

small Dq (solvent) value corresponding to weak solvation. In any event, the strong θ dependence of the angular function relating Dq to Dt makes angles of greater than approximately 98° highly unlikely.

Acknowledgment.—Support of this research by a National Science Foundation Predoctoral Fellowship is gratefully acknowledged. We also thank Dr. J. Perumareddi for providing his ligand field matrices prior to publication.

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Structure and Properties of an Unusual Mixed Cobalt(III)-Cobalt(II) Diamine Chloro Complex Salt

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Received October 23, 1967

The preparation of a compound assumed to be *trans*-dichlorobis(N-methylethylenediamine)cobalt(III) chloride has been described by Basolo.¹ The only analytical result reported was a chloride determination, which had to be rationalized on the basis of a formulation containing HCl of crystallization, *viz.*, $\text{Co}(\text{Meen})_2\text{Cl}_2 \cdot \text{Cl} \cdot 0.1\text{HCl}$ (Meen = $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). A recent re-investigation in our laboratory of some of the properties of this compound has led to the conclusion that it is not simply a dichlorocobalt(III) complex. It is instead a mixed cobalt(III)-cobalt(II) complex of empirical formula $\text{Co}_3(\text{Meen})_4\text{Cl}_8$. It contains dichlorobis(N-methylethylenediamine)cobalt(III) cations and tetrachlorocobaltate(II) anions in a ratio of 2:1.

Experimental Section

The preparative procedure duplicated that of Basolo¹ with minor modifications. Occluded HCl was removed from the crude material by dissolution in methanol and precipitation by addition of ethyl ether. The HCl-free complex was dried² for 2 days at 72° . Cobalt analyses were performed by the thermal decomposition of the complex as described by Charlot and Bezier,³ nitrogen by the Dumas method,⁴ and carbon and hydrogen by standard microchemical procedure.⁵ The chloride analyses, done by conductometric titration using a General Radio Type 1650A impedance bridge in conjunction with bright platinum electrodes, were of two types: (1) immediate titration with aqueous silver nitrate of a freshly prepared aqueous solution of the complex ("exterior ionic chloride"); (2) back titration by

chloride of excess silver nitrate remaining after boiling the aqueous complex solution containing the silver salt for 30 min. (This "total chloride" determination was confirmed by weighing the silver chloride precipitated in the boiling treatment just described.)

The infrared spectrum over the range $250\text{--}4000\text{ cm}^{-1}$ was obtained with a Perkin-Elmer Model 521 grating spectrophotometer utilizing solid complex and the KBr pellet technique. Spectra of aqueous and methanolic solutions of the complex were run on a Perkin-Elmer Model 202 spectrophotometer over the range $200\text{--}750\text{ m}\mu$. The solid reflectance spectrum of the complex diluted with lithium fluoride *vs.* a lithium fluoride standard was obtained with a suitably modified Beckman DU spectrophotometer. The proton magnetic resonance spectrum of a 10% solution of the complex in D_2O was recorded on a Varian A60 instrument using tetramethylsilane as a reference. Magnetic susceptibility measurements were made with a Varian water-cooled electromagnet (Model V4004) connected with a Model V2301A current regulator and a Model V2300A power supply. The field was standardized using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Results and Discussion

The analytical data are presented in Table I. It is to be noted that the observed total composition figures agree closely with calculations based on the trinuclear empirical formula already mentioned.

TABLE I

	Co	N	C	H	Cl ^a	Cl ^b
% calcd ^c	23.4	14.80	19.03	5.28	37.5	18.8
% obsd	23.5	14.81	18.96	5.75	37.5	18.8

^a "Total chloride." ^b "Exterior ionic chloride." ^c On the basis of the formula $\text{Co}_3(\text{Meen})_4\text{Cl}_8$.

The infrared spectrum has bands characteristic of the coordinated diamine and two strong bands attributed to a cobalt-chloride stretch at 275 and 295 cm^{-1} .⁶⁻⁸ Upon replacement of the tetrahedrally bound and part of the octahedrally bound chloride by reaction of the complex with silver carbonate, the band at 295 cm^{-1} disappears, but the band at 275 cm^{-1} , apparently due to the more firmly bonded octahedrally coordinated Cl, remains.

The visible reflectance spectrum of the solid has a number of bands between 600 and $700\text{ m}\mu$, characteristic of CoCl_4^{2-} as reported by Katzin,⁹ which are not obtained from an aqueous or methanolic solution of the complex. The visible solution spectrum of the complex from 350 to $700\text{ m}\mu$ is that normally associated with a *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$ type of cation. However, the addition of large amounts of LiCl or $(\text{CH}_3)_4\text{NCl}$ to methanolic solutions reestablishes the missing bands in the $600\text{--}700\text{-m}\mu$ region. From this observation one concludes that the complex ion CoCl_4^{2-} is present in the solid state, but hydrolyzes rapidly in dilute aqueous solution as expected. The "exterior chloride" data support this concept completely.

