was deposited electrolytically⁸ with a Sargent-Slomin electrolytic analyzer (Sargent Scientific Company). The precision was 0.5–1%.

Carbon and hydrogen determinations were performed by Dr. Alfred Bernhardt, Mulheim (Ruhr), Germany.

Results and Discussion

Complexes of hexanethiol with cobalt have been prepared by two methods: (a) direct combination of the mercaptan with cobalt(II) and oxygen and (b) reaction of the mercaptan with *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride. The products have a highly distinctive appearance, quite similar to that observed previously for the tris-(3-mercaptopropionato)-cobalt(III) and triscysteinatocobalt(III)² complexes. All these complexes were first obtained as exceedingly voluminous red precipitates, which clearly entrained much solvent, but which could be filtered only with difficulty. As the solvent was removed, in part by filtration and finally by drying, the materials greatly diminished in volume and assumed a green color with a metallic sheen, although they still looked red when a thin layer was viewed in transmitted light. The ultraviolet and visible spectra of products (a) and (b) were identical and very similar to those of the mercaptopropionato and cysteinato complexes, as can be seen from Table I, which lists the position of the absorption maxima between 250 and 600 $m\mu$ and, in parentheses, the molar absorptivity coefficients.

Products (a) and (b) differed with respect to their solubility in chloroform, the only solvent, of the many tested, which would dissolve appreciable amounts; the solubility of the former was about 3 g./l., that of the latter 30 g./l. These values could be determined only approximately, because the process of dissolution was

TABLE I

Hexanethiolato complex in chloroform	270 (8,430); 417 (8,590); 510 (23,400)
Tris-(3-mercaptopropionato)-cobalt(III) in 0.1 <i>M</i> NaOH	270 (8,200); 417 (6,400); 510 (22,600)
Triscysteinatocobalt(III) in 0.1 <i>M</i> NaOH	270 (8,900); 417 (8,000); 510 (24,100)

slow and accompanied by a change in the solid phase, which at first swelled and turned red, qualitatively a reversal of the changes observed on drying. However, the solubility difference between the two products was distinct.

Analysis of the complexes corresponded to the formula $[\text{Co}(\text{Shex})_3]$ where $(\text{Shex})^-$ is the hexanethiolate anion. Agreement with the calculated percentage composition was less accurate in the case of product (a), which was the more difficult to purify by reason of its lower solubility and filterability. Formulation of the complexes as involving cobalt(III) is in accordance with the facts that reaction (a) required oxygen while reaction (b) did not, as well as with the high absorbancy of the complexes in the visible region and their remarkable inertness toward acid. Cobalt(III) exhibits a strong tendency to form six coordinate, octahedrally oriented bonds. To achieve this coordination in the present case, polymeric structures would have to be formed. That such structures might in fact be involved was indicated in a general way by the properties already discussed and more evidence was sought from viscosity, diffusion, and osmotic pressure measurements.

Solutions of the tris-hexanethiolato complexes, both (a) and (b), did indeed exhibit a strikingly large viscosity; in moderate concentrations, *ca.* 1.8 g./l., the flow time was double that of the solvent. The absolute value of the property was somewhat variable; the intrinsic viscosity of the samples studied ranged from 3.2 to 3.8 dl./g.⁻¹. Such values indicate a high molecular weight, but unfortunately no quantitative estimate can be made in the absence of empirical data on similar compounds. A molecular weight of several tens of thousands is a reasonable lower limit, and the range of possibility extends to 10–100 times this value.⁹

Diffusion measurements, performed in a cell of the diaphragm type,¹⁰ provided additional qualitative evidence for the polymeric nature of the complexes. The diaphragm used was a solvent-resistant membrane which, according to the manufacturer, had pores of 20–30 $m\mu$ diameter. As a basis for comparison, the diffusion of a monomeric, neutral complex, tris-(acetylacetonato)-cobalt(III), was measured, and equilibrium, *i.e.*, even distribution of the complex throughout the cell, was attained in less than 10 hr. By contrast, tris-hexanethiolatocobalt(III) passed through the membrane to the extent of only 1–2% in 45 hr. This very slow diffusion must be due, first of all, to a smaller diffusion coefficient, and also it may be that some of the

(8) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, New York, N. Y., 1953, p. 419.

