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Tetraethylammonium Carbonylbis[difluoro(glyoximato)borato]copper(I)*†

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Abstract. $C_{17}H_{32}B_2CuF_4N_5O_5$, monoclinic, $P2_1/c$, a = 13·681 (1), b = 25·634 (3), c = 15·687 (2) Å, β = 115·35 (3)°, Z = 8, D_x = 1·463 Mg m^{-3}; R = 0·054 for 5000 reflections out to sin θ/λ = 0·50 Å^{-1} (Cu $K\alpha$ radiation). The two independent anions have the same conformation, the coordination about Cu$^{\rm I}$ being square-pyramidal with the Cu atom displaced by 1·03 Å from the plane of the N ligands toward the apical carbonyl group. The macrocyclic ligands are severely puckered into a boat conformation.

Introduction. To a hot methanolic solution (40 ml) of dimethylglyoxime (2·32 g) was slowly added a hot slurry of $Cu(OAc)_2.H_2O$ (1·99 g) in methanol (20 ml). The mixture was heated for 5 min, then filtered to give wine-red crystals of copper(II) dimethylglyoximate which was recrystallized from ethanol. This product was heated under reflux with excess $BF_3.Et_2O$ (10 ml) in dioxane (50 ml) for 15 min, then filtered and washed well with dioxane and ether to give bis[difluoro(glyoximato)borato]copper(II) (Gagné, Allison, Gall & Koval, 1977). Reduction was effected electrochemically as for similar compounds (Gagné *et al.*, 1977) using a platinum-gauze electrode in an acetone solution containing 0·10 *M* tetraethylammonium perchlorate as supporting electrolyte (−1·0 V *vs* Ag^+/Ag in CH_3CN). Single crystals of the carbonyl adduct were obtained by slow evaporation of an acetone solution of the Cu$^{\rm I}$ compound in a stream of CO.

Preliminary oscillation and Weissenberg photographs indicated 2/*m* Laue symmetry and systematic absences ($h0l$, l odd; $0k0$, k odd) characteristic of space group $P2_1/c$. Intensity data were collected on a Datex-automated GE quarter-circle diffractometer, using a crystal 0·2 × 0·3 × 0·5 mm with the long direction (**c**) approximately parallel to the φ axis. All reflections in the quadrant $\pm h,+k,+l$ out to 2θ = 100° (Ni-filtered Cu $K\alpha$ radiation) were collected using θ–2θ scans, leading to 5092 independent reflections of which exactly 5000 had net intensities greater than zero. The intensities of three check reflections (002, 0,10,0, $40\bar{2}$) remained effectively constant.

Positions of the Cu atoms and the framework atoms of the macrocycles were obtained using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974); the remaining heavy atoms were recovered from subsequent electron density and difference maps. H atoms of the tetraethylammonium cations were positioned on the basis of tetrahedral geometry and staggered conformations about the C–C bonds; those of the macrocyclic methyl groups were represented by sets of six half-populated sites, since difference maps in the expected planes showed no clear conformational preferences. The H parameters were not further adjusted.

Least-squares refinement was by minimization of the quantity $\sum w(F_o^2 - F_c^2)^2$, with the variances $\sigma^2(F_o^2) = 1/w$ based on counting statistics plus the empirical term (0·02 × scan count)^2. In the final cycles, the 454 parameters were distributed among three matrices: all coordinates in one, anisotropic U's and isotropic B's of cation A and anion A in the second, U's and B's of ions B in the third. The scale factor and an isotropic extinction parameter (Larson, 1967) were included with the U's and B's of ions A. Anisotropic U's were assigned to the Cu, F, carbonyl O, and methyl and methylene C atoms; the remaining atoms were assigned isotropic B's. The final goodness-of-fit (GOF) was 3·5 for the 5092 measured reflections and R was 0·054 for the 5000 reflections with positive net intensities; a difference map showed no pimples or dimples greater than 0·5 e Å^{-3}. The relatively large GOF suggests errors in the model – non-spherical electron distributions, additional anisotropies, and such – that are emphasized by the low observational variances associated with the heavily diffracting crystal. Final coordinates are given in Table 1.‡

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[*] Alternative name: tetraethylammonium carbonyl(2,2,9,9-tetrafluoro-5,6,12,13-tetramethyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-*N*,*N*′,*N*″,*N*‴)copper(I).

