Preparation of [Co₂(tren)₂OH](ClO₄)₃·H₂O (tren = Tris(2-aminoethyl)amine) and Magnetic Exchange Interactions in Binuclear Monohydroxo-Bridged Copper(II) and Cobalt(II) Complexes

Preparation of $[Co_2(tren)_2OH](ClO_4)_3 \cdot H_2O$ (tren = Tris(2-aminoethyl)amine) and Magnetic Exchange Interactions in Binuclear Monohydroxo-Bridged Copper(II) and Cobalt(II) Complexes

A. BENCINI,[1a] C. BENELLI,[1b] and D. GATTESCHI*[1b]

The complex $[Co_2(tren)_2OH](ClO_4)_3 \cdot H_2O$ (tren = tris(2-aminoethyl)amine) has been prepared and characterized through electronic spectroscopy and magnetic susceptibility measurements. The complex is dinuclear with two trigonal-bipyramidal chromophores bridged by one –OH ligand. The magnetic susceptibility data show that the two moieties are antiferromagnetically coupled with $J = -38$ cm^{-1}. This result is discussed in comparison with those for similar monohydroxo-bridged copper(II) complexes through an angular-overlap model.

Introduction

The magnetic exchange interactions in polynuclear metal complexes are intensively studied,[2-6] and some structural-magnetic correlations are becoming available.[7-11] Monohydroxo-bridged complexes are not numerous for dipositive metal ions, although quite recently some examples have been reported for copper(II) complexes.[12-15] We are currently interested in the characterization of cobalt(II) complexes[16] and decided to try to prepare a cobalt complex analogous to the reported copper(II) complex. A reasonable candidate to obtain that was the Co(tren)²⁺ moiety since cobalt(II) is known to yield trigonal-bipyramidal complexes with tren[17] (tren = tris(2-aminoethyl)amine), like copper.

We wish to report here the characterization of [Co₂(tren)₂OH](ClO₄)₃·H₂O.

Experimental Section

The synthesis of the cobalt complex was performed under a rigorously oxygen-free atmosphere, since the solution of the complex is extremely sensitive toward oxidation. The green complex was prepared by following the procedure previously outlined for the copper analogue. Anal. Calcd for $C_{12}H_{39}N_8Co_2Cl_3O_{14}$: C, 19.38; H, 5.29; N, 15.07; Co, 15.85. Found: C, 19.40; H, 5.24; N, 15.19; Co, 15.2.

Magnetic susceptibility data were obtained with an homemade Faraday balance equipped with a Bruker electromagnet and a R-100 Cahn microbalance. The cooling apparatus was a CF 200 flow cryostat from Oxford Instruments Co. Electronic spectra were recorded on a Varian Cary 17D spectrophotometer, and the EPR spectra were recorded with a Varian E-9 spectrometer equipped with X band (9 GHz) and an Oxford continuous-flow cryostat.

Results

The cobalt complex was analyzed satisfactorily for [Co₂-(tren)₂OH](ClO₄)₃·H₂O. Analogous results were obtained also with zinc(II). The IR spectra show a band at 3590 cm⁻¹, which was assigned to the O–H stretching vibration.[12] The electronic spectrum of the solid compound is shown in Figure 1. It is typical of trigonal-bipyramidal cobalt(II) complexes,[18,19] with absorption maxima at 6.5 × 10³, 13.8 × 10³, 16.7 × 10³, and 21.8 × 10³ cm⁻¹. In aqueous solution the spectra were found to be pH dependent, as shown in Figure 1. At pH 7 the three peaks in the visible region correspond to 14.3 × 10³, 17.6 × 10³, and 21.3 × 10³ cm⁻¹. At pH 9.3 the three peaks are shifted to 14.3 × 10³, 17.2 × 10³, and 21.6 × 10³ cm⁻¹ and a shoulder at 16.0 × 10³ cm⁻¹ appears. No isosbestic points were detected, suggesting that the equilibrium is rather complicated.