(9) H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," 2nd Ed., Interscience Publishers, New York, N. Y., 1950, pp. 279–306.

(10) L. J. Gosting, *Advan. Protein Chem.*, **11**, 430 (1956).

complex molecules could not pass through the membrane pores. It is clear, in any case, that molecules of the trishexanethiolato complex must be much larger than those of the monomeric complex.

Osmotic pressure measurements were done only with the more soluble form of trishexanethiolatocobalt(III) and, unfortunately, were not entirely successful. In a representative experiment, the solution contained about 20 g./l., and it was observed that a pressure head of *ca.* 10 cm. (of chloroform) would develop near the beginning of the experiment, but then decrease to 1–3 mm. For a molecular weight of, say, 5×10^4 , a pressure head of 1 cm. would be expected. The possibility of leakage was excluded, and a possible explanation for the observed behavior is that the complex was contaminated with low-molecular-weight impurities, which soon diffused through the membrane. There is some possibility that further aggregation of the solute occurred with the passing of time, but no indication of this was obtained by viscosity measurements. The quantitative significance of these results must be regarded as doubtful, but, qualitatively, a high molecular weight for the solute is indicated.¹¹

Viscosity and diffusion measurements were also made on solutions of tris-(3-mercaptopropionato)-cobalt(III) and triscysteinatocobalt(III). The intrinsic viscosities in 0.1 *M* sodium hydroxide were 0.2 and 0.1, respectively. These values are much lower than the viscosity of trishexanethiolatocobalt(III), but still may correspond to fairly large molecular weights. For comparison, the flow time of a solution containing 1.0 g. of dichlorobis-(ethylenediamine)-cobalt(III) chloride in 100 ml. of water was found to be only 1% greater than that of pure solvent. The dissolution of the complexes in sodium hydroxide involves salt formation, and it may be that there is, in addition, some substitution of hydroxo for mercapto groups causing partial depolymerization.

There was no appreciable diffusion of the 3-mercaptopropionato or of the cysteinato complexes through dialysis tubing in a 12-hr. period. In the same conditions, a monomeric complex of the same charge type, potassium (ethylenedinitrilo)-tetraacetatocobalt(III), diffused freely. These experiments indicate in a very simple way that the former complexes are not monomeric. They do not necessarily indicate a very high molecular weight, since the pores of dialysis tubing are sufficiently fine to retard or prevent the passage of comparatively small polymers, *e.g.*, lysozyme, of molecular weight 14,000.

On the basis of the empirical formula and the other properties discussed, we suggest that trishexanethiolatocobalt(III) has a polymeric structure in which the mercaptide groups act as bridges between pairs of cobalt(III) atoms. Triple bridges would result in a linear polymer (Fig. 1a), while double and single bridges would give a two-dimensional structure (Fig. 1b). The available evidence does not afford a clear distinction be-

