Inorganica Chimica Acta, *169* (1990) 151–155

Linear Trinuclear Copper(II) Complex with Aminoalcohol and Fluoroacetic Acid. The Crystal and Molecular Structures of Bis[μ-(2-diethylaminoethanolato-*N*,μ-*O*)]-bis[μ-fluoroacetato-*O*,*O*′]-bis(fluoroacetato)-bis(ethanol)tricopper(II)

KIMMO SMOLANDER* and KIRSTI LEISTO

Department of Chemistry, University of Joensuu, P.O. Box 111, SF-80101 Joensuu (Finland)

(Received April 17, 1989)

Abstract

The crystal and molecular structures of the linear trinuclear copper(II) complex with 2-diethylaminoethanol and fluoroacetic acid were determined by three-dimensional X-ray crystallography. Bis[μ-(2-diethylaminoethanolato-*N*,μ-*O*)]-bis[μ-fluoroacetato-*O*,*O*′]-bis(fluoroacetato)-bis(ethanol)tricopper(II) crystallizes in the triclinic space group $P\bar{1}$ with a = 7.963(6), b = 8.443(7), c = 13.553(6) Å, α = 76.16(5), β = 81.82(5), γ = 87.62(6)°, Z = 1. The structure was solved by direct methods and refined to the R value 0.050 using 2738 independent reflections. Like the F(2) atom, some of the C atoms of the aminoethanolato ligands are disordered with one or more rotational orientations.

The three Cu(II) ions are in linear arrangement bridged by one bidentate carboxylate O atom and one 2-diethylaminoethanolato O atom. The Cu(1) atom is in 4 + 1 and the Cu(2) atom in 4 + 2 environment, and the Cu(1)–Cu(2) distance is 3.126(1) Å. A 2-diethylaminoethanolato O atom, two fluoroacetate O atoms and an amino N atom form a distorted square-plane around the Cu(I) atom with Cu(1)–O bonds of 1.903(4)–1.966(4) Å and a Cu(1)–N bond of 2.030(4) Å; the apical site is occupied by an ethanolato O atom and the Cu(1)–O(6) distance is 2.623(7) Å. The square-plane of the central Cu(2), which lies on the inversion centre, consists of two 2-diethylaminoethanolato O atoms and two carboxylato O atoms with Cu(2)–O bonds of 1.946(3) and 1.954(4) Å, respectively. The apical sites are occupied by ethanolato O atoms with a Cu(2)–O(6) distance of 2.525(5) Å.

Introduction

The coordination chemistry of aminoalcohols and copper(II) has been receiving increasing attention and the structures and magnetic properties of the complexes have been intensively studied. Numerous copper(II) complexes with 2-dialkylaminoethanols (abbreviated DR-noH) have been reported [1–7], with structures typically dimeric, polymeric with dimeric units or cubane-like tetrameric distorted into different types [1–3]. By contrast, only two trinuclear complexes are known, namely [Cu_3(DEt-no)$_2$(benzoato)$_4$(EtOH)$_2$] [6] and [Cu_3(DBu-no)$_2$(benzoato)$_4$(EtOH)$_2$] [7].

Trinuclear copper(II) complexes in general can be classified into four types (a) the equilateral triangle, where oxygen or hydroxyl ion is coordinated to three Cu(II) ions [8–10]; (b) the isosceles triangle, where Cu(II) ions and oxygens occur alternately forming a triangle [11]; (c) chains of different types of trinuclears [12–14]; (d) the linear trinuclears [6, 7, 11, 14–19]. The bridging system in the linear trinuclears varies from a single Cu–O–Cu bridge [16] to one Cu–N–C–N–Cu and two Cu–Cl–Cu bridges [14] with many other variations.

In the present work, the linear trinuclear copper(II) complex bis[μ-(2-diethylaminoethanolato-*N*,μ-*O*)]-bis[μ-fluoroacetato-*O*,*O*′]-bis(fluoroacetato)-bis(ethanol)tricopper(II) was prepared and its molecular and crystal structures investigated.

Experimental

Preparation of the Complex

The blue [Cu_3(DEt-no)$_2$(FH_2CCOO)$_4$(H_5C_2OH)$_2$] complex was prepared by combining a warm ethanol solution of the copper(II) fluoroacetate with 2-diethylaminoethanol (DEt-noH; Fluka Ag) in molar ratio 1:1.15. The solution was refluxed, filtered and left to evaporate slowly at ambient temperature. After a few days blue crystals were collected, washed with cold ethanol/ether mixture and dried in a desiccator.

