stretching frequencies in the 1200–1500-cm^{-1} region and $\delta(NO_2)_s$ at 825 cm^{-1}.

Figure 6 compares the infrared spectra of the four complexes in the 400–600-cm^{-1} region as measured on disks of pure complex. The three meridial isomers show a very similar pattern of bands, with especially strong doublets at 600 and 500 cm^{-1} due to $\delta(NO_2)_w$ and $\nu(Co-N(NH_3))$, respectively.

As previously noted by Nakagawa and Shimanouchi, the values of the observed and calculated spectra of *mer*-$Co(NH_3)_3(NO_2)_3$, while in fair agreement, are not exactly the same because of the oversimplified assumption of the C_{2v} model for the complex. One must therefore expect a lower order of symmetry for either or both isomers of $Co(NH_3)_3(NO_2)_3$ and should not rely as heavily on infrared data for the purpose of identification as one does for the *cis–trans* isomers.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514, AND SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY, AIKEN, SOUTH CAROLINA 29801

The Magnetic Properties of Hexaamminecobalt(III) Pentachlorocuprate(II)

BY WILLIAM E. HATFIELD AND EDWIN R. JONES, JR.[1]

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The magnetic susceptibility of hexaamminecobalt(III) pentachlorocuprate(II) has been measured from 2.4 to 38°K. The susceptibility obeys the Curie–Weiss law, $\chi = C/(T + \Theta)$, in the temperature range 16–38°K, giving an effective magnetic moment of 1.95 BM with $\Theta = 17$°K. There is an antiferromagnetic transition near 8°K attributed to an intermolecular cation–anion–anion–cation mechanism.

Introduction

In the first report of the magnetism of the pentachlorocuprate(II) ion, Mori[2] noted that susceptibility data for $[Co(NH_3)_6][CuCl_5]$ obeyed the Curie–Weiss law from 4.2 to about 2°K, giving a magnetic moment of 1.47 BM. Our subsequent studies[3] in the temperature range 77–300°K yielded a magnetic moment of 1.85 BM. Because the $2A_1'$ ground electronic state[3,4] of the trigonal-bipyramidal $CuCl_5^{3-}$ ion is not expected to show a decrease in moment at low temperature, the magnetic properties of $[Co(NH_3)_6]$-$[CuCl_5]$ in the intervening temperature range need to be determined. Here we report the results of measurements from 2.4 to 38°K.

Experimental Section

Preparation of $[Co(NH_3)_6][CuCl_5]$.—Large, well-formed, orange crystals of hexaamminecobalt(III) pentachlorocuprate(II) were deposited from an aqueous solution (200 ml) of $[Co(NH_3)_6]$-Cl_3 (2 g) and $CuCl_2 \cdot 2H_2O$ (10 g). *Anal.* Calcd for $[Co(NH_3)_6]$-$[CuCl_5]$: Cl, 44.24; N, 20.86; H, 4.50. Found: Cl, 44.23; N, 20.79; H, 4.47.

Magnetic Susceptibility Determinations.—The magnetic properties of a powdered sample of $[Co(NH_3)_6][CuCl_5]$ (0.16177 g) in a plastic sample holder were determined with a Foner-type vibrating sample magnetometer[5] built by Princeton Applied Research Corp. Measurements were made at magnetic field strengths of 2000 and 10,000 Oe. The magnetometer was calibrated with a sphere of pure nickel metal. Correction was made for the diamagnetism of the sample holder assembly.

Results

The temperature variation of the inverse magnetic susceptibility of $[Co(NH_3)_6][CuCl_5]$ from 2.4 to 38°K is shown in Figure 1. The molar susceptibilities were calculated from the experimental observations after correction for (a) the diamagnetism (244×10^{-4} cgsu) of the constituent atoms using Pascal's constants and (b) the temperature-independent paramagnetism of the hexaamminecobalt ion (75×10^{-6} cgsu).[6] For temperatures above 16°K the susceptibility exhibits a Curie–Weiss behavior with an effective moment of 1.95 BM and a paramagnetic Curie temperature of 17°K. A single smooth curve fits the magnetic moments determined between 2.4 and 38°K by the vibrating sample magnetometer and the magnetic moments determined between 77 and 300°K by the Faraday method.[3]

