Crystal and Molecular Structure and Magnetic Properties of Linear Trimeric Copper(II) Complexes with Predominant Ferromagnetic Exchange Interaction†

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The crystal and molecular structure of bis(μ-benzoato-*O,O'*)-bis(benzoato-*O*)-bis[μ-(2-diethylamino)ethanolato-*O,N*]-bis(methanol)tricopper(II), (**1**), has been determined from single-crystal *X*-ray diffraction data and refined to $R = 0.045$ using 2 706 independent reflections. The space groups is $P\bar{1}$; $a = 14.793(3)$, $b = 10.533(3)$, $c = 8.127(2)$ Å, $\alpha = 73.84(1)$, $\beta = 84.40(1)$, $\gamma = 69.15(1)°$, and $Z = 1$. The Cu(1)–Cu(2) distance is 3.188(1) Å; the terminal copper atoms are square planar and the central copper is octahedrally co-ordinated. The structure of (**1**) is compared to that of bis(μ-benzoato-*O,O'*)-bis(benzoato-*O*)-bis[μ-(2-dibutylamino)ethanolato-*O,N*]-bis(ethanol)-tricopper(II), (**2**), reported previously. The molecular structures show no significant differences; their molecular packings in the crystalline state are discussed. The magnetic moments and susceptibilities of (**1**) and (**2**) were measured in the temperature range 5.1—298.6 K and reveal a predominant ferromagnetic exchange interaction. The exchange parameters ($\hat{H} = -2\sum_{i<j} J_{ij}\hat{S}_i\hat{S}_j$) obtained by fit procedures were $J_{12} = 30.1(5.0)$, $J_{13} = -6.1(3.0)$ cm^{-1}, $g = 2.09(0.02)$, $\theta = -1.0(0.5)$ K for (**1**) and $J_{12} = 28.7(5.0)$, $J_{13} = -7.5(3.0)$ cm^{-1}, $g = 2.09(0.02)$, $\theta = -2.3(0.5)$ K for (**2**).

Among the exchange-coupled copper(II) complexes the dimeric, tetrameric, and polymeric compounds are extensively studied, but the number of magnetically as well as structurally investigated trimeric compounds is limited. The molecular structures have revealed four kinds of trinuclear copper complexes. The equilateral-triangular[1–9] as well as the isosceles-triangular[10–19] systems exhibit, as far as the magnetic behaviour is studied, antiferromagnetic interactions except a μ_3-carbonato-bridged trimer for which a ferromagnetic ground state was found.[5] Only five examples of isolated linear trimers[20–32] are magnetically described. Four of these compounds[20–23] show an antiferromagnetic exchange coupling between neighbouring centres.[22,29–32] The fifth compound,[24] in which the copper centres are connected by a hydrogen-bond system, is nearly uncoupled. Moreover, chains of different types of trimers[33–38] were found and partly magnetically characterized.

In the present work we report the results of our studies on two linear trimeric complexes formed by copper(II) benzoate and dialkylaminoethanol. The structural and the magnetic properties of bis(μ-benzoato-*O,O'*)-bis(benzoato-*O*)-bis[μ-(2-diethylamino)ethanolato-*O,N*]-bis(methanol)tricopper(II), (**1**), are investigated as well as the magnetic properties of the related trimer bis(μ-benzoato-*O,O'*)-bis(benzoato-*O*)-bis[μ-(2-dibutylamino)ethanolato-*O,N*]-bis(ethanol)tricopper(II), (**2**), of which the structure was previously reported.[25]

