# Magnetic Properties of Mono-, Bi-, and Tri-nuclear Copper(II) Complexes of Novel Oxamato and Oxamido Ligands. Crystal Structure of a Mononuclear Precursor†

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Three novel ligands ($H_3L^i$ with $i$ = 1, 2, or 3) of the oxamato and oxamido types have been obtained and used to prepare the related 'mononuclear' entities $[CuL^i]^-$, $H_3L^1$ being *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid, $H_3L^2$ being *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamide, and $H_3L^3$ being *N*-methyl-*N*′-(4-methyl-6-oxo-3-azahept-4-enyl)oxamide. The complex of $H_3L^1$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a$ = 21.705(2), $b$ = 9.380(1), $c$ = 19.131(2) Å, and $\beta$ = 110.17(1)°. The structure consists of three mononuclear anions $[CuL^1]^-$ together with three sodium cations and four water molecules. From the mononuclear fragments, binuclear complexes $[CuL^iCuL]^+$ (L = 2,2′-bipyridine or diethylenetriamine) have been synthesized and spectroscopically characterized. A symmetrical binuclear complex $[Cu_2L^4]$ [$H_4L^4$ = *N*,*N*′-bis-(4-methyl-6-oxo-3-azahept-4-enyl)oxamide] and two trinuclear complexes, $[(CuL^1)_2Cu]$ and $[(CuL^1)_2Zn]$, have also been prepared. The magnetic properties of these complexes have been investigated in the range 5—290 K. The importance of the antiferromagnetic interactions mediated by the oxamato and oxamido bridges is discussed with respect to the nature of the $H_nL^i$ ($n$ = 3 or 4) and L ligands.

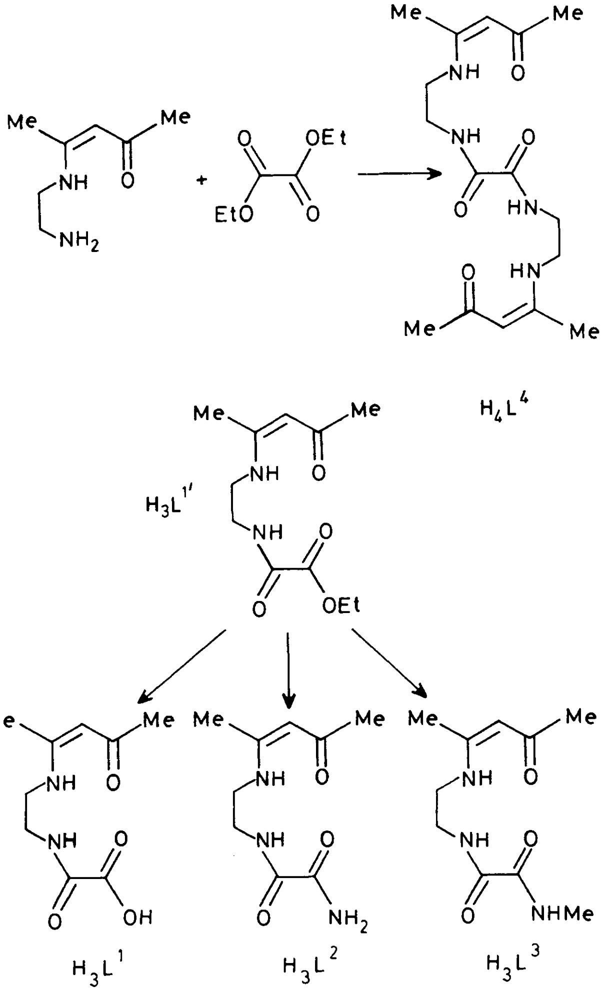
Polymetallic systems are attractive as synthetic models of the active sites of metallobiomolecules and also as materials for the study of correlations between structure and physical properties. In some instances, physical criteria may be used to ascertain the quality of synthetic biomodels. Among the known polynucleating ligands, particular attention has recently been paid to oxalic acid derivatives due to their wide range of possibilities. First, oxalates, oxamates, and oxamides are known to be very efficient in transmitting exchange interaction between magnetic ions in favourable geometries.[1–13] Further, these ligands are easily altered to give derivatives designed for a particular problem. In some instances, mononuclear precursors can be isolated and subsequently used as chelating ligands towards a second type of metal ion to yield heteropolynuclear species.

The present paper is devoted to copper(II) complexes derived from a new family of potentially polynucleating ligands, $H_nL^i$ ($n$ = 3 or 4). Mono-, bi-, and tri-nuclear complexes have been obtained and their magnetic properties studied.

## Results and Discussion

Depending on the experimental conditions, the half-unit 7-amino-4-methyl-5-aza-3-hepten-2-one reacts with diethyl oxalate to give either an oxamato derivative ($H_3L^{1'}$) or a symmetrical oxamido compound ($H_4L^4$). Interestingly, $H_3L^{1'}$ can react further with ammonia or a primary amine to yield unsymmetrical oxamido ligands $H_3L^2$ and $H_3L^3$.

As expected, we succeeded in isolating the mononuclear complexes (**1**), (**2**), and (**3**) derived from the ligands $H_3L^1$, $H_3L^2$, and $H_3L^3$, respectively. They are anionic. Analytical data and charge balance consideration suggest that they may be



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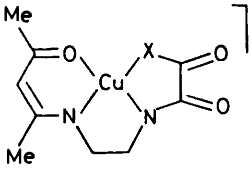
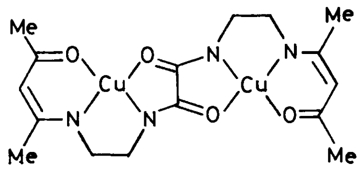
† [*N*-(4-Methyl-6-oxo-3-azahept-4-enyl)oxamato(3 – )]cuprate(II).

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

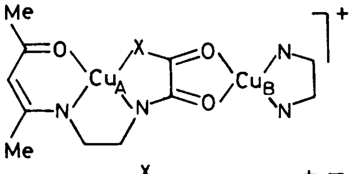
*Non-S.I. units employed:* B.M. ≈ $9.27 \times 10^{-24}$ J $T^{-1}$, G = $10^{-4}$ T.



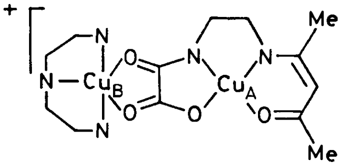
| | X |
|---|---|
| **(1)** | O |
| **(2)** | NH |
| **(3)** | NMe |



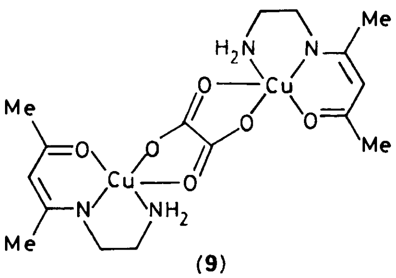
**(4)**



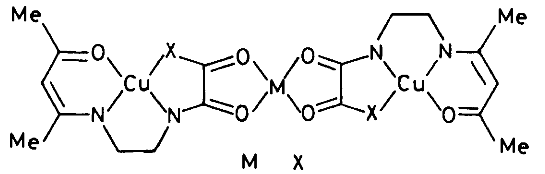
| | X |
|---|---|
| **(5)** | O |
| **(6)** | NH |
| **(7)** | NMe |



**(8)**



**(9)**



| | M | X |
|---|---|---|
| **(10)** | Cu | O |
| **(11)** | Zn | O |
| **(12)** | Zn | NH |

represented by the crude formulation $[CuL^i]^-$ ($i$ = 1, 2, or 3) which is definitely established in the case of (1) by a structural determination. It is noteworthy that the ester function of $H_3L^{1'}$ has been hydrolyzed so that the ligand actually involved in complex (1) is the acidic form, $H_3L^1$.

The mononuclear complexes (1)—(3) were then used as chelating ligands towards a second metal centre, M′, to yield homo- or hetero-, bi- or tri-nuclear complexes, depending on the nature of M′ (M′ = M or M′ ≠ M) and the mono- or bis-bidentate behaviour of the second ligand L co-ordinated to M′. If L is a bidentate ligand such as 2,2′-bipyridine (bipy) or a tridentate ligand such as diethylenetriamine (dien), binuclear complexes (5)—(8) are obtained. Trinuclear complexes (10)—(12) result from the use of $H_3L^i$ ($i$ = 1, 2, or 3) as a second ligand. As expected, the binucleating ligand $H_4L^4$ yields a dicopper complex (4).

