References

Bökman, F. & Bertagnolli, H. (1994). *Ber. Bunsenges. Phys. Chem.* **98**, 947–954.
Duraj, S. A., Towns, R. L. R., Baker, R. J. & Schupp, J. (1990). *Acta Cryst.* C**46**, 890–892.
Erker, G., Sarter, C., Albrecht, M., Dehnicke, S., Krüger, C., Raabe, E., Schlund, R., Benn, R., Rufinska, A. & Mynott, R. (1990). *J. Organomet. Chem.* **382**, 89–102.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Galeffi, B., Simard, M. & Wuest, J. D. (1990). *Inorg. Chem.* **29**, 951–954.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Manzer, L. E. (1982). *Inorg. Synth.* **21**, 135–140.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Young, D. A. (1988). *J. Mol. Catal.* **88**, 1405–1407.

Acta Cryst. (1996). C**52**, 568–570

Tetrakis[μ-(3-bromobenzoato)-μ-(2-dimethylaminoethanolato)-copper(II)]

Urho Turpeinen, Reijo Hämäläinen, Ilpo Mutikainen and Olli Orama

Department of Chemistry, PO Box 55, FIN-00014, University of Helsinki, Finland

(*Received 4 May 1995; accepted 5 September 1995*)

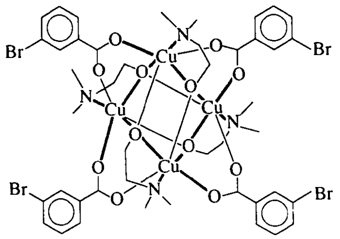
Abstract

A cubane-type Cu_4O_4 core has been found in the title tetrameric copper(II) complex {tetrakis(μ-3-bromobenzoato)-1κO:2$\kappa O'$;2κO:3$\kappa O'$;3κO:4$\kappa O'$;-4κO:1$\kappa O'$-tetrakis[μ-2-(dimethylamino)ethanolato]-1κN,1:2:3$\kappa^3 O$;2κN,2:3:4$\kappa^3 O$;3κN,3:4:1$\kappa^3 O$;4κN,4:1:2$\kappa^3 O$-tetracopper(II), $[Cu_4(C_7H_4BrO_2)_4(C_4H_{10}NO)_4]$}. The short Cu—$O_{\text{ethanolato}}$ bonds form an eight-membered ring folded in a boat-like conformation. The Cu···Cu distances vary between 3.121 (2) and 3.796 (3) Å. Each Cu atom has a distorted octahedral environment. Two ethanolato O atoms, a carboxy O atom and an amino N atom form the equatorial coordination plane, with Cu—O bond lengths in the range 1.914 (12)–1.954 (14) Å and Cu—N bond lengths in the range 2.011 (12)–2.057 (13) Å. The axial sites are occupied by an ethanolato O atom and an O atom of the carboxylate group, with Cu—O distances in the range 2.443 (8)–2.877 (9) Å.

Comment

Monomeric, dimeric, tetrameric, hexameric and nonameric complexes have been obtained from the reactions between 2-dimethylaminoethanol and Cu^{II} carboxylates (Turpeinen, Hämäläinen & Ahlgrén, 1980, 1985; Turpeinen, Hämäläinen & Reedijk, 1987, 1988). It has been found that when copper(II) 4-bromobenzoate reacts with 2-dimethylaminoethanol, a centrosymmetric structure is formed which is composed of three dimers. The dimers are bridged into a hexametallic unit by carboxylate O atoms, with Cu···Cu separations of 2.896 (2) and 2.988 (2) Å (Turpeinen, Hämäläinen & Reedijk, 1988).

The title structure, (I), consists of discrete cubane-like tetrameric molecules which are built up of four $[Cu(BrC_6H_4COO)(Me_2NCH_2CH_2O)]$ units joined together by the ethanolato O atom and carboxylate bridges. Within the Cu_4O_4 core, the long Cu···Cu distances are 3.794 (3) and 3.796 (3) Å, and the four short Cu···Cu distances vary from 3.121 (2) to 3.222 (3) Å.



