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Inorganica Chimica Acta 269 (1998) 241–245

**Inorganica
Chimica Acta**

Synthesis and single crystal X-ray structure of a novel trinuclear copper(II) methoxide complex

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Received 18 April 1997; accepted 7 July 1997

Abstract

Reaction of the ligand *cis,cis*-1,3,5-tri-(*E,E*)-3-(2-furyl)prop-2-en-1-ylidene-aminocyclohexane (tfct) with copper(II) ions and sodium tetrafluoroborate in methanol leads to the assembly of a novel trinuclear copper(II) complex. Single crystal X-ray diffraction shows that the complex contains a linear trinuclear array of copper(II) ions in which the central copper ion is coordinated by four methoxides, in a near square-planar coordination environment. The compound $\{[\text{Cu}(\text{tfct})]_2\text{Cu}(\mu\text{-OMe})_4 \cdot 2\text{BF}_4\}$ crystallises in the monoclinic system, space group $P2_1/c$, with $a=9.924(6)$, $b=14.620(13)$, $c=21.490(12)$ Å, $\beta=97.67(5)^\circ$ and $Z=2$. The $\{[\text{Cu}(\text{tfct})\text{BF}_4]\}^{2+}$ units are related by a crystallographic inversion centre on the copper(II) ion of the central $[\text{Cu}(\mu\text{-OMe})_4]^{2-}$ moiety. © 1998 Elsevier Science S.A.

Keywords: Crystal structures; Copper complexes; Trinuclear complexes; Alkoxide complexes; Copper(II) ion trimer; Solvent mediated assembly

1. Introduction

The coordination chemistry of *cis,cis*-1,3,5-triaminocyclohexane (tach) and tach-based complexes has been extensively studied [1–7]. Recently, we have developed new Schiff-base ligands based on tach, as effective models of metalloenzyme active sites [8,9], which are novel insofar as the complexes contain a stereochemically 'rigid' cavity, Fig. 1. In this paper we describe the preparation and structure of a novel trinuclear complex of a tach-based ligand, which contains an unusual $\{\text{Cu}(\mu\text{-OMe})_2\text{Cu}(\mu\text{-OMe})_2\text{Cu}\}^{2+}$ unit encapsulated within a rigid 'cavity' of two intercalated *cis,cis*-1,3,5-tri-(*E,E*)-3-(2-furyl)prop-2-en-1-ylidene-aminocyclohexane (tfct) ligands, see Scheme 1.

2. Experimental

2.1. Materials and methods

All reagents with the exception of phloroglucinol (Lancaster Chemicals Ltd.) were purchased from the Aldrich Chemical Company and used without further purification. *Cis,cis*-1,3,5-tri-(*E,E*)-3-(2-furyl)prop-2-en-1-ylidene-aminocyclohexane (tfct) was synthesised according to a previ-

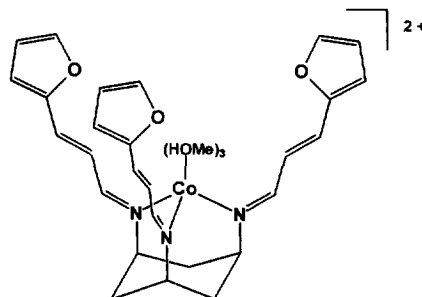
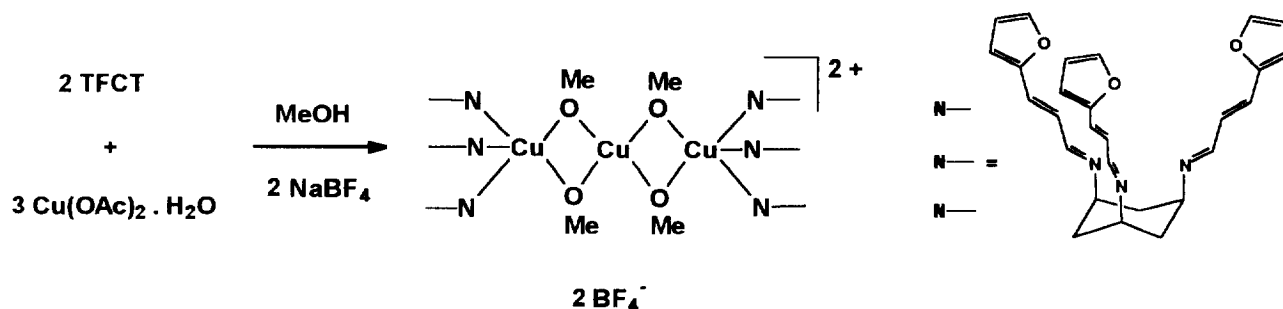


