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Notes

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Estimation of Exchange Integrals for Antiferromagnetically Coupled Binuclear Copper(II) Complexes from Room-Temperature Magnetic Moments

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The traditional method for determining the singlet–triplet splitting for antiferromagnetically coupled pairs of copper(II) ions, which conform to the spin Hamiltonian $H = 2J\hat{S}_1\cdot\hat{S}_2$ and the Van Vleck equation (eq 1),[1] is to measure the molar susceptibility, χ_M,

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

as a function of temperature, T, and determine the best-fit line of the theoretical equation to the data by using a nonlinear regression analysis. If g, the Landé spliting factor, cannot be determined from, e.g., EPR measurements, reasonable estimates of both g and $-2J$ (the exchange integral or singlet–triplet splitting) are used until, after a reiterative process, an appropriate error function (eq 2) is minimized.

$$E = \sum_i W_i(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2 \qquad W_i = (\chi_i^{\text{obsd}})^{-1} \qquad (2)$$

The common experimental techniques for measuring molar susceptibilities as a function of temperature comprise the traditional Gouy and Faraday methods,[2] which involve the measurement of forces on samples suspended in external magnetic fields, the Foner[3] method, using a vibrating sample magnetometer, and the SQUID (superconducting quantum interference device) method, based on the Josephson effect.[4-6] Of these the SQUID and Faraday methods are currently the most popular. The SQUID technique provides the greatest sensitivity and has been used successfully to measure exchange integrals for weakly paramagnetic copper protein extracts,[7-9] while the Faraday method allows susceptibility measurements over a wide dynamic range. The cost of purchasing state of the art SQUID or Faraday susceptometers can be prohibitive for many individuals interested in determining exchange integrals for spin-coupled binuclear complexes. Also, proximity to a source of supply of liquid helium is essential, unless one uses an electromagnet and a sealed helium refrigeration unit for temperature control or liquid nitrogen (Faraday).

Our interest in variable-temperature magnetic measurements has focused on the synthesis and study of antiferromagnetically coupled binuclear copper(II) complexes involving single hydroxide bridges and tetradentate (N_4) phthalazine and pyridazine ligands[10-13] and sexadentate (N_6) phthalazine ligands.[14] In a series of related complexes involving $d_{x^2-y^2}$ ground-state copper the magnitude of the exchange integral ($-2J$) was found to vary in a linear fashion with respect to the hydroxide bridge angle.[10-12] A similar relationship has been demonstrated for dihydroxo-bridged binuclear copper(II) complexes involving $d_{x^2-y^2}$ ground-state copper.[15] Also, the room-temperature magnetic moment was found to vary in a linear fashion with the Cu–O(H)–Cu bridge angle. Two unrelated monohydroxo-bridged copper complexes (with $d_{x^2-y^2}$ ground states) from other research groups fitted the lines approximately but d_{z^2} ground-state complexes, as would be expected, did not conform to the relationships.[11] If the dozen or so structurally documented monohydroxo-bridged binuclear copper(II) complexes[10-13] (ref c and d in Figure 1) are examined, a roughly linear relationship is found between the effective

