perturbed by delocalization effects only when orbital overlap between the sites is appreciable and should be unaffected by changes in the orbital pathway involved if delocalization is slight.

Acknowledgment. Acknowledgments are made to Army Research Office, Durham, N.C., under Grant No. DAAG29-76-G-0135 and to the National Institutes of Health under Grant No. 2-R01-GM15238-10 for support of this research.

Registry No. $[(bpy)_2ClRu(pym)](PF_6)$, 66792-58-3; $[(bpy)_2ClRu(pymH)]^{2+}$, 66792-59-4; $[(bpy)_2ClRu(pym)]^{2+}$, 66792-60-7; $[(bpy)_2ClRu(pym)RuCl(bpy)_2](PF_6)_2$, 66792-62-9; $[(bpy)_2ClRu(pym)RuCl(bpy)_2]^{3+}$, 66808-68-2; $[(bpy)_2ClRu(pym)RuCl(bpy)_2]^{4+}$, 66792-63-0; $[(bpy)_2ClRu(NO)](PF_6)_2$, 58575-12-5.

References and Notes

(1) R. W. Callahan, G. M. Brown, and T. J. Meyer, *Inorg. Chem.*, **14**, 1443 (1975).

(2) R. W. Callahan and T. J. Meyer, *Chem. Phys. Lett.*, **39**, 82 (1976); R. W. Callahan, F. R. Keene, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **99**, 1064 (1977).

(3) R. W. Callahan, Ph.D. Thesis, The University of North Carolina, Chapel Hill, N.C., 1975.

(4) (a) M. J. Powers, D. J. Salmon, R. W. Callahan, and T. J. Meyer, *J. Am. Chem. Soc.*, **98**, 6731 (1976); (b) M. J. Powers, Ph.D. Dissertation, The University of North Carolina, 1977; (c) T. J. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978).

(5) M. J. Powers, R. W. Callahan, T. J. Meyer, and D. J. Salmon, *Inorg. Chem.*, **15**, 1457 (1976).

(6) (a) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967); (b) *Electrochim. Acta*, **13**, 1005 (1968).

(7) H. Taube, *Proc. N.Y. Acad. Sci.*, in press.

(8) P. C. Ford, D. F. Rudd, R. Gaudner, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

(9) P. R. Taylor, B.Sc. Honors Thesis, University of Sydney, 1973; P. R. Taylor and N. S. Hush, private communication.

(10) W. Lange and E. Müller, *Chem. Ber.*, **63**, 1058 (1930).

(11) (a) S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, F. J. Miller, and T. J. Meyer, *J. Am. Chem. Soc.*, **94**, 300 (1972); (b) S. A. Adeyemi, E. C. Johnson, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, **12**, 2371 (1973); (c) M. J. Powers and T. J. Meyer, submitted for publication.

(12) G. M. Bryant, J. E. Fergusson, and H. K. J. Powell, *Aust. J. Chem.*, **24**, 257 (1971).

(13) Solutions of the oxidized ions in acetonitrile are unstable over long periods and after 2 h, noticeable decomposition occurs as shown by changes in cyclic voltammograms. The decomposition chemistry, which is unusual given the high chemical stability of related Ru(III)–Ru(III) dimeric systems, is currently under investigation. Its origin may lie in the close proximity at which the pyrimidine bridging ligand holds the Ru(III) sites. Experiments involving the oxidized ions were carried out before noticeable decomposition had occurred.

(14) The same result was obtained by generating the mixed-valence ion either by electrochemical oxidation or by oxidation with Ce(IV). However, the electrochemical experiment proved more satisfactory because a precipitate (probably a Ce(III) salt) appears following chemical oxidation and the precipitate leads to experimental difficulties in the determination of extinction coefficients.

(15) E. Kober, unpublished results.

(16) J. Curtis and T. J. Meyer, *J. Am. Chem. Soc.*, in press.

