rate-determining step in the formation and dissociation of the complex involved Np–O fission. However, the presence of HF at concentrations comparable to those in the formation–dissociation studies did not alter the NpO_2^+–H_2O exchange rate. Further HF did not modify the rates of H_2O exchange with either Rh(III) or Cr(III). Unfortunately, it was not possible to study fluoride catalysis of the NpO_2^+–H_2O exchange at $\mu = 8$ to 10 and 1 M $HClO_4$ where the complex formation was studied. On the basis of this work 10^{-3} M F^- or HF catalyzes the formation and dissociation of the complex but does not affect the rate of H_2O exchange of NpO_2^+, Cr(III), or Rh(III).

These observations are even more perplexing in view of the result that 1 M HCl has little or no effect on the rate of dissociation.

The only metal ions which form binuclear complexes with NpO_2^+ at a slow rate are those whose water exchange rates are slow. If the rapidly exchanging equatorial waters of $NpO_2^+ \cdot H_2O$ were being substituted by $M(H_2O)_6^{3+}$, one would expect fast reactions in all cases. Thus it is doubtful that equatorial waters play the dominant role in complex formation or dissociation. Rather it appears that a neptunyl oxygen is replaced in the kinetically important step.

At $\mu = 8$–10 and 1-2 M $HClO_4$ the NpO_2^+–H_2O exchange can be estimated from this work to be very rapid compared to the formation and dissociation of the complex. In view of the fact that Rh(III) and Cr(III) are nearly identical in their behavior it is reasonable to suggest that $M(H_2O)_6^{3+}$ competes with solvent H_2O for the active intermediate formed in the oxygen exchange of NpO_2^+. Because of its high (3+) charge, the metal ion is relatively unsuccessful compared to water, and the rate of water exchange is much greater than that for complexation. Since it was not possible to demonstrate fluoride catalysis of the rate of oxygen exchange of the metal ions in question the catalytic effect is not useful in attempting to more fully understand the mechanism of complex formation. We are unable to present a plausible and meaningful explanation for this marked fluoride catalysis.

The infrared spectra on neptunium complexes establish a small change in the asymmetrical stretching frequency, ν_3, as a function of equatorial environment. In the solid state several frequencies are sometimes observed, suggesting that all lattice positions are not equivalent. In aqueous media at low acid concentrations there is only a small observable change in the stretching frequency as association with Rh^{3+} takes place. The infrared spectra of the solid complex fluoride also showed no significant change. These observations suggest either that bonding is so weak that the O–Np–O bonds are hardly altered or that bonding is not through the axial oxygens. For reasons cited above, the former explanation appears more reasonable.

Magnetic Properties of Potassium Tribromocuprate(II) and Cesium Tribromocuprate(II)

BY MOTOMICHI INOUE, MICHIHIKO KISHITA, AND MASAJI KUBO

The magnetic susceptibilities of potassium tribromocuprate(II) and cesium tribromocuprate(II) have been determined over a temperature range of 80–300°K. The magnetic behavior of potassium tribromocuprate(II) conforms to a modified Bleaney–Bowers equation, indicating the existence of a weak antiferromagnetic spin interaction between $[Cu_2Br_6]^{2-}$ dimer ions as well as of a strong spin coupling within the dimers. On the other hand, the slight paramagnetism of cesium tribromocuprate(II) obtained after corrections for diamagnetic contributions shows no variation with temperature, indicating that the unpaired electrons are completely coupled.

Introduction

The binuclear structure of copper(II) acetate monohydrate has been established by X-ray crystal analysis.[1] The compound is a typical example of isolated binuclear clusters, the temperature dependence of its magnetic susceptibility being clearly interpreted by a simple singlet–triplet formula proposed by Bleaney and Bowers.[2]

A recent X-ray crystal analysis carried out by Willett, et al.,[3] has shown that potassium trichlorocuprate(II) contains $[Cu_2Cl_6]^{2-}$ dimer ions piled on top of one another to form one-dimensional infinite arrays. They have also reported that potassium tribromocuprate(II) is isomorphous with potassium trichlorocuprate(II). In view of the crystal data, one would suspect a possible spin interaction between copper atoms belonging to different dimer ions as well as between copper atoms within the dimers. However, the magnetic moment of

(1) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(2) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952).

(3) R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).

potassium trichlorocuprate(II) is 1.77 BM[4,5] at room temperature, a value only slightly reduced from the value of 1.9–2.0 BM normally observed for copper(II) compounds. This suggests that interaction between unpaired electrons is not very strong in the trichloro complex. A maximum of the susceptibility has been observed at about 30°K.[3] No detailed reports have been published as yet.

In the majority of copper(II) complexes, the spin-exchange interaction is stronger through bromine ions than through chlorine ions.[5] Therefore, we have undertaken to determine the temperature dependence of the magnetic susceptibilities of potassium and cesium tribromocuprates(II).