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[‡] Lists of structure factors, thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35806 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coordinates* (× 10⁴) *and isotropic thermal parameters*

	Molecule *A*				Molecule *B*			
	x	*y*	*z*	*B* (Å²)	*x*	*y*	*z*	*B* (Å²)
Cu	4690·5 (0·5)	−743·3 (0·3)	7115·9 (0·5)	4·01 (1)*	29·7 (0·5)	4124·1 (0·3)	7067·4 (0·5)	4·65 (1)*
N(1)	3608 (3)	−99 (1)	6708 (3)	3·7 (1)	−1377 (3)	4582 (1)	6653 (3)	3·8 (1)
N(2)	3141 (3)	−1035 (1)	6147 (3)	3·6 (1)	−1271 (3)	3695 (1)	5982 (3)	3·7 (1)
N(3)	5119 (3)	−1170 (1)	6138 (3)	3·3 (1)	742 (3)	3947 (2)	6130 (3)	4·1 (1)
N(4)	5583 (3)	−233 (1)	6668 (3)	3·5 (1)	624 (3)	4844 (2)	6778 (3)	4·3 (1)
C(1)	2603 (4)	−178 (2)	6178 (4)	3·5 (1)	−2295 (4)	4400 (2)	6063 (4)	3·6 (1)
C(2)	2326 (4)	−726 (2)	5899 (4)	3·5 (1)	−2219 (4)	3890 (2)	5647 (4)	3·5 (1)
C(3)	5699 (3)	−939 (2)	5796 (4)	3·3 (1)	1239 (4)	4308 (2)	5918 (4)	4·3 (1)
C(4)	6016 (3)	−398 (2)	6137 (3)	3·4 (1)	1139 (4)	4834 (2)	6258 (4)	4·0 (1)
C(5)	1780 (4)	242 (2)	5800 (4)	5·2 (1)*	−3338 (4)	4691 (2)	5761 (4)	5·5 (1)*
C(6)	1176 (4)	−888 (2)	5326 (5)	5·8 (1)*	−3194 (4)	3659 (2)	4845 (5)	5·8 (1)*
C(7)	5980 (5)	−1164 (2)	5047 (4)	5·5 (1)*	1825 (5)	4231 (2)	5306 (5)	7·1 (1)*
C(8)	6702 (5)	−76 (2)	5814 (5)	5·9 (1)*	1530 (4)	5309 (2)	5955 (4)	6·0 (1)*
O(1)	3936 (2)	416 (1)	6874 (2)	4·1 (1)	−1401 (3)	5082 (1)	6964 (3)	4·5 (1)
O(2)	2931 (2)	−1540 (1)	5812 (2)	4·1 (1)	−1144 (2)	3252 (1)	5528 (2)	4·3 (1)
O(3)	4698 (2)	−1648 (1)	5746 (2)	3·7 (1)	723 (3)	3464 (1)	5740 (3)	4·8 (1)
O(4)	5755 (2)	291 (1)	6907 (2)	4·1 (1)	375 (3)	5328 (1)	7007 (3)	4·7 (1)
B(1)	3927 (5)	−1849 (2)	6093 (5)	4·1 (1)	0 (5)	3087 (2)	5909 (5)	5·0 (1)
B(2)	5116 (5)	476 (2)	7408 (5)	4·3 (1)	−303 (5)	5301 (2)	7528 (5)	4·7 (1)
F(1)	4429 (2)	−1908 (1)	7075 (2)	4·3 (1)*	388 (2)	2973 (1)	6871 (2)	5·1 (1)*
F(2)	3608 (2)	−2336 (1)	5674 (2)	5·1 (1)*	14 (2)	2644 (1)	5410 (2)	6·0 (1)*
F(3)	5474 (2)	238 (1)	8284 (2)	5·3 (1)*	207 (2)	5024 (1)	8354 (2)	5·7 (1)*
F(4)	5300 (2)	1012 (1)	7499 (2)	5·4 (1)*	−484 (3)	5815 (1)	7708 (2)	6·2 (1)*
C(9)	5159 (4)	−997 (2)	8281 (4)	4·6 (1)	656 (5)	3842 (2)	8212 (4)	5·6 (1)
O(5)	5402 (4)	−1174 (2)	8997 (4)	8·7 (1)*	1072 (4)	3647 (2)	8916 (4)	11·1 (1)*
Tetraethylammonium cations								
N(5)	7048 (3)	−1991 (1)	2091 (3)	3·8 (1)	7824 (3)	2120 (1)	7278 (3)	3·8 (1)
C(10)	7681 (5)	−2113 (2)	1538 (4)	6·0 (1)*	8570 (5)	1905 (2)	8218 (4)	6·2 (1)*
C(11)	7089 (8)	−2272 (3)	544 (7)	10·7 (2)*	9721 (6)	1854 (3)	8372 (6)	9·3 (2)*
C(12)	6229 (4)	−1565 (2)	1608 (4)	5·3 (1)*	7817 (4)	1787 (2)	6479 (4)	4·8 (1)*
C(13)	6676 (5)	−1060 (2)	1458 (5)	5·7 (1)*	7518 (5)	1226 (2)	6490 (5)	6·6 (1)*
C(14)	6417 (4)	−2461 (2)	2148 (5)	6·1 (1)*	6703 (4)	2136 (2)	7257 (4)	5·7 (1)*
C(15)	7058 (5)	−2935 (2)	2636 (6)	7·3 (1)*	5816 (5)	2367 (3)	6392 (6)	8·0 (1)*
C(16)	7859 (5)	−1828 (2)	3056 (4)	5·7 (1)*	8155 (5)	2660 (2)	7129 (4)	5·5 (1)*
C(17)	7348 (8)	−1721 (3)	3728 (6)	9·9 (2)*	8217 (6)	3057 (2)	7835 (5)	7·7 (1)*