Contribution from the Department of Applied Science,
Faculty of Engineering, Kyushu University,
Fukuoka 812, Japan

Exchange Interactions in Diamminecopper(II) Carbonate

Kusuo Kamase, Keiji Osaki, and Norikiyo Uryû*

Received February 24, 1978

Some years ago, Jeter et al.[1] reported the results of investigation on the antiferromagnetic properties of the complex $Cu(NH_3)_2CO_3$. As shown in Figure 1, the structure of this complex[2,3] consists of chains of copper(II) ions. The superexchange interactions are thought to be operative through the bridging carbonate ligands or through incipient bond formation between pairs of copper ions in adjacent chains. Jeter et al. have analyzed their magnetic susceptibility measurements of a powdered sample based on two models: (A) the anisotropic Ising model of infinite chains of $s = {}^1/_2$ ions assuming that the spin–spin interactions are only operative through the bridging carbonate groups and (B) the dimer model assuming that pairs of copper ions in neighboring chains interact and give rise to singlet and triplet states only.

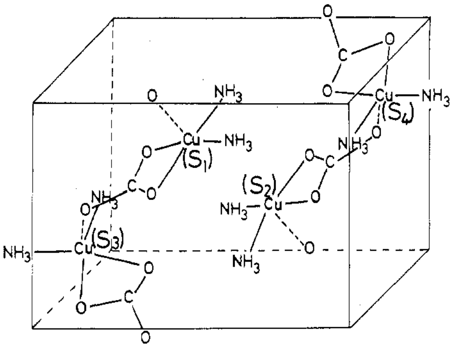

Figure 1. The structure of $Cu(NH_3)_2CO_3$. The four cluster spins $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, and $\mathbf{s}_4$ assigned to each Cu^{2+} ion are also shown.

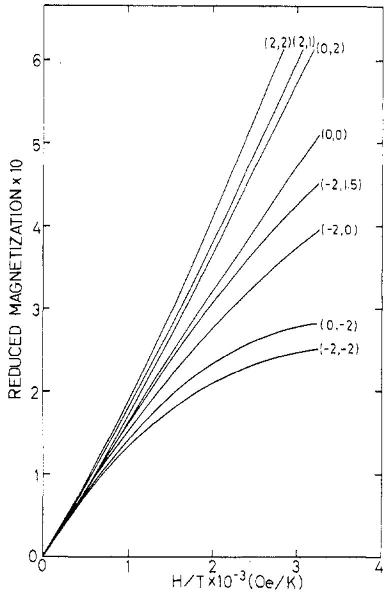

Figure 2. Variations of the reduced magnetic moment $\langle \mu \rangle$ vs. H/T calculated for various sets of values of J and J' and with $g = 2.18$. Numerical values in the parentheses denote the values of J and J' in units of cm^{-1}.

Model A turned out to be a rather poor approximation of the observation with the parameters $g = 2.20$, the Landé factor, and $J = -6.2$ cm^{-1}, the intrachain exchange coupling constant. On the contrary, model B with the use of the modified equation by Kubo et al.[4] gave a somewhat better fit with $g = 2.19$ and $J' = -4.5$ cm^{-1}, the interchain exchange coupling constant. By using the value of $2J'$, the energy separation between the singlet and triplet spin states, the magnetic moment in the dimer model B can be calculated by the Brillouin function for a system with $S = 1$. In an attempt to clarify the cooperative magnetic phenomenon, Jeter et al.[1] have also analyzed their magnetization data, comparing them with the above Brillouin function. However, the variation of the experimental magnetic moment $\langle \mu \rangle$ vs. H/T showed a marked deviation from the theoretical curves each calculated with $g = 2.19$ and $g = 2.0$. Thus it is evident that neither model A nor model B is sufficient to describe the magnetic behaviors of the present complex. Rather, both models should be reconciled to the