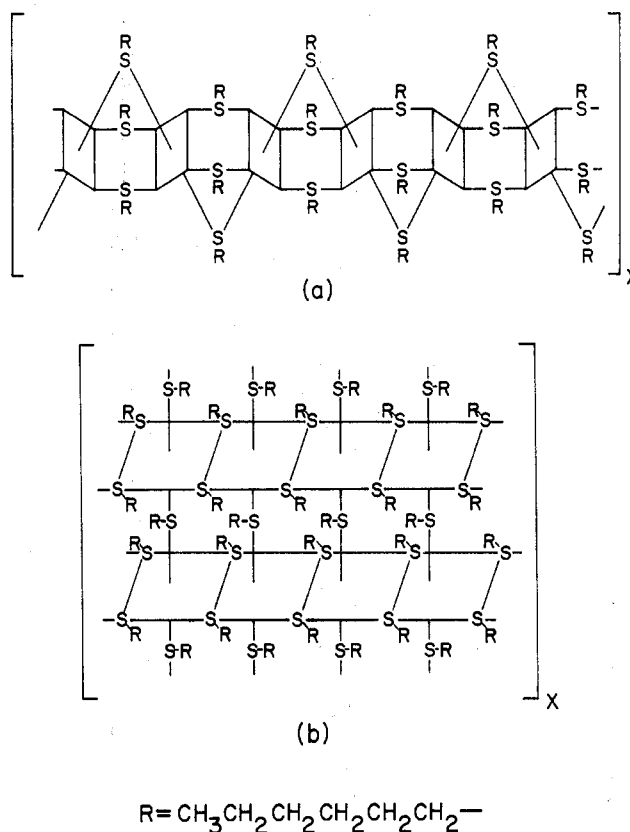


Fig. 1.—Possible structures of trishexanethiolatocobalt(III).

tween these possibilities, although the appreciable solubility of the polymer in chloroform and the high viscosity of the resulting solutions favor a linear structure. It is possible, indeed likely, that the degree of cross linking may vary, and this is the explanation offered for the difference in solubility observed for the products of preparations (a) and (b).¹² Several instances are known in which polymeric structures are formed to satisfy the preferred coordination number of the metal ion.¹³ A polymeric formula has been proposed by Jensen for a complex of nickel(II) with ethanethiol, $[\text{Ni}(\text{SCH}_2\text{CH}_3)_2]$, although that formulation was not supported with direct experimental evidence.¹⁴

In a previous paper,² it had been suggested that tris-(3-mercaptopropionato)-cobalt(III) and triscysteinatocobalt(III) complexes have structures involving coordination of the mercapto and carboxyl groups to form chelate rings. The present findings indicate, however, that the carboxyl group is not bound. The infrared spectra of the complexes have been examined to obtain more information on this point. Carboxylic acids show a strong absorption band at 1690–1740 cm^{-1} , which is ascribed to the hydrogen-bonded carboxyl group; in simple ionic salts the two carbon-oxygen bonds become equivalent and the band shifts to 1560–1620 cm^{-1} . In complexes that contain a coordinated carboxyl group, the 1690–1740 band will be

(12) We are indebted to a referee for helpful suggestions concerning the structure.

(13) D. P. Graddon, "An Introduction to Coordination Chemistry," Pergamon Press, New York, N. Y., 1961, pp. 39–49.

(14) K. A. Jensen, *Z. anorg. Chem.*, **252**, 227 (1944).

(11) D. W. Kupke, *Advan. Protein. Chem.*, **15**, 57 (1960).

shifted to lower frequencies; this is well illustrated by complexes of (ethylenedinitrilo)-tetraacetic acid, which show only a band at ~ 1650 cm^{-1} if all the carboxyl groups are coordinated to cobalt, and also have a band at ~ 1750 cm^{-1} if one or more carboxyl groups are not bound.¹⁵ Propionic acid has a band at 1725–1730 cm^{-1} ¹⁶ and tris-(3-mercaptopropionato)-cobalt-

(15) F. A. Cotton, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., pp. 387–390.

(16) P. J. Corish and D. Chapman, *J. Chem. Soc.*, 1746 (1957).

(III) a band at 1710 cm^{-1} ; this indicates no coordination between the carboxyl group and the cobalt ion. The potassium salt, $\text{K}_3[\text{Co}(\text{SCH}_2\text{CH}_2\text{COO})_3]$, has a strong band at 1575 cm^{-1} , in the same range as ionic carboxylate salts, *i.e.*, again there is no indication of coordination. The infrared spectrum of triscysteinato-cobalt(III) is rather complex and no analysis of it was attempted.