Results and Discussion

Molecular Structure.—The molecular structure of (**1**) is shown in Figure 1. Final positional parameters are given in Table 1; Table 2 contains selected bond lengths and angles. The three copper atoms form an exact linear arrangement with Cu(2) on the inversion centre and a Cu(1)–Cu(2) distance of 3.188(1) Å. The co-ordination sphere is formed by four benzoato-groups, acting as unidentate or bidentate ligands (two of each), two diethylaminoethanolato-groups, and two methanol molecules. Two adjacent copper centres are bridged by the oxygen atom O(1) of the diethylaminoethanolato-ligand and by the two carboxylato-oxygen atoms, O(2) and O(3), of a benzoato-ligand. The terminal copper atom Cu(1) has distorted square-planar co-ordination, by O(1), O(2), O(4), and N(1) (plane A, Table 3). Cu(2) is octahedrally co-ordinated by O(1), O(1'), O(3), and O(3'), (symmetry code for primed atoms $-x$, $-y$, $-z$), which form an exact plane B and the methanolic oxygen atoms O(6) and O(6') [Cu(2)–O(6) 2.478(4) Å]. Thus the different co-ordination numbers at the terminal and central copper atoms of the trimer can be summarized as a four–six–four co-ordination sequence. The dihedral angle φ_{AB} between the two equatorial co-ordination planes A and B is 60.7°. The planes C and D (Table 3), representing the carboxylato- and alkoxo-bridges form a dihedral angle φ_{CD} of 111.7°.

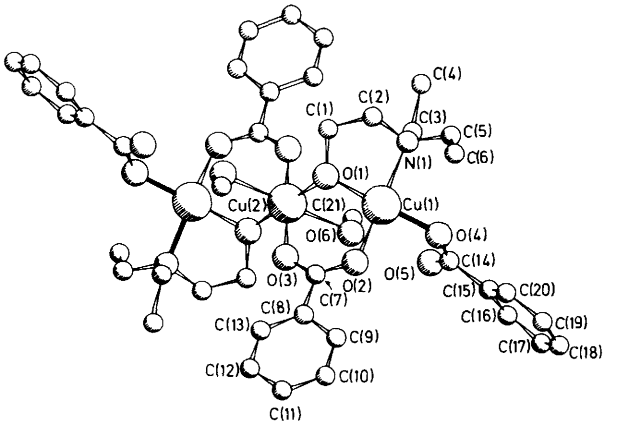

Figure 1. Molecular structure of (**1**)

The distance Cu(1) ··· O(6) [2.983(5) Å] appears to be too long to present a bonding character. However, the O(5) ··· O(6)

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† *Supplementary data available* (No. SUP 56327, 8 pp.): H-atom co-ordinates, thermal parameters, experimental and calculated magnetic susceptibilities and magnetic moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Positional parameters with estimated standard deviations in parentheses for (**1**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu(1)	0.1942(1)	0.0562(1)	−0.1455(1)	C(7)	0.1844(4)	−0.1364(5)	0.1862(6)
Cu(2)	0.0000	0.0000	0.0000	C(8)	0.2429(3)	−0.2475(5)	0.3347(6)
O(1)	0.1021(2)	−0.0247(3)	−0.1703(4)	C(9)	0.3358(4)	−0.2563(6)	0.3623(7)
O(2)	0.2280(2)	−0.0632(4)	0.0851(4)	C(10)	0.3887(4)	−0.3557(7)	0.5025(7)
O(3)	0.0985(2)	−0.1258(4)	0.1773(4)	C(11)	0.3485(5)	−0.4448(7)	0.6148(8)
O(4)	0.2812(3)	0.1477(4)	−0.1188(5)	C(12)	0.2563(5)	−0.4371(7)	0.5881(8)
O(5)	0.1783(3)	0.2887(5)	0.0212(7)	C(13)	0.2031(4)	−0.3387(6)	0.4480(7)
O(6)	0.0237(3)	0.2121(4)	0.0357(5)	C(14)	0.2588(4)	0.2347(6)	−0.0287(7)
N(1)	0.1811(3)	0.1380(4)	−0.4029(5)	C(15)	0.3410(4)	0.2701(5)	0.0172(6)
C(1)	0.0817(4)	−0.0110(6)	−0.3429(6)	C(16)	0.3227(4)	0.3772(6)	0.0983(7)
C(2)	0.1589(5)	0.0293(7)	−0.4563(7)	C(17)	0.3992(6)	0.4053(8)	0.1451(8)
C(3)	0.0991(5)	0.2739(7)	−0.4259(8)	C(18)	0.4916(6)	0.3303(9)	0.1109(9)
C(4)	0.0584(7)	0.3437(9)	−0.6042(9)	C(19)	0.5112(4)	0.2261(8)	0.0336(8)
C(5)	0.2664(5)	0.1671(9)	−0.4965(8)	C(20)	0.4357(4)	0.1949(6)	−0.0158(7)
C(6)	0.3606(4)	0.0469(8)	−0.4578(10)	C(21)	−0.0593(4)	0.3359(7)	0.0095(9)

