have had little success; certainly steric factors are important in forming those complexes we report. In order to coördinate to mercury(II) these ligands have struck a fine balance in the electronegativity of the donor oxygen atom and the charge on it. A major factor also may be that oxygen in these covalent molecular oxides cannot π-bond with the metal in the manner discussed by Leden and Chatt.[11]

We now are investigating other post-transition metal perchlorates in an attempt to make complexes with high coördination numbers.

Acknowledgment.—We wish to thank Dr. Helmut Kirner for taking the X-ray powder patterns and Professor G. B. Carpenter for helping to interpret them. This research was supported in part by the Atomic Energy Commission.

Experimental[12]

Preparation of the Complexes.—Interaction of either a methanol or ethanol solution of the appropriate ligand with a similar solution of hydrated mercuric(II) perchlorate results in the precipitation of white crystals. These can be recrystallized from the same solvent. Each complex was dried *in vacuo* at 60°. Several attempts to prepare a six-coördinate mercury complex of 4-methyl-pyridine N-oxide were unsuccessful. The basic ligand precipitated mercuric oxide, whereupon a small amount of perchloric acid was added to prevent hydrolysis. A solid compound of indeterminate analysis then was obtained by evaporation of solvent. New cobalt(II) and nickel(II) complexes of this ligand were prepared easily, and they are listed in Table I, along with the mercury compounds.

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[11] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

[12] Microanalyses by Schwarzkopf Microanalytical Laboratory.

CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AMHERST, MASSACHUSETTS

Sulfone Ligands in Cobalt(II) Complexes

BY C. H. LANGFORD AND P. O. LANGFORD

Received June 22, 1961

Tetramethylene sulfone[1] has attracted recent attention as a dipolar aprotic solvent of interesting properties.[2] The complexing power of sulfones with transition metal ions usually is assumed to be low; preliminary attempts to isolate sulfone complexes have failed.[3] However, sulfone complexes with antimony trichloride have been reported[4] and a number of complexes with the related solvent tetramethylene sulfoxide are known.[5] In the course of an investigation in this Laboratory using tetramethylene sulfone as a solvent, two *unstable* complexes consistent with the formulas $[Co(C_4H_8SO_2)Cl_2]$ and $[Co(C_4H_8SO_2)_3](ClO_4)_2$ have been isolated.

Cobalt (II) Chloride–Tetramethylene Sulfone Adduct.—Tetramethylene sulfone, purified as previously described,[2] was used to dissolve anhydrous cobalt chloride. When two volumes of benzene were added to one volume of the deep blue solution, a fine blue precipitate formed which had the empirical formula $CoCl_2 \cdot C_4H_8SO_2$. Cobalt was determined by titration with ethylenediaminetetraacetic acid using murexide indicator[6] and carbon by commercial microanalysis in the laboratories of G. Weiler and F. B. Strauss, Oxford. *Anal.* Calcd. for $[Co(C_4H_8SO_2)Cl_2]$: Co, 23.6; C, 19.2. Found: Co, 22.8; C, 20.2.

The blue complex is a non-electrolyte in tetramethylene sulfone. The specific conductance of a solution 4.32×10^{-4} *M* $CoCl_2$ in the sulfone was less than 4×10^{-7} ohm at 30°. Conductance measurements were made using a conventional Wheatstone bridge and a cell with bright Pt electrodes (cell constant = 0.354). Burwell and Langford[2] reported typical ionic salts with conductances 10 to 100 times the limit given here. Despite difficulties in excluding moisture, a crude molecular weight for the blue complex was determined using a simple Beckmann cryoscopic apparatus and the sulfone as solvent. A value of 300 was obtained. The calculated molecular weight for $[Co(C_4H_8SO_2)Cl_2]$ is 250.

It is concluded that the blue complex is a monomeric non-electrolyte consistent with the formula given above. The visible spectrum of this complex shows peaks at 687 and 590 mμ, with log ε values of 2.49 and 2.19, respectively. The spectrum is unlike that of $CoCl_4^{=}$, which shows peaks at 690, 672, and 640 in the sulfone solvent. Addition of two equivalents of chloride to the sulfone complex in solution converts it to the tetrachloro anion.

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[1] Tetramethylene sulfone is known commercially as sulfolane and is available from the Phillips Petroleum Company, Bartlesville, Okla.

[2] R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

[3] F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

[4] I. Lindquist and P. Einarsson, *Acta Chem. Scand.*, **13**, 420 (1959).

[5] R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).

[6] F. J. Welcher, "Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Princeton, N. J., 1958, p. 230.