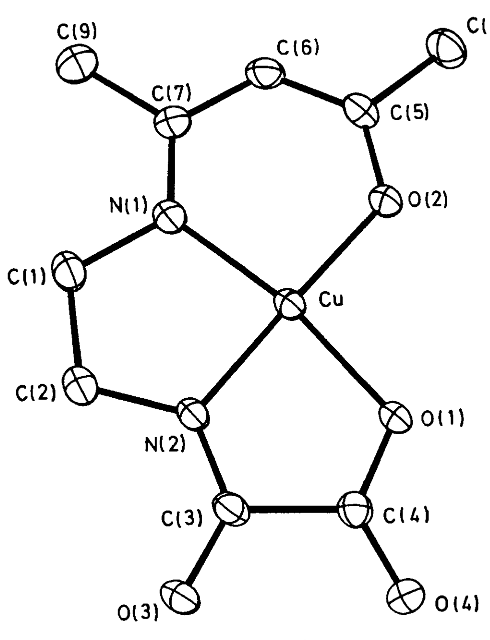


**Figure 1.** ORTEP plot of one of the $CuL^1$ molecules with the labelling scheme. Hydrogen atoms are omitted for clarity

Finally, an oxalato complex (9) is obtained by substituting the anion $C_2O_4^{2-}$ for the two $MeCO_2^-$ anions in the binuclear complex $[\{CuL'(\mu\text{-}MeCO_2)\}_2]$ (L′ = 7-amino-4-methyl-5-aza-3-hepten-2-onate).

We have been able to grow single crystals suitable for structural study only in the case of complex (1). However, spectroscopic data allow a good characterization of all the complexes and leave little doubt concerning the nature and the geometry of the chromophore involved in each case.

*Description of the Structure of Complex* (1).—The unit cell comprises three complex anions together with three sodium cations and four water molecules, one of them being shown in Figure 1, along with the atomic numbering. The structure is shown in Figure 2, with the sodium atom environment and the hydrogen bonding. Relevant atomic distances and angles are given in Table 1, atomic co-ordinates in Table 2.

Within each complex anion the copper atom is surrounded by two nitrogen and two oxygen atoms. These atoms show deviations from coplanarity with opposite atoms moving in the same direction to yield a tetrahedral distortion. The distortion increases from anion (1) to (2) and (3). In the latter instance, deviations up to 0.11 Å from the least-squares plane are observed. The displacements of the metal atoms from their related least-squares planes are less important than the tetrahedral distortions except in the case of anion (1) where they have similar magnitudes. The bond angles around the metal atoms are largely asymmetric. The O(1)–Cu–N(2) and N(2)–Cu–N(1) angles which are included in five-membered rings are less than 90° whereas the O(1)–Cu–O(2) and N(1)–Cu–O(2) angles are larger than this value. The copper–amidic nitrogen distances, Cu–N(2) [from 1.886(4) to 1.894(3) Å], are shorter than those generally reported (from 1.930 to 1.938 Å) for di- and tri-copper complexes involving oxamido bridges.[10] However, a short Cu–N distance of 1.899(6) Å has been reported.[9a] The copper–acidic oxygen distances [from 1.983(2) to 1.991(3) Å] are within the range of known values.

In the three anionic units, the C–O bond lengths display the same trend, *i.e.* C(4)–O(4) ⩽ C(3)–O(3) < C(4)–O(1) < C(5)–O(2), which likely reflects the importance of the interactions at the oxygen atoms. The longer distances correspond

**Table 1.** Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex (**1**)

| | Molecule | | | | Molecule | | |
|---|---|---|---|---|---|---|---|
| | (1) | (2) | (3) | | (1) | (2) | (3) |
| Cu–N(1) | 1.922(3) | 1.923(3) | 1.933(4) | O(1)–Cu–O(2) | 95.1(1) | 95.0(1) | 95.6(1) |
| Cu–N(2) | 1.891(3) | 1,894(3) | 1.886(4) | Cu–N(1)–C(1) | 113.9(2) | 114.2(2) | 113.3(3) |
| Cu–O(1) | 1.984(2) | 1.983(2) | 1.991(3) | Cu–N(1)–C(7) | 125.1(2) | 124.5(2) | 124.3(3) |
| Cu–O(2) | 1.880(2) | 1.884(2) | 1.885(3) | C(1)–N(1)–C(7) | 120.9(3) | 120.9(3) | 122.0(4) |
| N(1)–C(1) | 1.479(4) | 1.464(4) | 1.464(6) | N(1)–C(1)–C(2) | 112.4(3) | 111.3(3) | 109.6(4) |
| C(1)–C(2) | 1.511(5) | 1.530(5) | 1.537(8) | C(1)–C(2)–N(2) | 110.6(3) | 108.6(3) | 107.8(4) |
| C(2)–N(2) | 1.457(5) | 1.454(4) | 1.448(6) | Cu–N(2)–C(2) | 116.8(2) | 117.2(2) | 116.7(3) |
| N(2)–C(3) | 1.301(4) | 1.293(4) | 1.296(6) | Cu–N(2)–C(3) | 117.3(2) | 117.3(2) | 117.9(3) |
| C(3)–O(3) | 1.258(4) | 1.257(4) | 1.248(5) | C(2)–N(2)–C(3) | 124.4(3) | 123.7(3) | 125.2(4) |
| C(3)–C(4) | 1.551(5) | 1.543(4) | 1.550(6) | N(2)–C(3)–C(4) | 110.8(3) | 110.5(3) | 111.0(4) |
| C(4)–O(4) | 1.229(4) | 1.236(4) | 1.231(6) | N(2)–C(3)–O(3) | 129.2(3) | 130.2(3) | 128.6(4) |
| C(4)–O(1) | 1.277(4) | 1.272(4) | 1.287(5) | C(4)–C(3)–O(3) | 120.0(3) | 119.3(3) | 120.4(4) |
| O(2)–C(5) | 1.293(5) | 1.305(5) | 1.309(7) | O(1)–C(4)–C(3) | 115.2(3) | 116.4(3) | 115.5(4) |
| C(5)–C(6) | 1.374(5) | 1.364(5) | 1.355(9) | O(1)–C(4)–O(4) | 124.9(3) | 124.3(3) | 124.8(4) |
| C(6)–C(7) | 1.424(5) | 1.433(5) | 1.422(8) | C(3)–C(4)–O(4) | 119.9(2) | 119.2(3) | 119.7(4) |
| C(7)–N(1) | 1.303(4) | 1.297(5) | 1.303(7) | Cu–O(1)–C(4) | 112.8(2) | 111.9(2) | 112.1(3) |
| C(5)–C(8) | 1.499(5) | 1.509(5) | 1.512(7) | Cu–O(2)–C(5) | 124.1(2) | 122.3(2) | 122.4(3) |
| C(7)–C(9) | 1.507(5) | 1.504(5) | 1.499(8) | O(2)–C(5)–C(6) | 125.6(3) | 126.3(3) | 126.3(5) |
| | | | | O(2)–C(5)–C(8) | 113.7(3) | 113.7(3) | 112.6(5) |
| N(1)–Cu–N(2) | 85.7(1) | 84.9(1) | 84.7(2) | C(6)–C(5)–C(8) | 120.7(3) | 120.0(4) | 121.1(5) |
| N(1)–Cu–O(1) | 168.5(1) | 167.6(1) | 166.4(1) | C(5)–C(6)–C(7) | 127.1(3) | 127.4(4) | 127.9(5) |
| N(1)–Cu–O(2) | 96.3(1) | 97.4(1) | 97.1(2) | C(6)–C(7)–N(1) | 121.8(3) | 121.6(3) | 121.7(5) |
| N(2)–Cu–O(1) | 82.9(1) | 82.8(1) | 83.1(1) | C(6)–C(7)–C(9) | 116.8(3) | 117.3(3) | 116.9(5) |
| N(2)–Cu–O(2) | 178.0(1) | 176.8(1) | 175.1(1) | N(1)–C(7)–C(9) | 121.4(3) | 121.1(3) | 121.4(5) |