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Transition Metal Complexes of Secondary Phosphines. III.¹ Four- and Five-Coordinate Complexes of Nickel(II) Halides with Diphenylphosphine

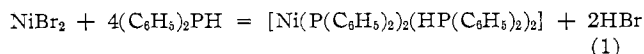
By R. G. HAYTER

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The reactions of diphenylphosphine with nickel halides in nonionizing solvents have yielded *trans*- $[\text{NiI}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_2]$ and the five-coordinate complexes $[\text{NiI}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The properties and structures of the complexes have been investigated and are discussed.

Introduction

It has previously been reported that diphenylphosphine reacts with ethanolic nickel bromide to give the yellow diamagnetic complex $[\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2)_2(\text{HP}(\text{C}_6\text{H}_5)_2)_2]$ ² according to eq. 1.



We have found from our investigation of the reactions of diphenylphosphine with palladium halides that the nature of the complex obtained is influenced both by the solvent and by the particular halide used.³ In particular, polar solvents such as ethanol favored acid elimination and the formation of phosphido complexes as in (1), whereas reactions in benzene were found to give complexes of the type $[\text{PdX}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_n]$ ($n = 2, 3$). It was therefore of interest to study the effect of solvent on the reactions of nickel halides with diphenylphosphine. It was also anticipated that a study of the properties of the complexes $[\text{NiX}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_2]$ (if capable of existence) would yield further information about the factors which affect the structure of nickel(II) complexes.⁴

Experimental

Microanalyses, molecular weights, dipole moments, and conductivity measurements and the preparation of diphenylphosphine were carried out as described in parts I³ and II¹ of this

series. The absorption spectra were measured with a Cary Model 14 spectrophotometer, using the method developed by Shibata and described by Maki⁵ for the solid state measurements.

The magnetic susceptibilities of the finely powdered solids were measured at room temperature by the Faraday method on a sensitive magnetobalance, which had been calibrated using a platinum standard of high purity.

Anhydrous nickel bromide and iodide were obtained from City Chemical Corporation, New York, N. Y. "Anhydrous" nickel chloride was prepared from the hexahydrate (J. T. Baker Chemical Company) by drying under vacuum at 100°; on the basis of hydrogen analysis the formula suggested for the light brown solid thus produced is $\text{NiCl}_2 \cdot \text{H}_2\text{O}$. *Anal.* Calcd. for $\text{NiCl}_2 \cdot \text{H}_2\text{O}$: H, 1.4. Found: H, 1.1.

Preparation of the Complexes.—All preparations were carried out under nitrogen. The anhydrous nickel halides dissolve slowly in refluxing benzene, toluene, or dichloromethane solutions of diphenylphosphine (two moles for $[\text{NiI}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_2]$, four moles for the remaining complexes) to give intensely colored solutions. After removal of residual nickel halide by filtration, the complexes either crystallized on standing or on addition of ether or *n*-hexane. The reaction times, yields, solvent systems, and analytical data are given in Table I and the physical properties of the complexes in Table II. A typical reaction procedure is described below.

Anhydrous nickel bromide (0.505 g., 2.31 mmoles) and diphenylphosphine (1.72 g., 9.23 mmoles) were refluxed together in dichloromethane (50 ml.) for 2 hr. to give a dark brown solution. After filtration through a fine sintered glass disk, the solution was diluted with ether (75 ml.) and cooled to give dark brown needles of $[\text{NiBr}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_3]$.

In the reaction of NiCl_2 with diphenylphosphine, pure $[\text{NiCl}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_3]$ crystallized first and was filtered off. On longer standing, a further crop of the dark brown chloro complex was obtained along with large yellow crystals. Attempted separation by fractional crystallization from benzene resulted in the decomposition of $[\text{NiCl}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_3]$ and the resulting orange-red solution deposited yellow rods (20% yield, m.p. 168–175°

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