Synthesis, Structure, and Magnetism of the Trinuclear Copper(II) Complex $[Cu(CuL)_2][ClO_4]_2$ [H_2L = 3,3′-(trimethylenedinitrilo)bis(2-butanone oxime)]†

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The trinuclear copper(II) complex $[Cu(CuL)_2][ClO_4]_2$ [H_2L = 3,3′-(trimethylenedinitrilo)bis-(2-butanone oxime)] has been synthesized. It crystallizes in monoclinic space group $C2/c$, with $Z = 4$, $a = 14.253(1)$, $b = 18.798(2)$, $c = 12.675(1)$ Å, and $\beta = 106.92(1)°$. The structure consists of trinuclear cations $[Cu(CuL)_2]^{2+}$ and perchlorate ions. The central copper is co-ordinated by oximate oxygens of two CuL entities and the configuration around the metal is significantly distorted from tetrahedral with a dihedral angle of 33.31(6)°. Each terminal copper adopts an essentially planar configuration with the nitrogen atoms of L^{2-}. The three chromophores in the cation are bent at the edges of the bridging oximate oxygens, with a dihedral angle of 55.88(9)°, to afford a butterfly shape for the cation. In the crystal the trinuclear cations interact with each other at the terminal copper, in the so-called out-of-plane mode, through oximate oxygen to form an infinite chain along the c axis. Cryomagnetic investigations in the range 80—300 K revealed a strong antiferromagnetic spin-exchange interaction within the molecule; the magnetic moment per cation is 2.00 μ_B at room temperature but converges to 1.80 ± 0.01 μ_B at 170 K. The exchange integral J, based on the isotropic exchange model $\mathscr{H} = -2\Sigma J_{ij}\hat{S}_i\hat{S}_j$, is -290.8 cm^{-1}.

Studies on magnetic exchange interaction in polynuclear metal complexes in terms of structural factors and the nature of bridging groups are of continuing interest to co-ordination chemists. Recently there has been an intensive effort to design and understand new molecular-based magnets.[1,2] In particular, new bridging systems which can mediate a strong antiferromagnetic spin coupling between paramagnetic centres have been exploited in the hope of developing ferrimagnetic materials.

In previous papers[3] we described the synthesis of linear trinuclear copper(II) complexes bridged by dimethylglyoximate, diphenylglyoximate, or *o*-benzoquinonedioximate groups [Figure 1(*a*)]. They are the first examples of linear trinuclear copper(II) systems, with double oximate bridges in a *cis* arrangement. Cryomagnetic investigations of these complexes have revealed that the spin exchange through the double bridges is strongly antiferromagnetic so as to cause complete spin coupling even at room temperature. In this study we aimed to synthesize other examples of linear trinuclear copper(II) complexes with double oximate bridges in *cis* arrangement, in order to gain further evidence for effective spin coupling in such bridging systems. Here we report the synthesis, structure, and cryomagnetic properties of a new trinuclear copper(II) complex $[Cu(CuL)_2][ClO_4]_2$ [H_2L = 3,3′-(trimethylenedinitrilo)bis(2-butanone oxime)], see Figure 1(*b*).

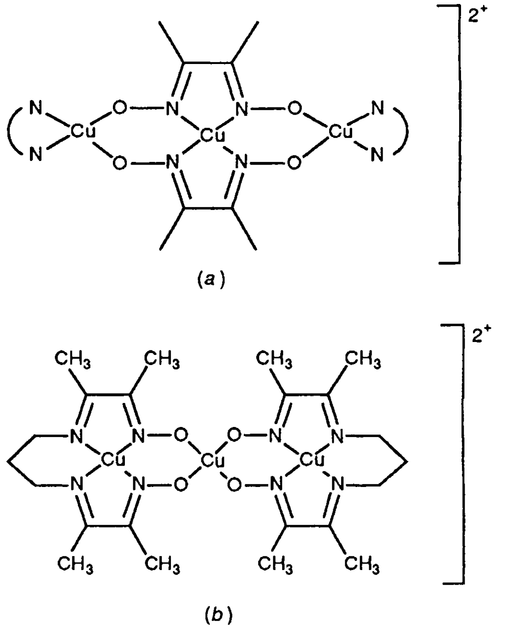

Figure 1. Chemical structures of linear trinuclear copper(II) complexes with double oximate bridges in *cis* arrangement

Experimental

Materials.—All chemicals were of reagent grade and were used as commercially obtained. 3,3′-(Trimethylenedinitrilo)-bis(2-butanone oxime), H_2L, and its copper(II) complex $[Cu(HL)]ClO_4{\cdot}H_2O$ were obtained by the literature method.[4]