* B_{eq} for atoms with anisotropic *U*'s: $8\pi^2/3\,[U_{11}/\sin^2\beta + U_{22} + U_{33}/\sin^2\beta + 2U_{13}\cos\beta/\sin^2\beta]$.

Discussion. The coordination about the five-coordinate Cu^{I} atoms is square-pyramidal, with the four N atoms of the macrocycle in the basal plane and a CO group in the apical position (Fig. 1). In both anions the Cu^{I} atom is displaced an extraordinarily large 1·03 Å

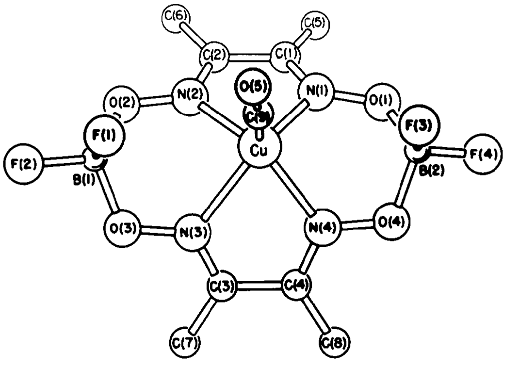

Fig. 1. A drawing of the anion, showing the numbering system.

Table 2. *Average bond lengths* (Å) *and angles* (°)

Numbers in square brackets are 'scatter e.s.d.'s' – e.s.d.'s in a single value as calculated from the dispersion of the *N* values in a group; numbers in parentheses are average e.s.d.'s in a single value as obtained from the coordinate e.s.d.'s.

	N			*N*	
Cu–N	8	2·135 [22](4)	N(1)–Cu–N(2)	4	73·0 [2](3)
Cu–C(9)	2	1·780 [2](5)	N(1)–Cu–N(4)	4	79·9 [11](3)
C(9)–O(5)	2	1·122 [0](7)	C(9)–Cu–N	8	118·9 [31](4)
N(1)–C(1)	8	1·281 [5](7)	Cu–C(9)–O(5)	2	176·3 [3](4)
N(1)–O(1)	8	1·381 [6](6)	Cu–N–C	8	118·9 [10](4)
C(1)–C(2)	4	1·480 [5](7)	Cu–N–O	8	124·8 [5](3)
C(1)–C(5)	8	1·496 [8](7)	C–N–O	8	116·1 [7](4)
B–O	8	1·479 [7](9)	N(1)–C(1)–C(2)	8	114·4 [6](5)
B–F	8	1·390 [8](8)	N(1)–C(1)–C(5)	8	124·2 [5](5)
			C(2)–C(1)–C(5)	8	121·2 [8](5)
Cu···F(1)	4	3·016 [13](3)	N–O–B	8	112·5 [6](5)
			O–B–O	4	114·4 [5](6)
			F–B–F	4	110·4 [8](6)
			O–B–F(1)	8	110·5 [4](5)
			O–B–F(2)	8	105·4 [6](5)
Tetraethylammonium ion					
N–C	8	1·507 [9](8)	C–N–C	12	109·5 [22](5)
C–C	8	1·495 [14](12)	N–C–C	8	116·0 [17](7)

Table 3. *Bond lengths* (Å) *and angles* (°) *about the* Cu^I *atoms*

E.s.d.'s are 0·004–0·005 Å for the distances and 0·3–0·4° for the angles.