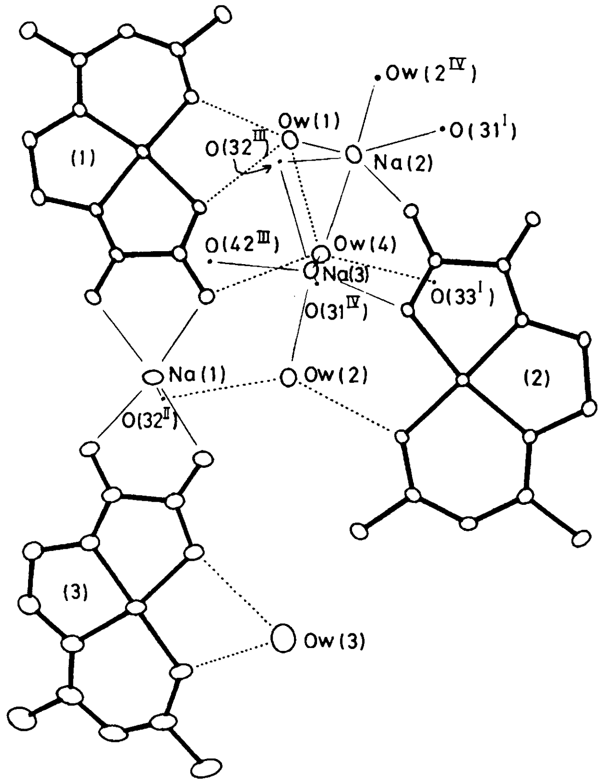


**Figure 2.** Molecular packing with a schematic representation of hydrogen bonds and the sodium atom environment. Symmetry operations as follows: I $x, -1 + y, z$; II $x, 1 + y, z$; III $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; IV $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$

to the oxygen atoms O(2) and O(1) bonded to copper centres. Within the oxamato moiety, the difference between C(4)–O(1) and C(4)–O(4) is suggestive of a partial localization of the negative charge on the bonded oxygen atom O(1). A similar suggestion has been made regarding the mononuclear complex $[Cu(dien)_2(C_2O_4)]$.[4a,14,15]

As for the 7-amino-4-methyl-5-aza-3-hepten-2-one moiety, the Cu–N(1) and Cu–O(2) distances do not significantly differ from those previously obtained for a binuclear complex, $[L'Cu(im)NiL']^+$ (im = imidazolate anion),[16] in which the copper atom is also four-co-ordinated. Interestingly, the $-N(CH_2)_2N-$ chain does not adopt the same conformation in the three units since the conformation is *gauche* in the units (1) and (2) but right in (3). This is the first example of such a right conformation in complexes derived from the above heptenone ligand. The dihedral angles between the least-squares planes of the three anionic units are 16.9, 20.2, and 3.5° for units (1) and (2), (1) and (3), and (2) and (3), respectively.

The sodium atoms and the water molecules play an important part in stabilizing the structure since they are simultaneously bonded to atoms belonging to different unit cells.

The sodium atoms are surrounded by either five [Na(1)] or six [Na(2), Na(3)] oxygen atoms at distances ranging from 2.276(3) to 2.587(3) Å. These oxygen atoms pertain to the water molecules Ow(1), Ow(2), and Ow(4), and to the three anionic complexes (Figure 2). Interestingly, Na(1) which lies between anions (1) and (3) is also bonded to one anion (2) of a different unit cell whereas Na(2) and Na(3) are linked to anions (1) and (2) only. Furthermore, Na(1) is not bonded to any water molecule whereas Na(2) and Na(3) are bonded to Ow(1), Ow(2), and Ow(4). Surprisingly, the water molecule Ow(3) is only involved in hydrogen bonding with two oxygen atoms of the same anionic complex (3). This is in marked contrast with the fact that the other water molecules, Ow(1), Ow(2), and Ow(4), are bonded not only to anions but also to sodium ions and/or water molecules belonging to the same unit cell or not. The net result of this complicated hydrogen-bonding framework is that short distances are observed between copper of different cells, *i.e.* 3.441(1) Å between Cu(1) and Cu(1)($1 - x, 1 - y, 1 - z$), 3.575(1) Å between Cu(1) and Cu(2)($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), and 3.786(1) Å between Cu(2) and Cu(3)($x, 1 + y, z$).

**Table 2.** Fractional atomic co-ordinates with (e.s.d.s) in parentheses for complex (**1**)

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cu(1) | 0.432 14(2) | 0.429 25(4) | 0.514 22(2) |
| N(11) | 0.440 3(1) | 0.534 7(3) | 0.603 1(2) |
| C(11) | 0.430 5(2) | 0.690 0(4) | 0.591 1(2) |
| C(21) | 0.409 8(2) | 0.730 2(4) | 0.509 8(2) |
| N(21) | 0.413 9(2) | 0.607 3(3) | 0.465 0(2) |
| C(31) | 0.393 6(2) | 0.606 1(3) | 0.392 6(2) |
| O(31) | 0.369 5(1) | 0.706 0(2) | 0.347 5(1) |
| C(41) | 0.401 7(2) | 0.455 8(4) | 0.363 2(2) |
| O(41) | 0.393 2(1) | 0.438 6(3) | 0.296 8(1) |
| O(11) | 0.417 1(1) | 0.357 1(2) | 0.412 2(1) |
| O(21) | 0.449 6(1) | 0.249 1(3) | 0.559 8(1) |
| C(51) | 0.465 5(2) | 0.228 3(4) | 0.630 7(2) |
| C(61) | 0.469 4(2) | 0.331 9(4) | 0.682 8(2) |
| C(71) | 0.457 0(2) | 0.480 4(4) | 0.669 8(2) |
| C(81) | 0.478 3(2) | 0.075 0(4) | 0.653 2(2) |
| C(91) | 0.464 3(2) | 0.572 2(5) | 0.736 8(2) |
| Cu(2) | 0.239 59(2) | −0.031 01(4) | 0.019 79(2) |
| N(12) | 0.226 4(1) | −0.115 3(3) | −0.075 9(1) |
| C(12) | 0.209 8(2) | −0.267 1(4) | −0.080 5(2) |
| C(22) | 0.227 2(2) | −0.333 2(4) | −0.002 9(2) |
| N(22) | 0.231 6(2) | −0.219 9(3) | 0.050 5(1) |
| C(32) | 0.245 0(2) | −0.241 5(3) | 0.120 9(2) |
| O(32) | 0.252 8(1) | −0.356 2(2) | 0.156 9(1) |
| C(42) | 0.252 4(2) | −0.098 4(3) | 0.162 7(2) |
| O(42) | 0.261 3(1) | −0.098 9(2) | 0.230 1(1) |
| O(12) | 0.248 9(1) | 0.013 9(2) | 0.124 2(1) |
| O(22) | 0.251 7(1) | 0.158 3(2) | −0.005 8(1) |
| C(52) | 0.252 7(2) | 0.193 0(4) | −0.071 4(2) |
| C(62) | 0.240 4(2) | 0.104 5(4) | −0.131 3(2) |
| C(72) | 0.225 3(2) | −0.044 7(4) | −0.134 6(2) |
| C(82) | 0.268 1(3) | 0.348 2(4) | −0.078 2(2) |
| C(92) | 0.208 3(2) | −0.116 6(4) | −0.209 1(2) |
| Cu(3) | 0.402 31(3) | 0.950 68(6) | −0.011 70(3) |
| N(13) | 0.426 4(2) | 1.148 9(4) | −0.012 2(2) |
| C(13) | 0.446 6(3) | 1.215 2(5) | 0.061 6(3) |
| C(23) | 0.415 5(2) | 1.134 7(5) | 0.111 0(2) |
| N(23) | 0.407 5(2) | 0.987 2(4) | 0.087 1(2) |
| C(33) | 0.399 2(2) | 0.881 1(5) | 0.126 4(2) |
| O(33) | 0.396 6(1) | 0.882 5(3) | 0.190 5(1) |
| C(43) | 0.392 5(2) | 0.738 9(5) | 0.083 1(2) |
| O(43) | 0.389 6(2) | 0.625 6(3) | 0.114 3(2) |
| O(13) | 0.388 7(2) | 0.750 7(3) | 0.014 8(2) |
| O(23) | 0.389 4(2) | 0.912 5(4) | −0.112 5(2) |
| C(53) | 0.394 8(2) | 1.011 1(7) | −0.158 4(3) |
| C(63) | 0.414 6(3) | 1.147 4(7) | −0.140 6(3) |
| C(73) | 0.431 6(2) | 1.214 8(6) | −0.069 9(3) |
| C(83) | 0.376 5(3) | 0.957 7(7) | −0.237 5(3) |
| C(93) | 0.454 7(3) | 1.366 3(6) | −0.064 9(3) |
| Na(1) | 0.375 85(8) | 0.652 1(2) | 0.229 08(8) |
| Na(2) | 0.334 16(8) | −0.048 4(2) | 0.350 63(7) |
| Na(3) | 0.256 28(7) | 0.184 9(1) | 0.216 98(7) |
| Ow(1) | 0.418 0(2) | 0.064 4(3) | 0.439 3(1) |
| Hw(11) | 0.412(2) | 0.148(2) | 0.408(2) |
| Hw(21) | 0.443(2) | 0.082(4) | 0.491 6(4) |
| Ow(2) | 0.254 9(2) | 0.345 1(3) | 0.115 8(2) |
| Hw(12) | 0.286(1) | 0.419(3) | 0.117(2) |
| Hw(22) | 0.262(2) | 0.299(4) | 0.074(1) |
| Ow(3) | 0.344 5(3) | 0.633 3(5) | −0.138 2(3) |
| Hw(13) | 0.349(3) | 0.633(6) | −0.085 6(6) |
| Hw(23) | 0.359(3) | 0.726(3) | −0.150(3) |
| Ow(4) | 0.369 0(1) | 0.125 5(3) | 0.272 5(1) |
| Hw(14) | 0.388(2) | 0.219(2) | 0.275(2) |
| Hw(24) | 0.383(2) | 0.064(3) | 0.240(2) |

