$[TiO(C_2O_4)_2]^{2-}$,[12-14] a ring structure is formed. Ion-exchange behavior of Ti(IV) in aqueous perchloric acid solutions, in particular the similar elution rate to VO^{2+}, has previously indicated a mononuclear 2+ species.[2]

Registry No. Ti(IV), 16043-45-1; Cr^{2+}, 22541-79-3; VO^{2+}, 20644-97-7; $CrCl^{2+}$, 14931-91-0; Cl^-, 16887-00-6; TiO^{2+}, 12192-25-5.

References and Notes

(1) Attempts to detect ν(Ti–O) by Raman solution spectroscopy, [Ti(IV)] = 0.05 M, $[HClO_4]$ = 2.0 M, have proved unsuccessful.
(2) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 537 (1973).
(3) T. R. Duke and P. R. Quinney, *J. Am. Chem. Soc.*, **76**, 3800 (1954).
(4) P. Moore and F. Basolo, *Inorg. Chem.*, **4**, 1670 (1965); T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).
(5) Los Alamos Report LA 2367, 1959, and Addenda by R. H. Moore and R. K. Zeigler.
(6) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569, 1964; *J. Phys. Chem.*, **68**, 228 (1964).
(7) J. H. Espenson, *Inorg. Chem.*, **4**, 1533, 1965.
(8) A. M. Chelmnick and D. Fiat, *J. Chem. Phys.*, **51**, 4238 (1969).
(9) A. M. Chelmnick and D. Fiat, *J. Magn. Reson.*, **8**, 325 (1972).
(10) W. S. Melvin and G. Gordon, *Inorg. Chem.*, **11**, 1912 (1972).
(11) W. Haase and H. Hoppe, *Acta Crystallogr., Sect. B*, **24**, 282 (1968).
(12) R. J. H. Clark "The Chemistry of Titanium and Vanadium", Elsevier, Amsterdam, 1968, p 195.
(13) W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
(14) G. M. H. Van De Velde, S. Harkema, and P. J. Gellings, *Inorg. Chim. Acta*, **11**, 243 (1974).

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Structural and Magnetic Properties of Binuclear Copper(II) Complexes

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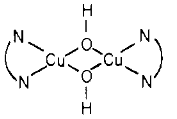
The structural and magnetic properties of binuclear copper(II) complexes of the types **1** and **2** have been the subjects of considerable recent research.[1-13] This large body of data clearly suggests that the geometry of the four-membered Cu–O–Cu–O ring is the dominant feature in determining the magnitude and the sign of the magnetic exchange parameter *J*, which is defined by the exchange Hamiltonian



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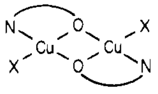


2

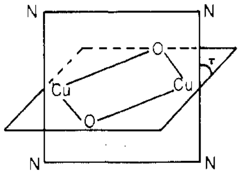
$$H_{ex} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2)$$

There is, however, some apparent difference of interpretation concerning the precise structural feature (or parameter) which dominates the magnetic exchange. Hatfield and Hodgson[7,10,11,14,15] have demonstrated an experimental correlation for complexes of type **1** between *J* and the Cu–O–Cu bridging angle, ϕ, and this relationship has been placed on a sound theoretical basis through the application of molecular orbital theory;[11,16,17] Sinn and his co-workers,[3,8] however, have noted that for a variety of complexes of type **2** which demonstrate large antiferromagnetic interactions the magnitude of *J* is influenced by the deviation from planarity at the copper atom and is relatively insensitive to changes in ϕ. In this communication the apparent distinction between these two sets of observations will be explained.

Discussion

As has been noted elsewhere,[11,16] the Cu_2O_2 bridging fragment has approximate D_{2h} symmetry since in virtually all of the complexes studied this moiety is planar and the Cu–O bond lengths are all equal. In complexes of type **1**, it is also found that the entire $Cu_2O_2N_4$ system is approximately planar.[18] Thus, if one examines the σ-bonding framework of the bridge (neglecting oxygen 2s orbitals) the eight σ orbitals transform[11] as $2\ A_g + 2\ B_{1g} + 2\ B_{2u} + 2\ B_{3u}$. At $\phi = 90°$ (again neglecting 2s orbitals) the highest occupied molecular orbitals (HOMO) are the accidentally degenerate B_{1g}^* and B_{2u}^* orbitals, each of which is singly occupied. Hence, under these conditions, the ground state is the triplet and, therefore, $J > 0$. Any appreciable change in ϕ from this value raises the degeneracy of these two orbitals and eventually leads to a singlet ground state ($J < 0$).[17,21] If the contribution of the oxygen 2s orbitals is included, this view is not qualitatively changed, i.e., there is some ϕ_0 (near 90°) at which B_{1g}^* and B_{2u}^* are degenerate, and at angles of $\phi_0 + \Delta\phi$ this degeneracy is lifted.[9] Experimentally, it is observed that at $\phi > 97.6°$ the value of *J* is negative, i.e., that the ground state is the singlet.[15]

The effect of distorting the geometry at the copper atom can be understood within this molecular orbital framework. Sinn and co-workers[8] have defined the angle τ (**3**) as the angle between the bridging Cu_2O_2 plane and the $Cu_2N_2X_2$ (in **2**) or Cu_2N_4 (in **1**) plane; this angle, which is zero for square-planar geometry at copper and would be 90° for tetrahedral geometry, gives an excellent measure of the distortion toward tetrahedral geometry which is often observed[8] in complexes of type **2**.