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
Cu–N(1)	2·126	2·106	C(9)–Cu–N(1)	119·4	121·3	N(1)–Cu–N(2)	73·0	72·8
–N(2)	2·146	2·165	–N(2)	114·4	117·9	N(3)–Cu–N(4)	72·8	73·2
–N(3)	2·159	2·133	–N(3)	117·1	116·4	N(1)–Cu–N(4)	81·1	80·5
–N(4)	2·105	2·142	–N(4)	124·4	120·1	N(2)–Cu–N(3)	78·8	79·2
–C(9)	1·781	1·778				N(1)–Cu–N(3)	123·1	122·2
						N(2)–Cu–N(4)	121·2	122·0

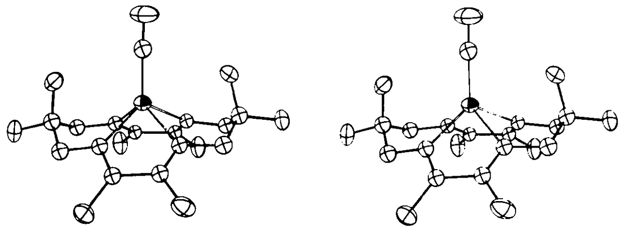

Fig. 2. A stereoscopic view (Johnson, 1965) of anion *A*.

above the plane of the N atoms, which are themselves coplanar within 0·01 Å. The Cu–C and C–O bond lengths, 1·78 and 1·12 Å, and the approximately linear Cu–C–O bond angle of 176° are typical of Cu^I–CO adducts (Gagné *et al.*, 1977; see also Churchill, DeBoer, Rotella, Aba Salah & Bruce, 1975; Pasquali, Marchetti & Floriani, 1978, and references therein).

A stereoscopic view of anion *A* is shown in Fig. 2. Geometries of the two independent anions are effectively identical, and average values for chemically equivalent bond lengths and angles are given in Table 2. The Cu–N distances are rather long and somewhat scattered; the range of values, 2·11 to 2·16 Å, is the same in both anions (see Table 3). The scatter is larger than for any other type of bond in the compound, and is of high statistical significance. We see no obvious explanation for this asymmetry, and can only suggest that it reflects some peculiar and as yet unappreciated subtleties in Cu^I bonding.

The dimethylglyoximate macrocycle is severely distorted from planarity, being best described as having a dome, boat conformation (Gagné *et al.*, 1977; Gagné, Allison & Lisensky, 1978). A result of this conformation is that two of the F atoms, F(1) and F(3), assume axial positions with relatively short (3·02 Å) Cu···F distances. The structure of the macrocycle is, overall, rather similar to that of an analogue in which one of the O–BF_2–O linkages is replaced by a trimethylene CH_2–CH_2–CH_2 link (Gagné *et al.*, 1978). That compound also shows a large out-of-plane displacement of the Cu^I atom (0·96 Å) and a short Cu···F distance (3·07 Å). Measurements of equilibrium binding constants of CO for it and related compounds had suggested that the Cu···F interaction might help to stabilize the five-coordinate species (Gagné, Allison & Ingle, 1979); however, some very recent studies of CO binding to a number of analogous Ni^I compounds (Gagné & Ingle, 1980) appear to rule out any such effect. In the present compound, there is no geometrical evidence to suggest that the Cu···F interactions lead to further stability; to the contrary, comparison of the two types of O–B–F angles (Table 2) suggests that the interaction might be repulsive.

References

Churchill, M. R., DeBoer, B. G., Rotella, F. J., Abu Salah, O. M. & Bruce, M. I. (1975). *Inorg. Chem.* **14**, 2051–2056.

Gagné, R. R., Allison, J. L., Gall, R. S. & Koval, C. A. (1977). *J. Am. Chem. Soc.* **99**, 7170–7178.

Gagné, R. R., Allison, J. L. & Ingle, D. M. (1979). *Inorg. Chem.* **18**, 2767–2774.

Gagné, R. R., Allison, J. L. & Lisensky, G. C. (1978). *Inorg. Chem.* **17**, 3563–3571.

Gagné, R. R. & Ingle, D. M. (1980). *Inorg. Chem.* Submitted.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Pasquali, M., Marchetti, F. & Floriani, C. (1978). *Inorg. Chem.* **17**, 1684–1688.