Table 2. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses for the copper environments in (**1**)

Cu(1)–Cu(2)	3.188(1)	O(1)–Cu(1)–N(1)	85.2(1)
		O(1)–Cu(1)–O(2)	92.5(1)
Cu(1)–N(1)	2.028(4)	O(2)–Cu(1)–O(4)	88.4(1)
Cu(1)–O(1)	1.897(3)	O(4)–Cu(1)–N(1)	94.7(2)
Cu(1)–O(2)	1.940(3)	O(2)–Cu(1)–N(1)	165.9(2)
Cu(1)–O(4)	1.919(3)	O(1)–Cu(1)–O(4)	176.6(2)
		Cu(1)–O(1)–Cu(2)	112.2(1)
Cu(2)–O(1)	1.944(3)	O(1)–Cu(2)–O(3)	88.1(1)
Cu(2)–O(3)	1.982(3)	O(1)–Cu(2)–O(6)	92.0(1)
Cu(2)–O(6)	2.478(4)	O(3)–Cu(2)–O(6)	91.8(1)

Table 3. Definitions of planes and least-squares planes in (**1**) with deviations (Å) of atoms from the plane

Plane A

O(1) 0.15, O(2) −0.15, O(4) 0.14, N(1) −0.14, Cu(1) 0.09*

Plane B

O(1), O(1′), O(3), O(3′)

Plane C

Cu(1) −0.06, O(2) 0.11, C(7) −0.04, O(3) −0.06, Cu(2) 0.05

Plane D

Cu(1), O(1), Cu(2)

Dihedral angles (°): φ_{AB} = 60.7, φ_{CD} = 111.7

* Atom not included in the calculation of the plane.

distance [2.664(7) Å] is a significant hydrogen bond. This is confirmed by the position of the methanolic hydrogen atom H[O(6)] found in the difference Fourier synthesis. Thus the alcohol molecule appears to stabilize the structure by fixing the non-co-ordinated benzoate oxygen atom in the hydrogen-bond system O(5) ··· O(6). Distances and angles within the ligands agree with those found in related compounds.

The molecular structures of the comparable parts of (**1**) and (**2**) show only insignificant differences. The replacement of the butyl group by an ethyl group at the aminoethanol nitrogen N(1) leads to a more linear O(2)–Cu(1)–N(1) arrangement [165.9(2)° in (**1**), 159.8(9)° in (**2**)]. A great influence of the different alkyl groups on the Cu(1)–O(1)–Cu(2) angle [well studied for alkoxo-bridged copper(II) dimers and tetramers [39–41]] was not found [112.2(1)° for (**1**), 111(1)° for (**2**)]. The dihedral angles φ_{AB} and φ_{CD} [60 and 111° respectively in (**2**)]* are similar. The parameters of the unit cell of (**2**) which we have determined show slight deviations from the reported [25] ones (see Experimental section) which might be caused by a temperature effect.

Crystal Packing.—Figure 2 shows a projection of (**1**) along [001]. The centres of the molecules in (**1**) are situated on 000; the phenyl groups of the unidentate benzoato-ligands are arrayed along [110], the phenyl groups of the bidentate ones point in the [$\bar{1}$10] direction. Although the intramolecular geometries in (**1**) and (**2**) are nearly the same, the space groups, $P\bar{1}$ and $P2_1/c$, differ. However, if the triclinic unit cell is transformed in a centred unit cell $\boldsymbol{a}'$, $\boldsymbol{b}'$, $\boldsymbol{c}'$ with $\boldsymbol{a}' = -\boldsymbol{c}'$, $\boldsymbol{b}' = 2\boldsymbol{a} - \boldsymbol{b}$, and $\boldsymbol{c}' = \boldsymbol{b}$ (A'-centred) the dimensions of the transformed cell [a' = 8.127(2), b' = 27.65(1), c' = 10.533(3) Å, α' = 90.01(1), β' = 106.16(1), γ' = 89.01(1)°] are comparable to those observed for (**2**). So the molecular centres in (**1**) are situated on nearly the same positions as in (**2**), related to the transformed cell.

