CHEMISTRY LETTERS, pp. 443-444, 1989.

Synthesis and Structure of Completely Spin-coupled Trinuclear Copper(II) Complex, $[Cu(dmg)_2\{Cu(bipy)(CH_3OH)\}_2](NO_3)_2$, Bridged by Bis(dimethylglyoximato)cuprate(II) Dianion

Dominique LUNEAU, Hiroki OSHIO, Hisashi ŌKAWA,*† and Sigeo KIDA†
Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashiku, Fukuoka 812

A linear trinuclear copper(II) complex $[Cu(dmg)_2\{Cu(bipy)(CH_3OH)\}_2](NO_3)_2$ in which bis(dimethylglyoximato)cuprate(II) dianion $[Cu(dmg)_2]^{2-}$ bridges two copper(II) ions through its deprotonated oxime oxygens has been synthesized and structurally characterized. Magnetic studies in the 80-300 K range revealed complete spin-coupling at room temperature (μ_{eff}: 1.85 μ_B/3Cu).

Studies of spin-exchange interaction in polynuclear metal complexes in relation to stereochemical factors and the nature of bridging groups are of continuing interest.1) One of the recent subjects in this field is to seek new bridging systems which can mediate a strong antiferromagnetic spin-exchange between dissimilar metal ions, in the hope of the development of ferrimagnetic materials.2) In most polynuclear copper(II) complexes the spin-exchange mediated by bridging groups is generally antiferromagnetic, but complete spin-coupling has rarely been attained at room temperature.3) Here we report a linear trinuclear copper(II) complex $[Cu(dmg)_2\{Cu(bipy)(CH_3OH)\}_2](NO_3)_2$, which shows complete spin-coupling through oximate bridges at room temperature.

The complex was obtained as purple microcrystals by the reaction of stoichiometric amounts of bis(dimethylglyoximato)copper(II) $[Cu(dmgH)_2]$, copper(II) nitrate trihydrate, and 2,2'-bipyridyl (bipy) in absolute methanol.4)

Single crystals were grown by slow diffusion technique. Crystal data: $C_{30}H_{36}N_{10}O_{12}Cu_3$; triclinic $P\bar{1}$; Z=1; a=11.732(8), b=12.037(9), c=8.618(4) A; α= 112.82(5), β=96.27(6), γ=119.50(5)°; V=905.4(14) Å^3; D_x=1.693 g cm^{-3}, D_m=1.702 g cm^{-3}; μ(Mo Kα)=18.93 cm^{-1}. Intensity data were collected on a Rigaku AFC-5 diffractometer with graphite monochromated Mo Kα radiation and 2801 reflections ($2<\theta<50°$; -h-kl and hkl) were corrected for absorption ($|F_0| > 3\sigma(F_0)$). The structure was solved by the heavy atom method and refined by a block diagonal least squares method. The weighting scheme was $w=[\sigma_C^2 + (0.030|F_0|)^2]^{-1}$. Final R and R_w values are 0.038 and 0.049, respectively.

A perspective drawing of the structure is given in Fig. 1. The complex forms a molecule consisting of a trinuclear cation and two nitrate ions and has the inversion center at the central copper Cu(1). The $[Cu(dmg)_2]^{2-}$ dianion bridges two copper ions through its deprotonated oxime oxygens with the Cu(1)-Cu(2) separation of 3.754(2) Å. The mean Cu-N bond distance of $[Cu(dmg)_2]^{2-}$ is 1.99 Å, which is slightly longer than that (1.91-1.96 Å) of $[Cu(dmgH)_2]$.⁵⁾ The nitrate ions are located on each side of the CuN_4 plane and the shortest Cu(1)-O(n1) distance is 2.613(3) Å. Each terminal copper atom Cu(2) is in a distorted square-pyramidal surrounging with two nitrogen atoms of bipy and two oxime oxygens of $[Cu(dmg)_2]^{2-}$ in the basal plane and the oxygen atom of a methanol molecule at the apical site. The Cu-N and Cu-O bond distances in the basal plane fall in the range 1.901-2.048 Å, whereas the apical Cu(2)-O(m) distance is elongated (2.356 Å). The deviation of Cu(2) from the basal plane is very small (0.184(1) Å) and the whole trinuclear cation is nearly coplanar.

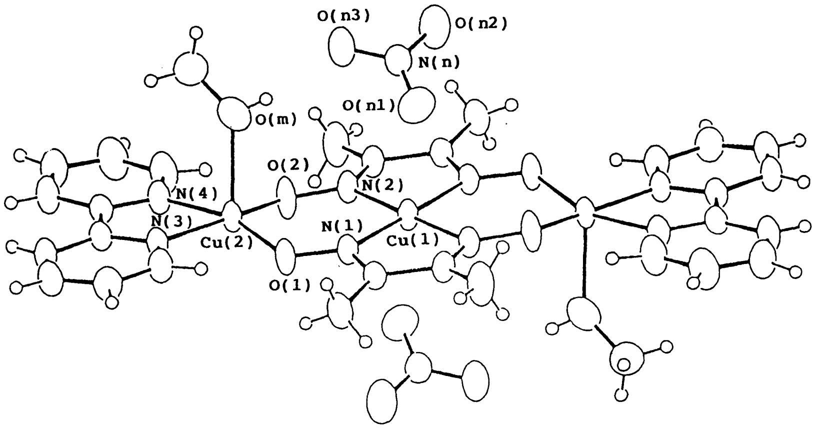

Fig. 1. ORTEP view of the complex. Thermal ellipsoids are drawn at 50% probability.

The magnetic moment of this complex is subnormal, suggesting an antiferromagnetic spin-exchange interaction within a molecule. Cryomagnetic studies over the 80-300 K range revealed that the magnetic moment is practically constant in the temperature range ($1.85 \pm 0.01\ \mu_B/3Cu$). The result clearly demonstrates that complete spin-coupling occurs in this complex even at room temperature. To our best knowledge this is the first example of linear trinuclear copper(II) complex exhibiting complete spin-coupling at room temperature.

References

1) For example: C. J. O'Connor, Prog. Inorg. Chem., 29, 203 (1982); M. Melnic, Coord. Chem. Rev., 42, 259 (1982); W. E. Hatfield, Comments Inorg. Chem., 1, 105 (1981).
2) Y. Pei, O. Kahn, and J. Sletten, J. Am. Chem. Soc., 108, 3143 (1986); Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, and J. Renard, Inorg. Chem., 26, 138 (1987).
3) For example: V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch, and C. A. Reed, J. Am. Chem. Soc., 106, 4765 (1984); S. Gupta, K. C. Kalia, and A. Chakravorty, Inorg. Chem., 10, 1534 (1971); J. A. Bertrand, J. H. Smith, and P. G. Eller, ibid., 13, 1649 (1974).
4) Analytical results. Found: C, 39.15; H, 3.95; N, 15.30; Cu, 20.33%. Calcd: C, 39.16; H, 3.92; N, 15.24; Cu, 20.74%.
5) E. Frasson, R. Bardi, and S. Bezzi, Acta Crystallogr., 12, 201 (1959).

(Received December 14, 1988)