Preparation of Materials

Potassium Tribromocuprate(II).—In accordance to Sabatier's method,[6] a solution of copper(II) dibromide and potassium bromide in equimolar amounts was allowed to evaporate in a vacuum desiccator over concentrated sulfuric acid. Dark brown needle-like crystals were obtained. *Anal.* Calcd for KCuBr$_3$: Cu, 18.6; Br, 70.0. Found: Cu, 18.6; Br, 70.0.

Cesium Tribromocuprate(II).—This was synthesized by a method described by Wells and Walden.[7] Cesium bromide was dissolved in a concentrated solution of copper(II) dibromide. When the solution was allowed to evaporate over concentrated sulfuric acid, dark brown prismatic crystals separated. *Anal.* Calcd for CsCuBr$_3$: Cu, 14.6; Br, 55.0. Found: Cu, 14.6; Br, 54.9.

Magnetic Measurements and Results

The magnetic susceptibility was determined by the Gouy method with a magnetic field strength of 10,000 oersteds using an Ainsworth recording semimicrobalance over a temperature range of 80–300°K. The temperature was automatically controlled.

The observed magnetic susceptibility of potassium tribromocuprate(II) is listed in Table I. The accuracy is estimated to be within ±1%. It is confirmed that the observed values were not altered by repeated recrystallization. The molar susceptibility has been corrected for the diamagnetic contribution (in cgs emu) of all ions: Cu^{2+}, -11×10^{-6}; Br$^-$, -36×10^{-6}; K$^+$, -13×10^{-6}; and Cs$^+$, -31×10^{-6}.[8] From the corrected molar susceptibilities χ_A, the magnetic moments μ were evaluated per copper atom using

$$\mu = 2.83[(\chi_A - N\alpha)T]^{1/2} \qquad (1)$$

where $N\alpha$ stands for the temperature-independent paramagnetism assumed to be equal to 60×10^{-6} cgs emu for Cu(II).[9]

Discussion

Willett, *et al.*,[3] have carried out a complete X-ray crystal analysis on potassium trichlorocuprate(II).

(4) E. Cotton-Feytis, *Ann. Chim.* (Paris), **4**, 9 (1925).

(5) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(6) P. Sabatier, *Bull. Soc. Chim. France*, **11**, 683 (1892).

(7) H. L. Wells and P. T. Walden, *Am. J. Sci.*, **47**, 94 (1894).

(8) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956.

TABLE I
MAGNETIC SUSCEPTIBILITY PER GRAM χ_g (CGS EMU), MOLAR MAGNETIC SUSCEPTIBILITY χ_A CORRECTED FOR DIAMAGNETIC CONTRIBUTIONS, AND MAGNETIC MOMENTS μ_{eff} (BM) OF POTASSIUM TRIBROMOCUPRATE(II)

Temp, °K	$10^6\chi_g$	$10^3\chi_A$	μ_{eff}
78	3.02	1.17	0.83
94	3.50	1.33	0.98
111	3.72	1.41	1.10
130	3.80	1.43	1.19
150	3.76	1.42	1.27
181	3.55	1.35	1.37
212	3.27	1.25	1.42
241	3.03	1.17	1.46
295	2.66	1.04	1.52

It has been found that the crystal contains planar centrosymmetric binuclear complex ions [Cu$_2$Cl$_6$]$^{2-}$, in which the Cu–Cl bond lengths are close to 2.30 A with the distances to the terminal chlorine atoms slightly shorter than the distances to the bridging chlorine atoms. The dimer ions are stacked obliquely in a one-dimensional infinite array along the crystallographic a axis so that two neighboring dimer ions are bonded by four Cu–Cl bonds of about 3.03 A to complete a distorted coordination octahedron about each copper atom. It is reported also that potassium tribromocuprate(II) is isomorphous with this structure.

Bleaney and Bowers[2] have proposed a theoretical equation for the susceptibility χ_A of isolated dimeric clusters as a function of temperature

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp\frac{J}{kT}\right]^{-1} + N\alpha \qquad (2)$$

where N is the Avogadro number, $g = 2.00$ is the electronic g factor, β is the Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, and J denotes the energy separation between the triplet and singlet states. The value of J/k can be determined directly from the temperature T_m corresponding to the maximum susceptibility as $J/k = 1.60T_m = 205$°K. Equation 2 is in good agreement with the experimental data of anhydrous copper(II) acetate as well as its monohydrate,[9] acetylacetonemono(o-hydroxyanil)copper(II),[10] and other copper(II) complexes having a binuclear structure.[5,11] Therefore, the susceptibility was calculated assuming the validity of the Bleaney–Bowers equation with the aforementioned value for J/k and is shown by a broken curve in Figure 1. The observed susceptibility is smaller than the value calculated for isolated clusters at all temperatures studied, the maximum deviation appearing at the temperature of the maximum susceptibility. The discrepancy between the observed and calculated curves is not due to the choice of $N\alpha$, because the two curves cannot be fitted with each other by a simple shift along the χ_A axis and also because a negative value would be required for $N\alpha$ in order to fit the theoretical curve with the observed

(9) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(10) G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961).