Magnetic Properties.—The magnetic moments of (**1**) and the magnetic susceptibilities of (**2**) are shown in the temperature range 5.1—298.6 K [Figure 3(*a*) and (*b*)]. Both compounds reveal the same magnetic behaviour which is characteristic of predominant ferromagnetic spin coupling. The magnetic moments increase with decreasing temperature, reach maxima at 8 and 20 K for (**1**) and (**2**) respectively, and decrease with further cooling.

To characterize the exchange interaction in linear symmetric trimers the Hamilton operator (1) based on the isotropic HDvV

$$\hat{H} = -2J_{12}(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) - 2J_{13}\hat{S}_1\hat{S}_3 \qquad (1)$$

model may be written. The exchange integral J_{12} refers to two adjacent centres and J_{13} to the interaction between the terminal centres. The energies of the spin states are given in terms of $E(S_T, S^+)$ with total spin $S_T = S_1 + S_2 + S_3$ and $S^+ = S_1 + S_3$. For three interacting $S = \frac{1}{2}$ centres, a quartet state, $E(\frac{3}{2}, 1) = -J_{12} - \frac{1}{2}J_{13}$, and two doublet states, $E(\frac{1}{2}, 0) = \frac{3}{2}J_{13}$ and $E(\frac{1}{2},1) = 2J_{12} - \frac{1}{2}J_{13}$, are obtained. The temperature dependence of the magnetic susceptibility is obtained from van Vleck's equation. To take into account the decrease of the magnetic moments at low temperatures a Weiss constant θ is

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* Calculated from the given data.[25]