(I)

The coordination geometry around the Cu atoms is distorted octahedral (4+2). The four equatorial bonds are directed towards two ethanolato O atoms, an amino N atom and a carboxy O atom, with mean values of 1.93, 2.04 and 1.94 Å, respectively. The axial bonds are directed towards an ethanolato O atom and a carboxy O atom, with mean values of 2.75 and 2.60 Å, respectively. The molecular symmetry of the present complex, C_1, has also been found in the related complex $[Cu(Me_2NCH_2CH_2O)(F_3CCOO)]_4$ (Ahlgrén, Turpeinen & Hämäläinen, 1982). The symmetry of the

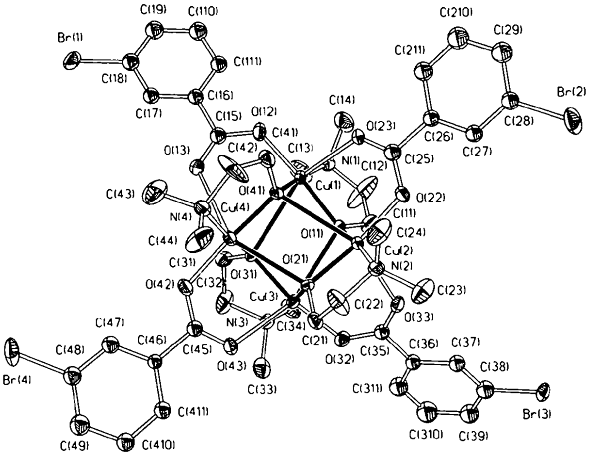


Fig. 1. A view of the title structure (*SHELXTL/PC*; Sheldrick, 1990). Displacement ellipsoids are drawn at the 20% probability level.

molecules, however, is lower than the point symmetry C_2 found in $[Cu(Me_2NCH_2CH_2O)(Cl_2CHCOO)]_4$ (Turpeinen, Hämäläinen & Ahlgrén, 1980) or S_4 found in $[Cu(Me_2NCH_2CH_2O)(ClCH_2COO)]_4$ (Turpeinen, Ahlgrén & Hämäläinen, 1979).

Experimental

Dark blue crystals of $[Cu_4(C_7H_4BrO_2)_4(C_4H_{10}NO)_4]$ were prepared by slow evaporation of an ethanol solution containing copper(II) 3-bromobenzoate and 2-(dimethylamino)ethanol in a molar ratio of approximately 1:1.

Crystal data

$[Cu_4(C_7H_4BrO_2)_4(C_4H_{10}NO)_4]$
$M_r = 1406.7$
Triclinic
$P\bar{1}$
$a = 14.487 (5)$ Å
$b = 14.978 (6)$ Å
$c = 15.081 (5)$ Å
$\alpha = 118.45 (3)°$
$\beta = 110.79 (3)°$
$\gamma = 86.76 (3)°$
$V = 2664 (2)$ Å^3
$Z = 2$
$D_x = 1.753$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7–14°$
$\mu = 4.63$ mm^{-1}
$T = 293$ K
Irregular
0.30 × 0.30 × 0.25 mm
Dark blue

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.77$, $T_{max} = 1.00$
5977 measured reflections
5977 independent reflections
3134 observed reflections $[F > 6\sigma(F)]$

$\theta_{max} = 23°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 200 reflections intensity decay: <2%

Refinement

Refinement on *F*
$R = 0.0540$
$wR = 0.0647$
$S = 1.36$
3134 reflections
434 parameters
H atoms included using a riding model