Preparation of $[Cu(CuL)_2][ClO_4]_2$.—To a solution of $[Cu(HL)]ClO_4{\cdot}H_2O$ (0.5 mmol) in boiling methanol (15 cm^3) were added successively a solution of NaOH (0.5 mmol) in methanol (5 cm^3) and a solution of copper(II) perchlorate hexahydrate (0.25 mmol) in methanol (10 cm^3). The resulting red solution was heated under reflux for 1 h, filtered while hot, and concentrated slowly to a small volume to afford red-wine crystals. Yield 60% (Found: C, 30.50; H, 4.35; Cu, 22.10; N,

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† Bis[μ-(trimethylenedinitrilo)bis(2-butanone oximato)]-1κ^4*N*: 2κ^2*O*; 2κ^2*O*: 3κ^4*N*-tricopper(II) diperchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Summary of crystal data, intensity data collection, and structure refinements

Formula	$C_{22}H_{36}Cl_2Cu_3N_8O_{12}$
M	866.1
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	14.253(1)
b/Å	18.798(2)
c/Å	12.675(1)
β/°	106.92(1)
$U/Å^3$	3 249.0(4)
Z	4
$D_c/g\ cm^{-3}$	1.770
$D_m/g\ cm^{-3}$	1.749
$\mu(Mo\text{-}K_\alpha)/cm^{-1}$	22.58
T/*k*	29
Scan type	θ—2θ
Scan width/°	1.2 + 0.4tanθ
Scan speed °/min	3
$2\theta_{max.}/°$	60
Octant measured	$+h, \pm k, \pm l$
No. of reflections measured	9 715
No. of unique reflections $[\lvert F_o\rvert > 3\sigma(F_o)]$	3 895
No. of reflections per parameter	12.3
Maximum, minimum residual electron density/e $Å^{-3}$	0.4, −0.4
Maximum shift/e.s.d.	0.2
Weighting scheme (*w* =)	$[\sigma_c^2 + (0.03\lvert F\rvert)^2]^{-1}$
R^a	0.037
R'^b	0.053

[a] $\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$. [b] $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$.

Table 2. Positional parameters ($\times 10^5$ for Cu and Cl, $\times 10^4$ for other atoms) of $[Cu(CuL)_2][ClO_4]_2$

Atom	*x*	*y*	*z*
Cu(1)	0	1 515(2)	25 000
Cu(2)	9 978(2)	−8 002(1)	49 959(2)
Cl(1)	−50 000	−29 000(4)	−25 000
Cl(2)	−50 000	9 789(6)	−25 000
O(1)	1 227(1)	397(1)	3 563(1)
O(2)	−743(1)	−42(1)	3 540(1)
O(3)	−4 672(2)	−2 468(1)	−3 243(2)
O(4)	−5 789(2)	−3 339(1)	−3 109(2)
N(1)	1 653(1)	−125(1)	4 239(1)
N(2)	2 372(1)	−1 090(1)	5 673(2)
N(3)	382(2)	−1 590(1)	5 560(2)
N(4)	−382(1)	−609(1)	4 184(1)
C(1)	2 596(2)	−185(1)	4 505(2)
C(2)	3 212(2)	306(2)	4 055(3)
C(3)	2 989(2)	−768(1)	5 297(2)
C(4)	4 072(2)	−939(2)	5 572(4)
C(5)	2 675(2)	−1 681(2)	6 458(3)
C(6)	1 900(3)	−1 840(2)	7 029(3)
C(7)	956(3)	−2 125(2)	6 330(3)
C(8)	−531(2)	−1 648(1)	5 098(2)
C(9)	−1 160(3)	−2 256(2)	5 279(3)
C(10)	−995(2)	−1 086(1)	4 309(2)
C(11)	−2 056(2)	−1 075(2)	3 693(3)
O(5)	−4 269(4)	1 487(3)	−2 366(8)
O(6)	−5 565(8)	1 092(6)	−1 855(10)
O(5′)	−5 518(6)	375(3)	−2 835(8)
O(6′)	−4 524(6)	1 047(5)	−1 389(6)

