

ateship during his stay at Arizona State University. The diffractometer was obtained and upgraded with financial assistance from the National Science Foundation.

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Acta Cryst. (1991). **C47**, 1814–1816

A Mixed Bridged Trinuclear Copper(II) Complex with Diethylaminoethanolato and 3-Methylbenzoato Ligands

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(Received 21 November 1990; accepted 31 January 1991)

Abstract. Bis[μ -2-(diethylamino)ethanolato-*O,N*]-bis(methanol)-bis(μ -3-methylbenzoato-*O,O'*)-bis(3-methylbenzoato-*O*)-tricopper(II), [Cu₃(C₆H₁₄NO)₂(C₈H₇O₂)₄(CH₄O)₂], *M_r* = 1027.6, monoclinic, *P*2₁/*c*, *a* = 8.302 (2), *b* = 30.794 (8), *c* = 10.688 (3) Å, β = 110.12 (1)°, *V* = 2565.7 Å³, *Z* = 2, *D_x* = 1.330 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 1.231 mm⁻¹, *F*(000) = 1074, *T* = 297 K. Final *R* = 0.059 for 3145 independent reflections [*F_o* > 2σ(*F_o*)]. Linear Cu₃ arrangement; adjacent copper centres are bridged by a bidentate carboxylato group and an aminoethanolato oxygen atom.

Introduction. Trinuclear copper(II) complexes with benzoato/diethylaminoethanolato bridging, [Cu₃{(C₂H₅)₂NC₂H₄O}₂(C₆H₅CO₂)₄(CH₃OH)₂] (Haase & Gehring, 1985) or benzoato/dibutylaminoethanolato bridging, [Cu₃{(n-C₄H₉)₂NC₂H₄O}₂(C₆H₅CO₂)₄(C₂H₅OH)₂] (Muhonen, Pajunen & Hämäläinen, 1980), are systems with a quartet spin ground state due to a ferromagnetic exchange coupling in the Cu^{II}—RO/RCO₂—Cu^{II} moiety (Gehring & Haase, 1990). As part of these investigations (Gehring, 1990) we synthesized new Cu₃ complexes with methyl-substituted benzoato ligands as reported in a preliminary

communication (Gehring, Paulus, Haase, Bill & Trautwein, 1990). The present work deals with the molecular structure of the 3-methyl derivative.

Experimental. Cu₂CO₃(OH)₂ (0.05 mol) was stirred into a melt of 3-methylbenzoic acid (0.2 mol) to prepare the starting material Cu(3-CH₃-C₆H₄CO₂)₂. The reaction was completed by further heating of the powdered mixture to 423–443 K (0.5 h). Residual acid was removed by washing with dichloromethane or ether. For purification, the crude product (50 g) was treated with acetone (analytical grade, 300 ml) in a Soxhlet extractor and dried *in vacuo*.

Diethylaminoethanol (3.90 mmol in 5 ml methanol) was added to a methanolic suspension of Cu(3-CH₃-C₆H₄CO₂)₂ (1.95 mmol in 50 ml). After filtration blue single crystals precipitated from the turquoise solution standing at 279 K. Elemental analysis, calculated values for Cu₃(C₄₆H₆₄N₂O₁₂) in parentheses: C 53.76 (53.76), H 6.08 (6.28), N 2.75 (2.73)%.

For data collection a single crystal with the approximate dimensions 0.3 × 0.4 × 1 mm was sealed in a Lindemann capillary containing mother liquor. Lattice constants determined on a Stoe-Siemens AED2 diffractometer by a least-squares treatment of the setting angles of 56 reflections in the

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range $14 < 2\theta < 43^\circ$. Intensities of 6071 reflections with $0 \leq h \leq 8$, $-33 \leq k \leq 16$, $-11 \leq l \leq 10$, $3 \leq 2\theta \leq 45^\circ$ were measured in the $\omega:2\theta = 1:1$ mode. Standard intensities (253, 253, 202) monitored after each hour of measuring time showed no evidence of crystal decay. The data were corrected for Lorentz and polarization effects; numerical absorption correction led to 3145 unique reflections with $F_o > 2\sigma(F_o)$, $R_{\text{int}} = 0.018$ (SHELX76; Sheldrick, 1976).

Structure solution (direct methods) and refinement with SHELX76 (Sheldrick, 1976). Anisotropic temperature factors for non-hydrogen atoms, geometrically calculated positions for aromatic and aliphatic hydrogen atoms with C—H = 0.96 Å, $U_{\text{iso}}(\text{H}) = U_{\text{eq}}$ of the corresponding carbon atom, fixed. The position of the methanolic H(O6) was localized in a difference Fourier map and fixed. Final values of $R = 0.059$, $wR = 0.055$, $w = k[\sigma(F_o)]^{-1}$, k determined by least squares. 302 parameters, maximum residual electron densities 0.79, -0.72 e \AA^{-3} . $|\Delta/\sigma|_{\text{mean}} = 0.06$.

Scattering factors for Cu^0 were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), others as supplied by SHELX76.