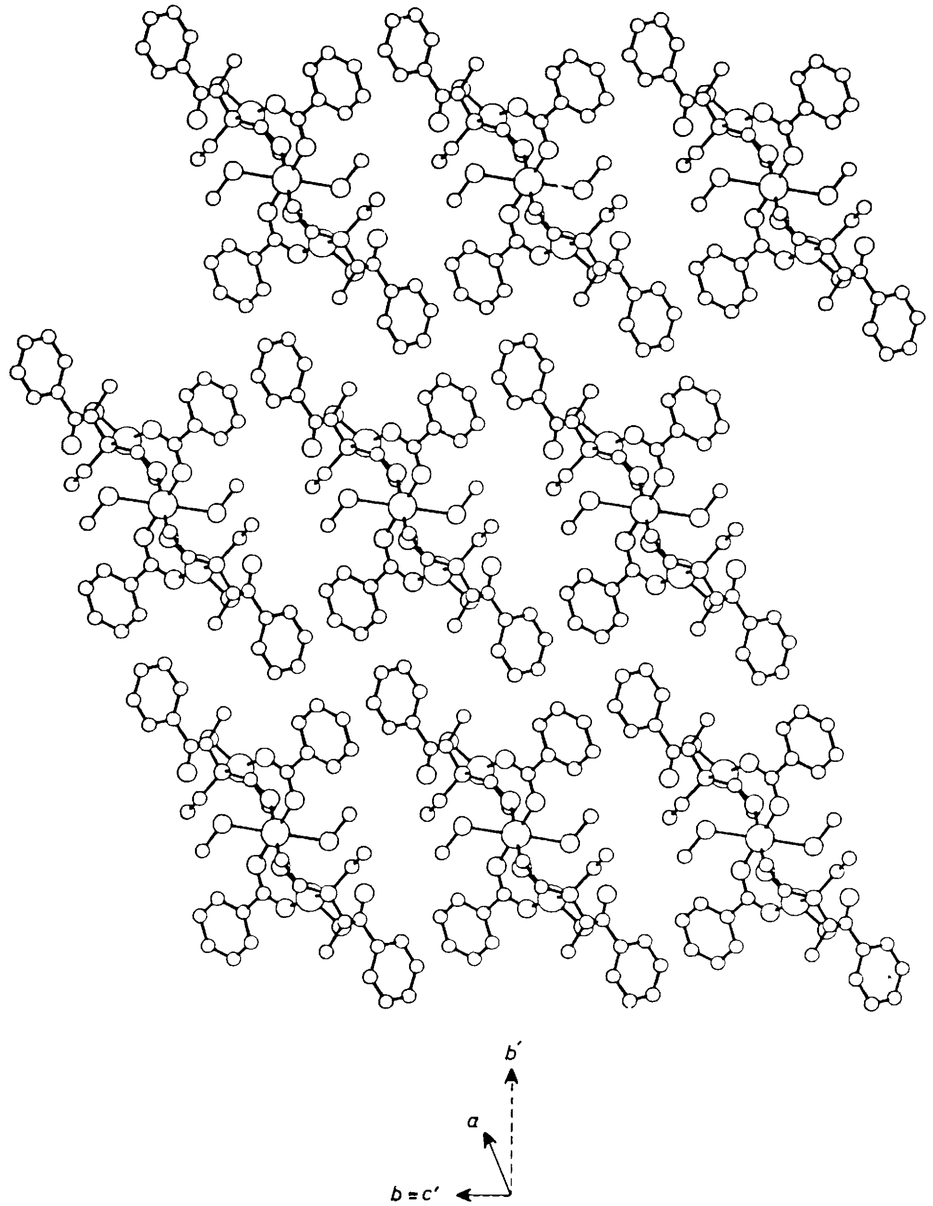

Figure 2. Crystal packing of (**1**): view along [001]; *a* and *b* are original axes, *b*′ and *c*′ are transformed axes

introduced. Then, the calculated susceptibility per mole of copper is given by equation (2). The parameters J_{12}, J_{13}, g, and θ were evaluated by fitting equation (2) to the experimental susceptibilities ($N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}). For (**1**) the fit procedure converged at $J_{12} = 30.1(5.0)$ cm^{-1}, $J_{13} = -6.1(3.0)$ cm^{-1}, $g = 2.09(0.02)$, $\theta = -1.0(0.5)$ K ($R = 0.51$ †) and for (**2**) at $J_{12} = 28.7(5.0)$ cm^{-1}, $J_{13} = -7.5(3.0)$ cm^{-1}, $g = 2.09(0.02)$, $\theta = -2.3(0.5)$ K ($R = 0.37$). The magnetic moments of (**1**) and the magnetic susceptibilities of (**2**) calculated with these parameters are shown in Figure 3(*a*) and (*b*). With constant $J_{13} = 0$ we obtained for (**1**), $J_{12} = 17.7(5.0)$ cm^{-1}, $g = 2.13(0.02)$, $\theta = -1.3(0.5)$ K ($R = 1.19$) and for (**2**), $J_{12} = 15.5(5.0)$ cm^{-1}, $g = 2.13(0.02)$, $\theta = -2.8(0.5)$ K ($R = 1.97$). The results of the temperature dependent e.s.r. spectra of (**1**) and (**2**)[42] are not suitable to fix the g values clearly. The signals obtained from powder samples are unusually broad and cannot be interpreted in the normal way.

$$\chi_{\text{calc.}} = \frac{N_A g^2 \mu_B^2}{12k(T-\theta)} \cdot \frac{10\exp(J_{12}/kT) + \exp(-2J_{12}/kT) + \exp(-2J_{13}/kT)}{2\exp(J_{12}/kT) + \exp(-2J_{12}/kT) + \exp(-2J_{13}/kT)} + N\alpha \qquad (2)$$

Linear trimers with ferromagnetic ground states (Figure 4) have not been reported previously. The results of the calculations show that the predominant ferromagnetic coupling is due to the interaction between neighbouring centres. A smaller antiferromagnetic contribution results from interaction between the terminal centres. Although the value of J_{13} is expected to be zero or very small, from studies of other linear trimers,[29,30,32] the considerably worse agreement between experimental and calculated susceptibilities using $J_{13} = 0$

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† $R = 10^{-3}\Sigma(\chi_{\text{exp.}} - \chi_{\text{calc.}})^2 T^2$.