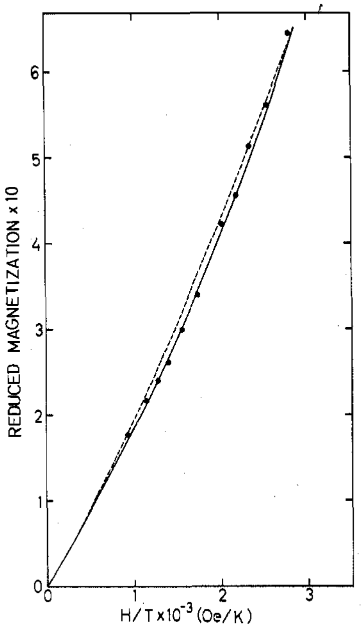

Figure 3. Comparison of the present calculation of the magnetic moment with the experimental data of Jeter et al. shown by solid circles. The results giving the best fit by the cluster model and by the modified effective field model are shown by the dotted and solid lines, respectively.

model in which the intra- and interchain exchange interactions are equally taken into consideration.

Let us consider a cluster of four spins $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, and $\mathbf{s}_4$ as shown in Figure 1 and take into account the intrachain exchange interaction between spins $\mathbf{s}_1$ ($\mathbf{s}_2$) and $\mathbf{s}_3$ ($\mathbf{s}_4$) and the interchain exchange between spins $\mathbf{s}_1$ and $\mathbf{s}_2$. Other spin–spin interactions operating through the bridging carbonate groups (i.e., along the chains) will be considered as an effective molecular field afterward. The spin Hamiltonian of the Heisenberg exchange interactions in the present four-spin cluster under an external magnetic field is given by

$$\mathcal{H} = -2J(\mathbf{s}_1\cdot\mathbf{s}_2) - 2J'[(\mathbf{s}_1\cdot\mathbf{s}_3) + (\mathbf{s}_2\cdot\mathbf{s}_4)] + g\mu_B H\sum_{i=1}^{4}s^z_i \quad (1)$$

Here, we have neglected the antisymmetric exchange interactions[5] which may coexist with the intrachain exchange interactions.

The conventional vector-model approach to the cluster spin system cannot be applied for the present spin Hamiltonian (eq 1), because the composite spins $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, $\sigma_1 = \mathbf{s}_1 + \mathbf{s}_3$, and $\sigma_2 = \mathbf{s}_2 + \mathbf{s}_4$ are not diagonalized simultaneously. For convenience, we choose the basis wave functions which diagonalize the second term of eq 1. Then the 16 × 16 secular matrix for the Hamiltonian (eq 1) breaks up into two 1 × 1, two 4 × 4, and one 6 × 6 submatrices.

With the use of spin wave functions $\psi(s_i)$ which are either α or β when $s^z_i = +^1/_2$ or $-^1/_2$, respectively, the basis wave functions $\psi(s_1)\ \psi(s_3)\ \psi(s_2)\ \psi(s_4)$ for each submatrix are given as follows:

$$\begin{array}{l}
\left.\begin{array}{l}\alpha\alpha\alpha\alpha\\ \beta\beta\beta\beta\end{array}\right\}(m=\pm2)\\
\left.\begin{array}{l}(\alpha\alpha\alpha\beta \pm \alpha\alpha\beta\alpha)/2^{1/2}\\ (\alpha\beta\alpha\alpha \pm \beta\alpha\alpha\alpha)/2^{1/2}\end{array}\right\}(m=1)\\
\left.\begin{array}{l}(\beta\beta\alpha\beta \pm \beta\beta\beta\alpha)/2^{1/2}\\ (\alpha\beta\beta\beta \pm \beta\alpha\beta\beta)/2^{1/2}\end{array}\right\}(m=-1)\\
\left.\begin{array}{l}\alpha\alpha\beta\beta\\ \beta\beta\alpha\alpha\\ (\alpha\beta\alpha\beta \pm \alpha\beta\beta\alpha + \beta\alpha\alpha\beta \pm \beta\alpha\beta\alpha)/2\\ (\alpha\beta\alpha\beta \pm \alpha\beta\beta\alpha - \beta\alpha\alpha\beta \mp \beta\alpha\beta\alpha)/2\end{array}\right\}(m=0)
\end{array} \quad (2)$$

m is the z component of the total composite spin and has the definite diagonal elements in each submatrix. The eigenvalues of each secular submatrix are obtained as a function of exchange parameters J and J' and the magnetic field H.