The electronic spectra of [Cu₂(tren)₂OH](clO₄)₃·H₂O are shown in Figure 2. In the solid state only a broad band with a maximum at 12.5 × 10³ cm⁻¹ and a shoulder at 15.2 × 10³ cm⁻¹ is observed. Also in this case the water solution spectra are pH dependent. At low pH a peak at 12.1 and a shoulder at 14.1 × 10³ cm⁻¹ are neatly resolved, while in the low-frequency region there is some evidence of additional absorption. With an increase in pH, the intensity of the band increases and the peak and shoulder move to 11.9 × 10³ and 14.6 × 10³ cm⁻¹, respectively. The residual absorbance in the low-frequency region seems to decrease.

The temperature dependence of the magnetic susceptibility of the cobalt complex is shown in Figure 3. The curve is the best fit curve with use of the Bleaney–Bowers equation for two $S = ^3/_2$ systems, as described in the next section.

The polycrystalline powder EPR spectra of the pure cobalt(II) complex do not show any signal in the range of temperature 4.2–300 K. If the complex is doped with some zinc, a signal, centered at $g = 6$, shows up at low temperature (4.2–20 K), but no other feature could be detected in the spectrum up to 1.4 T. By an increase in the concentration of cobalt, satellite lines, presumably due to intermolecular interactions, appear at both high and low field. Attempts were made also to record single-crystal spectra, although the crystal structure of the complex is not known. In some crystal orientations a g value close to the extreme of the powder spectra was observed. With rotation of the crystal a few degrees from this position, the signal broadened, moving to high field. It was impossible therefore to follow this resonance, and it was not possible to obtain the g tensor.

The polycrystalline powder EPR spectra of the pure copper(II) complex show, as reported,[12] one signal at $g = 2.12$. It remains practically unchanged down to 4.2 K. If the copper complex is doped with some zinc, also additional signals at both