Much larger values characterize the Cu ⋯ Cu distances within the same unit cell: 9.915(1) Å for Cu(1) ⋯ Cu(2), 9.955(1) Å for Cu(2) ⋯ Cu(3), and 11.004(1) Å for Cu(1) ⋯ Cu(3).

*E.S.R. Spectra.*—(*a*) *Solution.* Well resolved hyperfine (h.f.) and superhyperfine (s.h.f.) structures are observed for the isotropic room-temperature spectra of the mononuclear species (**1**)—(**3**). They originate in the interactions of the free electron with the nuclear spins of the copper atoms ($I = \frac{3}{2}$) and the adjacent $^{14}$N nuclei ($I = 1$). The latter coupling offers an easy means to determine the number of nitrogen atoms surrounding the copper centre. From this criterion and the number of s.h.f. lines actually observed, *i.e.* five for complex (**1**) and seven for complexes (**2**) and (**3**), an $N_2O_2$ environment is assigned to the copper ion in (**1**) in accordance with the structural data whereas $N_3O$ surroundings are present in (**2**) and (**3**). At low temperature (120 K), axial $S = \frac{1}{2}$ spectra with h.f. and s.h.f. structures are observed. The related $g$ and $A$ values (Table 3) are consistent with a $d_{x^2-y^2}$ ground state.

The spectrum of the binuclear complex (**4**) displays one broad absorption at $g = 2.089$ at 300 K. This feature decreases in intensity on cooling and vanishes at *ca.* 120 K. This behaviour is in accordance with the temperature dependence of the magnetic susceptibility and therefore supports the occurrence of a strong antiferromagnetic interaction between the copper atoms.

The spectra of the trinuclear complexes at 120 K can be interpreted by using a $S = \frac{1}{2}$ spin Hamiltonian with $g_{\parallel} = 2.162$ and $g_{\perp} = 2.04$ for (**10**), $g_{\parallel} = 2.203$ and $g_{\perp} = 2.08$ for (**11**), and $g_{\parallel} = 2.197$ and $g_{\perp} = 2.08$ for (**12**).

Hyperfine splitting of the parallel component is not observed in the spectra of the homopolynuclear complexes (**4**)—(**7**), (**9**), and (**10**). This is consistent with a strong coupling between adjacent copper ions. Interestingly, in (**11**) and (**12**) where the interaction is extensively reduced by the interposition of a zinc atom, the splitting is clearly discernible.

(*b*) *Polycrystalline powder.* The spectra of the three mononuclear complexes are almost identical. At 300 K they display a quasi-isotropic feature at $g \approx 2.10$. The broadness of these signals is likely due to dipolar interactions resulting from short intermolecular Cu ⋯ Cu distances. In the case of (**4**), a broad signal is observed at $g \approx 2.06$ but a bump of low intensity is also discernible at $g \approx 2.20$. The related *Q*-band spectrum displays two well resolved signals at $g_{\parallel} \approx 2.181$ and $g_{\perp} \approx 2.058$. Very similar data are obtained for (**5**) and (**6**). In any case, the spectra of these binuclear complexes show neither fine structure nor 'half-field' transition.

The trinuclear complexes give spectra which can be interpreted as doublet-state spectra. However, the spectra related to the heterotrinuclear complexes (**11**) and (**12**) show no significant dependence on temperature whereas, for complex (**10**), the width and the positions of the signals do vary with temperature. The broadening characterizing the spectrum at 300 K may be due to either inter- or intra-molecular exchange phenomena. An intramolecular nature is supported by the fact that, at 4 K, where only the lowest doublet is populated (see below), the spectrum is exchange-narrowed and not broadened. Several explanations can be given for the temperature dependence of the $g$ values. By analogy with a recently reported tricopper complex,[17] we suggest that this dependence is related to the fact that the spectrum observed at 4 K is that of the lowest doublet while the spectrum at 300 K is the thermal average of the spectra of the three multiplets. Finally, it may be recalled that, for all the complexes but (**8**), well resolved spectra are

**Table 3.** E.s.r. results (solution and solid state) and visible absorptions ($\lambda_{max.}$ in nm)

| Complex | $\lambda_{max.}$[a] | Solvent | E.s.r. data | | | | |
|---|---|---|---|---|---|---|---|
| | | | $g_{iso}$[b] | $A_{iso}$[b]/G | $g_{\parallel}$[c] | $A_{\parallel}$[c]/G | $g_{\perp}$[c] |
| **(1)** | 542 | dmso–$H_2O$ | 2.095 | 84 | 2.204 | 187 | 2.05 |
| **(2)** | 517 | dmso–$H_2O$ | 2.087 | 91 | 2.184 | 204 | 2.05 |
| **(3)** | 502 | dmso–$H_2O$ | 2.087 | 90 | 2.183 | 203 | 2.05 |
| **(4)** | 562 | $CH_2Cl_2$ | 2.089 | *d* | *e* | *e* | *e* |
| | | Solid,[f] 300 K | — | — | 2.181 | — | 2.06 |
| **(5)** | 598 | Solid[g] | — | — | 2.215 | — | 2.06 |
| **(6)** | 600 | Solid[g] | — | — | 2.213 | — | 2.06 |
| **(7)** | 600 | Solid[g] | — | — | 2.210 | — | 2.06 |
| **(8)** | | $H_2O$ | 2.104 | 79 | — | — | — |
| | 570, 620 | Solid[g] | 2.090 | — | — | — | — |
| **(9)**[h] | 636 | dmso | — | — | 2.164 | — | 2.115, 2.054 |
| | | Solid[f,g] | — | — | 2.169 | — | 2.121, 2.057 |
| **(10)** | 576 | dmso | — | — | 2.162 | — | 2.04 |
| | | Solid, 300 K | — | — | 2.167 | — | 2.07 |
| | | Solid, 4 K | — | — | 2.179 | — | 2.04 |
| **(11)** | 570 | dmso–$H_2O$ | 2.098 | 82 | 2.203 | 190 | 2.08 |
| | | Solid[g] | — | — | 2.188 | — | 2.05 |
| **(12)** | 528 | dmso | 2.085 | 92 | 2.197 | 195 | 2.08 |
| | | Solid[g] | — | — | 2.180 | — | 2.05 |

[a] In dimethyl sulphoxide (dmso). [b] At 300 K. [c] At 90 K. [d] No h.f. structure. [e] No signal at low temperature. [f] *Q* Band. [g] At 300 and 90 K. [h] Three *g* values.

observed. They can be interpreted as doublet-state spectra with $g_{\parallel} > g_{\perp}$ in accordance with a $d_{x^2-y^2}$ ground state. These spectra do not display any feature attributable to triplet or quadruplet spectra. This behaviour is very reminiscent of that reported for similar complexes.[10]

*Electronic Spectra.*—Electronic spectra of copper(II) complexes with multidentate ligands are not, usually, precise indicators of the actual geometry at the metal centre. However, within a series of closely related compounds displaying only minor variations of the ligand field, they may offer the possibility to distinguish the limiting geometries from each other.