$w = 1/[\sigma^2(F) + 0.0011F^2]$
$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.82$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
Cu(1)	0.0161 (1)	0.3178 (1)	0.1932 (1)	0.048 (1)
Cu(2)	0.2180 (1)	0.3672 (1)	0.3920 (1)	0.044 (1)
Cu(3)	0.2462 (1)	0.4982 (1)	0.2881 (1)	0.047 (1)
Cu(4)	0.1926 (1)	0.2712 (1)	0.1006 (1)	0.049 (1)
Br(1)	−0.2758 (2)	0.0076 (2)	−0.4695 (2)	0.127 (2)
Br(2)	0.1225 (2)	0.2347 (2)	0.7534 (2)	0.113 (2)
Br(3)†	0.4255 (2)	0.8417 (2)	0.9497 (2)	0.066 (1)
Br(30)‡	0.3724 (7)	1.0166 (6)	0.7483 (6)	0.096 (5)
Br(4)	0.4196 (2)	0.2165 (2)	−0.2693 (2)	0.111 (2)
O(11)	0.1088 (6)	0.4269 (7)	0.3288 (7)	0.046 (5)
O(12)	−0.0854 (7)	0.2300 (9)	0.0531 (8)	0.076 (7)
O(13)	−0.0083 (9)	0.2182 (9)	−0.0561 (8)	0.089 (7)
O(21)	0.2915 (6)	0.3866 (6)	0.3165 (6)	0.038 (5)
O(22)	0.1447 (7)	0.3189 (8)	0.4506 (7)	0.066 (7)
O(23)	0.0077 (8)	0.2361 (8)	0.2997 (8)	0.072 (7)
O(31)	0.1492 (6)	0.4043 (6)	0.1473 (6)	0.041 (5)
O(32)	0.3077 (7)	0.6110 (7)	0.4354 (8)	0.057 (6)
O(33)	0.2884 (8)	0.5437 (7)	0.5334 (7)	0.064 (6)
O(41)	0.1214 (6)	0.2352 (7)	0.1670 (7)	0.044 (5)
O(42)	0.2842 (8)	0.2996 (7)	0.0456 (8)	0.069 (7)
O(43)	0.3744 (7)	0.4450 (8)	0.1935 (8)	0.061 (6)
N(1)	−0.0897 (9)	0.4100 (10)	0.2326 (10)	0.063 (8)
N(2)	0.3426 (8)	0.3142 (10)	0.4593 (9)	0.055 (8)
N(3)	0.2135 (10)	0.6022 (9)	0.2337 (9)	0.060 (8)
N(4)	0.2138 (10)	0.1230 (9)	0.0342 (10)	0.058 (8)
C(11)	0.0660 (11)	0.4995 (12)	0.3966 (12)	0.077 (11)
C(12)	−0.0383 (13)	0.4864 (19)	0.3434 (15)	0.232 (19)
C(13)	−0.1304 (14)	0.4577 (17)	0.1650 (18)	0.122 (19)
C(14)	−0.1709 (12)	0.3580 (15)	0.2331 (15)	0.103 (15)
C(15)	−0.0816 (12)	0.2034 (12)	−0.0400 (13)	0.062 (5)§
C(16)	−0.1775 (6)	0.1458 (7)	−0.1342 (7)	0.054 (4)§
C(17)	−0.1800 (6)	0.1057 (7)	−0.2397 (7)	0.059 (4)§
C(18)	−0.2700 (6)	0.0593 (7)	−0.3282 (7)	0.070 (5)§
C(19)	−0.3573 (6)	0.0529 (7)	−0.3112 (7)	0.077 (5)§
C(110)	−0.3548 (6)	0.0930 (7)	−0.2056 (7)	0.078 (5)§
C(111)	−0.2649 (6)	0.1394 (7)	−0.1171 (7)	0.065 (5)§
C(21)	0.3963 (10)	0.3888 (11)	0.3692 (12)	0.057 (10)
C(22)	0.4103 (12)	0.3123 (16)	0.4060 (15)	0.103 (17)
C(23)	0.3859 (14)	0.3777 (13)	0.5768 (12)	0.101 (13)
C(24)	0.3241 (14)	0.2110 (12)	0.4380 (14)	0.106 (14)
C(25)	0.0603 (12)	0.2605 (12)	0.3919 (14)	0.058 (4)§
C(26)	0.0279 (7)	0.2141 (7)	0.4495 (7)	0.052 (4)§
C(27)	0.0844 (7)	0.2386 (7)	0.5567 (7)	0.055 (4)§
C(28)	0.0523 (7)	0.1953 (7)	0.6065 (7)	0.061 (4)§
C(29)	−0.0363 (7)	0.1276 (7)	0.5492 (7)	0.083 (5)§
C(210)	−0.0927 (7)	0.1032 (7)	0.4421 (7)	0.096 (6)§
C(211)	−0.0607 (7)	0.1465 (7)	0.3922 (7)	0.070 (5)§
C(31)	0.1094 (11)	0.4440 (11)	0.0763 (12)	0.064 (10)
C(32)	0.1726 (15)	0.5398 (12)	0.1141 (11)	0.102 (14)
C(33)	0.3037 (12)	0.6678 (12)	0.2640 (13)	0.083 (12)
C(34)	0.1433 (13)	0.6669 (13)	0.2735 (15)	0.088 (14)
C(35)	0.3094 (11)	0.6149 (12)	0.5225 (12)	0.049 (4)§
C(36)	0.3443 (7)	0.7201 (7)	0.6221 (7)	0.052 (4)§
C(37)	0.3674 (7)	0.7290 (7)	0.7243 (7)	0.060 (4)§
C(38)	0.3966 (7)	0.8255 (7)	0.8170 (7)	0.074 (5)§
C(39)	0.4028 (7)	0.9130 (7)	0.8076 (7)	0.083 (5)§
C(310)	0.3797 (7)	0.9041 (7)	0.7055 (7)	0.107 (7)§
C(311)	0.3505 (7)	0.8076 (7)	0.6127 (7)	0.085 (5)§
C(41)	0.1025 (12)	0.1310 (11)	0.1261 (13)	0.069 (11)
C(42)	0.1639 (19)	0.0746 (14)	0.0705 (19)	0.174 (19)
C(43)	0.1752 (16)	0.0721 (14)	−0.0846 (13)	0.125 (16)
C(44)	0.3170 (13)	0.1058 (14)	0.0668 (16)	0.124 (15)
C(45)	0.3549 (11)	0.3710 (13)	0.1013 (13)	0.052 (4)§
C(46)	0.4250 (6)	0.3684 (7)	0.0451 (7)	0.041 (4)§
C(47)	0.3983 (6)	0.3015 (7)	−0.0661 (7)	0.059 (4)§
C(48)	0.4624 (6)	0.2989 (7)	−0.1176 (7)	0.066 (5)§
C(49)	0.5531 (6)	0.3633 (7)	−0.0580 (7)	0.079 (5)§
C(410)	0.5799 (6)	0.4302 (7)	0.0532 (7)	0.067 (5)§
C(411)	0.5158 (6)	0.4328 (7)	0.1047 (7)	0.056 (4)§

