CONTRIBUTION FROM THE METCALF CHEMICAL
LABORATORIES OF BROWN UNIVERSITY,
PROVIDENCE 12, RHODE ISLAND

Sulfur Donors: Cobalt(II) with Chelating Alkyl Sulfides

BY RICHARD L. CARLIN AND EDWARD WEISSBERGER

Received December 16, 1963

Attempts in this laboratory to produce complexes of cobalt(II) halides with dialkyl sulfides have resulted in the formation of deep blue solutions, but no stable sulfide complexes have been isolated. On the other hand, by utilizing the chelate effect, others have been able to prepare stable crystalline complexes containing sulfur atoms as donors.[1,2] In this report complexes of cobalt(II) halides with 2,5-dithiohexane ($CH_3SCH_2CH_2SCH_3$) and 3,6-dithiooctane ($C_2H_5SCH_2CH_2SC_2H_5$) are described.

Experimental[3]

Reagents.—Commercial reagent grade $CoCl_2$ and $CoBr_2$ were used. CoI_2 was prepared by reaction of $CoCO_3$ with HI. The commercial ligands (K and K Chemical Company) were used without further purification.

Compounds.—All complexes were formed by direct reaction of the anhydrous cobalt salt and the pure ligand. The preparation could also be effected in ethanol solution. The complexes were washed with alcohol and dried under vacuum over $CaCl_2$ (1.5–2 weeks used here). The following crystalline complexes were prepared.

Dichlorobis-(2,5-dithiohexane)cobalt(II).—A purple solid. *Anal.* Calcd. for $C_8H_{20}S_4CoCl_2$: C, 25.62; H, 5.38. Found: C, 24.51; H, 5.41. A strong odor of the ligand is easily detected above this and all other complexes.

Dibromobis-(2,5-dithiohexane)cobalt(II).—The neat reaction yielded red-brown crystals. *Anal.* Calcd. for $C_8H_{20}S_4CoBr_2$: C, 20.75; H, 4.35. Found: C, 20.96; H, 4.60.

Diiodobis-(2,5-dithiohexane)cobalt(II).—A brown material. *Anal.* Calcd. for $C_8H_{20}S_4CoI_2$: C, 17.24; H, 3.61. Found: C, 17.87; H, 3.57.

Bis-(2,5-dithiohexane)cobalt(II) Perchlorate.—Hexaaquocobalt(II) perchlorate was treated with ligand, filtered, retreated with ligand, and allowed to stand under vacuum over $CaCl_2$ for 2 weeks. The pink complex is insoluble in chloroform, nitrobenzene, and benzene; insignificantly soluble in nitromethane and nitroethane; and decomposes in ethanol and acetone. *Anal.* Calcd. for $C_8H_{20}S_4Co(ClO_4)_2$: C, 19.19; H, 4.01; S, 25.50. Found: C, 19.46, 19.23; H, 4.01, 4.50; S, 25.16.

Complexes with 3,6-Dithiooctane.—Analogous complexes are formed by the neat reaction of this ligand with the cobalt halides; the colors are all the same. In each case the compounds with this ligand are less stable, in either the solid phase or in nonaqueous solution, than those formed by 2,5-dithiohexane. *Anal.* Calcd. for $C_{12}H_{28}S_4CoCl_2$: C, 33.45; H, 6.53. Found: C, 34.89; H, 6.37. Calcd. for $C_{12}H_{28}S_4CoBr_2$: C, 27.75; H, 5.42. Found: C, 29.44; H, 5.91. Calcd. for $C_{12}H_{28}S_4CoI_2$: C, 23.50; H, 4.59. Found: C, 23.33; H, 4.68. Attempts to synthesize a complex of this ligand with cobaltous perchlorate were unsuccessful.

TABLE I

REFLECTANCE SPECTRA OF THE COMPLEXES[a]

	ν_1	ν_2	ν_3
$[CoL_2Cl_2]$	8,000	15,200	19,400
$[CoL_2Br_2]$	7,500	15,200	18,000
$[CoL_2I_2]$	7,500	13,500	20,400
$[NiL_2Cl_2]$	8,850	14,700	24,000
$[NiL_2Br_2]$	8,720	14,550	23,600
$[NiL_2I_2]$	8,620	14,700	23,100
$[NiL_3](ClO_4)_2$	10,600	17,000	28,000

[a] In cm.$^{-1}$; L is 2,5-dithiohexane.

TABLE II

MAGNETIC DATA ON THE COBALT COMPLEXES AT 296°K.