(1) (a) ISSECC, CNR. (b) Università di Firenze.
(2) Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199.
(3) Kokoszka, G. F.; Duerst, R. W. *Coord. Chem. Rev.* **1970**, *5*, 209.
(4) Ginsberg, A. P. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 45.
(5) Hatfield, W. E. *ACS Symp. Ser.* **1974**, No. 5, 108.
(6) Glick, M. D.; Lintvedt, R. L. *Prog. Inorg. Chem.* **1976**, *21*, 233.
(7) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.
(8) Bencini, A.; Gatteschi, D. *Inorg. Chim. Acta* **1978**, *31*, 11.
(9) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
(10) Kahn, O. *Mol. Phys.* **1975**, *26*, 1036.
(11) Banci, L.; Bencini, A.; Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1981**, *20*, 393.
(12) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, *28*, L121.
(13) Haddad, M. S.; Wilson, S. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384.
(14) Burk, P. L.; Osborn, J. A.; Youinou, M. T.; Angus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1274.
(15) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc. Dalton Trans.* **1981**, 1868.
(16) Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Struct. Bonding (Berlin)* **1982**, *52*, 37.
(17) Ciampolini, M.; Paoletti, P. *Inorg. Chem.* **1967**, *6*, 1621.
(18) Ciampolini, M. *Struct. Bonding (Berlin)* **1969**, *6*, 52.
(19) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 43.
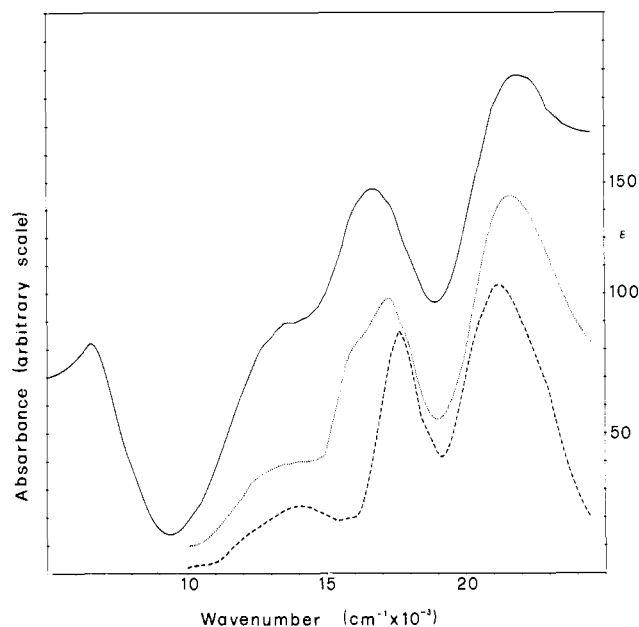
Figure 1. (—) Diffuse-reflectance electronic spectrum of [Co$_2$-(tren)$_2$OH](ClO$_4$)$_3$·H$_2$O. (···) Electronic spectrum of a water solution of cobalt(II) sulfate (3.30 M) + tren (3.43 M) at pH 9.3. (- - -) Electronic spectrum of the same solution at pH 7.
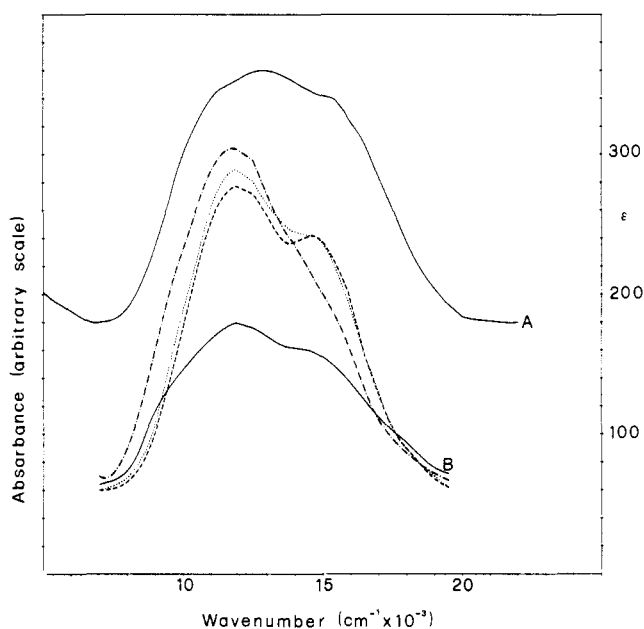

Figure 2. (A) Diffuse-reflectance electronic spectrum of [Cu$_2$-(tren)$_2$OH](ClO$_4$)$_3$·H$_2$O. (B) Electronic spectra of a water solution of copper(II) sulfate (3.82 M) + tren (4.05 M): (—) pH 4; (-·-·) pH 8.8; (···) pH 10.2; (- - -) pH 11.6.

low and high field are observed, but they cannot be easily analyzed. If the zinc complex is doped with some copper, an axial spectrum with $g_{\parallel}$ = 2.0, $A_{\parallel}$ = 90 G and $g_{\perp}$ = 2.2, $A_{\perp}$ = 100 G is observed.

Discussion

On the basis of the stoichiometry of the cobalt complex, identical with that of the copper analogue, and of the identical IR spectra we formulate also the former as a dinuclear complex bridged by one hydroxo group. The coordination environment around each metal ion is trigonal bipyramidal, as shown by the electronic spectra.

The electronic spectra of the cobalt complex in the solid state can be compared to those of the Co(tren)X$^+$ complexes (X = I, NCS), which have been previously reported,[20,21] and also
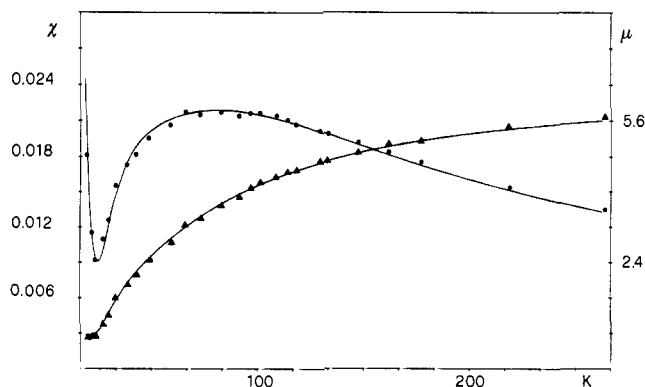

