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Out-of-Plane Interactions in Dichlorobis(2-methylpyridine)copper(II) and Dibromobis(2-methylpyridine)copper(II)

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Received October 26, 1970

The magnetic susceptibilities of dichlorobis(2-methylpyridine)copper(II) and dibromobis(2-methylpyridine)copper(II) have been measured in the temperature range 4.2-300°K. The data for both compounds obey the Van Vleck equation for exchange coupled copper ions with the singlet-triplet separation being 5 cm^{-1} for the bromo-complex and 7.4 cm^{-1} for the chloro-complex. The singlet state is the ground state in both cases.

Introduction

In recent years many copper(II) complexes of the type CuL_2X_2, where X is chloride or bromide and L is pyridine or substituted pyridine, have been prepared and characterized.[2] These complexes are mainly polymeric, having six coordination about the copper ion with halide ligands from adjacent molecules occupying the out-of-plane coordination positions. However, the complexes of 2-methylpyridine were found to have properties somewhat different to those found for the analogous pyridine complexes,[3] and it was postulated that the methyl group in the 2-position provides steric hindrance to the usual octahedral coordination. Subsequently, Duckworth and Stephenson[4] determined that such was the case for dichlorobis(2-methylpyridine)copper(II). The coordination about copper in this complex is tetragonal pyramidal with the fifth position (out-of-plane) occupied by a chloride ligand from an adjacent planar moiety, and the sixth position is effectively blocked by the methyl groups of the pyridine ligands. In continuing our program devoted to the study of the factors which determine the extent and nature of electronic and magnetic interactions between copper ions, we have determined the magnetic susceptibilities of Cu(2-methylpyridine)$_2$Cl$_2$ and Cu(2-methylpyridine)$_2$Br$_2$ in the temperature range 4.2-300°K. The results of our studies are described in this paper.

Experimental Section

The complexes were prepared in the manner described by Allen *et al.*[5] *Anal. Calcd for* $Cu(CH_3C_5H_4N)_2Cl_2$: C, 44.94; H, 4.40; N, 8.74. Found: C, 45.14; H, 4.54; N, 8.85. Calcd for $Cu(CH_3C_5H_4N)_2Br_2$: C, 35.18; H, 3.44; N, 6.84. Found: C, 35.34; H, 3.45; N, 6.83.

The magnetic susceptibility measurements of powdered samples in the temperature range 77-295°K, were determined using a Faraday balance.[6] In the temperature range 4.2-56°K, a Foner-type vibrating sample magnetometer[7] was used. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,[8] and diamagnetic corrections for the substituent atoms were estimated from Pascal's constants.[9]

Since the structure of the bromo-complex has not been determined previously, the powder photograph of the complex was compared with that of the chloro-

Table I. Powder Pattern D-spacings

Cu(2-methylpyridine)$_2$Cl$_2$	Cu(2-methylpyridine)$_2$Br$_2$
5.1672 (w)*	5.4645 (w)
3.8404 (s)	
3.5394 (s)	3.6304 (s)
2.8174 (w)	2.7866 (m)
2.5880 (s)	2.5552 (m)
2.4069 (m)	
2.1779 (m)	2.1356 (s)
2.0077 (s)	1.8983 (s)
1.8358 (m)	1.8166 (s)
1.7473 (s)	1.7092 (s)
1.6595 (m)	1.5578 (m)
1.5221 (m)	1.5073 (m)
1.4638 (m)	1.4543 (w)
1.4277 (m)	
1.3993 (w)	
1.3669 (w)	1.3982 (w)
1.3380 (w)	
1.3043 (w)	1.3160 (m)
1.2598 (m)	1.2704 (m)
1.2112 (m)	1.2003 (w)
1.1767 (m)	1.1666 (w)
1.1266 (m)	
1.0194 (w)	1.0213 (w)
0.9881 (w)	0.9709 (w)

* Line intensity: w = weak, m = medium, and s = strong.

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(1) NSF Trainee, 1968-1971.

(2) W.E. Hatfield and R. Whyman, *Transition Metal Chemistry*, *5*, 53 (1969).

(3) D.P. Graddon, R. Schulz, E.C. Watton, and D.G. Weeden, *Nature*, *198*, 1299 (1963).

(4) V.F. Duckworth and N.C. Stephenson, *Acta Cryst.*, *25*, 1795 (1969).

(5) J.R. Allen, D H. Brown, R.H. Nutall, and D.W.A. Sharp, *J. Chem. Soc.* (*A*), 1031 (1966).

(6) W.E. Hatfield, C.S. Fountain, and R. Whyman, *Inorg. Chem.*, *5*, 1855 (1966).