The observation that the complex is soluble only in polar solvents supports the conclusion that it is a salt in the solid state. The pH of a 0.1 M aqueous solution of the complex is about 4, thus indicating about 10^{-3}

(1) F. Basolo, *J. Am. Chem. Soc.*, **75**, 227 (1953).

(2) Preparations at temperatures above 80° resulted in partial decomposition of the complex with the formation of more cobalt(II) species. Drying at temperatures up to 120° resulted in no detectable decomposition; however, decomposition resulted at about 135° .

(3) G. Charlot and D. Bezier, "Quantitative Inorganic Analysis," translated by R. C. Murray, John Wiley and Sons, Inc., New York, N. Y., 1957, p 408.

(4) Courtesy of the Testing and Inspection Spectral Laboratory of the National Aniline Division of Allied Chemical Corp., Buffalo, N. Y.

(5) Performed by Weiler and Strauss Microanalytical Laboratory, Oxford England.

(6) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

(7) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

(8) G. W. Watt and D. S. Klett, *Inorg. Chem.*, **3**, 782 (1964).

(9) L. I. Katzin, *J. Am. Chem. Soc.*, **76**, 3089 (1954).

mole of HCl to 1 mole of complex as the maximum residual acid present.

The proton nmr indicates the presence of the following initial relative number of various types of hydrogen: NH, 3.0; CH₃, 3.0, CH₂, 4.0; OH, 0.0. The amine hydrogen exchanges with the D₂O leading to appearance of an OH peak within a few hours. The nmr spectral peak locations are very concentration dependent, probably because of the presence of the paramagnetic cobalt(II) species. The mean magnetic moment for the compound was 2.8 BM. Since the two cobaltic ions are diamagnetic, the magnetic moment for the cobaltous ion is calculated as 4.9 BM. Nyholm¹⁰ reported corresponding values of 2.7 and 4.6 BM, respectively, for the compound [Co(diars)₂Cl₂]₂CoCl₄. By treatment of an alcoholic solution of the complex with aqueous perchloric acid, as suggested by Nyholm,¹⁰ a light green diamagnetic precipitate forms, presumably [Co(Meen)₂Cl₂]₂ClO₄. The magnetic moment calculated for the cobaltous ion indicates three unpaired electrons and, hence, a tetrahedral ion as evidenced from the solid reflectance spectrum and solution spectrum in the presence of excess Cl⁻.

All of the experimental evidence is compatible with the assignment of the structure of the complex as [Co(Meen)₂Cl₂]₂CoCl₄.

Other compounds prepared by Basolo¹ seem to fall into the same general category in that the *cis* compounds could not be prepared from what were thought to be the *trans* compounds. In Table II the experimental values for per cent chloride are those reported by Basolo¹ and the calculated values are based on the general formulas [Co(en*)₂Cl₂]₂CoCl₄ and [Co(en*)₂Cl₂]₂Cl, where en* = substituted ethylenediamine.

TABLE II

COMPARISON OF THE TOTAL CHLORIDE ANALYSES CALCULATED FOR [Co(en*)₂Cl₂]₂CoCl₄ AND [Co(en*)₂Cl₂]₂Cl WITH LITERATURE VALUES FOR SEVERAL COMPLEXES THOUGHT TO BE OF THE FORM [Co(en*)₂Cl₂]₂Cl·xHCl

en*	Exptl ¹	Total Cl	
		Calcd	
		[Co(en*) ₂ Cl ₂] ₂ CoCl ₄	[Co(en*) ₂ Cl ₂] ₂ Cl
N-Methylethylenediamine	37.2	37.5	34.0
N-Ethylenediamine	35.4	34.9	31.1
N- <i>n</i> -Propylethylenediamine	32.2	32.6	28.7
Isobutylenediamine	33.9	34.9	31.1
C,C',C'-Tetramethylethylenediamine	30.6	30.7	26.6

The agreement between the experimental and calculated values for per cent chloride in the cobalt(III)-cobalt(II) species indicates that the series of compounds are probably all of this same general type.¹¹⁻¹⁴

(10) R. S. Nyholm, *J. Chem. Soc.*, 2072 (1950).