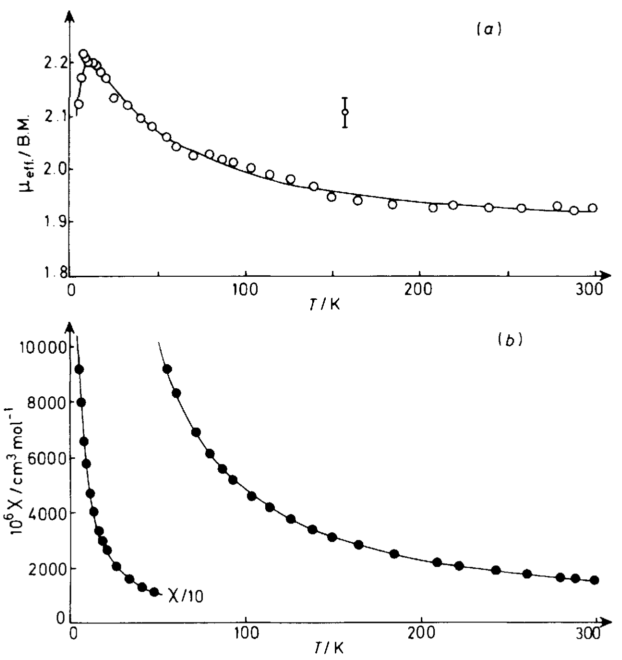

Figure 3. (*a*) Experimental (○) and calculated (——) temperature dependence of the magnetic moments (B.M. = 9.274×10^{-24} J T^{-1}) of (**1**). (*b*) Experimental (●) and calculated (——) temperature dependence of the magnetic susceptibilities of (**2**)

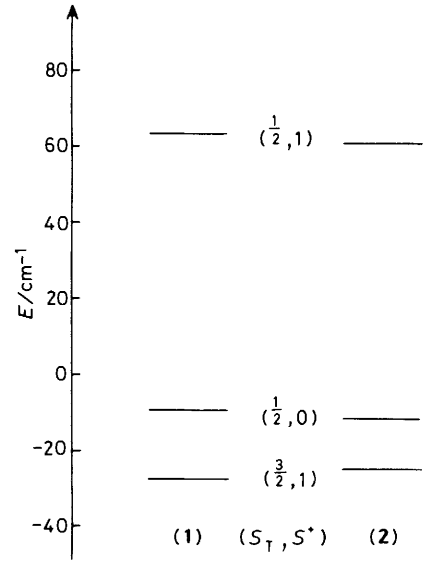

Figure 4. Schematic energy splitting diagrams for (**1**) and (**2**)

implies an interaction which is far from negligible. The exchange parameters of (**1**) and (**2**) agree within the error limits as expected from structure analyses. The g values evaluated from susceptibility measurements are comparable to those found in other trimeric compounds.[29–31]

To understand the ferromagnetic exchange interaction it is necessary to know the factors leading to orthogonal magnetic orbitals on Cu(1) and Cu(2). For the linear trimers studied so far[20–24] qualitative statements about the nature of the magnetic orbitals can be made from the structures and the antiferromagnetic coupling is as predicted. In (**1**) and (**2**) a three-atom carboxylate bridge and an one-atom oxygen bridge connect the copper centres [Cu(1), Cu(1′)], which lead to the loss of the coplanarity of the co-ordination planes around Cu(1) and Cu(2). Therefore not even qualitative statements about the magnetic orbitals in (**1**) and (**2**) can be made; moreover, the different co-ordination numbers and geometries at Cu(1) (square planar) and Cu(2) (octahedral) should be taken into account also. For a better interpretation of the ferromagnetic coupling in (**1**) and (**2**) calculations of the magnetic orbitals are necessary. Up to now only these two compounds of this type are known and correlations between structural effects and magnetic properties are not available. So we are looking for more experimental data to obtain a better understanding of this interesting exchange coupling problem.