Figure 3. Temperature dependence of the magnetic susceptibility and of the effective magnetic moment of [Co$_2$(tren)$_2$OH](ClO$_4$)$_3$·H$_2$O. Solid circles and triangles denote experimental points for susceptibility and moment, respectively. Solid lines are the curves calculated as described in the text.

to the [Co(Me$_6$tren)X]X spectra (Me$_6$tren = tris(2-(di-methylamino)ethyl)amine; X = Cl, Br, I, NCS). The electronic spectra in aqueous solution of the Co(II) complex have been previously reported, limited to the low-pH region, and they were attributed to a trigonal-bipyramidal Co-(tren)(H$_2$O)$^{2+}$ species.[22] The pH dependence of the spectra show that other species are formed in solution at higher pH, presumably containing hydroxyl ions but not necessarily only the monohydroxo species that is isolated in the solid state. That this is indeed the case is suggested by the fact that at no pH are spectra identical with the solid-state spectrum observed.

In view of the interest in the electronic spectra of aquo and hydroxo derivatives of cobalt(II) complexes[23] it is worth commenting on the spectra of Co(tren)(H$_2$O)$^{2+}$ and Co$_2$-(tren)$_2$(OH)$^{3+}$. For the former we will refer to solution and for the latter to solid-state data. The main differences are seen in the positions of the two highest d–d transitions, namely, in those that can be attributed to the $^4A_2 \rightarrow$ $^4A_2$(P) and $^4A_2 \rightarrow$ ^4E(P) transitions (C_{3v} notation). It may be safely assumed that the spectra of the dinuclear species are identical with those of the mononuclear moiety due to the small value of the coupling constant between the two metal ions (see below). As one passes from the water to the hydroxo derivative, the splitting of the two highest bands increases, in the sense that the A$_2$(P) transition moves to lower energy, while the E(P) transition moves to higher frequency. This behavior can be rationalized by considering that the hydroxo group is exerting a stronger ligand field strength than the water molecule and also that the π contribution increases in the same direction. Angular-overlap calculations confirm this prediction, showing that the splitting of the two F $\rightarrow$ P transitions increases as the Dq ($^3/_{10}e_\sigma - ^4/_{10}e_\pi$) of the axial ligand increases and as the e_π/e_σ ratio of the same ligand is increased.

For the electronic transitions of the dinuclear species we used for the sake of simplicity the same geometrical coordinates and the e_λ parameters previously used.[21] The OH ligand was set in an axial position, and its e_λ parameters were varied until a fit of the observed electronic transitions was found. The corresponding parameters are $e_\sigma^{N_{ax}}$ = 3460 cm^{-1}, $e_\sigma^{N_{eq}}$ = 4750 cm^{-1}, e_σ^{OH} = 6860 cm^{-1}, e_π^{OH} = 2470 cm^{-1} (B = 750 cm^{-1}, ζ = 533 cm^{-1}, k = 0.9), and the calculated transitions are 6.3 × 10^3 14.0 × 10^3, 16.7 × 10^3 and 21.6 × 10^3 cm^{-1}