12.85. Calc. for $C_{22}H_{36}Cl_2Cu_3N_8O_{12}$: C, 30.50; H, 4.20; Cu, 22.00; N, 12.95%).

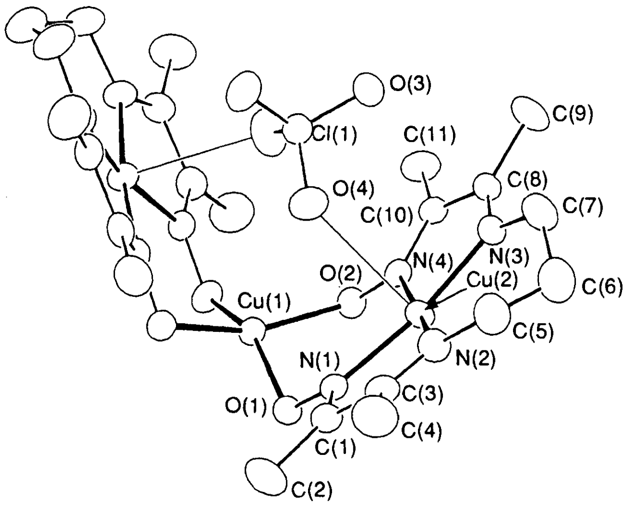

Figure 2. A perspective view of $[Cu(CuL)_2][ClO_4]_2$ with the numbering system

X-Ray Crystal Structure Determination.—A crystal with dimensions 0.56 × 0.44 × 0.26 mm was used for data collection. Crystal data and details of the data collection are given in Table 1. Intensity data were collected at room temperature on a Rigaku AFC-5 four-circle diffractometer with Mo-K_α irradiation and a graphite monochromator. Three reference intensities were recorded periodically throughout the data collection and showed no sign of deterioration. Cell constants were obtained from a least-squares fit of 50 reflections. The intensity data were corrected for Lorentz and polarization effects and for absorption, and were reduced by the use of UNICS III program system of the Computer Centre of the Institute for Molecular Science. Absorption corrections were made with a numerical Gaussian integration method.

Structure solution and refinement. The copper and co-ordinated atoms were located by direct methods using the MULTAN package.[5] The remaining non-hydrogen atoms were located in a succession of Fourier difference syntheses. After anisotropic refinement the hydrogen atoms were located in a Fourier difference synthesis and refined with isotropic thermal parameters. During the structure determination it seemed that one of the two perchlorate anions was disordered. Thus, the refinement was carried out with two sets of oxygen atoms with occupancy 0.5. The atomic scattering factors were taken from ref. 6. The final block-diagonal least-squares refinement converged at $R = 0.037$ and $R' = 0.053$. Atomic parameters for non-hydrogen atoms are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Magnetic Measurements.—Magnetic susceptibilities on powder samples were determined in the temperature range 80—300 K by the Faraday method. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine).[7] Diamagnetic corrections were made by the use of Pascal's constants.[8]

Results and Discussion

Crystal Structure.—A perspective view of the complex is shown in Figure 2, together with the numbering system. Relevant bond lengths and angles are listed in Table 3.

The crystal consists of trinuclear cations $[Cu(CuL)_2]^{2+}$ and perchlorate ions. The central copper atom Cu(1) is located on the two-fold axis and co-ordinated by oximate oxygens of two

Table 3. Selected bond lengths (Å) and angles (°) of $[Cu(CuL)_2][ClO_4]_2$

Cu(1)–O(1)	1.928(1)	Cu(1)–O(1)	1.950(2)
Cu(2)–N(1)	1.981(2)	Cu(2)–N(2)	1.972(2)
Cu(2)–N(3)	1.962(2)	Cu(2)–N(4)	1.969(2)
Cu(1) ••• Cu(2)	3.551 4(5)	Cu(1) ••• Cu(2^{I})	4.026 3(4)
Cu(2) ••• Cu(2^{I})	4.142 3(5)		
O(1)–Cu(1)–O(2)	97.61(7)	O(1)–Cu(1)–O(2^{II})	87.54(7)
O(1)–Cu(1)–O(1^{II})	152.26(7)	O(2)–Cu(1)–O(2^{II})	158.47(7)
N(1)–Cu(2)–N(2)	80.73(8)	N(1)–Cu(2)–N(3)	170.04(9)
N(1)–Cu(2)–N(4)	99.76(7)	N(2)–Cu(2)–N(3)	97.22(9)
N(2)–Cu(2)–N(4)	172.73(9)	N(3)–Cu(2)–N(4)	81.04(8)

Key to symmetry operations: I, $-x, 1-y, 1-z$; II, $-x, y, \frac{1}{2}-z$.