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(8) B.N Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(9) E. König, *Magnetic Properties of Transition Metal Compounds*, Springer - Verlag, Berlin, 1966.

complex for which the structure is known.[4] The similarity of intensities of the lines and the progressions of the d-spacings, tabulated in Table I, suggest that the complexes have the same structure, although previous spectral data[5] have been interpreted as indicating structural differences.

Results

As shown in Figure 1, the magnetic susceptibility data for both Cu(2-methylpyridine)$_2$Cl$_2$ and Cu(2-methylpyridine)$_2$Br$_2$ obey the Curie-Weiss law, $\chi = C/T + \vartheta$, in the range 295°K to approximately 30°K. For the chloro-complex, the Curie constant $C = 0.394$, $\vartheta = -1$°K, and μ_{eff} is calculated from the equation $\mu_{eff} = 2.828C^{1/2}$ to be 1.78 B.M. The data for the bromo-complex are $C = 0.384$, $\vartheta = -6$°K, and $\mu_{eff} = 1.76$ B.M. However, at the low temperature limit it is apparent that the Curie-Weiss law fails. There is a distinct minimum in the χ^{-1} *versus* T plot at approximately 7°K for the chloro-complex, and, at the low temperature limit of our measurements, the data for the bromo-complex exhibits the same characteristic behavior of magnetically coupled pairs of copper ions. Although the Néel temperature was not measured directly for Cu(2-methylpyridine)$_2$Br$_2$, the data obey the Van Vleck equation (1)[10]

$$\chi_m = 2g^2N\beta^2/3kT[1 + 1/3\exp(-2J/kT)] + N\alpha \tag{1}$$

for magnetically coupled pairs of copper ions yielding a singlet-triplet splitting of 5 cm^{-1} and $g = 2.11$. For the chloro-complex, the best least squares fit of the data yield $g = 2.15$ and $-2J = 7.4$ cm^{-1}

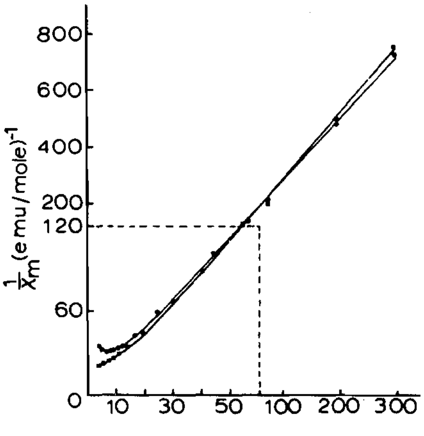

Figure 1. The temperature variation of the experimental inverse susceptibility of Cu(2-methylpyridine)$_2$Cl$_2$ (●) and Cu(2-methylpyridine)$_2$Br$_2$ (■).

Discussion

The structure of Cu(2-methylpyridine)$_2$Cl$_2$ is shown schematically in Figure 2. As can be seen, the two copper atoms in this dimer are more than 4 Å apart, but are bridged by chloride atoms with a Cu–Cl–Cu angle of about 101°. It was postulated by Kanamori[11] that if the bridging angle is close to or equal to 90°, the sign of the coupling constant should be positive. Such was the case in the dimer bis(pyridine N-oxide)-copper(II) nitrate,[12] where a bonding angle of 103° is present and the exchange coupling constant is positive. In the current system, however, this is not the result. The transition at 7°K is indictative of a weak interaction of the opposite sign which must be transmitted via the chloride bridges. It must be noted that Dudley and Hathaway[13] have postulated from electron paramagnetic resonance experiments that no exchange coupling occurs in this complex. It seems very likely, however, that their experiments would not be sensitive to a spin-spin interaction as small as that found for this complex through our magnetism studies, since undiluted samples were studied. It has been observed previously[12] that line width broadening can become quite large in such magnetically concentrated complexes, and only upon dilution do the lines due to the coupling become more easily observed if the degree of interaction is small. As would be expected, the lengthening of the metal-halogen bonds anticipated for the bromo-complex seems to decrease the extent of exchange as reflected in the smaller value of $-2J$ for Cu(2-methylpyridine)$_2$Br$_2$. It should also be noted that more electron delocalization in Cu(2-methylpyridine)$_2$Br$_2$ due to a greater mixing of the metallic wave functions with those of the bromide ligands should produce a smaller g value than that resulting from Cu(2-methylpyridine)$_2$Cl$_2$ even though there is a substantial delocalization in both complexes.

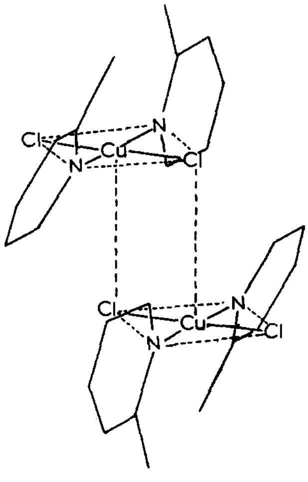

Figure 2. Structure of Cu(2-methylpyridine)$_2$Cl$_2$.