(20) Bertini, I.; Ciampolini, M.; Gatteschi, D. *Inorg. Chem.* **1973**, *12*, 693.
(21) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1975**, *14*, 812.
(22) Vacca, A.; Paoletti, P. *J. Chem. Soc. A* **1968**, 2378.
(23) Bertini, I.; Canti, G.; Luchinat, C.; Mani, F. *Inorg. Chem.* **1981**, *20*, 1670.
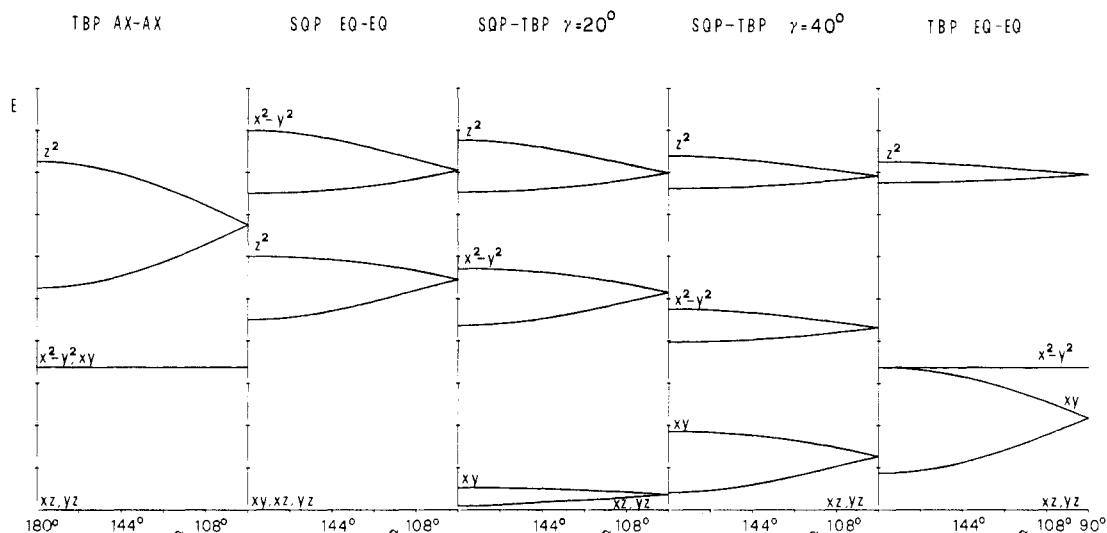
Figure 4. Splitting of the d orbitals of the two metal ions due to the exchange interaction. The orbitals are labeled according to their main component.

The calculated zero-field splitting is 14 cm^{-1}, with $\pm^3/_2$ lying lowest. This seems to be confirmed by the EPR spectra of the zinc-doped complex, which shows a parallel feature at $g = 6$.[24]

Also for the copper(II) complex the electronic spectra are indicative of a trigonal-bipyramidal coordination of the metal ion.[25,26] The water solution spectra are indicative of a complex equilibrium. They are similar to those previously reported, but not discussed, by Paoletti et al. for copper(II) complexes with similar amine coligands.[22]

Confirmation of the suggested coordination comes from the EPR spectra of the zinc-doped copper complex and copper-doped zinc complexes, which apparently show that the unpaired electron is in an essentially d_{z^2} orbital.

The EPR spectra of the pure compound indicate the presence of exchange-coupled copper ions. Since, however, the EPR spectra remain practically unchanged down to liquid-helium temperature, they cannot be attributed to the strongly antiferromagnetically coupled species. Alternative explanations may be that another coupled polynuclear species is present or that a mononuclear species is coprecipitated. Evidence of paramagnetic impurities was obtained from the temperature dependence of the magnetic susceptibility.[12]

The electronic and EPR spectra were fit with a procedure analogous to that used for the cobalt complex. The parameters used for the best fit are $e_\sigma^{N_{ax}} = 5200$ cm^{-1}, $e_\sigma^{N_{eq}} = 5400$ cm^{-1}, $e_\sigma^{OH} = 9600$ cm^{-1}, and $e_\pi^{OH} = 4000$ cm^{-1}. The calculated electronic transitions are 12.0×10^3 and 15.1×10^3 cm^{-1}, while the calculated g values are $g_\parallel = 1.99$ and $g_\perp = 2.21$. Comparing the AO parameters for the cobalt(II) and the copper(II) ions, one notices smaller values for the former.