Fig. 1. An example of a monomeric compound with the tfct ligand coordinated to a cobalt(II) ion. The cavity is formed by three stereochemically rigid 3-(2-furyl)prop-2-en-1-ylidene moieties, surrounding three coordinated methanol molecules. See Ref. [9] for the synthesis of this complex.

ous literature method [9]. Solvents for synthesis (AR grade) were supplied by Fisons Ltd. and were also used without further purification. Deuterated solvents were obtained from Goss Scientific. Melting points were determined using an Electrothermal 1100 microprocessor controlled apparatus. Densities were measured by flotation of crystals in a mixed solvent system, bromoform/hexane. Fourier transform (FT) ^1H NMR spectra were acquired on a JEOL EX270 spectrometer and spectra were referenced using the signal from the residual solvent protons. IR spectra were acquired using KBr pressed pellets (pressed under 7.0 t pressure) on a Mattson Sirius Research Series FT-IR spectrometer. Mass spectra were acquired on a Fisons Instruments Autospec using a

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Scheme 1. The formation of the trimer. The tfct is pictured with its stick structure.

0–650°C temperature range. Crystallographic data were collected with an MSC Rigaku AFC6S diffractometer. Elemental analyses were performed by Butterworth Laboratories Ltd., 54–56 Waldegrave Road, Teddington, Middlesex, UK.

2.2. Preparation of $Cu_3(tfct)_2(OMe)_4(BF_4)_2$

A solution of diacetatocopper(II) monohydrate (0.034 g, 0.17 mmol) and sodium tetrafluoroborate (0.012 g, 0.11 mmol) in methanol (4 ml) was mixed with a solution of *cis,cis*-1,3,5-tri-(*E,E*)-3-(2-furyl)prop-2-en-1-ylidene-amino-cyclohexane [3] (tfct) (0.05 g, 0.11 mmol) in methanol (5 ml) which gave an instant colour change from blue to dark green. On standing for a period of 4 days the solution precipitated the product as large dark green crystals. (0.045 g, 0.033 mmol, 29% yield), m.p. 200–210°C (dec.). *Anal.* Found: C, 50.99; H, 4.72; N, 6.10. Calc. for $C_{58}H_{66}N_6O_{10}Cu_3B_2F_8$: C, 50.80; H, 4.85; N, 6.13%. IR (cm^{-1} , KBr pressed pellet): 3429(m), 2917(m), 2805(m), 1623(s), 1611(s), 1467(m), 1173(m), 1126(s), 1084(s), 1015(s), 980(m), 755(m). Measured density = 1.56(10) $g\ cm^{-3}$.

2.3. Crystallographic data collection and structure determination

A crystal of dimensions 0.2 × 0.2 × 0.2 mm was mounted on a thin glass fibre using epoxy cement. X-ray diffraction data were collected at 298(2) K using graphite-monochromated Mo K α radiation ($\lambda = 0.71069\ \text{\AA}$). Cell constants and an orientation matrix for the data collection were obtained from a least-squares refinement of the positions of 20 automatically centred reflections $13.78 \leq 2\theta \leq 15.84^\circ$. A summary of the crystallographic data and structure parameters is given in Table 1. A total of 6021 unique reflections was recorded in the range $5.14 \leq 2\theta \leq 50.00^\circ (+h, +k, l)$ using an $\omega/2\theta$ scan technique. Three standard reflections were monitored throughout the data collection (every 150 reflections) and showed no significant intensity loss. Equivalent reflections were merged ($R_{int} = 0.049$) and the data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods with SHELXS 86 and expanded using Fourier techniques with DIRDIF. Full-matrix least-squares refinement on