(11) In aquation¹² and base hydrolysis^{13,14} kinetic studies conducted on several of these complexes, the concentrations were determined assuming the high chloride analyses were the result of excess HCl. It does not seem, however, that this error vitiates in any serious way their kinetic conclusions, since only the cobalt(III) cation reactions were observed in their studies.

(12) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

(13) R. G. Pearson, R. E. Meeker, and F. Basolo, *ibid.*, **78**, 709 (1956).

(14) S. C. Chan, *J. Chem. Soc., Sect. A*, 142 (1966).

Chromatographic Separations of Symmetrical and Unsymmetrical *trans*-Co(Meen)₂Cl₂⁺.¹⁵—Since the cation *trans*-Co(Meen)₂Cl₂⁺ can exist in two geometrically different forms,¹⁴ attempts were made to separate and identify these two forms. Treatment of *trans*-(Co(Meen)₂Cl₂)₂CoCl₄, as originally prepared, by a column chromatographic technique,¹⁶ produced two green bands. When the material was separated by an ascending paper chromatographic method,¹⁶ *R_f* values of 0.72 ± 0.02 and 0.59 ± 0.02 were obtained for two components. Material isolated by the evaporation of an aqueous solution of *trans*-(Co(Meen)₂Cl₂)₂CoCl₄ at approximately 100° had a single *R_f* value of 0.60. Equilibration of a dilute solution of *trans*-(Co(Meen)₂Cl₂)₂CoCl₄ in methanol for 1 week produced material having a single *R_f* value of 0.73. The perchlorate salt of *trans*-Co(Meen)₂Cl₂⁺, prepared as described earlier, had *R_f* values of 0.71 ± 0.02 and 0.59 ± 0.02. The equilibration for 1 week of a methanolic solution of the perchlorate salt in the presence of 2 *M* LiCl gave material with an *R_f* value of 0.59.

Swamping an alcoholic solution of the complex with LiCl should stabilize the more unsymmetrical form of the cation inasmuch as it should be more highly ion paired than the symmetrical form. The form stabilized under these forcing conditions had the lower *R_f* value. Consequently, the higher *R_f* value has been assigned to the symmetrical form.

The preparation of salts containing the two separate *trans* isomers of Co(Meen)₂Cl₂⁺ is thus demonstrated through their chromatographic separation. The *R_f* values obtained for the symmetrical form (0.72 ± 0.02) and for the unsymmetrical form (0.59 ± 0.02) were independent of the identity of the anion when the anion was either perchlorate or tetrachlorocobalt(II).

The position of the *trans-trans* isomerization equilibrium of Co(Meen)₂Cl₂⁺ in methanol seems to be easily controlled and very dependent on the chloride concentration.

The visible spectra of symmetrical and unsymmetrical *trans*-(Co(Meen)₂Cl₂)₂CoCl₄ are somewhat different, and the half-time for the unsymmetrical to symmetrical isomerization has been estimated to be about 17 hr at room temperature (approximately 23°).

Preparation of *cis*-(Co(Meen)₂Cl₂)Cl.—Treatment of *trans*-(Co(Meen)₂Cl₂)₂CoCl₄ with excess methanolic NaOCH₃ results in the formation of a deep red solution. Addition of excess methanolic HCl to this solution causes a fast color change to purple. This purple color is replaced by green on standing overnight.¹⁷

(15) The designations symmetrical and unsymmetrical are based on the possible *trans* cation configurations. Symmetrical refers to the two methyl groups *trans* to each other (see Chan,¹⁴ Figure 2B) and unsymmetrical to the methyl groups *cis* to one another (see Chan,¹⁴ Figure 2A).

(16) Whatman acid-washed cellulose powder was used in the column and Whatman No. 1 acid-washed filter paper was used for the ascending paper chromatography. The solvent in each case was 85% ethanol and 15% water.

(17) Alcoholic solutions of the N-ethyl and N-*n*-propyl derivatives undergo the same color changes. However, the *cis* to *trans* isomerizations indicated by the color changes from purple to green are much more rapid. In contrast, an alcoholic solution of the isobutylenediamine complex turns orange when treated with NaOCH₃ and returns to green on acidification with HCl. The perchlorate salts of the N-ethyl, N-*n*-propyl, and isobutylenediamine complexes were obtained from Dr. Basolo.

Diamagnetic *cis*-(Co(Meen)₂CO₃)₂CO₃ has been prepared by the reaction of aquated (Co(Meen)₂Cl₂)₂CoCl₄ with Ag₂CO₃ and isolated by the evaporation of the aqueous solution resulting, after filtration to remove AgCl and CoCO₃. Reaction of methanolic HCl with the carbonate produces a purple solution which slowly changes to green on standing overnight.