	Dia. cor. $\times 10^6$	$\chi_M^{cor} \times 10^6$	μ, B.M.	θ, °K.
$[CoL_2Cl_2]$	143	9,720	4.92	−10
$[CoL_2Br_2]$	165	10,260	5.15	−22
$[CoL_2I_2]$	197	9,950	5.07	−21

The nickel complexes[1] with these ligands were prepared for comparison purposes.

Spectra.—Electronic spectra were obtained on a Cary Model 14 spectrometer by the reflectance technique with a magnesium carbonate reference.

Magnetic Susceptibilities.—These were obtained by the Gouy method on a magnetic balance of standard design. Measurements were made below room temperature (77, 195°K.) with a silvered double-walled dewar. Measurements were also made at several field strengths. $HgCo(NCS)_4$ served as the calibrant, and molar susceptibilities were corrected for diamagnetism in the usual way. Curie–Weiss plots were constructed by usual methods, the best value of the Curie constant, C, and the molecular field constant, θ, being obtained by a least-squares procedure. We use the equation $\chi = C/T - \theta$.

X-Ray Powder Patterns.—These were obtained on both the cobalt and nickel complexes with 2,5-dithiohexane by standard procedures.

Results

The X-ray powder patterns of the cobalt halide complexes with 2,5-dithiohexane are identical with those of the corresponding derivatives of nickel. In agreement with the stoichiometry, the complex with cobalt perchlorate is not isomorphous with tris-(2,5-dithiohexane)nickel(II) perchlorate.

Spectral data for the complexes of 3,6-dithiooctane (L′) were found to be the same as for the complexes formed by 2,5-dithiohexane (L); since the latter complexes were found to be the more stable, only the data pertaining to them will be reported here. The data are in Table I.

The magnetic susceptibility results, again limited to the complexes derived from 2,5-dithiohexane, are summarized in Table II.

Discussion

The fact that the cobalt halide complexes with the chelating sulfur donors are octahedral is proved by their isomorphism with the corresponding nickel compounds; the latter were shown by Nyholm[1] to be octahedral. The magnetic moments of the cobalt compounds show the large orbital contribution expected[4] for octahedral cobalt(II). The spectra (Fig. 1)

---

[1] R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

[2] H. C. E. Mannerskantz and G. Wilkinson, *ibid.*, 4454 (1962).

[3] Microanalyses by Schwarzkopf Microanalytical Laboratory.

[4] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

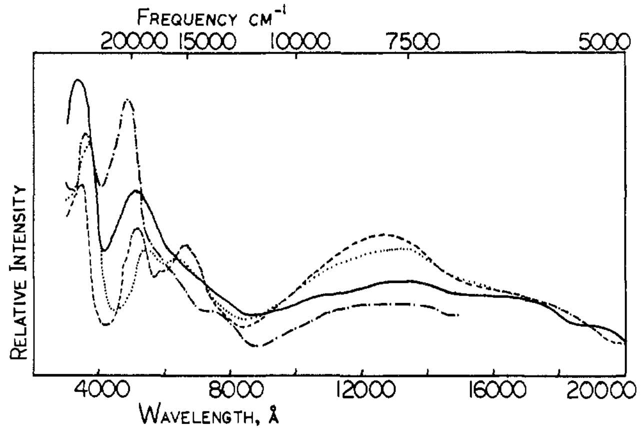

Fig. 1.—Spectra of the cobalt complexes: – – – –, chloride; . . . . ., bromide; - · -, iodide; ———, perchlorate.

may be interpreted on the same basis.[5] The assignment leads to values of an average Dq of 830 (Cl^-), 800 (Br^-), and 770 (I^-) cm.$^{-1}$.

The position of dialkyl sulfide in the spectrochemical series is not well established. Chatt and co-workers[6] have correlated the spectra of some complexes of the type *trans*-[L(piperidine)$PtCl_2$], where L = dialkyl sulfide, selenide, or telluride; or arsine, phosphine, or amine. A reliable comparison with the spectra of aquo and ammine complexes is, however, difficult to obtain in this manner. By using the nomograph of Liehr and Ballhausen,[7] satisfactory spectral assignments can be obtained for the nickel complexes with sulfide donor.