Copper analyses were carried out by atomic absorption spectroscopy using a Perkin-Elmer 2380 instrument.

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

Data Collection

The crystal and refinement data are given in Table 1. The unit cell parameters and the orientation matrix were determined by a least-squares refinement based on 24 well-centred reflections measured at 20 °C on a Nicolet R3m diffractometer.

Intensity data were collected on the same diffractometer by the ω-scan technique using graphite crystal monochromated Mo Kα radiation (λ = 0.71069). The intensity of one check reflection recorded after every 99 measurements remained essentially constant throughout the data collection. The intensities were corrected for Lorentz and polarization effects and for absorption from empirical ψ-scan data from 6 reflections.

TABLE 1. Crystal data, data collection and refinement data

Formula	$C_{24}H_{48}Cu_3F_4N_2O_{12}$
Formula weight	823.27
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.963(6)
b (Å)	8.443(7)
c (Å)	13.553(6)
α (°)	76.16(5)
β (°)	81.82(5)
γ (°)	87.62(6)
V (Å^3)	875.7
Z	1
D_o (g cm^{-3})	1.57
D_c (g cm^{-3})	1.56
λ (Å) (Mo Kα)	0.71069
Monochromator	graphite
Linear absolute coefficient (cm^{-1})	18.85
Crystal size (mm)	0.12 × 0.30 × 0.30
Diffractometer	Nicolet R3m
Data collection method	ω
2θ range (°)	3 to 55
Scan rate (° min^{-1})	2.5 to 29.3
No. standard reflections	1
Variation in standard intensities	±1%
Reflections collected	4020
Reflections used in refinement $I > 2.5\sigma(I)$	2732
No. of variables	396
R (= $\Sigma\Delta/\Sigma\lvert F_o\rvert$)[a]	0.050
R_w (= $\Sigma\Delta^{1/2}/\Sigma\lvert F_o\rvert w^{1/2}$)[b]	0.054
Residual electron density (e A^{-3})	0.42
T (K)	293
F(000) (e)	425
h range	0–11
k range	−11 to 11
l range	−18 to 18

[a] $\Delta = \lVert F_o\rvert - \lvert F_c\rVert$. [b] $w^{-1} = \sigma^2(F_o) + 0.0005F_o^2$.

Structure Determination

The structures were solved by direct methods and Fourier techniques and refined by blocked-cascade full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms.

The disorder of the carbon atoms of the DEt-no ligands was evident in the distances involving these atoms and in the shape and size of the thermal ellipsoids. A difference map calculated without the disordered carbon atoms showed severe dispersion of the electron density. The disordered atoms were given a site occupation factor of 0.5, and the corresponding bond length of pairs of the atoms fixed together were refined. The positions of the disordered atoms C(2), C(3), C(5) and C(6) refined well, giving site occupation factors of about 0.5. These atoms were considered fixed in subsequent calculations. The disorders were judged to arise from the mixture of two configurations of the DEt-no ligand, generated by in one or more rotational orientations of the ethyl groups and the amine around the N–Cu axis. The F(2) atom showed disorder too, and the site occupation factors were fixed at 0.75 and 0.25.

The hydrogen atoms bonded to carbon atoms were included at calculated positions with fixed bond lengths (C–H = 0.96 Å) and constrained angles,

TABLE 2. Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters (×10^3)

Atom	x	y	z	U
Cu1	1779(1)	−1645(1)	1906(1)	49(1)
Cu2	0	0	0	45(1)
O1	1365(5)	−1854(4)	594(3)	46(1)
N1	1025(3)	−3998(5)	2447(2)	57(2)
C1	934(4)	−3485(6)	607(3)	56(2)
C2a	3(9)	−4256(11)	1625(4)	38(2)[a]
C2b	1346(28)	−4739(10)	1512(5)	148(4)
C3a	2506(9)	−5084(10)	2486(7)	54(3)
C3b	2034(17)	−5309(12)	3003(21)	192(4)
C4	3743(7)	−4850(9)	3168(4)	105(3)
C5a	−153(12)	−4122(18)	3383(5)	74(3)
C5b	−790(6)	−4253(25)	2694(16)	209(4)
C6a	−1200(21)	−5520(21)	3776(11)	98(4)
C6b	−1459(26)	−3769(23)	3631(12)	113(4)
O2	3207(5)	269(5)	1257(3)	59(1)
O3	1948(5)	1400(5)	−121(3)	54(1)
C7	3062(7)	1320(7)	449(4)	47(2)
C8	4402(8)	2589(8)	155(5)	60(2)
F1	4115(6)	3797(6)	−692(4)	103(2)
O4	2157(6)	−1396(5)	3231(3)	79(2)
O5	846(7)	1001(6)	3219(4)	64(2)
C9	1724(9)	−158(8)	3581(5)	64(2)
C10	2487(8)	−163(6)	4529(5)	89(2)
F2a	2097(11)	1291(5)	4855(5)	135(3)
F2b	3789(17)	−1315(17)	4768(14)	108(4)
O6	−907(6)	263(6)	1817(3)	73(2)
C11	−2655(10)	207(11)	2184(7)	93(3)
C12	−3397(13)	1603(14)	2433(8)	122(3)