Referring to the generally proposed criteria,[18] it appears that the values of the maximum of absorption ($\lambda_{max.}$) reported in Table 3 are not consistent with trigonal-bipyramidal geometry which is supposedly characterized by an absorption in the 800—850 nm region. This is in accordance with the e.s.r. data which support a $d_{x^2-y^2}$ ground state* for all the complexes but **(8)**, the unresolved spectrum obtained in the latter case not allowing any firm conclusion concerning stereochemistry. Finally, a joint examination of e.s.r. and electronic spectra leads to the conclusion that, in all the complexes, the copper environment can be ideally described in terms of either square-planar or square-pyramidal geometry.

In a recent paper[7] devoted to a series of oxalato- (oxamato-) complexes very similar to those reported in Table 3, $\lambda_{max.}$ values of *ca.* 570 nm were attributed to a square-planar $CuN_2O_2$ and $CuN_3O$ chromophores, while the maximum of absorption for the related square-pyramidal chromophore is reported to occur at lower energies (630—650 nm). Therefore, it seems reasonable to assign essentially a square-planar geometry to the copper centres in complexes **(1)**—**(4)** and **(10)**—**(12)**. It may be recalled that structural data show that in **(1)** the environments of the copper ions are distorted square planar and do not involve any axial co-ordination. The shift of the maximum from 542 nm for **(1)** to 517 and 502 nm for **(2)** and **(3)**, respectively, is not consistent with a change of geometry from planar to square pyramidal which would cause a shift to lower energies, but can readily be attributed to a change of the copper surroundings from $N_2O_2$ to $N_3O$, as established by e.s.r. spectroscopy. This is in accordance with the generally accepted assumption that a shift of $\lambda_{max.}$ towards shorter wavelengths is associated with an increase of the number of nitrogen atoms bonded to copper.[7,19] This rationale is further supported by the observation of high $\lambda_{max.}$ values of 562 and 570 nm for **(4)** and **(11)**, respectively, where the environment of the copper ions is $N_2O_2$. Conversely, a low $\lambda_{max.}$ value (528 nm) characterizes **(12)** where the copper ions are very likely in a $N_3O$ environment (see below).

The ligand-field spectrum of complex **(8)** displays two well separated features peaking at 570 and 620 nm which are attributable to nothing but a square-planar chromophore, $Cu_AN_2O_2$, and a square-pyramidal chromophore, $Cu_BN_3O_2$, respectively. Indeed, a literature survey[2,4c,10,14,15] shows that, in all the structurally characterized binuclear copper(II) complexes involving an oxalato- (or oxamato-) bridge and triamines as complementary ligands, two ideal geometries have to be considered, *i.e.* square pyramidal or trigonal bipyramidal, the former being preferred in the absence of steric interaction created by the triamines as is the case for **(8)**.

The ligand-field spectrum of complex **(9)**, with one maximum located at 636 nm, is consistent with the occurrence of two copper ions in a nearly square-pyramidal geometry.[2] In this instance, the two equatorial planes of the $CuN_2O_2$ type would be virtually parallel.

No unambiguous conclusion can be extracted from the electronic spectra of complexes **(5)**—**(7)**. These spectra display a rather broad absorption peaking at almost the same position ($\approx$600 nm) in the three cases. This unexpected constancy could be tentatively ascribed to the presence of two overlapping absorptions. Despite many attempts, no resolved spectrum has yet been obtained. By extension of the previous data, we think that the $Cu_AN_2OX$ chromophores adopt a nearly square-planar geometry. As for the geometry of the second ion, $Cu_B$, the possibility of axial ligation of a $ClO_4^-$ anion or intermolecular interaction cannot be ruled out. However, the i.r. spectra of

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* A slight tetrahedral deformation leading to a 'compressed tetrahedron' does not modify the nature of the ground state [B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55] so that the conclusions concerning the magnetic properties remain valid.

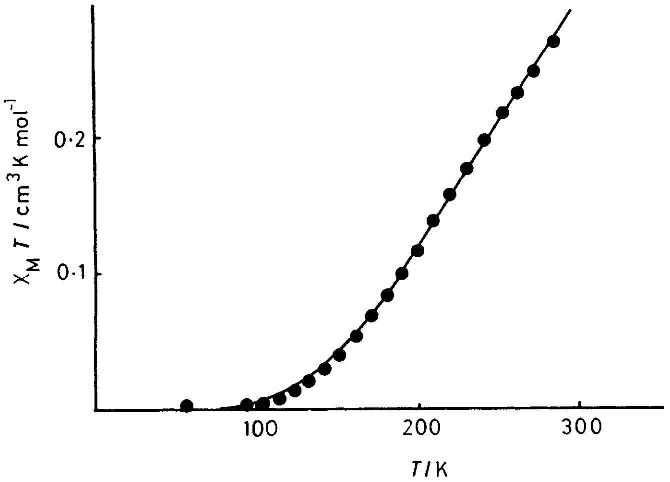

**Figure 3.** Experimental (●) and calculated (—) temperature dependence of $\chi_M T$ for complex (**5**). Calculated with $J = -470$ cm$^{-1}$, $g = 2.12$, $p = 0$, and $\chi_{corr.} = -240 \times 10^{-6}$ c.g.s. units

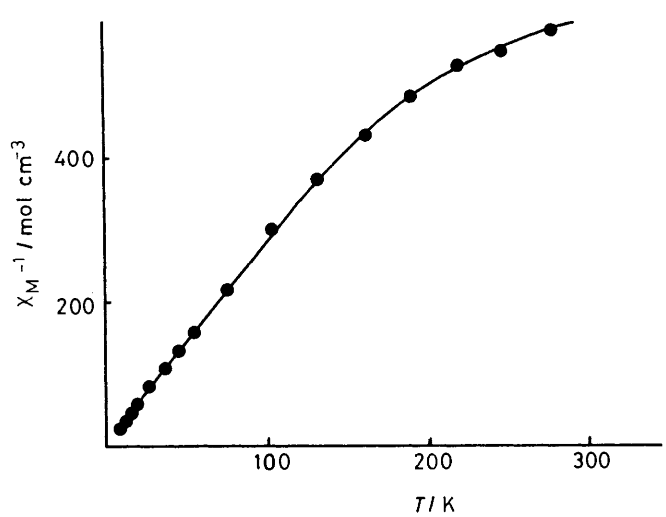

**Figure 4.** Experimental (●) and calculated (—) inverse of the molar susceptibility *versus* $T$ for complex (**10**). Calculated with $J = -370$ cm$^{-1}$, $g = 2.05$, $\theta = -1$ K, and $\chi_{corr.} = -200 \times 10^{-6}$ c.g.s. units

(**5**)—(**7**) show a broad band at 1 090 cm$^{-1}$ and a sharper one at 623 cm$^{-1}$, attributed to the perchlorate ($\nu_3$ and $\nu_4$), respectively.[20] The lack of any splitting would be consistent with a non-co-ordinated tetrahedral $ClO_4^-$.[21]

We have previously indicated that, according to the observed $\lambda_{max.}$, the most likely environment for the copper ions in the trinuclear complexes (**10**)—(**12**) is square planar. This implies that in (**11**) and (**12**) the water molecules revealed by analysis and i.r. spectra are co-ordinated to the zinc atom. This is in accord with the absence of water in the homotrinuclear complex (**10**) and with the affinity of zinc for oxygenated ligands so that the zinc atom fixes two water molecules to complete an octahedral co-ordination. This environment makes unlikely an intermolecular interaction that could raise the co-ordination of copper to five in (**11**) and (**12**). Such an interaction is still possible in (**10**) but should be sufficiently feeble not to give a significant modification of the electronic spectrum. Due to the neutrality of (**10**), an axial co-ordination (or semi-co-ordination) of an anionic ligand is ruled out.

*Magnetic Susceptibilities.*—For complex (**1**), analysis of the temperature variation of the inverse susceptibility with use of a Curie–Weiss law [$\chi^{-1} = (T - \theta)/C$] yields a $C$ value of 0.43 cm$^3$ K mol$^{-1}$ which corresponds to $g = 2.13$ and a $\theta$ value of $-0.55$ K. From the small negative value of $\theta$, it can be estimated that a slight antiferromagnetic interaction ($|J| \leqslant 1$ cm$^{-1}$) is operative between the mononuclear entities in accordance with the short intermolecular Cu $\cdots$ Cu distances evidenced in the structural study.