The temperature dependence of the magnetic susceptibility of [Co$_2$(tren)$_2$OH](ClO$_4$)$_3\cdot$H$_2$O complex was analyzed with use of the Bleaney–Bowers equation, including a temperature-independent paramagnetism of 250×10^{-6} and a 1.5% paramagnetic impurity. The best fit parameters are $J = -38$ cm^{-1} and $g = 2.32$ for an exchange Hamiltonian defined as $H = -J(S_1\cdot S_2)$. An alternative method for analyzing the data is that of taking into account also the zero-field contributions of the single cobalt(II) ions, which in principle may be of the same order of magnitude as the calculated J values.[27] With the inclusion of an axial zero-field splitting the experimental

points were fit with $J = -30 \pm 4$ cm^{-1} and $D = 80 \pm 50$ cm^{-1}. With use of a mapping procedure it was found that J and D are strongly correlated in the sense that decreasing J in the indicated range requires an increase of D in order to keep good agreement with the experimental data. The calculated D values appear to be very large and contrast with the values we calculate with the AOM. Therefore, we believe the simple Bleaney–Bowers parameters are more appropriate in the present case.

It is interesting at this point to consider how the exchange interactions are determined by the coordination environments of the metal ion and the relative geometries of the two moieties constituting the dinuclear complex. In order to do that, we applied an angular-overlap model we proposed recently for dinuclear complexes.[8] This is in principle identical with the AOM for mononuclear complexes in the sense that it evaluates the energy of the metal d orbitals through a perturbation treatment not taking explicitly into consideration the ligand orbitals.[28] For the nonbridge ligands the treatment is identical with that for the usual AOM, while the bridge ligands are considered to influence the orbitals of both the metal ions. A 10 × 10 Hamiltonian matrix of the two sets of d orbitals is diagonalized, yielding the eigenvalues and the eigenvectors. According to the models suggested by Hoffmann[9] and Kahn,[10] the antiferromagnetic interaction between the two metal ions is determined by the splitting of the d orbitals in the dinuclear complex, in the sense that the larger the splitting of a pair of orbitals, the larger the antiferromagnetic coupling.

First we considered two trigonal bipyramids bridged by one monoatomic ligand in the axial position (TBP ax–ax). For the sake of simplicity we considered only a σ metal-to-ligand interaction. In Figure 4 the energy levels calculated for these dinuclear complexes when the M–L–M angle is varied are shown. It is apparent that only the z^2 orbitals are split by the exchange interaction. This is true only as long as π interactions are neglected, but it may be safely assumed that in any case they will be less effective than the σ interaction in determining the coupling. The splitting is maximum for $\alpha = 180°$ and goes to zero when $\alpha = 90°$. This pattern might be slightly varied by including the interaction with s ligand orbitals.

Another limiting case, depicted in Figure 4, is that of two square pyramids bridged through two equatorial positions (SP eq–eq). In this case the orbitals that are split by the interaction are $x^2 - y^2$ and z^2. The two splittings are identical. They have

(24) Benelli, C.; Gatteschi, D. *Inorg. Chem.* **1982**, *21*, 1788.
(25) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.
(26) Bencini, A.; Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1978**, *17*, 3194.
(27) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 1944.

(28) Schäffer, C. E. *Struct. Bonding (Berlin)* **1968**, *5*, 68.

Table I. J and Cu–O–Cu Angle, α, Values for Binuclear Monohydroxo-Bridged Copper(II) Complexes

| complexes	J, cm^{-1}	α, deg	ref
$[Cu_2(tren)_2OH](PF_6)_3$	−700		12
$[Cu_2(tren)_2OH](ClO_4)_3 \cdot H_2O$	−760		12
$[Cu_2(bpy)_4OH](ClO_4)_3{}^a$	−322	141.6	13
$[Cu_2(phen)_4OH](ClO_4)_3{}^a$	−354		13
$[Cu_2LOH](BF_4)_3{}^a$	−850	132.2	14
$[Cu_2(Lig)OH](ClO_4)_3 \cdot H_2O^a$	−240	141.7	15

^{a} Abbreviations: bpy = 2,2'-bipyridine; phen = phenanthroline; L = 1,4-bis[(1-oxa-4,10-dithia-7-azacyclododec-7-yl)methyl]-benzene; Lig = 30-membered macrocycle derived from the condensation of 2 molecules of 2,6-diacetylpyridine and 2 molecules of 3,6-dioxaoctane-1,8-diamine.

a maximum when the M–L–M angle, α, is 180° and go to zero when α = 90°.