[a] The site occupation factors are 0.5 and 0.5 and for atom F2 0.75 and 0.25.

and their thermal parameters were set at 1.2 times the equivalent isotropic thermal parameters for the corresponding carbon atom. The alcoholic hydrogen atom was located from a difference Fourier map.

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL software for minicomputer (Nova 3) [20]. The program uses neutral atom scattering factors from ref. 21 and takes anomalous dispersion into account. The figures were drawn with the SHELXTL program on a Zeta plotter.

The final atomic coordinates and thermal parameters with their e.s.d.s for non-hydrogen atoms are given in Table 2.

Results and Discussion

Description of the Structure

The stereoview with the labelling of the atoms is shown in Fig. 1 and the packing in Fig. 2. Bond lengths and bond angles are given in Table 3.

The three Cu(II) ions are in linear arrangement with Cu(2) on the inversion centre; the Cu(1)–Cu(2) distance is 3.126(1) Å. The Cu(II) ions are bridged by a bidentate carboxylate group and the oxygen O(1) of 2-diethylaminoethanolato. The two terminal Cu(1) atoms are in 4 + 1 and the central Cu(2) atom in 4 + 2 environment.

A 2-diethylaminoethanolato O atom, two fluoroacetato O atoms and an amino N atom form the tetrahedrally distorted square-plane around Cu(1) with Cu(1)–O bonds of 1.903(4)–1.966(4) Å and a Cu(1)–N bond of 2.030(4) Å. An ethanolato O(6) atom occupies the apical site at a Cu(1)–O(6) distance of 2.623(7) Å. The dihedral angle between the Cu(1)O(1)O(2) and Cu(1)O(2)O(4) planes is 18.7°. The square-plane of the central Cu(2) atom consists of two 2-diethylaminoethanolato O atoms and two carboxylato O atoms, with bonds Cu(2)–O(1) of 1.946(3) and Cu(2)–O(3) of 1.954(4) Å, respectively. The apical sites are occupied by ethanolato O atoms at Cu(2)–O(6) distances of 2.525(5) Å.

The molecular structures of the previously reported trinuclear dialkylaminoethanolato complexes [Cu_3(DEt-no)$_2$(ben)$_4$(EtOH)$_2$] [6] and [Cu_3(DBu-no)$_2$(ben)$_4$(EtOH)$_2$] [7] are nearly equal. The replacement of the benzoate by a fluoroacetate group produces a square-pyramidal environment around the terminal Cu(1): in our complex the coordination sphere of Cu(1) is tetrahedrally distorted square-pyramidal (4 + 1), whereas in the other two complexes it is almost square-planar, or 4 + 0 + 1. The apical Cu(1)–O(6) distances of the terminal Cu(1) deviate, being 2.623(5), 2.983(5) and 2.85(2) Å in the (DEt-no)(FAcO), (DEt-no)(ben) and (DBu-no)(ben) complexes, respectively. The apical Cu(2)–O(6) distances of the central Cu(2)

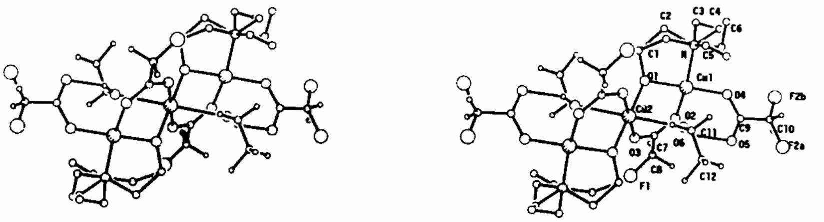

Fig. 1. Stereoview of [Cu_3(DEt-no)$_2$(FH_2CCOO)$_4$(H_5C_2OH)$_2$].