Very similar variations of the molar susceptibility are observed for the four binuclear complexes (**4**)—(**7**). In the four cases we have low values of $\chi_M$ and a maximum of $\chi_M$ at temperatures higher than room temperature, while for complex (**8**) the maximum occurs at 120 K. In one instance, (**4**), a Curie tail at low temperature supports the presence of a small amount ($p = 0.2\%$) of uncoupled (paramagnetic) impurity. The experimental data, corrected for diamagnetism, were fitted to the Bleaney–Bowers relation. Surprisingly, in order to obtain a satisfactory fit (Figure 3), it was necessary to allow the temperature-independent paramagnetism (t.i.p.) to vary. The resulting values [0 for (**4**), (**5**), and (**7**) and 30 × 10$^{-6}$ for (**6**)] differ significantly from the generally retained estimation of 60 × 10$^{-6}$ c.g.s. units per Cu atom. This probably reflects the uncertainty in estimating diamagnetic corrections which, for these binuclear complexes, are of the same order of magnitude as the uncorrected molar susceptibilities. Another possible explanation would originate in the choice of the same $g$ values for both copper atoms. However, this explanation does not hold for complex (**4**). Finally, we chose to fit these uncorrected data with the form (1) of Bleaney–Bowers equation, the diamagnetic

$$\chi_M = \frac{2N\beta^2 g^2}{kT}[3 + \exp(-J/kT)]^{-1}(1 - p) + \frac{N\beta^2 g^2}{kT} \cdot p + \chi_{corr.} \quad (1)$$

correction and the t.i.p. being included in the term $\chi_{corr.}$. The resulting values are $J = -550$ cm$^{-1}$ and $g = 2.12$ for (**4**), $J = -470$ cm$^{-1}$ and $g = 2.12$ for (**5**), $J = -492$ cm$^{-1}$ and $g = 2.12$ for (**6**), $J = -495$ cm$^{-1}$ and $g = 2.10$ for (**7**), and $J = -148$ cm$^{-1}$ and $g = 2.15$ (t.i.p. = 120 × 10$^{-6}$ c.g.s. units) for (**8**). In marked contrast with the behaviour of the aforementioned binuclear complexes, the thermal variation of the susceptibility of (**9**) can be accurately represented by a Curie–Weiss law with $C = 0.846$ cm$^3$ K mol$^{-1}$ ($g = 2.10$) and $\theta = -0.46$ K.

The data obtained for the tricopper complex (**10**) are represented in Figure 4 in the form of the temperature dependence of the inverse molar susceptibility (corrected for diamagnetic contributions and t.i.p.) which points to a Curie–Weiss behaviour at low temperature with $C = 0.39$ cm$^3$ K mol$^{-1}$ ($g = 2.04$) and $\theta \approx -0.9$ K. When the complex is cooling from room temperature, the moment $\mu$ slightly decreases from 2.08 B.M. to reach a plateau below 100 K with $\mu \approx 1.7$ B.M. A further decrease to 1.6 B.M. is observed at very low temperatures (<20 K). These data can easily be understood. For a trinuclear species involving individual spins equal to $\frac{1}{2}$, the low-lying states are two doublets and a quartet. In the temperature range 20—100 K the linear dependence of $\chi_M^{-1}$ *vs.* $T$ and the plateau observed for $\mu$ are consistent with a doublet ground state. The slight decrease of $\mu$ below 20 K is indicative of a non-negligible antiferromagnetic interaction between trinuclear entities. However, this interaction is actually small as demonstrated by the low value of $\theta$.

A quantitative analysis of the data is readily achieved in the case of an ideal geometry where the two terminal copper atoms Cu(1) and Cu(3) are symmetry-related.[22] In this case, two coupling constants have to be considered, *i.e.* $J = J_{12} = J_{23}$ and $j = J_{13}$. With the additional assumption that the three multiplets have the same $g$ value, the expression of the susceptibility is (2). As noted by previous authors,[10] the quality

$$\chi_M = \frac{N\beta^2 g^2}{2k(T - \theta)} \left[\frac{1 + \exp(J - j/kT) + 10\exp(3J/2kT)}{1 + \exp(J - j/kT) + 2\exp(3J/2kT)}\right] + \chi_{corr.} \quad (2)$$

of the fit is almost independent of the value of $j$ which, therefore, cannot be determined. An excellent agreement between calculated and experimental values (Figure 4) is obtained by imposing $j = 0$, while the other parameters are $g = 2.05$, $\theta = -1.0$ K, $J = -370$ cm$^{-1}$, and $\chi_{corr.} = -200 \times 10^{-6}$ c.g.s. units.

In order to estimate the interaction between the terminal copper atoms Cu(1) and Cu(3) in complex (**10**), we have studied the magnetic properties of (**11**) in which the central atom is the diamagnetic zinc. For this complex the molar susceptibility follows a Curie–Weiss law ($C = 0.88$ cm$^3$ K mol$^{-1}$, $\theta = -2.01$ K) in the whole temperature range (275—4.7 K). The moment $\mu$ is almost constant and equal to 2.60 B.M. from 275 to 45 K. Below 40 K, $\mu$ decreases and reaches 2.13 B.M. at 4.7 K. This decrease and the non-zero value of $\theta$ in the Curie–Weiss representation can be ascribed to the occurrence of intramolecular and/or intermolecular interactions. Due to the weakness of the interaction, it is difficult to distinguish between the two possibilities. However, the presence of two water molecules co-ordinated to the central zinc atom makes an intermolecular interaction unlikely. Indeed, fitting the experimental data by the theoretical law for a pair of copper(II) ions leads to $J \leqslant -1.0$ cm$^{-1}$ with $g = 2.16$. The proper conclusion is that the antiferromagnetic interaction between the non-adjacent copper(II) ions is at the best very weak and equal to 1.0 cm$^{-1}$.

The magnetic data characterizing the complexes under study are very similar to those for similar complexes.[2,4,6,10] These analogies support the conclusions suggested by the analytical and spectroscopic data regarding the structure of the complexes.

As expected from previous work,[2,4,6,10,23] the $J$ values for the dimeric Cu(L$^i$)CuL complexes depend on the nature of the $H_3L^i$ and L ligands. Within the framework of the localized non-orthogonal orbitals model,[23] it has been shown that in binuclear complexes with extended bridging ligands the ferromagnetic contribution is very small and the magnitude of the antiferromagnetic interaction depends on the square of the overlap integral between the magnetic orbitals. Other models[2,24] as well as an *ab initio* scheme[25] have been used to understand the factors that govern the magnitude of the magnetic interaction in $\mu$-oxalato-copper complexes.

For complexes (**4**)—(**7**) we can infer from the e.s.r. and electronic spectra that the geometry of the copper ion is square planar or, eventually, square pyramidal. In both cases, the magnetic orbitals of the $d_{x^2-y^2}$ type point from the metal centres towards the four nearest neighbours. They are located in the same plane and overlap on each side of the bridge, favouring strong antiferromagnetic coupling. Interestingly, the greatest $J$ value ($-550$ cm$^{-1}$) is observed for (**4**) in which the oxamide bridge has the *trans* configuration and the two copper atoms the same environment so that the two magnetic orbitals are equal in energy. Considering complexes (**5**)—(**7**), we note that substituting NH and NMe groups for O at the X position of the bridge causes a slight increase of the antiferromagnetic interaction $J$ between the two copper atoms from $-470$ (**5**) to $-492$ (**6**) and $-495$ cm$^{-1}$ (**7**). This is in accordance with the previously reported rationale,[6,26] concerning the influence of the electronegativity of the atoms of the bridge on the magnitude of the antiferromagnetic coupling.