The cobalt sulfone bond seems to be weak. When water is added, the visible spectrum shifts. At 3% water (by vol.) the 687 mμ peak is shifted to 675 mμ and the extinction coefficient at the maximum increased by 4%. The spectrum is insensitive to further addition of water until the water content reaches 10%. Above this the blue color disappears and a spectrum similar to $[Co(H_2O)_6]^{++}$ in water develops. It appears that water begins to displace sulfone from the complex immediately but displaces chloride only when there is a large excess of water.

Cobalt(II) Perchlorate–Tetramethylene Sulfone Adduct.—A red complex of cobalt(II) containing tetramethylene sulfone was prepared by heating hexaaquocobalt(II) perchlorate and the sulfone to dryness in a drying pistol at 110° in the presence of P_2O_5. The solid was extremely sensitive to moisture. Analysis for cobalt was carried out as before and perchlorate was determined by conductometric titration using analytical reagent tetraphenylarsonium chloride from G. F. Smith Chemical Co. as a precipitant. Although other analyses would be more convincing, these suggest the empirical formula $Co(ClO_4)_2{\cdot}(C_4H_8SO_2)_3$. *Anal.* Calcd: Co, 9.5; ClO_4, 32.3. Found: Co, 9.4; ClO_4, 32.7. Unfortunately, the instability of the complex rendered further analysis difficult.

This substance is an electrolyte in tetramethylene sulfone. The equivalent conductance of a 1.10×10^{-3} *M* solution is 18.4 ohms^{-1} cm.$^{-2}$, which should be compared[2] to values of about 12 for sodium thiocyanate and 10 for tetraphenylarsonium chloride in this solvent. Thus it appears that this substance is a 2:1 electrolyte, consistent with the formula $[Co(C_4H_8SO_2)_3](ClO_4)_2$. This is supported by the visible spectrum in the sulfone solvent. There is a maximum at 532 mμ which is similar to the maximum for hexaaquocobalt(II) perchlorate at 523 in this solvent. It is interesting that the hexaaquo complex gives a distinct spectrum in tetramethylene sulfone, indicating that water is not displaced from the coördination sphere by the sulfone.

In summary, it appears that tetramethylene sulfone may form weak complexes with Co(II) which are more easily decomposed by water than those with similar solvents. The formulations suggest that the sulfone acts as a bidentate ligand, presumably bonding through the two oxygens. It is not unlikely that the blue complex is roughly tetrahedral and the red one octahedral.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE 39, MASSACHUSETTS

Vinyl Derivatives of Metals. XII. Some Perchlorovinylmercury Compounds[1]

BY DIETMAR SEYFERTH AND ROLF H. TOWE

Received September 18, 1961

Bis-(perchlorovinyl)-mercury has been known since 1908 through the work of Hofmann and Kirmreuther.[2] The synthesis of this compound and of related chlorovinylmercurials has been the subject of further studies.[3,4] The reactions of bis-(perchlorovinyl)-mercury have received practically no study. It has been noted that the cleavage of this compound by chlorine proceeds well only with strong illumination,[5] that its reaction with ammonium sulfide produces mercuric sulfide and trichloroethylene, and that almost no reaction is observed with hot 10% hydrochloric acid or with potassium cyanide solution.[2] We report here some further reactions of mercurials containing the perchlorovinyl group.

The cleavage of diorganomercurials by the halogens and by hydrogen halides is well-known. Bis-(perchlorovinyl)-mercury underwent carbon–mercury bond cleavage when treated with two equivalents of bromine in carbon tetrachloride or with two equivalents of iodine in refluxing xylene solution, giving the respective mercuric halide and halotrichloroethylene. When these reactions were carried out with the mercurial and the halogen in 1:1 molar ratio, the expected perchlorovinylmercuric halides were not obtained. Isolated instead was the respective mercuric halide, and *ca.* one half of the starting mercurial was recovered. This could be due either to the instability toward disproportionation of perchlorovinylmercuric bromide and iodide under the experimental conditions, or to a significantly greater rate of cleavage of the perchlorovinylmercuric halide when compared with bis-(perchlorovinyl)-mercury. This question remains unresolved, although further studies (see below) showed that perchlorovinylmercuric bromide is capable of existence, but that perchlorovinylmercuric iodide

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[1] Part XI: D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).

[2] K. A. Hofmann and H. Kirmreuther, *Ber.*, **41**, 314 (1908).

[3] M. Fitzgibbon, *J. Chem. Soc.*, 1218 (1938).

[4] H. E. Parker, British Patent 427,079 (1935); *Chem. Abstr.*, **29**, 6608 (1935).

[5] K. A. Hofmann and H. Kirmreuther, *Ber.*, **42**, 4232 (1909).