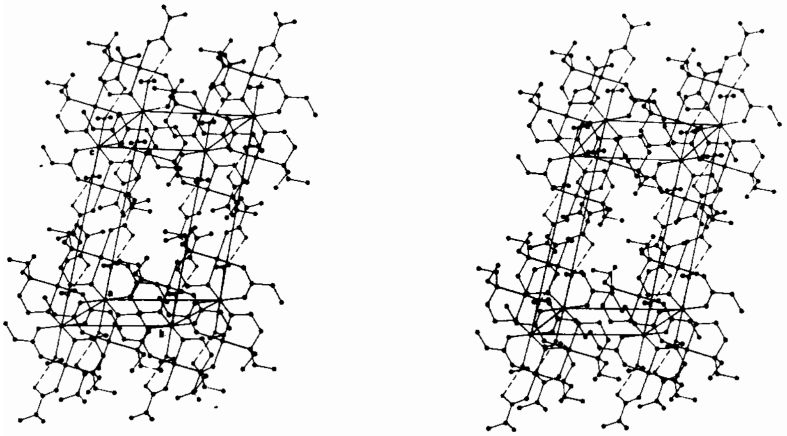

Fig. 2. Stereoview of the packing.

atom are about the same: 2.525(2), 2.478(4) and 2.52(2) Å, while the Cu(1)–Cu(2) distances differ slightly, being 3.126(1), 3.188(1) and 3.211(6) Å in the three complexes respectively.

The bridging angle Cu(1)–O(1)–Cu(2) at the aminoalcohol O atom is 108.6(2), which is slightly smaller than the corresponding angles of 112.2(1) and 111(1)°, in the (DEt-no) and (DBu-no) complexes. The angle N–Cu(1)–O(2) is 161.1(1), 165.9(2) and 159.8(9) in the (DEt-no)(FAcO), (DEt-no)(ben) and (DBu-no)(ben) complexes, respectively.

An intramolecular hydrogen bond exists between the unbonded carboxylate oxygen atoms O(5) and ethanolato oxygen atom O(6). The distance 2.710 Å indicates a medium strong hydrogen bond (O(6)–H(O6) = 0.746, O(5)...H(O6) = 2.051 Å and <O(5)...H–O(6) = 147.4° [21–23]. The shortest intermolecular contact of 3.227 Å is between F(2a) and F(2b) (1 – *x*, –*y*, 1 – *z*).

TABLE 3. Bond lengths (Å) and angles (°)

The copper environments			
Cu(1)–N	2.030(4)	Cu(1)–Cu(2)	3.126(1)
Cu(1)–O(1)	1.903(4)	Cu(2)–O(1)	1.946(3)
Cu(1)–O(2)	1.966(4)	Cu(2)–O(3)	1.954(4)
Cu(1)–O(4)	1.925(5)	Cu(2)–O(6)	2.525(5)
Cu(1)–O(6)	2.623(5)		
O(1)–Cu(1)–N	86.9(1)	O(1)–Cu(2)–O(3)	88.5(2)
O(1)–Cu(1)–O(2)	90.4(2)	O(1)–Cu(2)–O(6)	86.2(2)
O(1)–Cu(1)–O(4)	178.7(2)	O(3)–Cu(2)–O(6)	90.4(2)
O(2)–Cu(1)–N	161.1(1)	O(3)–Cu(2)–O(1′)	91.5(2)
O(2)–Cu(1)–O(4)	89.4(2)	O(3)–Cu(2)–O(6′)	89.6(2)
N–Cu(1)–O(4)	93.7(2)		
The 2-diethylaminoethanolato ligand[a]			
C(1)–O(1)	1.429(6)	Cu(1)–O(1)–Cu(2)	108.6(2)
C(1)–C(2)	1.483(7)	C(1)–O(1)–Cu(1)	112.0(3)
N–C(2)	1.529(8)	C(1)–O(1)–Cu(2)	121.4(3)
N–C(3)	1.463(8)	C(2)–C(1)–O(1)	109.3(5)
N–C(5)	1.452(8)	C(1)–C(2)–N	108.1(5)
C(4)–C(3)	1.493(11)	C(2)–N–Cu(1)	102.6(3)
C(5)–C(6)	1.424(21)	C(2)–N–C(3)	109.6(6)
		C(2)–N–C(5)	107.0(5)
		C(3)–N–Cu(1)	109.9(3)
		C(3)–N–C(5)	117.7(6)
		C(5)–N–Cu(1)	108.9(5)
		N–C(3)–C(4)	116.2(7)
		N–C(5)–C(6)	120.2(12)
The bidentate fluoroacetato ligand			
C(7)–O(2)	1.250(6)	C(7)–O(2)–Cu(1)	128.4(4)
C(7)–O(3)	1.247(7)	C(7)–O(2)–Cu(2)	130.4(3)
C(7)–C(8)	1.488(8)	O(2)–C(7)–O(3)	127.3(5)
C(8)–F(1)	1.380(7)	O(2)–C(7)–C(8)	114.6(5)
		O(3)–C(7)–C(8)	118.1(5)
		C(7)–C(8)–F(1)	112.6(5)
The unidentate fluoroacetato ligand			
C(9)–O(4)	1.263(8)	C(9)–O(4)–Cu(1)	124.7(4)
C(9)–O(5)	1.224(8)	O(4)–C(9)–O(5)	128.0(7)
C(9)–C(10)	1.497(10)	O(4)–C(9)–C(10)	112.4(6)
C(10)–F(2a)	1.410(8)	O(5)–C(9)–C(10)	119.6(5)
C(10)–F(2b)	1.410(15)	C(9)–C(10)–F(2a)	111.2(6)
		C(9)–C(10)–F(2b)	116.6(10)
The ethanolato ligand			
C(11)–O(6)	1.409(9)	C(11)–O(6)–Cu(2)	117.9(5)
C(11)–C(12)	1.389(15)	C(12)–C(11)–O(6)	117.2(8)