In the case of complex (**8**) the ligand-field spectrum points to a significant difference between the two copper ions. As already noted, one of the ions, namely Cu$_A$, has a square-planar geometry, whereas the most likely limiting geometry for the second ion, Cu$_B$, is square pyramidal with the three nitrogen atoms of diethylenetriamine and one oxygen of the bridge forming the equatorial plane. The second oxygen of the bridge is at the apex of the pyramid. In this instance, the two magnetic orbitals would be located in the planes (Cu$_A$O$_2$N$_2$) and (Cu$_B$ON$_3$), respectively and could overlap only on one side of the bridge. This would cause the magnitude of the interaction to be roughly one-fourth of what it was in the previous case where the overlap occurs on both sides of the bridge. Actually, comparing the $J$ values for (**5**) and (**8**) leads to a reduction factor of *ca.* 0.3, in reasonable agreement with the expected value of 0.25. The possibility remains that Cu$_B$ acquires some trigonal-bipyramidal character with the resulting presence of some $d_{z^2}$ character in the corresponding magnetic orbital and a non-zero spin density on the apical site. This would allow the magnetic orbitals to overlap again on each side of the bridge, giving a $|J|$ value intermediate between those attributable to the two limiting geometries, *i.e.* square-planar and square-pyramidal. The agreement observed between the experimental and the expected values of the reduction factor (see above) shows that Cu$_B$ in complex (**8**) is essentially square pyramidal.

The very weak interaction ($J \leqslant -1$ cm$^{-1}$) actually observed in the case of complex (**9**) is consistent with the two copper ions having a square-pyramidal geometry. The magnetic orbitals would then be located in largely separated parallel planes and would not interact. A slight modification of the geometry of the metal ions from square pyramidal to trigonal bipyramidal could explain the non-zero $J$ value.

In the trinuclear complex (**10**) the interaction between adjacent copper atoms is weaker ($J = -370$ cm$^{-1}$) than in the related binuclear complex where the magnetic orbitals have the same relative orientations. This may be due to the fact that the bridging network, Cu$_A$(C$_2$N$_2$O$_2$)Cu$_B$, is not rigorously planar. However, the $J$ value observed for (**10**) is slightly greater than the value ($-353.6$ cm$^{-1}$) recently reported for a similar complex,[10] which, however, has a bis trinuclear structure. Judging from the heterotrinuclear complex (**11**), the interaction between the terminal copper ions is, at the best, very weak.

## Experimental

*Ligand Preparation.*—$H_3L^{1'}$. To a stirred solution of diethyl oxalate (15 g, 0.1 mol) in diethyl ether (100 cm$^3$) was added 7-amino-4-methyl-5-aza-3-hepten-2-one[27] (5 g, 0.035 mol). A few minutes later a white precipitate appeared. The solid was filtered off, dissolved in $CH_2Cl_2$ (200 cm$^3$), and the resulting solution was filtered again. Removal of the solvent yielded a white powder (7 g, 82%) (Found: C, 54.4; H, 7.6; N, 12.0. $C_{11}H_{18}N_2O_4$ requires C, 54.5; H, 7.4; N, 11.6%). N.m.r. ($CDCl_3$): $\delta_H$ 1.36 (3 H, t, $CH_3$), 1.92 (3 H, s, $CH_3$), 1.98 (3 H, s, $CH_3$), 3.44 (4 H, m, $CH_2$), 4.32 (2 H, q, $CH_2$), 4.99 (1 H, s, CH), 7.58 (1 H, t, NH), and 10.84 (1 H, t, NH).

$H_3L^2$. 7-Amino-4-methyl-5-aza-3-hepten-2-one (5 g, 35.2 mmol) and ethyl oxamate (4.1 g, 35.2 mmol) were mixed together in $CH_2Cl_2$ and heated for 15 min. A white precipitate appeared upon cooling. It was filtered off, washed with ethanol, and dried (6.5 g, 86%) (Found: C, 50.5; H, 7.1; N, 19.9. $C_9H_{15}N_3O_3$ requires C, 50.7; H, 7.0; N, 19.7%). This ligand can also be prepared by reaction of a methanolic solution of $H_3L^{1'}$ with an aqueous $NH_3$ solution. N.m.r. [$(CD_3)_2SO$]: $\delta_H$ 1.96 (3 H, s, $CH_3$), 2.02 (3 H, s, $CH_3$), 3.43 (4 H, m, $CH_2$), 5.05 (1 H, s, CH), 7.89 and 8.15 (2 H, br, s, $NH_2$), 8.93 (1 H, t, NH), and 10.70 (1 H, t, NH).

$H_3L^3$. To the ligand $H_3L^{1'}$ (2 g, 8.3 mmol) dissolved in $CH_2Cl_2$ (50 $cm^3$) was added a slight excess of a 8 mol $dm^{-3}$ solution of methylamine in absolute ethanol (1.3 $cm^3$). After heating and stirring for 15 min, a white precipitate appeared upon cooling. The product was filtered off and dried (1.8 g, 96%) (Found: C, 52.4; H, 7.4; N, 18.2. $C_{10}H_{17}N_3O_3$ requires C, 52.9; H, 7.5; N, 18.5%). N.m.r. [$(CD_3)_2SO$]: $\delta_H$ 1.96 (3 H, s, $CH_3$), 2.02 (3 H, s, $CH_3$), 2.79 (3 H, d, $CH_3$), 3.58 (4 H, m, $CH_2$), 5.05 (1 H, s, CH), 8.80 (1 H, q, NH), 8.96 (1 H, t, NH), and 10.70 (1 H, t, NH).

$H_4L^4$. To a stirred solution of diethyl oxalate (2.6 g, 17.6 mmol) in $CH_2Cl_2$ (50 $cm^3$) was added 7-amino-4-methyl-5-aza-3-hepten-2-one (5 g, 35.2 mmol). The solution ws refluxed for 15 min. After cooling, the white powder which appeared was filtered off and dried (5.8 g, 97%) (Found: C, 56.4; H, 7.8; N, 16.4. $C_{16}H_{26}N_4O_4$ requires C, 56.8; H, 7.7; N, 16.6%). N.m.r. [$(CD_3)_2SO$]: $\delta_H$ 1.95 (3 H, s, $CH_3$), 2.01 (3 H, s, $CH_3$), 3.39—3.48 (4 H, m, $CH_2$), 5.18 (1 H, s, CH), 9.05 (2 H, t, NH), and 10.70 (2 H, t, NH).

*Preparation of the Complexes.*—$Na[CuL^1(H_2O)]\cdot0.33H_2O$, (**1**). To $H_3L^{1'}$ (0.5 g, 2.07 mmol) in MeOH (40 $cm^3$) was added an aqueous solution (10 $cm^3$) of NaOH (0.25 g, 6.2 mmol). Copper ethanoate, $Cu(O_2CMe)_2\cdot H_2O$ (0.41 g, 2.07 mmol), in water (20 $cm^3$) was then added dropwise, giving a purple solution. The filtered solution was concentrated to 40 $cm^3$ and acetone (100 $cm^3$) was added. Crystals appeared 72 h later (0.33 g, 50%) (Found: C, 33.3; H, 4.2; Cu, 20.0; N, 8.8; Na, 7.3. $C_{27}H_{41}Cu_3N_3Na_3O_{16}$ requires C, 33.6; H, 4.2; Cu, 19.8; N, 8.7; Na, 7.2%).

$Na[CuL^2]\cdot2H_2O$, (**2**). To $H_3L^2$ (0.9 g, 2.39 mmol) suspended in MeOH (40 $cm^3$) was added an aqueous solution (10 $cm^3$) of NaOH (0.28 g, 7.04 mmol). Copper ethanoate (0.47 g, 2.35 mmol) in water (20 $cm^3$) then was added dropwise, giving a red solution. Acetone (60 $cm^3$) was added to the filtered solution, giving a powdered red product (0.55 g, 70%) (Found: C, 32.1; H, 4.8; Cu, 18.6; N, 12.3; Na, 6.8. $C_9H_{16}CuN_3NaO_5$ requires C, 32.4; H, 4.8; Cu, 19.0; N, 12.6; Na, 6.9%).

$Na[CuL^3]\cdot2H_2O$, (**3**). Complex (**3**) was obtained with the same procedure. Yield: 75% (Found: C, 34.2; H, 5.4; Cu, 17.9; N, 11.8; Na, 6.5. $C_{10}H_{18}CuN_3NaO_5$ requires C, 34.6; H, 5.2; Cu, 18.3; N, 12.1; Na, 6.6%).