Table 1
Crystallographic information

Empirical formula	$C_{58}H_{66}N_6O_{10}Cu_3B_2F_8$
Formula weight	1371.40
Crystal size (mm)	0.2 × 0.2 × 0.2
Crystal system	monoclinic
Space group	$P2_1/c$
a (\AA)	9.924(6)
b (\AA)	14.620(13)
c (\AA)	21.490(10)
β ($^\circ$)	97.67(5)
V (\AA^3)	3090(4)
Z	2
Density calc./meas. ($g\ cm^{-3}$)	1.47/1.56(10)
μ (cm^{-1})	11.08
Range of transmission factors	0.91–1.00
Temperature (K)	293(2)
Scan type	$\omega/2\theta$
Scan width ($^\circ$)	$0.84 + 0.3 \tan \theta$
2θ range ($^\circ$) (+ h , + k , l)	5.14–50.00
No. reflections/unique reflections	6159/6021
R_{int}	0.049
No. observed	2875 ($I \geq 2\sigma(I)$)
No. parameters	440
Residuals $R(F_o)^a/R_w(F_o^2)^b$	0.0623/0.2035
GOF	1.033
ΔQ in final ΔF map ($e\ \text{\AA}^{-3}$)	0.49 to -0.38
Largest shift/e.s.d., last cycle	0.021

Radiation = Mo K α , $\lambda = 0.71069\ \text{\AA}$.

^a Conventional $R = R = \sum ||F_o| - |F_c|| / \sum |F_o|$ for 2875 observed reflections having $F_o^2 > 2\sigma(F_o^2)$.

^b $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ for 5423 data.

F^2 was carried out with SHELXL 93 with all non-hydrogen atoms anisotropic and hydrogens refined using a riding model. Programs used are given in Ref. [10]. The asymmetric unit contains a BF_4^- anion which was disordered and refined by splitting the anion over two positions. The occupations of each position were refined to 53 and 47%. The B–F distances and the F···F distances were restrained to be equal in the refinement.

3. Structural results

The unit cell ($P2_1/c$, $Z = 2$) is composed of two $\{[Cu(tfct)]_2Cu(\mu_2-OMe)_4 \cdot 2BF_4\}$ molecules with the central copper(II) ion located on an inversion centre of

symmetry. Therefore, the three copper ions lie on a straight line with the central copper(II) on the inversion centre (Fig. 2). The copper–copper distance is 2.978(2) Å, which does not represent a bonding distance. The copper coordination sphere of the terminal copper ions is occupied by the three face-capping nitrogen atoms of the tfct ligand and two methoxide ions, which bridge to the central copper atom in a μ_2 coordination mode. The central copper(II) ion has a distorted square planar coordination geometry, being coordinated to four methoxide ions: Cu(2)–O(4) and Cu(2)–O(5) at a distance of 1.958(4) and 1.959(4) Å respectively. The O(4)–Cu(2)–O(5) and O(4)–Cu(2)–O(5) angles are

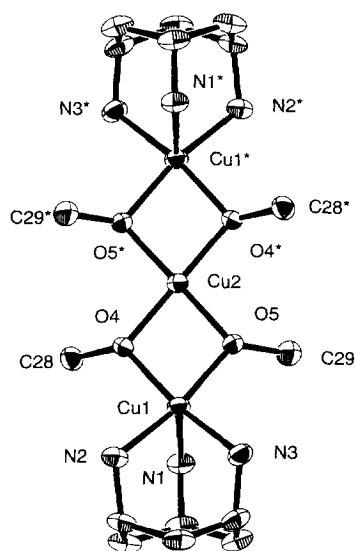


Fig. 2. An ORTEP representation of the tri-copper unit in $\text{Cu}_3(\text{tfct})_2(\text{OMe})_4(\text{BF}_4)_2$ with 30% probability ellipsoids. The ligands 'arms', tetrafluoroborate anions and the hydrogen atoms are omitted for clarity.