Experimental

Preparation of Complexes.—Dialkylaminoethanol, $R_2NC_2H_4OH$ (5.5 mmol), dissolved in absolute alcohol, R′OH (15 cm^3), was added dropwise to a suspension of copper(II) benzoate[43] (2.75 mmol) in hot R′OH (45 cm^3) [for (**1**), R = C_2H_5, R′ = CH_3; for (**2**), R = n-C_4H_9, R′ = C_2H_5]. After standing overnight, blue needles precipitated from the green solution. Recrystallisation from R′OH by slow cooling in a Dewar flask gave well formed crystals suitable for *X*-ray analysis. Elemental analysis (%) with calculated values in parentheses: (**1**), C, 51.75 (51.90); H, 5.60 (5.80); N, 2.90 (2.90). (**2**), C, 56.10 (56.20); H, 6.75 (6.90); N, 2.55 (2.50).

Crystal Data.—Both *X*-ray measurements were performed on a computer-controlled Stoe-Stadi 4 four-circle diffractometer. (**1**), $C_{42}H_{56}Cu_3N_2O_{12}$, M = 971.5, triclinic, a = 14.793(3), b = 10.533(3), c = 8.127(2) Å, α = 73.84(1), β = 84.40(1), γ = 69.15(1)°, U = 1 136.6 Å^3 (by least-squares refinement with 48 strong reflections, λ = 0.710 69 Å), space group $P\bar{1}$ (no. 2),[44a] Z = 1, T = 299 K, D_m (flotation) = 1.43(3), D_c = 1.42 g cm^{-3}. Blue, moisture sensitive needles, pasted in cyanoacrylate. Crystal dimensions: *ca.* 1 × 0.2 × 0.14 mm, μ(Mo-K_α) = 13.87 cm^{-1}. (**2**) (Reported parameters in square brackets[25]), $C_{52}H_{76}Cu_3N_2O_{12}$, M = 1 111.8, monoclinic, a = 8.201(5) [8.210(9)], b = 29.58(2) [29.77(5)], c = 12.600(8) [12.71(1) Å], β = 114.06(2) [113.90(5)°], U = 2 791.3 [2 839 Å^3] (by least-squares refinement with 38 strong reflections, λ = 0.710 69 Å), space group $P2_1/c$ (no. 14) [$P2_1/c$],[44a] T = 294 K [not given in ref. 25].

Data Collection and Processing.—(**1**): scan ω–θ = 1:1 in the range $3 \leqslant 2\theta \leqslant 45°$, graphite-monochromated Mo-K_α radiation, 2 968 reflections measured, 2 796 unique after absorption correction (max., min. transmission factors = 0.84, 0.73) giving 2 706 with $F \geqslant 2\sigma(F)$. Three standard reflections ($\bar{1}1\bar{1}$, $\bar{2}11$, 011) recorded every 50 reflections showed the stability of the measurements.

Structure Analysis and Refinement.—The structure was solved by direct methods. All non-hydrogen atoms were located after several Fourier syntheses. Block-matrix least-squares refinement converged at R = 0.109, anisotropic refinement with hydrogen atoms geometrically positioned (C–H distance = 1.08 Å) converged at R = 0.045, R' = 0.044 [weighting scheme $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ from counting statistics]. The hydrogen atom bonded to the methanolic oxygen atom was located in a difference Fourier synthesis, a final difference map showed no peak higher than 0.66 e Å^{-3}.

Scattering factors of Cu^0 were taken from the International Tables,[44b] all others are stored in the program SHELX 76,[45] which was used for the calculations.

Magnetic Measurements and Calculations.—The magnetic susceptibilities were recorded by the Faraday method [39] in the temperature range 5.1—298.6 K. The magnetic susceptibilities were corrected for underlying diamagnetism [(**1**), -171.7×10^{-6}; (**2**), -209.6×10^{-6} cm^3 mol^{-1}). The magnetic moments are calculated from $\mu = 2.828\ (\chi T)^{\frac{1}{2}}$.* All calculations were performed on the IBM 370/168 and IBM 3081 D computers respectively of the Technische Hochschule Darmstadt.

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* To convert into S.I. units χ should be multiplied by $4\pi 10^{-6}$; this gives $\mu = 797.74(\chi T)^{\frac{1}{2}}$.

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