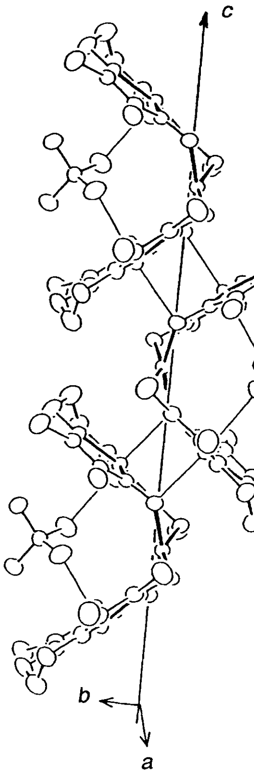

Figure 3. Crystal structure of the complex

CuL entities related by the symmetry operation $-x, y, \frac{1}{2}-z$. The co-ordination geometry around Cu(1) is a flattened tetrahedron: the dihedral angle between the planes defined by Cu(1), O(1), and O(2) and by Cu(1), O(1) ($-x, y, \frac{1}{2}-z$), and O(2) ($-x, y, \frac{1}{2}-z$) is 33.31(6)°. The Cu(1)–O(2) bond length [1.950(2) Å] is slightly longer than Cu(1)–O(1) [1.928(1) Å].

The terminal copper atom Cu(2) has an essentially square planar environment with four nitrogen atoms of L^{2-}; the deviations of the nitrogen atoms from the N_4 least-squares plane are within ± 0.03 Å. The Cu–N bond lengths fall in the range 1.962(2)—1.981(2) Å which are slightly elongated compared with the Cu–N bond lengths of $[Cu(HL)]ClO_4$ [1.937(5)—1.961(5) Å].[9] The atom Cu(2) is slightly displaced (by 0.145 Å) from the N_4 least-squares plane.

A noticeable feature of the trinuclear cation is that the whole cation is not coplanar and bent at the bridging oximate oxygens so that it assumes a butterfly shape. Thus, the Cu(1) ••• Cu(2) interatomic distance [3.551 4(5) Å] is significantly shorter compared with the corresponding Cu ••• Cu distances (3.74—3.75 Å) in our previous trinuclear copper(II) complexes[3] given in Figure 1(*a*). The dihedral angle between the mean plane defined by N(1), N(4), O(1), and O(2) and that defined by Cu(1), O(1), and O(2) is 55.88(9)°. One of the perchlorate ions is located inside the cavity of the cation and weakly bonding to Cu(2) and Cu(2) ($-x, y, \frac{1}{2}-z$) through O(4) and O(4) ($-x, y, \frac{1}{2}-z$), respectively; Cu(2) ••• O(4) is 2.838(2) Å. Another perchlorate ion is free from the co-ordination to copper and disordered.

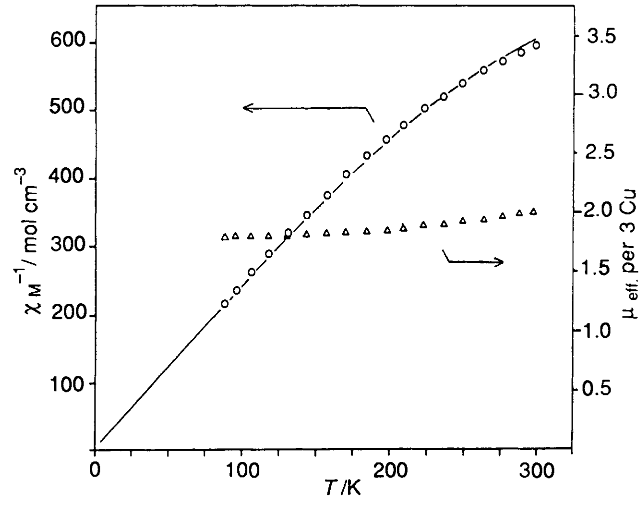

Figure 4. Plots of χ_M^{-1} and $\mu_{eff.}$ *vs.* *T* for the complex $[Cu(CuL)_2][ClO_4]_2$. The trace shows the theoretical curve based on the equation given in the text, using the magnetic parameters $g = 2.05$, $J = -290.8$ cm^{-1}, and $N_\alpha = 180 \times 10^{-6}$ cm^3 mol^{-1}

In the crystal the trinuclear cations interact with each other at the terminal copper ions in a so-called out-of-plane mode as found for $[Cu(HL)]ClO_4$,[9] $[Cu(Hdmg)_2]$[10] (H_2dmg = dimethylglyoxime), and $[Cu_4L'_4(ClO_4)_2][ClO_4]_2$[11] [HL′ = 2-(2′-aminoethyl)imino-3-butanone oxime]. That is, Cu(2) is weakly co-ordinated by the oxime oxygen O(2) ($-x, -y, 1-z$) of the centrosymmetrically related adjacent molecule translated by one unit cell along the *c* axis. Thus, the interactions between adjacent cations form a doubly bridged infinite chain along *c* (see Figure 3).