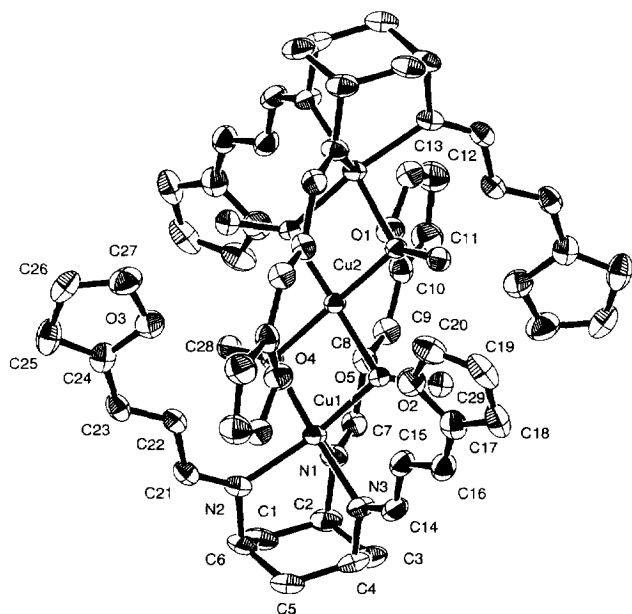


Fig. 3. An ORTEP representation of the crystal structure of $\text{Cu}_3(\text{tfct})_2(\text{OMe})_4(\text{BF}_4)_2$ with 30% probability ellipsoids. The hydrogen atoms and the tetrafluoroborate anions are omitted for clarity.

99.7(2) and 80.3(2) $^\circ$ respectively. The terminal copper ions adopt an approximate square pyramidal coordination geometry with two oxygens from the methoxide ions at the base of the pyramid [Cu(1)–O(4) = 1.958(4) Å, Cu(1)–O(5) = 1.959(4) Å, O(4)–Cu(1)–O(5) = 78.1(2) $^\circ$]. Two nitrogen atoms form the opposite side of the pyramid base [Cu(1)–N(2) = 2.032(6) Å, Cu(1)–N(3) = 2.013(6) Å, N(2)–Cu(1)–N(3) = 88.4(2) $^\circ$]. The apex of the pyramid is formed by the remaining nitrogen atom of the ligand N(1)–Cu(1) at a distance of 2.232(6) Å. The out of plane