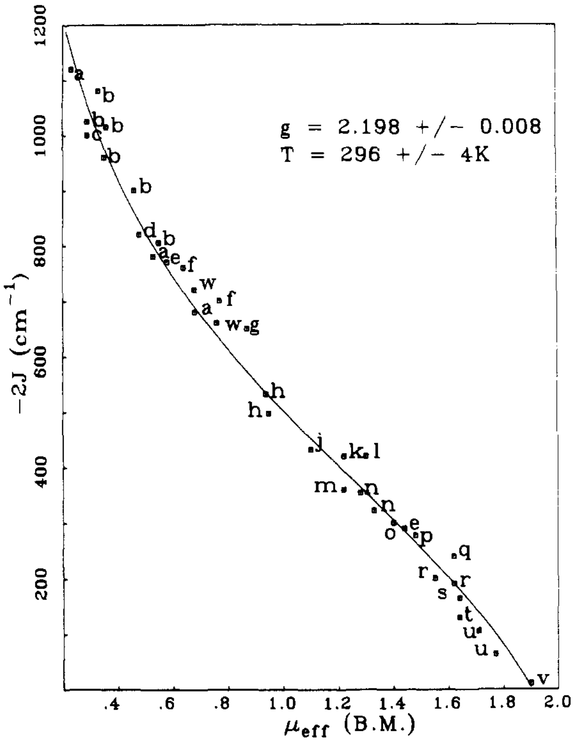

Figure 1. Experimental data (□) and the theoretical curve for $g = 2.198$, $T = 296$ substituted into eq 4. References: (a) Mikuriya, M.; Okawa, H.; Kida, S. *Inorg. Chim. Acta* **1980**, *42*, 233. (b) Mikuriya, M.; Harada, T.; Okawa, H.; Kida, S. *Inorg. Chim. Acta* **1983**, *75*, 1. (c) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228. (d) Burk, P. L.; Osborn, J. A.; Youinou, M.-T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273. (e) Reference 10. (f) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, *28*, L121. (g) Yamashita, M.; Ito, H.; Ito, T. *Inorg. Chem.* **1983**, *22*, 2102. (h) Reference 9. (j) Reference 11. (k) Berry, K. J.; Black, D. St. C.; Bos Vanderzalm, C. H.; Moss, G. I.; Murray, K. S. *Inorg. Chim. Acta* **1980**, *46*, L21. (l) Sorrell, T. N.; Jameson, D. L.; O'Connor, C. J. *Inorg. Chem.* **1984**, *23*, 190. (m) Reference 14. (n) Haddad, M. S.; Wilson, S. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384. (o) Kokoszka, G. F.; Gordon, G. *Transition Met. Chem. (N.Y.)* **1969**, *5*, 181. (p) McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765. (q) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868. (r) Thompson, L. K. *Can. J. Chem.* **1983**, *61*, 579. (s) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1983**, 1815. (t) Jeter, D. Y.; Lewis, D. L.; Hempel, J. C.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1972**, *11*, 1958. (u) Drew, M. G. B.; Nelson, J.; Esho, F.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1837. (v) Lambert, S. L.; Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, *29*, L223. (w) Tanaka, M.; Kitaoka, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2469.

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room-temperature magnetic moment and the exchange integral for values of μ_{eff}(RT) in the range 0.3–1.6 μ_{B} and $-2J$ in the range 190–1000 cm^{-1}. However, if one includes a larger selection of spin-coupled complexes involving a variety of ligand bridges and covering an extended range of $-2J$ and μ_{eff}(RT) it becomes apparent that the relationship is not linear. Figure 1 contains $-2J$ vs. μ_{eff}(RT) data for a varied selection of binuclear copper(II) complexes involving unrelated ligands, which have been synthesized and studied in a variety of different laboratories, where variable-temperature magnetic measurements have been carried out on a variety of different susceptometers with room-temperature magnetic moments quoted at different room temperatures.

Substitution of the Van Vleck equation (eq 1) into the expression (eq 3) (TIP, temperature-independent paramagnetism,

$$\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{1/2} \qquad (3)$$

not included in the corrected molar susceptibility term) for the effective magnetic moment gives (eq 4) an expression, in which

$$-2J = kT\ln\left(\frac{3.0003g^2}{\mu_{\mathrm{eff}}^2} - 3\right) \qquad (4)$$

the exchange integral ($-2J$) and the effective magnetic moment at temperature T are variables ($N\beta^2/3k = 0.12505$). A nonlinear regression analysis of the 36 data (Figure 1) using this two-parameter expression (eq 4) and using a weighting scheme in between a constant and proportional standard deviation[16] gave the theoretical line (Figure 1) and a two-parameter fit of $g = 2.198 \pm 0.008$ and $T = 295.6 \pm 4.5$ K.