† Occupancy of 0.75. ‡ Occupancy of 0.25. § U_{iso}.

Table 2. *Selected geometric parameters (Å, °)*

Cu(1)—Cu(2)	3.162 (2)	Cu(2)—O(41)	2.816 (9)
Cu(1)—Cu(4)	3.222 (3)	Cu(2)—N(2)	2.055 (13)
Cu(1)—Cu(3)	3.796 (3)	Cu(3)—Cu(4)	3.121 (2)
Cu(1)—O(11)	1.942 (7)	Cu(3)—O(21)	1.941 (10)
Cu(1)—O(12)	1.929 (8)	Cu(3)—O(31)	1.929 (6)
Cu(1)—O(23)	2.474 (15)	Cu(3)—O(32)	1.942 (7)

Cu(1)—O(41)	1.941 (9)	Cu(3)—O(43)	2.598 (12)
Cu(1)—O(31)	2.822 (9)	Cu(3)—O(11)	2.686 (7)
Cu(1)—N(1)	2.057 (13)	Cu(3)—N(3)	2.044 (16)
Cu(2)—Cu(3)	3.154 (4)	Cu(4)—O(31)	1.924 (9)
Cu(2)—Cu(4)	3.794 (3)	Cu(4)—O(41)	1.914 (12)
Cu(2)—O(11)	1.947 (10)	Cu(4)—O(42)	1.954 (14)
Cu(2)—O(21)	1.930 (12)	Cu(4)—O(21)	2.692 (10)
Cu(2)—O(22)	1.948 (14)	Cu(4)—O(13)	2.877 (9)
Cu(2)—O(33)	2.443 (8)	Cu(4)—N(4)	2.011 (12)
O(11)—Cu(1)—O(23)	86.6 (4)	O(21)—Cu(3)—O(31)	91.5 (4)
O(12)—Cu(1)—O(23)	101.7 (5)	O(21)—Cu(3)—O(32)	98.2 (4)
O(11)—Cu(1)—O(41)	92.1 (3)	O(21)—Cu(3)—O(43)	80.7 (4)
O(12)—Cu(1)—O(41)	95.3 (4)	O(31)—Cu(3)—O(43)	85.6 (3)
O(23)—Cu(1)—O(41)	84.9 (5)	O(32)—Cu(3)—O(43)	110.3 (4)
O(11)—Cu(1)—N(1)	84.3 (4)	O(31)—Cu(3)—N(3)	84.3 (4)
O(12)—Cu(1)—N(1)	88.5 (4)	O(32)—Cu(3)—N(3)	89.1 (5)
O(23)—Cu(1)—N(1)	93.0 (6)	O(43)—Cu(3)—N(3)	87.0 (5)
O(11)—Cu(2)—O(21)	89.6 (4)	O(31)—Cu(4)—O(41)	91.7 (4)
O(11)—Cu(2)—O(22)	95.5 (5)	O(31)—Cu(4)—O(42)	94.6 (5)
O(11)—Cu(2)—O(33)	85.6 (3)	O(41)—Cu(4)—N(4)	85.2 (6)
O(21)—Cu(2)—O(33)	85.8 (4)	O(42)—Cu(4)—N(4)	89.7 (6)
O(22)—Cu(2)—O(33)	104.7 (4)	Cu(1)—O(11)—Cu(2)	108.8 (5)
O(21)—Cu(2)—N(2)	85.7 (5)	Cu(2)—O(21)—Cu(3)	109.1 (4)
O(22)—Cu(2)—N(2)	89.6 (6)	Cu(3)—O(31)—Cu(4)	108.2 (4)
O(33)—Cu(2)—N(2)	90.8 (4)	Cu(1)—O(41)—Cu(4)	113.4 (6)