Thus it becomes apparent that it is not just the interaction angle, but also the characteristics of the bridging atoms which determine the type of exchange. Goodenough[14] has described a 90° cation-anion-cation interaction mechanism which, when applied to a d^9–d^9 system, can result in either a singlet or triplet ground state for a dimer. The mechanism predicts

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(10) J.H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities,* Oxford University Press, London, Chapter IX, 1932.

(11) J. Kanamori, *Phys. Chem. Solids, 10,* 87 (1959).

(12) W.E. Hatfield, J.A. Barnes, D.Y. Jeter, R. Whyman, and E.R. Jones, *J. Amer. Chem. Soc., 92,* 4982 (1970).

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(14) J.B. Goodenough, *Magnetism and the Chemical Bond,* Interscience Publishers, New York, N. Y., pp. 180 ff, 1963.

that the singlet state will lie lowest when the σ orbitals of the metal atoms are coupled through the *s* orbitals of the bridging atom and that the triplet state will be the ground state if electrons of like spin can be simultaneously excited from two different bridging atom *p* orbitals to the σ orbitals of the two metal atoms. Perhaps a more general statement may be that a negative exchange coupling constant results if a single orbital from the bridge, be it *s*, hybrid *sp*, or low lying *d*, can interact with both metal atoms, while positive exchange coupling constants result if two bridge orbitals are utilized to transmit the interaction. Although there are not enough magnetic susceptibility data on properly characterized copper dimers to reach definitive conclusions, it may be significant that negative coupling constants appear to be obtained for these out-of-plane interactions only when the bridging atom has low lying *d* orbitals.

While there are major structural differences, of the copper complexes with adequate magnetic data, the copper dimer $[Cu_2Cl_8]^{4-}$, which occurs in the compound $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 . 2H_2O$,[15] has perhaps the greatest similarity to the bridging arrangement found in these 2-methylpyridine complexes. The geometry of the $[Cu_2Cl_8]^{4-}$ dimer is best described as two distorted trigonal bipyramids sharing an edge. There is a center of symmetry, and the Cu_2Cl_2 ring is planar with a Cu–Cu separation of 3.714(8) A and a Cl–Cu–Cl angle of 84.8°. The magnetic susceptibility measurements for $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 . 2H_2O$[16] clearly indicate the presence of magnetic interactions yielding a singlet ground state with a triplet state lying some 17 cm^{-1} above it. The features of the two Cu_2Cl_2 units are compared in Figure 3. On the basis of interatomic separations, it is reasonable to expect, as is determined experimentally, that the smaller exchange coupling constant will result in the case of the 2-methylpyridine complex.

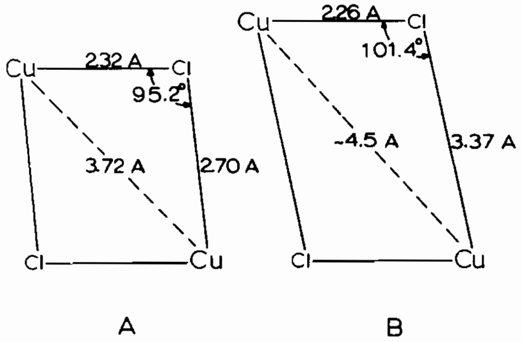

Figure 3. Geometrical details of the Cu_2Cl_2 rings in the complexes $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 . 2H_2O$ (A) and Cu(2-methylpyridine)$_2$Cl$_2$ (B).

The energy of the interaction is considerably larger than that expected for dipolar coupling. From the expression for the magnitude of dipolar coupling $(= 3/4\ g^2\beta^2 < (1-3\cos^2 \vartheta)/r_{1,2}^3 >)$ we calculate for the point-charge approximation an energy of only 0.035 cm^{-1}. To more carefully verify the mechanism of the interaction, a study of the electron paramagnetic resonance of these complexes has been undertaken. Unfortunately, no proper host lattice has yet been found.

Acknowledgments. This research was sponsored by the National Science Foundation through grants GP-7400 and GP-22887, and by the Materials Research Center of the University of North Carolina through Contract SD-100 with the Advanced Research Projects Agency. We are grateful for this continuing support.

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[15] D.J. Hodgson, P.K. Hale, J.A Barnes, and W.E. Hatfield, *Chem. Commun.*, 786 (1970).

[16] J.A. Barnes, W.E. Hatfield, and D.J. Hodgson, *Chem. Phys. Letters*, *7*, 374 (1970).