Magnetic Properties.—The magnetic moment of this complex is subnormal at room temperature (1.15 μ_B per copper). Magnetic susceptibilities were determined in the temperature range 80—300 K. The results are given in Figure 4 in the form of plots of χ_M^{-1} *vs.* *T* and $\mu_{eff.}$ *vs.* *T*, where χ_M and $\mu_{eff.}$ are the magnetic susceptibility and magnetic moment per three copper atoms, respectively.

The magnetic moment (per three copper atoms) at room temperature (2.00 μ_B) is very close to the spin-only value for one unpaired electron. The moment decreases with lowering of temperature and reaches a plateau ($\mu_{eff.} = 1.80 \pm 0.01$ μ_B) at 170 K. The plots of χ_M^{-1} *vs.* *T* obey the Curie–Weiss law [$\chi_M^{-1} = C/(T-\theta)$] in the range 80—170 K with a Weiss constant of -9 K and a Curie constant of 0.44. Above 170 K the plots deviate from a straight line, this becoming more pronounced at higher temperature. All these facts indicate that a strong antiferromagnetic spin exchange operates in this complex and perfect spin coupling is attained at 170 K.

The Hamiltonian for the spin exchange of the system Cu^2–Cu^1–Cu^3 is written as $\mathscr{H} = -J(\hat{S}_T{}^2 - \hat{S}_{23}{}^2)$, where $\hat{S}_T = \hat{S}_1 + \hat{S}_2 + \hat{S}_3$, $\hat{S}_{23} = \hat{S}_2 + \hat{S}_3$, and J = exchange integral. In this equation we neglect the exchange between the terminal copper ions. According to Kambe's approach,[12] two spin-doublet states, $S_T = \frac{1}{2}(S_{23} = 1)$ and $S_T = \frac{1}{2}(S_{23} = 0)$, and one spin-quartet state, $S_T = \frac{3}{2}$ $(S_{23} = 1)$, occur and their relative energies are given as 0, $-2J$, and $-3J$, respectively. By use of the Van Vleck equation, the magnetic susceptibility equation is[13] $\chi_M = (Ng^2\beta^2/4kT)[1 + \exp(2J/kT) + 10\exp(3J/kT)]/[1 + \exp(2J/kT) + 2\exp(3J/kT)]$. Each symbol having its usual meaning. The magnetic susceptibility of $[Cu(CuL)_2][ClO_4]_2$ is well simulated with this equation as shown by the trace in Figure 4 with a negative exchange integral $J = -290.8$ cm^{-1}. The discrepancy factor, $\sigma = [\Sigma(\chi_{obs.} - \chi_{calc.})^2/\Sigma\chi_{obs.}{}^2]^{\frac{1}{2}}$, in this least-squares fitting was 0.061. Thus, the spin-quartet state is about 870 cm^{-1} above the ground state.

It is interesting to compare the magnetic properties of the present complex with those of the trinuclear copper(II) complexes given in Figure 1(*a*), which were revealed previously to be almost spin-coupled even at room temperature. Their estimated exchange integrals ($-J$) are much larger than 300 cm^{-1}. Single-crystal *X*-ray analyses for two of those complexes have revealed that the whole of the trinuclear cation is nearly coplanar. Such a structure appears to be essential for perfect spin coupling at room temperature in those complexes. Oximate-bridged dinuclear and triangular trinuclear copper(II) complexes which have been shown to be perfectly spin-coupled retain such a coplanar structure.[14–18] For the present complex, antiferromagnetic spin exchange is weaker ($J = -290.8$ cm^{-1}) and spin coupling is completed at 170 K. As our *X*-ray analysis has demonstrated, the trinuclear cation of this complex is significantly distorted from coplanarity; *i.e.* (1) the configuration around the central copper is pseudo-tetrahedral and (2) three chromophores in the cation are bent at the edges to form a butterfly shape. Such structural distortions must be associated with the weakened antiferromagnetic interaction in this complex. However, emphasis should be placed on the fact that the antiferromagnetic spin exchange through the oximate bridge is unexpectedly strong despite such significant distortions in the molecule.

Acknowledgements

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