$[Cu_2L^4]$, (**4**). The ligand $H_4L^4$ (0.5 g, 1.5 mmol) and copper ethanoate (0.6 g, 3 mmol) in MeOH (40 $cm^3$) were stirred at ambient temperature for 2 h. The purple precipitate which appeared was filtered off, washed with MeOH, and recrystallized from $CH_2Cl_2$ (0.55 g, 80%) (Found: C, 41.7; H, 4.8; Cu, 27.1; N, 12.0. $C_{16}H_{22}Cu_2N_4O_4$ requires C, 41.6; H, 4.8; Cu, 27.5; N, 12.1%).

$[CuL^1Cu(bipy)]ClO_4$, (**5**). Complex (**1**) (0.32 g, 1 mmol) and $[Cu(bipy)_2][ClO_4]_2$[28] (0.57 g, 1 mmol) were mixed in MeOH (40 $cm^3$) and heated. The solution became brown and a few minutes later a brown precipitate appeared. Filtration, washing with MeOH, and drying afforded the desired product (0.55 g, 93%) (Found: C, 38.2; H, 3.0; Cl, 5.9; Cu, 20.6; N, 9.1. $C_{19}H_{19}ClCu_2N_4O_8$ requires C, 38.4; H, 3.2; Cl, 6.0; Cu, 21.4; N, 9.4%). The same procedure yielded $[CuL^2Cu(bipy)]ClO_4$ (**6**) (92%) and $[CuL^3Cu(bipy)]ClO_4$ (**7**) (95%) [Found: C, 38.0; H, 3.4; Cl, 6.2; Cu, 21.2; N, 11.6. $C_{19}H_{20}ClCu_2N_5O_7$, (**6**), requires C, 38.5; H, 3.4; Cl, 6.0; Cu, 21.4; N, 11.8. Found: C, 39.3; H, 3.7; Cl, 6.0; Cu, 20.3; N, 11.5. $C_{20}H_{22}ClCu_2N_5O_7$, (**7**), requires C, 39.6; H, 3.6; Cl, 5.8; Cu, 20.9; N, 11.5%].

$[CuL^1Cu(dien)]ClO_4\cdot2H_2O$, (**8**). To a MeOH solution of diethylenetriamine (0.16 g, 1.55 mmol) and copper perchlorate $Cu(ClO_4)_2\cdot6H_2O$ (0.57 g, 1.55 mmol) was added a MeOH solution of complex (**1**) (0.5 g, 1.55 mmol). After stirring for 1 h, the blue precipitate which appeared was filtered off and dried (0.6 g, 71%) (Found: C, 26.5; H, 4.8; N, 12.9. $C_{13}H_{28}ClCu_2N_5O_{10}$ requires C, 27.1; H, 4.8; N, 12.1%).

$[(CuL')_2(\mu\text{-}C_2O_4)]\cdot2H_2O$, (**9**). To $[\{CuL'(\mu\text{-}MeCO_2)\}_2]$[29] (0.5 g, 1.22 mmol) dissolved in water (30 $cm^3$) was added dropwise an aqueous solution (30 $cm^3$) of sodium oxalate (0.16 g, 1.22 mmol). The bright blue precipitate which appeared very quickly was filtered off, washed with water and methanol, and dried (0.6 g, 93%) (Found: C, 36.2; H, 5.5; Cu, 23.2; N, 10.5. $C_{16}H_{30}Cu_2N_4O_8$ requires C, 36.0; H, 5.6; Cu, 23.8; N, 10.5%).

$[(CuL^1)_2Cu]$, (**10**). Complex (**1**) (0.5 g, 1.55 mmol) dissolved in MeOH (20 $cm^3$) was added at once to copper ethanoate (0.15 g, 0.77 mmol) dissolved in water (20 $cm^3$). A brown precipitate appeared quickly. It was filtered off, washed with methanol, and dried (0.4 g, 84%) (Found: C, 35.6; H, 3.7; Cu, 30.3; N, 9.0. $C_{18}H_{22}Cu_2N_4O_8$ requires C, 35.3; H, 3.6; Cu, 31.1; N, 9.1%).

$[(CuL^1)_2Zn]\cdot2H_2O$, (**11**). Use of $ZnBr_2$ instead of copper ethanoate yielded the desired compound as a purple powder (70% yield) (Found: C, 33.1; H, 3.8; Cu, 19.4; N, 8.6; Zn, 10.2. $C_{18}H_{26}Cu_2N_4O_{10}Zn$ requires C, 33.2; H, 4.0; Cu, 19.5; N, 8.6; Zn, 10.0%).

$[(CuL^2)_2Zn]\cdot2H_2O$, (**12**). (73% yield) (Found: C, 32.9; H, 4.4; Cu, 19.1; N, 12.8; Zn, 9.7. $C_{18}H_{28}Cu_2N_6O_8Zn$ requires C, 33.3; H, 4.3; Cu, 19.6; N, 13.0; Zn, 10.0%).

*Physical Measurements.*—Microanalyses were performed by the Service Central du CNRS, Lyon. Infrared spectra of KBr discs were recorded using a Perkin-Elmer 577 spectrometer, visible spectra using a Varian Cary 2300 spectrophotometer. Magnetic susceptibility data were collected on powdered samples of the different compounds with use of a Faraday-type magnetometer using mercury tetra(thiocyanato)cobaltate (susceptibility at 20 °C, $16.44 \times 10^{-6}$ $cm^3$ $mol^{-1}$) as a standard. Data were corrected for the diamagnetism of the ligands, cations, and anions estimated from Pascal constants, and for t.i.p. The molar susceptibilities $\chi_M$, which are expressed in c.g.s. units in the present work, should be multiplied by $4\pi \times 10^{-6}$ to convert into S.I. units. E.s.r. spectra were recorded at *X*-band frequency (9.4—9.5 GHz) with a Bruker 200 TT spectrometer. Proton n.m.r. data of the ligands were run on a Bruker WH 90 spectrometer using $SiMe_4$ as internal reference.

*X-Ray Crystal-structure Determination of* $Na[CuL^1(H_2O)]\cdot0.33H_2O$ (**1**).—*Crystal data.* $C_{27}H_{41}Cu_3N_6Na_3O_{16}$, $M$ = 965.3, monoclinic, space group $P2_1/n$(no. 14), $a$ = 21.705(2), $b$ = 9.380(1), $c$ = 19.131(2) Å, $\beta$ = 110.17(1)°, $U$ = 3 656(1) Å$^3$, $D_m$ = 1.76, $Z$ = 4, $D_c$ = 1.75 g $cm^{-3}$, $F$(000) = 1 972, Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å, $\mu$ = 18.5 $cm^{-1}$, $T$ = 293 K.

*Data collection and processing.* A brown parallelepiped crystal of dimensions 0.40 × 0.35 × 0.10 mm was centred on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell dimensions were determined from the setting angles of 25 reflections in the range $11 < \theta < 14°$. A data set of 7 376 reflections ($1.5 < \theta < 26°$, $\pm h, k, l$) was recorded as described previously[30] by the $\theta$—$2\theta$ scan technique (scan width $0.80 + 0.35 \tan\theta$, scan speed 1.1—10.1° $min^{-1}$). The intensities of three standard reflections monitored every 2 h showed no significant variation during data collection. Data reflections were corrected for Lorentz and polarization effects[31] and for absorption[32] (maximum, minimum transmission factors 1.00, 0.84). Equivalent reflections ($hk0$ and $\bar{h}k0$) were merged ($R_{av.}$ = 0.015). 4 650 Reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered 'observed' and used for the structure solution and least-squares refinement.

*Structure determination.* The structure was solved by the heavy-atom method. After locating the three Cu atoms by a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps using SHELX[33] enabled all the non-hydrogen atoms in the structure to be located. They were refined anisotropically. All hydrogen atoms were located on a difference Fourier map. Water molecule hydrogens were refined isotropically with a fixed thermal parameter. All other hydrogens were introduced in calculations in constrained geometry (C–H 0.97 Å) with fixed isotropic thermal parameters. Neutral-atom scattering factors were used, those for non-hydrogen atoms being corrected for anomalous dispersion ($f'$, $f''$).[34] Unit weights were applied and gave satisfactory weight analysis. In the last full-matrix least-squares refinement cycle no shift was greater than 0.2 times the estimated standard deviation for non-hydrogen atom parameters and the final $R$ value was 0.024 ($R' = 0.028$). A final Fourier difference map showed a residual electron density of 0.3 e Å$^{-3}$. All calculations were performed on a VAX-11/730 DEC computer. Atomic co-ordinates 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.

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