The differences noted in Figure 1 between runs 1 and 2 are an indication of the precision and accuracy of the magnetic measurements. Thus, the magnetic moment calculated from the slope of either set of magnetic data is more reliable than a moment calculated from a line fitted to the data obtained in both

(1) ORAU Research Participant.
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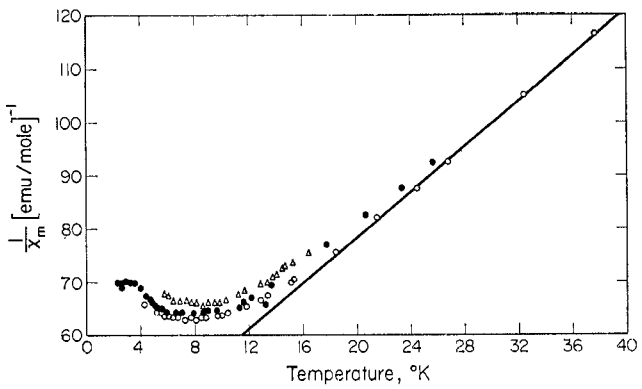

Figure 1.—The inverse magnetic susceptibility *vs.* temperature plot for $[Co(NH_3)_6][CuCl_5]$: O, run 1; ●, run 2 (both at 10,000 Oe); Δ, run 3 (at 2000 Oe).

runs. In this case both sets of data yield the same moment but slightly different Curie temperatures.

Our data below 4.2°K do not agree with those reported earlier by Mori,[2] who used an ac inductance method operating at low field strengths. The disparity might be explained as a field-strength effect, since the $1/\chi$ *vs.* T data (Figure 1) suggest an antiferromagnetic transition at about 8°K. Antiferromagnetic susceptibilities are frequently field dependent and show an increase in susceptibility with a decrease in field strength.[7] As shown in Figure 1, nearly the same susceptibilities were obtained on our samples at both 2000 and 10,000 Oe. We can offer no explanation for the difference between the present results and those reported by Mori; however, our measurements on two different samples did not show Curie–Weiss behavior below 4.2°.

Discussion

Although the detailed X-ray study of hexaamminecobalt(III) pentachlorocuprate(II)[8] has not been reported, the crystal structure of hexaamminechromium(III) pentachlorocuprate(II) was recently redetermined.[9] From three-dimensional X-ray studies, the compounds crystallize into a cubic crystal system with 32 molecules per unit cell and with copper atoms on positions of symmetry 32. Thus the pentachlorocuprate(II) ion must have a trigonal bipyramidal structure with symmetry D_{3h}.

The ^2D electronic state of the copper(II) ion is split by the trigonal-bipyramidal (D_{3h}) crystal field giving a $^2A_1'$ ground state with the $^2E'$ and $^2E''$ lying at higher energies.[3,10,11] Although there is no appropriate crystal containing the $CuCl_5^{3-}$ ion for selection-rule experiments, there is general agreement that the double maxima in the near-infrared region arise from the $^2A_1' \rightarrow {}^2E'$ (8200 cm^{-1}) and the $^2A_1' \rightarrow {}^2E''$ (10,000 cm^{-1}) transitions. The latter transition is not permitted by the electric dipole mechanism but is allowed by a vibronic interaction.

For a consideration of the magnetic properties,[12] spin–orbit coupling and magnetic moment operators are added to the crystal field perturbation Hamiltonian. This gives $\mathcal{H} = \mathcal{H}_{cf} + \lambda LS + \beta H(kL + 2S)$, where λ is the spin–orbit coupling constant and k is the Stevens orbital reduction factor.[13] Applying this operator to the basis set of functions given in Table I, one obtains the factored secular determinant

$$\begin{array}{cc} \underline{\Gamma_4^n(^2E'')} & \underline{\Gamma_4^n(^2A_1')} \\ \begin{vmatrix} -(\lambda/2) + Ds - 4Dt - E & \sqrt{(3/2)}\lambda \\ \sqrt{(3/2)}\lambda & 2Ds + 6Dt - E \end{vmatrix} = 0 \end{array}$$