Table 2
Fractional atomic coordinates

Cu(1)	1945(1)	8485(1)	378(1)	44(1)
Cu(2)	0	10000	0	39(1)
O(1)	23(5)	11808(4)	1449(3)	66(1)
O(2)	–2636(6)	7237(4)	–1107(3)	69(2)
O(3)	1827(6)	9649(4)	–2003(3)	79(2)
O(4)	1891(4)	9720(3)	22(2)	43(1)
O(5)	57(4)	8845(3)	421(2)	45(1)
N(1)	2921(6)	8797(4)	1352(3)	52(1)
N(2)	3760(6)	8151(4)	100(3)	50(1)
N(3)	1673(6)	7153(4)	562(3)	55(2)
C(1)	5051(8)	8045(6)	1188(4)	68(2)
C(2)	3897(8)	8086(6)	1583(4)	63(2)
C(3)	3173(9)	7161(6)	1606(4)	73(2)
C(4)	2803(8)	6695(5)	969(4)	63(2)
C(5)	4034(8)	6655(5)	611(4)	67(2)
C(6)	4698(7)	7590(5)	548(4)	59(2)
C(7)	2696(7)	9421(5)	1734(3)	53(2)
C(8)	1809(7)	10195(5)	1610(3)	53(2)
C(9)	1648(8)	10809(5)	2052(4)	58(2)
C(10)	796(8)	11597(6)	2015(4)	60(2)
C(11)	526(10)	12205(6)	2459(4)	81(2)
C(12)	–440(10)	12830(6)	2165(5)	84(3)
C(13)	–703(9)	12571(6)	1567(5)	74(2)
C(14)	634(8)	6665(5)	366(4)	59(2)
C(15)	–481(8)	6919(5)	–87(4)	60(2)
C(16)	–1591(8)	6395(6)	–221(4)	64(2)
C(17)	–2745(8)	6567(6)	–679(4)	64(2)
C(18)	–3971(9)	6153(6)	–805(5)	77(2)
C(19)	–4676(9)	6596(7)	–1332(5)	86(3)
C(20)	–3822(10)	7233(7)	–1504(4)	79(2)
C(21)	4176(7)	8380(5)	–419(4)	53(2)
C(22)	3373(7)	8848(5)	–930(3)	49(2)
C(23)	3937(7)	9135(5)	–1427(4)	56(2)
C(24)	3221(8)	9582(5)	–1970(4)	61(2)
C(25)	3612(10)	9934(6)	–2502(4)	77(2)
C(26)	2391(11)	10252(6)	–2866(4)	80(2)
C(27)	1363(10)	10059(6)	–2554(5)	86(3)
C(28)	2953(6)	10358(5)	141(3)	51(2)
C(29)	–668(7)	8606(5)	921(3)	59(2)
B(1)	–2394(18)	5160(13)	1177(9)	90(5)
F(1)	–3215(18)	4996(13)	645(7)	109(5)
F(2)	–2539(19)	6079(9)	1265(7)	126(6)
F(3)	–2729(17)	4674(11)	1665(7)	129(6)
F(4)	–1057(13)	5022(13)	1149(9)	159(8)
B(2)	–2523(23)	5130(16)	1283(10)	127(7)
F(21)	–2833(25)	4767(17)	721(9)	184(9)
F(22)	–3585(17)	5529(14)	1533(8)	155(6)
F(23)	–2157(19)	4450(12)	1700(10)	145(7)
F(24)	–1453(21)	5695(16)	1296(7)	147(6)

Table 3
Selected bond lengths (Å) and angles (°)