One of the 3-bromobenzoate groups was shown to be disordered. Two positions were assigned to the Br atom of this group, with site occupancies of 0.75 for Br(3) and 0.25 for Br(30). Some ethanolato C atoms bonded to N atoms were also shown to be disordered (high displacement parameters and short C—C bonds). Geometric restraints were therefore used for these atoms during the refinement. The four phenyl rings were refined isotropically as rigid groups. The other non-H atoms were refined anisotropically. H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Data collection: Nicolet *P*3 software. Cell refinement: Nicolet *P*3 software. Data reduction: Nicolet *P*3 software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahlgrén, M., Turpeinen, U. & Hämäläinen, R. (1982). *Acta Cryst.* B**38**, 429–433.

North, A. C. T, Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Realease 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Turpeinen, U., Ahlgrén, M. & Hämäläinen, R. (1979). *Acta Chem. Scand. Ser. A*, **33**, 593–596.

Turpeinen, U., Hämäläinen, R. & Ahlgrén, M. (1980). *Acta Cryst.* B**36**, 927–930.

Turpeinen, U., Hämäläinen, R. & Ahlgrén, M. (1985). *Acta Cryst.* C**41**, 1728–1730.

Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1987). *Inorg. Chim. Acta*, **134**, 87–93.

Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1988). *Inorg. Chim. Acta*, **154**, 201–207.

Acta Cryst. (1996). C**52**, 570–572

Sodium Tetraphenylcyclopentadienide Bis(dimethoxyethane)

Christian Näther, Tim Hauck and Hans Bock

Institut für Anorganische Chemie, der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany

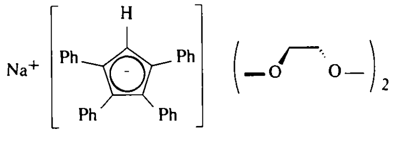
(*Received 11 October 1994; accepted 31 July 1995*)

Abstract

The title compound, $Na^+.C_{29}H_{21}^-.2C_4H_{10}O_2$, has been prepared and its crystal structure determined at 200 K. The structure shows isolated contact pairs containing a nine-coordinate Na^+ ion, which is surrounded by two dimethoxyethane molecules and one η^5-coordinated cyclopentadienyl ring.

Comment

Alkali metal salts of cyclopentadiene and its derivatives are still of synthetic and theoretical interest. The use of cyclopentadienylsodium in tetrahydrofuran for the preparation of the transition metal η^5-cyclopentadienyl derivatives (Fischer & Jira, 1953) remains the most widely applicable route to this important class of organometallic compounds. Only a few alkali metal cyclopentadienyl derivatives, predominantly the corresponding lithium compounds, have been structurally characterized. We are interested in the coordination chemistry of the ionic cyclopentadienyl metal complexes such as those containing sodium. Their structural diversity needs to be explored in detail, especially their dependency on solvent effects, charge distribution and the structure of the anion. Here we report the crystal structure of a novel monomeric tetraphenylcyclopentadienyl sodium compound, (I).



(I)

The crystal structure contains monomeric units of the tetraphenylcyclopentadienyl anion (Fig. 1) fivefold coordinated to the Na^+ cation, which is surrounded, in addition, by two molecules of dimethoxyethane (Fig. 2), making the structure comparable to that of pentamethylcyclopentadienylsodium pyridine (Rabe, Roesky, Stalke, Pauer & Sheldrick, 1991), which is the first reported monomeric cyclopentadienyl derivative of sodium. In general, the sodium salts of cyclopentadienyl anions,