$$\begin{array}{cc} \underline{(\Gamma_5 + \Gamma_6)^n(^2E'')} & \underline{(\Gamma_5 + \Gamma_6)^n\ (^2E')} \\ \begin{vmatrix} (\lambda/2) + Ds - 4Dt - E & \lambda \\ \lambda & -\lambda - 2Ds + Dt - E \end{vmatrix} = 0 \end{array}$$

$$\begin{array}{c} \underline{\Gamma_4^n\ (^2E')} \\ |\lambda - 2Ds + Dt - E| = 0 \end{array}$$

Here Ds and Dt are crystal field parameters, and the Γ^n ($n = a$ or b) are irreducible representations of the D_3 double group. The $^2E''(\Gamma_4^n)$ state is mixed into the $^2A_1'(\Gamma_4^n)$ ground state by spin–orbit coupling, and the first-order corrected wave functions for the Kramers-doublet ground state are

$$\Gamma_4^n = \Gamma_4^n(^2A_1') - [(\sqrt{3/2})\lambda/\Delta]\Gamma_4^n(^2E'')$$

where Δ is the energy separation between $^2A_1'$ and $^2E''$. Applying the magnetic moment operators $\mu_z = \beta(kL_z + 2S_z)$ and $\mu_x = \beta(kL_x + 2S_x)$, the first-order Zeeman terms are $\pm\beta H$ and $\pm\beta H(1 - 3k\lambda/\Delta)$. Substitution of these first-order terms and the second-order Zeeman terms calculated from μ_x into the Van Vleck expression for magnetic susceptibility gives

$$\chi_m = \frac{N\beta^2}{3kT}(3 - 6k\lambda/\Delta) + 3N\beta^2k^2/\Delta \qquad (1)$$

Ignoring the second term (the temperature-independent paramagnetism) and using the relationship $\mu_{eff}^2 = 3k\chi T/N\beta^2$, we can write $\mu_{eff} = \mu_{eff}^{spin\ only}(1 - 2k\lambda/\Delta)$, thus predicting a temperature-independent moment. The magnetic moment will become temperature dependent only when the second term in eq 1 is large. The temperature-independent magnetic moment of

TABLE I
BASIS FUNCTIONS FOR d^1 (ONE-HOLE) CONFIGURATION IN DOUBLE GROUP D_3

Irreducible representations	Eigenfunctions	Bethe's notation[a]
$^2A_1'$	$\lvert 0, \pm 1/2\rangle$	Γ_4^n
$^2E'$	$\lvert +2, +1/2\rangle$	Γ_4^n
	$\lvert \pm 2, \mp 1/2\rangle$	$(\Gamma_5 + \Gamma_6)^n$
$^2E''$	$\lvert \pm 1, \pm 1/2\rangle$	$(\Gamma_5 + \Gamma_6)^n$
	$\lvert \pm 1, \mp 1/2\rangle$	Γ_4^n

[a] $n = a$ or b.

(7) B. N. Figgis and J. Lewis in "Techniques in Inorganic Chemistry," Vol. 4, Interscience Publishers, New York, N. Y., 1965, p 137.

(8) I. Bernal, N. Elliott, R. A. Lalancette, and T. Brennan, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., Amsterdam, 1968, p 518; T. A. Brennan, Thesis, State University of New York, Stony Brook, N. Y., 1970.

(9) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

(10) C. A. L. Becker, D. W. Meek, and T. M. Dunn, *J. Phys. Chem.*, **72**, 3588 (1968).

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$[Co(NH_3)_6][CuCl_5]$ down to ~16°K is in agreement with this analysis.

The antiferromagnetic transition at 8°K must arise from coupling of the magnetic wave functions transmitted by chloride ligands of adjacent molecules. This mechanism has been designated the cation–anion–anion–cation interaction,[14] and for half-filled σ orbitals, moderately weak spin coupling is expected. The low Néel point of 8°K reflects weak spin coupling in $[Co(NH_3)_6][CuCl_5]$.