3

All of the complexes of type **2** which have been studied in detail have $\phi \gg 97.6°$, which means (vide supra) that the ground state is the singlet and that $J < 0$. In these cases, the effect of increasing τ from zero is to attenuate the overlap between the Cu (d_{xy} and $d_{x^2-y^2}$) and the oxygen (p_x and p_y) σ orbitals, since these orbitals are coplanar at $\tau = 0$ and become progressively less aligned as τ increases. Since the magnetic exchange depends on this orbital overlap, the principal magnetic effect of the geometric distortion is to reduce the magnitude of *J* without affecting its sign. Thus, for example, a progressive increase of τ from 33.1 to 39.3° leads to a decrease in $|J|$ from 240 to 146 cm^{-1} [8] for a series of complexes whose ϕ values are all close to 103°. It is to be expected that, at large values of ϕ, the magnitude of *J* is more sensitive to changes in τ than to changes in ϕ since (at $\phi \gg \phi_0$) the degree of orbital overlap varies more rapidly with τ. Our experience with chromium(III) dimers parallels this conclusion that the magnitude of *J* is largely determined by the degree of orbital overlap; the overlap between the Cr(III) (t_{2g}) orbitals containing the unpaired spin and the oxygen p orbitals is much less than is the case for copper(II), and hence the magnitude of *J* observed in Cr(III) complexes analogous to **1** is much less than that for the Cu(II) systems.[22] It remains true that the sign of *J* is determined largely by ϕ.

It is also noteworthy that at $\phi = \phi_0$, the effect of a small increase from zero in τ must also lead to a lifting of the degeneracy of the B_{1g}^* and B_{2u}^* orbitals. Unfortunately the available data do not allow an examination of this effect since complexes of type **1** have $\tau \approx 0°$ and complexes of type **2** have $\phi \gg \phi_0$.

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Registry No. Copper, 7440-50-8.

References and Notes

(1) E. Uhlig and K. Staiger, *Z. Anorg. Allg. Chem.*, **346**, 21 (1966); **360**, 39 (1968).
(2) C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 2723 (1968).
(3) E. Sinn, *Coord. Chem. Rev.*, **5**, 313 (1969).
(4) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, **4**, 203 (1970).
(5) J. A. Bertrand, J. A. Kelley, and J. L. Breece, *Inorg. Chim. Acta*, **4**, 247 (1970).
(6) A. Pajunen and M. Lehtonen, *Suom. Kemistil. B*, **44**, 200 (1971).
(7) E. D. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1654 (1974), and references therein.
(8) R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, **13**, 2013 (1974).
(9) J. A. Bertrand and P. G. Eller, *Prog. Inorg. Chem.*, **21**, 29 (1976).
(10) W. E. Hatfield, *ACS Symp. Ser.*, **No. 5**, Chapter 10 (1974).
(11) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975).
(12) E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **14**, 334 (1975).
(13) V. R. Mergehenn, W. Haase, and R. Allmann, *Acta Crystallogr., Sect. B*, **31**, 1847 (1975).
(14) K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, **9**, 423 (1973).
(15) V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976).
(16) J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, **6**, 248 (1972).
(17) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
(18) A notable exception is the $[Cu(bpy)OH]_2^{2+}$ cation in $[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$.[19,20]
(19) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).
(20) B. F. Hoskins and F. D. Whillans, *J. Chem. Soc., Dalton Trans.*, 1267 (1975).
(21) This discussion is presented in more detail in ref 11, pp 179–181.
(22) D. J. Hodgson, *ACS Symp. Ser.* **No. 5**, Chapter 9 (1974).

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Physical Properties of Linear-Chain Systems. 6. Single-Crystal Absorption Spectra of $RbCrCl_3$ and $CsCrCl_3$[1]

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$RbCrCl_3$ and $CsCrCl_3$ show the same crystal structure as a number of ABX_3 compounds (with A = a univalent alkali metal cation, B = a divalent first-row transition metal ion, and X = Cl, Br, or I).[1] This structural type contains $[BX_6]$ octahedra sharing faces to form linear chains; the chains are sufficiently separated by the A cations for the magnetic interactions between chains to be very weak. Thus the major interactions are one-dimensional, along the chains. These interactions produce very significant effects on the magnetic and spectroscopic properties in comparison to those of isolated BX_6^{4-} octahedra.[3] The spectrum of $CsCrCl_3$ has previously been examined at 77 K,[4] and an anomalous absorption was reported at 22 000 cm^{-1}, an energy approximately twice that observed for the $^5E \rightarrow {}^5T_2$ transition. This absorption was attributed to a pairwise excitation of $^5E \rightarrow {}^5T_2$ transitions associated with adjacent Cr^{2+} ions, (i.e., $2(^5E \rightarrow {}^5T_2)$). As this particular form of interaction has not otherwise been observed in the ABX_3 compounds, the optical spectrum of $RbCrCl_3$ has been examined and that of $CsCrCl_3$ reexamined to 4.2 K.