The very reasonable fit of the data with a sensible mean g value and mean room-temperature indicates, quite clearly, that realistic estimates of exchange integrals can be obtained for antiferromagnetically coupled binuclear copper(II) complexes by the use of this graphical fit or by substituting known values of g, T, and χ_{M} into the Van Vleck equation itself. The errors from this estimation are not likely to be unreasonable, and, in fact, for very strongly coupled systems, where variable temperature susceptibility measurements may involve large errors because of the weak paramagnetism involved, especially at low temperatures, measurements of $-2J$ values are likely to provide very reasonable results.

The upsurge of interest in spin-coupled copper compounds, which are relevant as models for spin-coupled binuclear copper protein active sites, has led to the synthesis and study of a large number of binuclear copper complexes, many of which have not been investigated by variable-temperature susceptibility studies because of the lack of suitable equipment. However, since most chemistry departments have room-temperature susceptibility equipment, which can be purchased or constructed at a modest cost, the results of room-temperature magnetic moment measurements can be used to provide reasonable estimates of exchange integrals. Of the simple techniques suitable for such measurements the Faraday method, using a sensitive microbalance with resolution at the microgram level, would be favored, especially for weakly paramagnetic, strongly coupled complexes.

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Crystal Structure of Bis(*p*-toluidine)bis(acetonitrile)tetraiodotetracopper: Correction of Space Group

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The crystal structure of the tetrameric copper cluster bis(*p*-toluidine)bis(acetonitrile)tetraiodotetracopper has recently been described.[1] It was reported in the triclinic space group $P\bar{1}$ with two formula weights in the unit cell. In fact it should be formulated in the monoclinic space group $C2/c$, with $Z = 4$.

The reported cell dimensions are $a = 14.274$ (5) Å, $b = 7.587$ (2) Å, $c = 14.239$ (5) Å, $\alpha = 88.61$ (2)°, $\beta = 110.07$ (2)°, and $\gamma = 88.70$ (2)°. The vectors $\mathbf{c} + \mathbf{a}$, $\mathbf{c} - \mathbf{a}$ and $-\mathbf{b}$ describe an effectively monoclinic cell with $a = 16.340$ Å, $b = 23.366$ Å, $c = 7.587$ Å, $\alpha = 90.05$, $\beta = 92.35°$, and $\gamma = 90.15°$. The atomic coordinates, transformed according to the relations $x_{\mathrm{m}} = {}^1/_2x_{\mathrm{t}} + {}^1/_2z_{\mathrm{t}} + {}^1/_4$, $y_{\mathrm{m}} = -{}^1/_2x_{\mathrm{t}} + {}^1/_2z_{\mathrm{t}} - {}^1/_4$, and $z_{\mathrm{m}} = -y_{\mathrm{t}}$, yield values that are compatible with the space group $C2/c$[2] within the reported esd's (Table I, supplementary material). Since the coordinate shifts necessary to achieve the higher symmetry are no greater than the esd's, the change in space group does not change the description of the structure, other than to introduce an exact crystallographic twofold axis in place of the approximate one. Further confirmation of the correctness of this description is obtained from the structure factors, which show the appropriate absences (triclinic hkh, $k = 2n + 1$)[3] for space group $C2/c$.

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Supplementary Material Available: Table I, positional parameters for $Cu_4I_4C_{18}H_{24}N_4$ in $C2/c$ (1 page). Ordering information is given on any current masthead page.

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(3) Of the 250 reflections of this type listed in the supplementary data, 119 had k odd and 118 of these were marked with an asterisk, presumably indicating unobserved. The sole exception, 14,1,14, had $F_{\mathrm{o}} = 208$ where some unobserved reflections had $F_{\mathrm{o}} = 164$*. Of the 131 such reflections with k even, 59 were not marked and were presumably considered observed.

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Synthesis and Characterization of a Ruthenium(II) Clathrochelate Complex

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Metal clathrochelates consist of a metal ion encapsulated by a bicyclic macrocyclic ligand.[2] These complexes often possess greater thermodynamic and kinetic stability than that found in analogous open-chain complexes, because of their greatly reduced

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