The octahedral compound tris-(2,5-dithiohexane)-nickel(II) perchlorate exhibits (Fig. 2) a spectrum similar to that of other nickel compounds,[7] and an immediate assignment, $10Dq = 10{,}600$ cm.$^{-1}$, can be made. This result shows that dialkyl sulfide is a stronger field donor than oxygen in either water or oxide and is almost as strong as ammonia.[7] It is as well a far stronger donor than ethylenethiourea,[8] which in the compound hexakis(ethylenethiourea)nickel(II) perchlorate yields a spectrum which may be assigned by $10Dq = 7700$ cm.$^{-1}$. The spectrum also allows a calculation of the $E(^3P)$–$E(^3F)$ term separation of 12,900 cm.$^{-1}$ in the sulfide complex; this corresponds to about 83% of the free ion value.

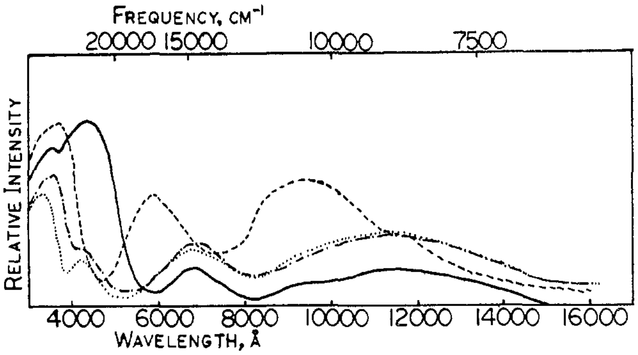

Fig. 2.—Spectra of the nickel complexes: . . . . ., chloride; - · -, bromide; ———, iodide; – – – –, perchlorate.

The halide complexes also exhibit spectra typical of octahedral nickel. In accord with the spectrochemical series, the spectra are assigned by the average parameter Dq = 880 (Cl^-), 870 (Br^-), and 860 (I^-) cm.$^{-1}$.

The Perchlorate Compound.—The stoichiometry of this compound, $Co(ClO_4)_2\cdot$(2,5-dithiohexane)$_2$, suggests either a coordination number of four or that perchlorate is coordinated. Due to insolubility, we have been unable to measure the electrolytic conductance in order to test the latter possibility. The infrared spectrum of the compound in Nujol mull, in the 1100 cm.$^{-1}$ region, is not clear enough to indicate whether or not the stretching frequencies of perchlorate are changed or split by coordination.

The effective magnetic moment at room temperature, 3.23 B.M., is unusual and forces us to conclude that the compound is neither tetrahedral nor octahedral.[4] The reflectance spectrum, with bands at 7400, 18,500, and 29,400 cm.$^{-1}$, is also not like that of tetrahedral cobalt, although it is perhaps similar to that of octahedral cobalt. The compound may even involve cobalt in more than one stereochemical arrangement, but we have been unable to grow any single crystals for an X-ray structure determination.

The compound also exhibits an unusual temperature dependent magnetic moment (Fig. 3).

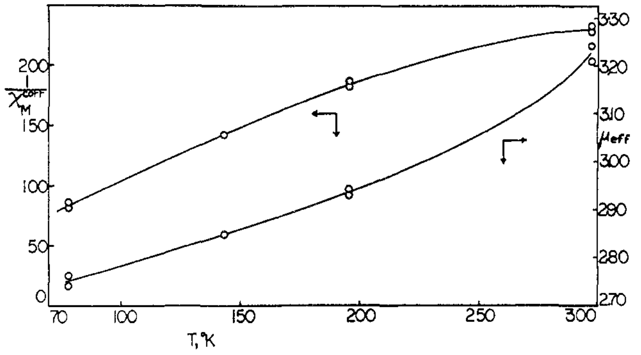

Fig. 3.—Molar susceptibility and effective magnetic moment of $Co(ClO_4)_2\cdot 2(CH_3SCH_2-)_2$ as a function of temperature.

These results lead us to suggest that the perchlorate compound may involve planar coordination. The pink color is similar to that reported[9] for square-planar $[Co(en)_2](AgI_2)_2$, but the latter has a magnetic moment of only 2.46 B.M. A moment of 2.0–2.4 B.M. has been suggested as typical of square-planar cobalt-(II).[4]

Acknowledgment.—We wish to thank A. D. Liehr for a preprint of his paper on the spectra of cobalt. Thanks are also due to J. S. Dubnoff and S. L. Holt, Jr. This research was supported in part by the National Science Foundation.

---

(5) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

(6) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1047 (1959).

(7) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

(8) S. L. Holt, Jr., and R. L. Carlin, to be published.

(9) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2552 (1963).