Experimental Section

Preparations. Anhydrous CsCl, RbCl, and $CrCl_2$ were purchased from ROC/RIC. The compounds $CsCrCl_3$ and $RbCrCl_3$ were prepared by mixing equimolar quantities of CsCl or RbCl and $CrCl_2$, sealing the mixture in an evacuated quartz ampule, and refining in a Bridgman furnance. The resulting single-crystal boules ~5 cm in length by 1.5 cm in diameter could readily be cleaved (along 1120) to give flakes $\parallel c$, suitable for σ and π spectroscopic measurements. Both crystals show strong pleiochroism, appearing red-brown in light polarized parallel to *c* and yellow in light polarized perpendicular to *c*. We were not able to obtain suitable crystals for measurement of the axial spectrum.

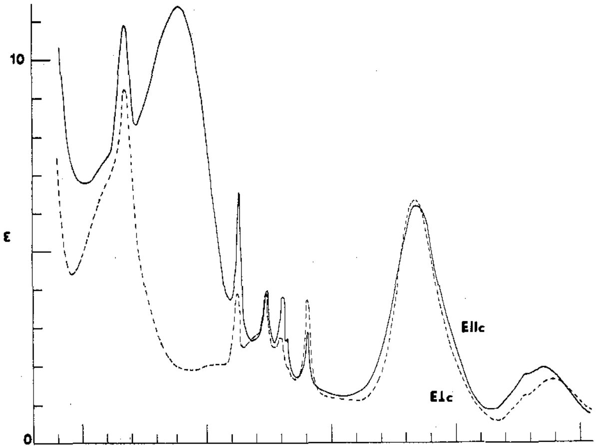

Figure 1. General spectrum of $CsCrCl_3$, 5000–26 000 cm^{-1}. The region 15 000–20 000 cm^{-1} is shown only in outline. ϵ is in units of $l. mol^{-1} cm^{-1}$ throughout.

Crystal Data. The crystal structure of $CsCrCl_3$ has been determined[4] and is similar to that of the type of compound $CsNiCl_3$.[5] While the cell is hexagonal, $P6_3mc$, with $a = 7.256$ (3) Å, $c = 6.224$ (3) Å, $CsCrCl_3$ differs however in that the site symmetry of the Cr^{2+} ion is C_{3v} ($3m$) and not D_{3d} ($\bar{3}m$).

The distortion takes the form of a small displacement of the Cr along the chain axis so that three Cr–Cl distances are 2.419 (5) Å and three are 2.618 (6) Å, with corresponding Cr–Cr–Cl angles within each group of 90.1 (2) and 81.7 (2)°, respectively. This distortion is presumably connected with the Jahn–Teller effect but does not of itself split the degenerate E level; this can only occur in this compound by a vibrational mechanism for which there is some evidence from anisotropic motion of the chloride ions parallel to the *c* axis.

The structure of $RbCrCl_3$ has not been determined, but preliminary x-ray photographs indicate a similar unit cell to that of $CsCrCl_3$, with $a = 7.06$ (3) Å and $c = 6.24$ (3) Å.

No complete magnetic data exist for either compound although $CsCrCl_3$ is reported to be antiferromagnetic below 108 K.[9]

Spectroscopic Measurements. The σ and π single-crystal absorption spectra of $CsCrCl_3$ and $RbCrCl_3$ were measured at various temperatures between 300 and ~4 K in the spectral range 5000–30 000 cm^{-1}, using techniques described in ref 1. Oscillator strengths were determined as in ref 1; while internal consistency is probably ~5%, due to inaccuracies in the measurement of crystal thickness and estimation of band areas, the absolute values are not likely to be accurate to better than 15–20%.

Results

The spectrum of $CsCrCl_3$ at 75 K is similar to that previously reported,[4] but there are significant changes at 4 K (Figures 1–3); the spectrum of $RbCrCl_3$ is generally similar to this but shows some unexpected variations in detail (Figures 2–5). The observed energy levels and oscillator strengths are listed in Table I.

The spectra can best be described in terms of four regions of absorption. From 5000 to 15 000 cm^{-1} there are two strong broad unstructured absorptions, attributed (see below) to the $^5E \rightarrow {}^3T_1$ and $^5E \rightarrow {}^5T_2$ transitions; from 15 000 to 19 000 cm^{-1} there is a complex group of weak bands; 19 000–25 000 cm^{-1} is occupied by the double exciton; the charge-transfer absorption occurs beyond about 25 000 cm^{-1}. In region I, the main bands at about 11 500 cm^{-1} are entirely structureless. The weaker bands, whose peak positions depend slightly on