The crystal structure for $[Cr(NH_3)_6][CuCl_5]$ shows that the shortest intermolecular chloride–chloride contacts occur for the axial chloride of one $CuCl_5^{3-}$ ion and axial chloride ligands of three adjacent $CuCl_5^{3-}$ units. The internuclear separations are 4.11 Å, and the copper–chloride(1)–chloride(2) angles are 144.74°. This separation is only 0.80 Å greater than the axial chloride–equatorial chloride intramolecular distance within a $CuCl_5^{3-}$ ion. The unpaired electron in the ground state is in a $3d_{z^2}$ orbital, which has a greater amplitude along the z axis than in the xy plane; thus, in the absence of angular dependencies, ligand axial–axial contacts are expected to be more important than ligand equatorial–equatorial contacts for the conduction of antiferromagnetic interactions.

(14) J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience Publishers, New York, N. Y., 1963, p 184.

The closest intermolecular equatorial chloride–other chloride separation, 4.14 Å, occurs between equatorial ligands of adjacent $CuCl_5^{3-}$ ions. In addition, there are four other equatorial chlorides at 4.75 Å. A detailed description of the cooperative magnetic interaction would be extremely difficult, although in principle a treatment similar to the classical work on the hexachloroiridate(IV) salts should be possible.[15] Another explanation would involve particle size or surface effects. We conclude that although the magnetism of the pentachlorocuprate(II) ion may be described by crystal field theory, below 16°K the susceptibility does not exhibit Curie–Weiss behavior but shows a complex behavior suggestive of antiferromagnetism.

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(15) M. E. Lines, *Proc. Roy. Soc.* (London), **A271**, 105 (1963), and references therein.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

The Chemistry of Macrocyclic Complexes of Cobalt(III). Hydrolysis Rates and Equilibria in *trans*-$Co^{III}LX_2$ Systems[1]

BY JOHN A. KERNOHAN AND JOHN F. ENDICOTT[2]

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The specific rates and equilibria have been investigated for the hydrolytic reactions of some *trans*-$CoLX_2^+$ complexes where L is a macrocyclic ligand (of the Curtis type) and $X^- = Cl^-$, Br^-, or NCS^-. The relative lability of these complexes can be ascribed partly to nonbonded steric interactions between ligand methyl groups and the axial ligands X and partly to the formation of relatively long-lived intermediates where L is the Schiff-base amine 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The kinetic and thermodynamic data for these systems can be related by linear free energy relations; however, the coefficients in the LFER's appear to be different for each system. The relatively positive values of $\Delta S^{\ddagger}$ found for many of the systems studied shows that $\Delta S^{\ddagger}$ is not generally correlated with stereochemical change and may not provide any simple information about the geometry of the activated complex.

Introduction

Despite extensive research and discussion, there remain many controversial issues pertaining to the mechanism of ligand substitution reactions in octahedral complexes.[3] Much of the recent discussion has centered around the stereochemical changes which occur during the exchange of ligands. It has been argued that such changes reflect the geometry of the activated

(1) (a) Presented in part before the Division of Inorganic Chemistry, 156th National Meeting of American Chemical Society, Atlantic City, N. J., Sept 1968. (b) Preliminary aspects of this work were also presented at the XIth International Conference on Coordination Chemistry, Haifa, Israel, Sept 1968; see R. E. Ball, J. A. Kernohan, and J. F. Endicott, "Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., Amsterdam, 1968. (c) Taken in part from the Dissertation submitted by J. A. K. to Boston University in partial fulfillment of the requirements of the Ph.D. degree, 1969. (d) Supported in part by the Public Health Service (Grant AM 08737) and in part by a Grant in Aid from the Graduate School, Boston University.

(2) Author to whom correspondence may be addressed at the Department of Chemistry, Wayne State University, Detroit, Mich. 48202.

(3) For recent reviews see: (a) C. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966; (b) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966); (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967; (d) C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, **19**, 193 (1968); (e) R. D. Archer, *Coord. Chem. Rev.*, **4**, 243 (1969).