Although it appears that *cis*-Co(Meen)₂Cl₂⁺ has been prepared in solution, as evidenced by the purple color, it has not been isolated free from both *trans*-Co(Meen)₂Cl₂⁺ and *cis*-Co(Meen)₂CO₃⁺. A half-time of about 8 hr at room temperature (about 23°), estimated by visible spectrophotometry, for the *cis*-*trans* isomerization of Co(Meen)₂Cl₂⁺ in methanol is comparable with the time for the same type of isomerization of Co(en)₂Cl₂⁺ or Co(pn)₂Cl₂⁺, as reported by Brasted and Hirayama.¹⁸

Acknowledgment.—Joint support of this research through a research fellowship to E. W. G. from Hooker Chemical Corp. and through a research contract with the USAEC is gratefully acknowledged.

(18) R. C. Brasted and C. Hirayama, *J. Am. Chem. Soc.*, **80**, 788 (1958).

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Contact Shifts of Acetonitrile Solutions of Cupric Chloride and Titanium Trichloride

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Received September 6, 1967

In solutions of solvated paramagnetic metal ions in which there is a chemical exchange of coordinated solvent molecules and bulk solvent, nuclear magnetic resonance absorptions of the solvent protons are shifted from the magnetic field values observed for the pure solvent.^{2,3} Contact interactions between the ligand and metal ion in the solvation complexes are the principal contributors to the resonance shift for solutions of first-row transition metal ions.⁴ When chemical exchange is rapid and the resonance absorptions of complexed and bulk protons are averaged, the observed shift, $\Delta\omega$, is related to the hyperfine coupling constant, A , in the paramagnetic molecule by

$$\frac{\Delta\omega}{\omega} = -\frac{\gamma_e}{\gamma_N} \frac{g\beta S(S+1)}{6kTS} CA \quad (1)$$

where ω is the resonance frequency, C is the concentration of complexed ligand protons, g is the g factor of the metal complex, and the remaining symbols have the

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(2) D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 108 (1965).

(3) J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

(4) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

usual significance. The temperature dependence is $1/T$ in this case. If the resonances of complexed and bulk protons are not completely averaged, *i.e.*, if chemical exchange is slow,⁵ the temperature dependence is not straightforward, but, in general, the resonance will shift toward the average as the temperature is increased. In either case, a positive hyperfine constant results in a downfield shift of the nmr absorption relative to the pure solvent, and a negative constant yields an upfield shift. Both the sign and magnitude of the shifts depend upon the detailed mechanism of spin density transfer in the paramagnetic molecule. It is the transfer of positive or negative spin density to a nucleus that results in a positive or negative hyperfine coupling with that nucleus.⁶ The transfer process may be considered in two parts: first, the transfer of unpaired spin density from metal to ligand, and, second, the distribution of unpaired spin throughout the ligand molecules. Eaton, Phillips, and co-workers^{7,8} and others^{9,10} have shown that the free-radical formalism developed by McConnell¹¹ and others¹² may be successfully applied to the second factor. This note is concerned with the first, specifically, the comparison of hyperfine coupling constants in acetonitrile-metal complexes in which the initial metal-ligand spin density transfer involves σ - or π -antibonding electrons.

Proton magnetic resonance contact shifts were measured as a function of temperature for copper(II) chloride and titanium(III) chloride solutions in acetonitrile. Both metal ions have single unpaired electrons, but in complexes of copper(II), a d^9 ion, unpaired spin transfer should be predominantly through σ -antibonding orbitals. Spin transfer in complexes of titanium(III), a d^1 ion, should be predominantly through π -antibonding orbitals. Acetonitrile coordinates through the nitrile group for which both σ and π bonding may be expected.

Experimental Section

Materials and Solutions.—Acetonitrile purified by the method of O'Donnell, Ayres, and Mann¹³ was used throughout. The cupric chloride solution (0.02 M) was prepared by adding acetonitrile to a weighed amount of the anhydrous salt in a volumetric flask. The titanium trichloride solution (0.01 M) was prepared under a nitrogen atmosphere with previously degassed solvent. The concentration of the titanium in solution was checked by adding 1-ml aliquots to ceric nitrate solution and back titrating with ferrous ammonium sulfate.

Nmr Measurements.—Proton magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer. Temperatures were controlled to $\pm 1^\circ$ by a Varian variable-temperature unit. A minimum of six spectra were taken at each

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(6) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 222.

(7) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(8) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(9) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

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(11) H. M. McConnell, *ibid.*, **24**, 632 (1956).

(12) A. Carrington, Lecture Series 1964, No. 3, The Royal Institute of Chemistry, London, 1964, and references quoted therein.

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