Symmetry code –*x*, –*y*, –*z*. [a]Only the a form of the disordered carbon atoms is tabulated.

References

1 K. Smolander, *Ann. Acad. Sci. Fenn., Ser A2, 200* (1983) 1, and refs. therein.

2 K. Smolander, *Inorg. Chim. Acta, 133* (1987) 317.

3 K. Smolander, *Inorg. Chim. Acta, 128* (1987) 61.

4 K. Smolander, *Inorg. Chim. Acta, 114* (1986) 1.

5 K. Nieminen, *Ann. Acad. Sci. Fenn., Ser. A2, 197* (1983) 1.

6 W. Haase and S. Gehring, *J. Chem. Soc., Dalton Trans.*, (1985) 2609.

7 H. Muhonen, A. Pajunen and R. Hämäläinen, *Acta Crystallogr., Sect. B, 36* (1980) 2790.

8 F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1983) 539.

9 K. Smolander, *Acta Chem. Scand., Ser. A, 37* (1983) 5, and refs. therein.

10 M. Näsäkkälä, *Ann. Acad. Sci. Fenn., Ser. A2, 181* (1977) 35.

11 H. Knuutila, *Inorg. Chim. Acta, 72* (1983) 11.

12 H. Knuutila, *Inorg. Chim. Acta, 50* (1981) 22.

13 D. D. Swank and R. D. Willet, *Inorg. Chim. Acta, 8* (1974) 143.

14 P. de Meester and A. C. Skapaski, *J. Chem. Soc., Dalton Trans.*, (1972) 2400.

15 G. Nieuwpoort, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1983) 531.

16 H. Muhonen and W. E. Hatfield, *Acta Chem. Scand. Ser. A, 40* (1986) 41.

17 N. Matsumoto, Y. Nishida, S. Kida and I. Ueda, *Bull. Chem. Soc. Jpn., 49* (1976) 117.

18 W. A. Baker and F. T. Helm, *J. Am. Chem. Soc., 97* (1975) 2295.

19 P. Arrizabalaga, P. Castan and F. Dahan, *Inorg. Chem., 22* (1983) 2245.

20 G. M. Sheldrick, *The SHELXTL System Computer Programs,* Nicolet XRD Corporation, Cupertino, U.S.A., 1981.

21 *International Tables for X-ray Crystallography,* Kynoch Press, Birmingham, 1974.

22 P. Schuster, G. Zundel and C. Sandorfy (eds.), *The Hydrogen Bond,* Vol. II, *Structure and Spectroscopy,* North-Holland, Amsterdam, 1976, pp. 401–452.

23 I. D. Brown, *Chem. Soc. Rev., 7* (1978) 359.