A third case that is relevant to the monohydroxo-bridged complexes is that of two trigonal bipyramids bridged through one equatorial ligand (TBP eq–eq, Figure 4). In this case the z^2 orbitals are not largely split since they are only moderately affected by the in-plane bridging ligand; a much larger splitting is anticipated for the xy orbitals, which point with one lobe toward the bridging ligands.

In Figure 4 we took into account also some cases in which the geometry around each metal ion is intermediate between a square pyramid and a trigonal bipyramid. The distortion is monitored by the angle γ. It is 0° for two angular square pyramids and 60° for two trigonal bipyramids. The splittings of the d orbitals are intermediate between those of the limit cases trigonal bipyramidal and square pyramidal, respectively.

The predictions that one can make using these diagrams are the following: for copper(II) complexes, with everything kept fixed, and with only the geometrical environments altered, the order of the J values should vary according to

$$\text{TBP ax–ax} > \text{SP eq–eq} > \text{TBP eq–eq}$$
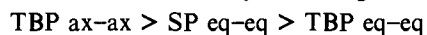
Another observation that can be made with use of the diagrams of Figure 4 is that, since for monohydroxo-bridged complexes the Cu–O–Cu angles are likely to be fairly large. (they vary from 131.2 to 141.7° in the reported structures),[13-15] the dependence of J on the angle is anticipated to be less marked as compared to that for the dihydroxo-bridged complexes.[7] In fact the slope of the levels is much smaller in the range

180–130° than in the 130–90° range. It is therefore to be expected that for monohydroxo-bridged complexes the variation of the angle is not the main factor in determining the J value especially if concomitant changes in bond distances and coordination environments are observed in a series of complexes. The J values and the Cu–O–Cu angle, when available, for monohydroxo-bridged copper(II) complexes are shown in Table I.

$[Cu_2(tren)_2OH](ClO_4)_3 \cdot H_2O$ is an example of TBP ax–ax: no structural data are available for this complex, but the fairly large value of J reported for this compound suggests that the angle is closer to the 180° than to the 90° limit. A very large J value is also reported for the "earmuff" complex in which the two copper ions are in essentially square-pyramidal environments.[23] The Cu–O–Cu angle is fairly small, 132.2°, and the Cu–OH distance is much shorter than usually observed in dihydroxo-bridged complexes. This short distance may be responsible for the fact that J in this complex is much larger than in the complex reported by Nelson,[15] for which the Cu–O–Cu angle is larger (141.7°).

Trying to use the diagrams of Figure 4 for cobalt(II) complexes, one must consider the splitting of the three highest magnetic orbitals. In the case of TBP ax–ax only the z^2 orbitals are split. Therefore, as one passes from copper to cobalt, a large decrease in the antiferromagnetic coupling is expected since only the z^2 orbitals are providing effective pathways. The other orbitals which are not split may yield ferromagnetic couplings. This should be particularly effective for xz and yz orbitals, which are expected to overlap to some extent.[29] Comparing the J value for $[Cu_2(tren)_2OH](ClO_4)_3 \cdot H_2O$ and that for the cobalt analogue, one finds $J_{Cu}/J_{Co} \simeq 18$, which is much larger than the expected ratio[29] of 9. This may be due either to stronger metal-to-bridge ligand interactions in copper as compared to cobalt or to ferromagnetic pathways operative in the cobalt(II) dinuclear complex.

(29) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567.
(30) Ball, P. W.; Blake, D. G. *J. Chem. Soc., Dalton Trans.* **1974**, 852.