Cu(1)–O(4)	1.958(4)	C(7)–C(8)	1.436(10)
Cu(1)–O(5)	1.959(4)	C(8)–C(9)	1.332(10)
Cu(1)–N(3)	2.013(6)	C(9)–C(10)	1.424(10)
Cu(1)–N(2)	2.032(6)	C(10)–C(11)	1.357(11)
Cu(1)–N(1)	2.232(6)	C(11)–C(12)	1.412(12)
Cu(2)–O(5)	1.913(4)	C(12)–C(13)	1.332(12)
Cu(2)–O(4)	1.915(4)	O(1)–C(13)	1.370(9)
N(1)–C(7)	1.268(9)	O(1)–C(10)	1.383(9)
N(1)–C(2)	1.462(9)	C(14)–C(15)	1.422(10)
N(2)–C(21)	1.285(9)	C(15)–C(16)	1.342(10)
N(2)–C(6)	1.491(8)	C(22)–C(23)	1.339(10)
N(3)–C(14)	1.278(9)	C(23)–C(24)	1.439(11)
N(3)–C(4)	1.487(9)		
O(4)–Cu(1)–O(5)	78.1(2)	C(21)–N(2)–C(6)	117.3(6)
O(4)–Cu(1)–N(3)	166.2(2)	C(21)–N(2)–Cu(1)	126.4(5)
O(5)–Cu(1)–N(3)	95.5(2)	C(6)–N(2)–Cu(1)	116.4(5)
O(4)–Cu(1)–N(2)	94.9(2)	C(14)–N(3)–C(4)	117.1(6)
O(5)–Cu(1)–N(2)	165.7(2)	C(14)–N(3)–Cu(1)	126.8(5)
N(3)–Cu(1)–N(2)	88.4(2)	C(4)–N(3)–Cu(1)	116.1(5)
O(4)–Cu(1)–N(1)	99.4(2)	N(1)–C(7)–C(8)	127.1(7)
O(5)–Cu(1)–N(1)	101.5(2)	C(9)–C(8)–C(7)	121.8(7)
N(3)–Cu(1)–N(1)	93.8(2)	C(11)–C(10)–O(1)	109.5(8)
N(2)–Cu(1)–N(1)	91.9(2)	C(11)–C(10)–C(9)	131.4(8)
O(5)–Cu(2)–O(4)	80.3(2)	O(1)–C(10)–C(9)	119.0(7)
O(5)–Cu(2)–O(4)'	99.7(2)	C(10)–C(11)–C(12)	107.1(8)
C(28)–O(4)–Cu(2)	124.8(4)	C(13)–C(12)–C(11)	106.4(9)
C(28)–O(4)–Cu(1)	124.1(4)	C(12)–C(13)–O(1)	111.6(8)
Cu(2)–O(4)–Cu(1)	100.5(2)	C(13)–O(1)–C(10)	105.3(7)
C(29)–O(5)–Cu(2)	126.3(4)	C(8)–C(9)–C(10)	129.2(8)
C(29)–O(5)–Cu(1)	123.7(4)	N(3)–C(14)–C(15)	126.8(7)
Cu(2)–O(5)–Cu(1)	100.5(2)	C(15)–C(16)–C(17)	127.4(8)
C(7)–N(1)–C(2)	117.2(6)	N(2)–C(21)–C(22)	125.2(7)
C(7)–N(1)–Cu(1)	131.5(5)	C(22)–C(23)–C(24)	125.2(7)
C(2)–N(1)–Cu(1)	111.0(5)		

distance of the Cu(1) atom for the least-squares best fit plane defined by N(2), N(3), O(4) and (O5) is 0.2261 Å.

The whole $\{\text{Cu}(\mu\text{-OMe})_2\text{Cu}(\mu\text{-OMe})_2\text{Cu}\}^{2+}$ unit is encapsulated within the six interdigitated furyl-prop-2-en-1-ylidene 'arms', of the two tfct ligands. Large Cu–N=C angles, averaging 128.2(5)°, indicate some steric strain between the furyl-propen-2-en-1-ylidene groups and the tri-copper unit. Two tetrafluoroborate anions complete the structure (Fig. 3).

Crystallographic details are summarised in Table 1, positional parameters are given in Table 2 and selected bond lengths and angles are given in Table 3. ORTEP representations [10] are shown in Figs. 2 and 3.

4. Discussion

We have found eleven examples using the Cambridge Structural Data base [11] of discrete linear trinuclear copper structures like the one described in this paper [12–22]. Of these, two main synthetic strategies have been used to prepare the linear tri-copper array, these are (i) programmed assembly where the alkoxide groups are covalently attached to the

ligand and (ii) solvent mediated assembly where the alkoxide groups originate from the alcoholic solvent. Ten [12–21] complexes have been prepared using programmed assembly with a ligand which coordinates directly to the peripheral copper(II) ion of the trinuclear array and provides two further ligating atoms which coordinate the central copper(II). There is one example [22] that uses the solvent mediated assembly approach, but in this complex two of the four bridged methoxy units are also in a μ_3 coordination mode bridging as axial ligands to a copper ion in an adjacent dimer. The structure reported in this paper is unusual insofar as it shows a discrete $\text{Cu}_3(\text{OMe})_4^{2+}$ unit. It is reasonable to suggest the steric bulk of the ligand is important in preventing aggregation of the unit with other units as observed in [22].

5. Supplementary material

Full crystal data including structure factors and complete bond distances are available from the authors on request. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, positional coordinates, and bond lengths and angles.

Acknowledgements

LC would like to thank the EPSRC for a maintenance grant.

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