Atomic coordinates and selected bond distances and angles are given in Tables 1 and 2.* Fig. 1 shows the molecular structure drawn with PLUTO (Motherwell & Clegg, 1978). Best planes were calculated with a locally written program (Costines, Foitzik & Gehring, 1984).

Discussion. The three copper atoms form a linear arrangement with Cu(2) on the inversion centre. The terminal copper atoms Cu(1) and Cu(1') [symmetry code: (') $1 - x, 1 - y, 1 - z$] have a distorted square planar geometry coordinated by O(1), O(2), O(4) and N(1) forming the best plane *A* with deviations of 0.16, -0.16 , 0.15 and -0.15 Å. The Cu(1) position is 0.10 Å above *A*. For the central Cu(2) a distorted octahedral geometry is realized with O(1), O(1'), O(3) and O(3') as basal plane *B* and the methanolic oxygen atoms O(6) and O(6') as axial ligands.

Adjacent copper centres are bridged by an amino-ethanol oxygen ligand [Cu(1)—O(1)—Cu(2) = 111.7 (2)°] and a bidentate carboxylato group O(2)—C(3)—O(3) leading to a mixed-bridged non-coplanar coordination geometry with Cu(1)—Cu(2) = 3.173 (1) Å. The non-coplanarity can be described by the dihedral angle $\varphi_{AB} = 61.0^\circ$ formed between the best plane *A* and the plane *B*. Correspondingly, the six-membered ring —Cu(1)—O(2)—C(3)—O(3)—

Table 1. Positional atomic parameters with *e.s.d.*'s in parentheses and equivalent isotropic thermal parameters

$$U_{\text{eq}} = \frac{10^3}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}, \mathbf{a}).$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Cu(1)	0.3564 (1)	0.5949 (1)	0.4125 (1)	46
Cu(2)	0.5	0.5	0.5	45
O(1)	0.3382 (4)	0.5444 (1)	0.5080 (3)	47
O(2)	0.5911 (5)	0.6054 (1)	0.5287 (4)	58
O(3)	0.6863 (5)	0.5389 (1)	0.6032 (4)	56
O(4)	0.3708 (5)	0.6438 (1)	0.3062 (4)	61
O(5)	0.5459 (6)	0.6131 (1)	0.2149 (4)	77
O(6)	0.5092 (6)	0.5331 (1)	0.2922 (4)	80
N(1)	0.0977 (6)	0.5921 (2)	0.3314 (5)	57
C(1)	0.1685 (7)	0.5339 (2)	0.4975 (7)	64
C(2)	0.0542 (10)	0.5683 (4)	0.4320 (12)	187
C(3)	0.6985 (7)	0.5795 (2)	0.6023 (5)	50
C(4)	0.8589 (7)	0.5998 (2)	0.6984 (5)	51
C(5)	0.8801 (8)	0.6433 (2)	0.7113 (6)	68
C(6)	1.0272 (11)	0.6617 (3)	0.7975 (8)	85
C(7)	1.1519 (12)	0.6360 (4)	0.8719 (9)	120
C(8)	1.1383 (11)	0.5925 (3)	0.8622 (9)	127
C(9)	0.9899 (9)	0.5741 (3)	0.7741 (7)	94
C(10)	0.4673 (7)	0.6449 (2)	0.2361 (6)	53
C(11)	0.4837 (7)	0.6876 (2)	0.1753 (5)	50
C(12)	0.3899 (9)	0.7229 (2)	0.1910 (6)	71
C(13)	0.4049 (11)	0.7624 (2)	0.1343 (7)	89
C(14)	0.5145 (11)	0.7660 (3)	0.0636 (8)	95
C(15)	0.6112 (9)	0.7313 (3)	0.0488 (7)	83
C(16)	0.5931 (8)	0.6921 (2)	0.1053 (6)	64
C(17)	0.4678 (14)	0.5063 (3)	0.1813 (7)	111
C(18)	0.0056 (10)	0.6328 (3)	0.3106 (12)	161
C(19)	0.0543 (12)	0.6686 (3)	0.3963 (9)	112
C(22)	0.0607 (10)	0.5700 (4)	0.1996 (11)	197
C(23)	-0.1220 (15)	0.5616 (5)	0.1181 (13)	279
C(26)	1.0520 (13)	0.7090 (3)	0.8093 (11)	146
C(27)	0.7385 (11)	0.7362 (3)	-0.0201 (9)	133