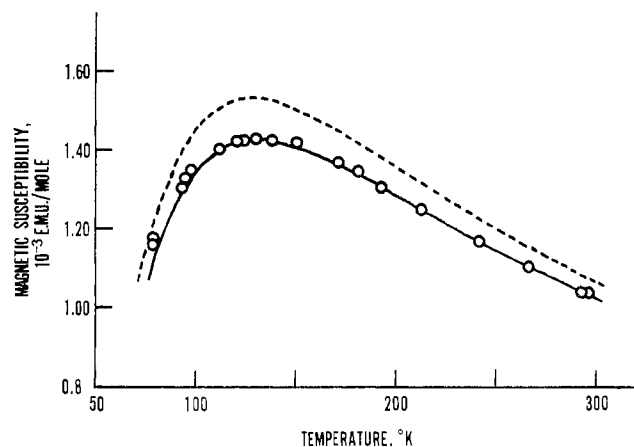(11) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

Figure 1.—Magnetic susceptibility of potassium tribromo-cuprate(II) as a function of temperature. The broken curve was calculated assuming the validity of the Bleaney–Bowers equation (eq 2); J/k = 205°K. The solid curve was calculated from the modified equation (eq 3) with J/k = 195°K and θ = −17°K.

one at their maxima. The assumption that g is equal to 2.00 also is not responsible for the discrepancy. It is very likely that g for copper is slightly greater than 2.00 owing to spin–orbit interactions. In this case, the theoretical data (eq 2) increase making the discrepancy still larger. Lewis, et al.,[12] have attributed the deviation of magnetic susceptibilities observed for some carboxylic acid derivatives of copper(II) from those predicted by eq 2 to the presence of a small amount of impurities in samples or to the existence of different crystal forms varying in magnetic interaction. Therefore, we have taken the X-ray powder patterns of the present sample. All of the diffraction lines could be accounted for by crystal data given by Willett, et al.,[3] while lines possibly due to copper(II) dibromide and potassium bromide were absent.

The foregoing facts suggest that $[Cu_2Br_6]^{2-}$ dimer ions in potassium tribromocuprate(II) are not completely isolated but are subject to magnetic interaction with one another. Since the copper–halogen bond length within a dimer ion is evidently shorter than the distance between a copper atom and the nearest halogen atoms belonging to adjacent dimers, it is reasonable to assume that the spin interaction within the dimer ions is dominant and that the resultant magnetic moments of the dimer ions are subject to the orienting effect of the Weiss field, which is opposed by the thermal agitation of the elementary magnetic moments. Under this condition, one is led to modify the Bleaney–Bowers expression as

(12) J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thompson, *J. Chem. Soc.*, 6464 (1965).

$$\chi_A = \frac{Ng^2\beta^2}{3k(T - \theta)}\left[1 + \frac{1}{3}\exp\frac{J}{kT}\right]^{-1} + N\alpha \qquad (3)$$

where θ is the Weiss constant that takes into account the spin interaction between the dimer ions. The susceptibility χ_A was calculated from this equation with J/k = 195°K and θ = −17°K and is shown by a solid curve in Figure 1. Excellent agreement is obtained between the experimental susceptibility values and the theoretical curve based on eq 3. The values of J/k and θ depend on the assumed value of g. If it is assumed that g = 2.10, one gets J/k = 205°K and θ = −16°K. However, agreement between observed and calculated values becomes poor in the range of high temperature. To be sure, g = 2.10 is an overestimation. The negative value for θ indicates the presence of antiferromagnetic spin interaction between dimer ions. The energy of the spin interaction is of the order of $k|\theta|$, which amounts to a few per cent of the energy of the spin interaction J within a dimer ion in this compound. Possibly, a transition takes place to an antiferromagnetic state below about 17°K, leading to the existence of long-range spin ordering.

Lithium trichlorocuprate(II) dihydrate[13] has a structure closely related to those of potassium trichlorocuprate(II) and potassium tribromocuprate(II). The magnetic property of this compound has been examined. It is reported that the ground state is a triplet rather than a singlet, whereas the ground state is a singlet in potassium tribromocuprate(II).

The magnetic susceptibility of cesium tribromocuprate(II) is −0.02 × 10^{-6} cgs emu/g over the whole temperature range of 80–300°K. Corrections for diamagnetic contributions yield a slight paramagnetism, χ_A = 0.14 × 10^{-3} cgs emu. The origin of the paramagnetism is open to speculation. Possibly, it arises from the so-called temperature-independent paramagnetism discussed by Van Vleck,[14] or it may be the residual paramagnetism of an antiferromagnetic state. Accordingly, it is concluded that the unpaired electrons of copper atoms are completely coupled. Since no X-ray crystal data have been available for cesium tribromocuprate(II), we have taken X-ray powder patterns and found that this compound is not isomorphous with cesium trichlorocuprate(II).[15,16]

(13) P. H. Vossos, L. D. Jenning, and R. E. Rundle, *J. Chem. Phys.*, 32, 1590 (1960).

(14) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

(15) A. F. Wells, *J. Chem. Soc.*, 1662 (1947).

(16) A. W. Schluester, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, 5, 277 (1966).