With the eigenvalues $\epsilon_{m,i}$, the magnetic moment can be calculated by

$$M = Ng\mu_B\sum_{m,i}m\exp(-\epsilon_{m,i}/kT)/\sum_{m,i}\exp(-\epsilon_{m,i}/kT) \quad (3)$$

For comparison with the experimental data, the numerical calculation has been done for $g = 2.18$, for the field strengths of 10.0, 12.5, and 15.0 kOe, and for various sets of values of J and J'. The calculation has been performed by the FACOM M-190 computing facility of Kyushu University. The reduced magnetic moment $\langle\mu\rangle = M/(N\mu_B/2)$ as a function of H/T should be compared with the experimental data by Jeter et al. The variation of $\langle\mu\rangle = f(H/T)$ for various sets of values of J and J' are shown in Figure 2. The fitting procedure, in consideration of these data, has resulted in the values $J = +2.34$ cm^{-1} and $J' = +2.52$ cm^{-1} which are both ferromagnetic contrary to the estimates of Jeter et al. As shown in Figure 3, the calculation of the magnetic moment with this set of values gives far better agreement with the experimental magnetic moment than those of the dimer model.

The intrachain exchange interactions other than those considered in the present cluster model result in an effective molecular field. Then the reduced magnetic moment may be modified in the first approximation as

$$\langle\mu\rangle = f(H/T)/(1 - \Theta/T) \quad (4)$$

The fitting procedure with the use of this modified expression gives a quite excellent agreement with the variation of the experimental magnetic moment as shown in Figure 3. The values of the parameters in this case have been estimated as $J = -2.0$ cm^{-1}, $J' = +1.0$ cm,$^{-1}$ and $\Theta = 1.5$ K. For negative values of J' the fitting procedures were unsuccessful, as in the case of the linear-chain model by Jeter et al. In view of the copper–carbonate–copper angle (119°), the ferromagnetic intrachain exchange coupling may be reasonable.[6] These values are also quite reasonable for the interpretation of the behavior of the magnetic susceptibility which is antiferromagnetic in nature. Thus, the present exchange model of a four-spin cluster provides a much improved analysis of magnetic interactions for diamminecopper(II) carbonate, and so may be a more realistic model than the antiferromagnetic linear-chain model or the dimer model previously proposed by Jeter et al.

Registry No. Cu(NH$_3$)$_2$CO$_3$, 21710-50-9.

References and Notes

(1) Y. Jeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **11**, 185 (1972).
(2) F. Hanic, *Acta Chim. Acad. Sci. Hung.*, **32**, 305 (1962).
(3) F. Hanic, *Chem. Zvesti*, **17**, 365 (1963).
(4) M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **6**, 900 (1967).
(5) T. Moriya, *Phys. Rev.*, **120**, 91 (1960).
(6) J. Kanamori, *J. Phys. Chem. Solids*, **10**, 87 (1959).

Contribution from the Department of Chemistry,
University of Vermont, Burlington, Vermont 05401

Physical and Chemical Properties of Squarate Complexes. 1. Spectral, Magnetic, and Thermal Behavior of Dimeric Iron(III) Squarate

James T. Wrobleski and David B. Brown*

Received December 22, 1977

Trivalent metal–ion complexes which contain the squarate dianion (I, Sq) with general formula M(Sq)(OH)(H$_2$O)$_3$ were