Table 2. Selected bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Cu(1)—Cu(2)	3.173 (1)	Cu(2)—O(3)	1.968 (4)
Cu(1)—O(1)	1.894 (3)	Cu(2)—O(6)	2.468 (4)
Cu(1)—O(2)	1.944 (4)	O(2)—C(3)	1.253 (7)
Cu(1)—O(4)	1.915 (4)	O(3)—C(3)	1.253 (7)
Cu(1)—N(1)	2.022 (5)	O(4)—C(10)	1.271 (7)
Cu(1)—O(6)	2.830 (5)	O(5)—C(10)	1.241 (7)
Cu(2)—O(1)	1.940 (3)		
Cu(1)—O(1)—Cu(2)	111.7 (2)	O(1)—Cu(2)—O(6)	89.1 (1)
O(1)—Cu(1)—O(2)	92.3 (1)	O(3)—Cu(2)—O(6)	89.5 (2)
O(2)—Cu(1)—O(4)	89.7 (2)	Cu(1)—O(2)—C(3)	129.5 (4)
O(4)—Cu(1)—N(1)	93.1 (2)	O(2)—C(3)—O(3)	126.7 (5)
O(1)—Cu(1)—N(1)	85.8 (2)	Cu(2)—O(3)—C(3)	130.7 (4)
O(1)—Cu(1)—O(4)	176.4 (2)	Cu(1)—O(4)—C(10)	123.5 (4)
O(2)—Cu(1)—N(1)	164.7 (2)	O(4)—C(10)—O(5)	124.3 (6)
O(1)—Cu(2)—O(3)	88.2 (2)		

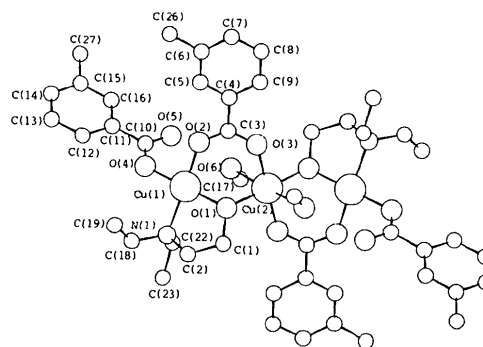


Fig. 1. Molecular structure of the title compound. [Atomic labeling changed in comparison to Haase & Gehring (1985) and Muhonen, Pajunen & Hämäläinen (1980) respectively.]

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53969 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cu(2)—O(1)— is folded with a dihedral angle $\varphi_{CD} = 111.2^\circ$ defined between the best plane *C* [deviations (Å) in parentheses], Cu(1) (0.04), O(2) (-0.07), C(3) (0.03), Cu(2) (-0.03), O(3) (0.03) and the plane *D*, Cu(1), O(1), Cu(2).

Two structural effects are associated with the methanolic oxygen atoms O(6), O(6'). (i) The hydrogen bridge O(5)⋯H(O6)—O(6), O(5)—O(6) = 2.650 (7) Å, O(5)—H(O6)—O(6) = 175 (2)°, stabilizes the folded structure. (ii) The *trans* angle O(2)—Cu(1)—N(1) = 164.7 (2)° is influenced by the Cu(1)—O(6) = 2.830 (5) Å distance as the O(6) position may be described as the apical position in a square-planar pyramidal Cu(1) coordination. This correlation is observed within the series of related trinuclear compounds (Gehring, 1990). A smaller Cu(1)—O(6) distance leads to a more distorted Cu(1) basal plane *A* with smaller angles O(2)—Cu(1)—N(1) while the other *trans* angle O(1)—Cu(1)—O(4) remains nearly unchanged at $176 \pm 1^\circ$.

Distances and angles within the ligands agree with those found in related compounds. The molecular structure of the 3-methyl derivative shows no sig-

nificant differences to the unsubstituted analogues mentioned in the *Introduction*.

Financial support of the Deutsche Forschungsgemeinschaft, Bonn Bad Godesberg, is gratefully acknowledged.

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Acta Cryst. (1991). **C47**, 1816–1819

Structure of a Nickel(II) Complex of the Deprotonated Anion of 3,10-Dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione Dioxime

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(Received 6 March 1990; accepted 6 February 1991)

Abstract. μ -[3,10-Dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioximato(1-)- μ -O,N,N',N'',N''']-nickel(II) perchlorate, [Ni(C₁₂H₂₁N₄O₂)⁺.ClO₄⁻], *M*_r = 411.5, triclinic, *P* $\bar{1}$, *a* = 6.533 (2), *b* = 10.840 (3), *c* = 12.979 Å, α = 103.57 (3), β = 95.76 (3), γ = 103.16 (2)°, *V* = 858.5 (5) Å³, *Z* = 2, *D*_x = 1.592 Mg m⁻³, λ (Mo *K*α) = 0.71073 Å, μ = 1.33 mm⁻¹, *F*(000) = 428, *R* = 0.0440, *wR* = 0.0494 for 2417 independent reflections at 296 K. An oxime proton is lost from the ligand in forming the complex and the remaining oxime proton forms an intramolecular hydrogen bond between the two oxime oxygens. The Ni^{II} atom is in a distorted square

planar coordination. The average values for the important bond distances are Ni—N(oxime) = 1.871, Ni—N(imine) = 1.907, O⋯O = 2.443 Å for the intramolecular hydrogen bond.

Introduction. It is well established that deprotonated tetradentate diimine dioximes and diamine dioximes coordinate with transition metal ions to form complexes having strong intramolecular hydrogen bonds between *cis* oxime groups (Wang, Chung, Cheng & Wang, 1990; Fair & Schlemper, 1978; Gavel & Schlemper, 1979; Liss & Schlemper, 1975). The O⋯O distance can be varied either by changing the ligand or by changing the size of the metal ion. The X-ray crystal structures of the complexes of deprotonated

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