KULPE, S., SEIDEL, I., SZULZEWSKY, K. & KRETSCHMER, G. (1982). *Acta Cryst.* **B38**, 2813–2817.
NAVRÁTIL, O., FOFANA, M. & SMOLA, J. (1984). *Z. Chem.* **24**(1), 30–31.
RICHTER, H., FLUCK, E., RIFFEL, H. & HESS, H. (1983). *Z. Anorg. Allg. Chem.* **496**, 109–116.
Syntex (1971). *XTL Structure Determination System.* Syntex Analytical Instruments, Cupertino, California, EU.

Acta Cryst. (1989). C**45**, 1689–1691

Structure of a Polyaminecopper(II) Complex

BY PETER SIVÝ, FEDOR VALACH AND BRANISLAV KOREŇ

Department of Chemical Physics and Nuclear Technique, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 *Bratislava, Czechoslovakia*

ĽUBOV MACÁŠKOVÁ

Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 *Bratislava, Czechoslovakia*

AND FRANTIŠEK PAVELČÍK AND JÚLIUS SIVÝ

Department of Analytical Chemistry, Faculty of Pharmacy, J. A. Komensky University, 832 32 *Bratislava, Czechoslovakia*

(*Received* 23 *September* 1988; *accepted* 1 *March* 1989)

Dedicated to Professor Ján Gažo in memoriam

Abstract. μ-(1,3-Propanediamine-*N*,*N'*)-tetrakis-(1,3-propanediamine-*N*,*N'*)dicopper(II) tetrafluoroborate, $[Cu_2(C_3H_{10}N_2)_5](BF_4)_4$, $M_r = 844{\cdot}9$, orthorhombic, *Pbca*, $a = 14{\cdot}573\ (11)$, $b = 15{\cdot}761\ (13)$, $c = 30{\cdot}669\ (13)$ Å, $V = 7044{\cdot}2$ Å^3, $Z = 8$, $D_m = 1{\cdot}58$, $D_x = 1{\cdot}59$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}36$ mm^{-1}, $F(000) = 3456$, $T = 293$ K. Final $R = 0{\cdot}082$ for 5220 unique reflections. The two molecules of $[Cu(tn)_{2\cdot5}](BF_4)_2$ (tn = 1,3-propanediamine) in the asymmetric unit are linked through one of the tn groups. The coordination polyhedron of both copper(II) ions is a distorted tetragonal pyramid. The four BF_4^- ions form no short intermolecular contacts.

Introduction. Gažo and co-workers (Gažo, 1974; Gažo, Boča, Jóna, Macášková, Šíma, Pelikán & Valach, 1982) have studied the relationship in Cu^{II} complexes between the central-atom—ligand distances in the equatorial plane and those in axial positions. It was found that for a given chromophore the mean values of central-atom—ligand distances in the equatorial plane (R_e) and those in the axial positions (R_a) correlate along a smooth curve in such a way that the values of R_a decrease with increasing R_e and *vice versa*. The tetragonal distortions of coordination polyhedra occur to the greatest extent in Cu^{II} complexes with planar metallocycles having π bonds in the equatorial plane. By contrast, comparatively short axial bonds were found in complexes with five-membered or non-planar six-membered metallocycles (*e.g.* in chair conformations).

The present work reports the X-ray structure of a Cu^{II} 1,3-propanediamine (tn) complex containing six-membered metallocycles (in chair conformation) in the equatorial plane. In the complex, of formula $[Cu_2(tn)_5](BF_4)_4$, it was initially assumed that three tn groups are bonded to one copper(II) ion and another two to the second copper(II) ion and moreover that BF_4^- ions are bonded to the $[Cu(tn)_{2\cdot5}]$ molecules. The reality is quite different.

Experimental. $[Cu_2(tn)_5](BF_4)_4$ was prepared by adding $Cu(BF_4)_2.6H_2O$ in methanol to a solution containing 1,3-propanediamine.

Dark-blue prismatic crystal with dimensions 0·27 × 0·27 × 0·60 mm; D_m by flotation in CCl_4; orthorhombic space group *Pbca* (No. 61); Syntex $P2_1$ diffractometer, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 50°$, time per reflection *ca* 60 s; two standard reflections, variation 2·8%; 25 reflections with $6{\cdot}0 < 2\theta < 18{\cdot}1°$ used for refinement of lattice parameters; absorption correction was not applied; index range $0 \le h \le 11$, $0 \le k \le 18$, $0 \le l \le 36$; 5930 reflections measured, 5220 unique, 1720 observed with $I > 2{\cdot}0\sigma(I)$. For identification of Bravais translation lattice program *UB* was used (Sivý, Sivý & Koreň, 1987). Data reduction carried out with program

Table 1. *Final atomic coordinates* ($\times 10^4$, *for* Cu $\times 10^5$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu(1)	57174 (1)	27768 (1)	17862 (1)	3·53 (13)
Cu(2)	60250 (1)	24639 (1)	44069 (1)	3·94 (14)
N(11)	6495 (13)	3777 (15)	1606 (6)	6·4 (8)
C(12)	6514 (20)	4561 (18)	1838 (10)	8·1 (11)
C(13)	5535 (22)	4923 (14)	1919 (10)	8·1 (11)
C(14)	4964 (20)	4368 (18)	2187 (10)	7·6 (10)
N(15)	4711 (13)	3589 (11)	1980 (7)	5·0 (6)
N(16)	6471 (12)	2033 (13)	1374 (6)	5·4 (9)
C(17)	6510 (20)	1105 (18)	1423 (8)	6·9 (10)
C(18)	5601 (20)	713 (18)	1438 (9)	7·4 (11)
C(19)	5037 (18)	946 (18)	1827 (8)	6·4 (9)
N(10)	4770 (13)	1854 (12)	1825 (6)	5·2 (6)
N(21)	4680 (12)	2111 (13)	4304 (6)	5·4 (6)
C(22)	4473 (20)	1248 (17)	4156 (9)	6·9 (10)
C(23)	4861 (20)	583 (15)	4452 (9)	6·6 (9)
C(24)	5867 (19)	566 (14)	4477 (8)	6·1 (9)
N(25)	6211 (14)	1326 (13)	4695 (7)	6·2 (7)
N(26)	5742 (15)	3622 (11)	4171 (7)	5·9 (7)
C(27)	5658 (19)	4311 (18)	4482 (11)	8·1 (11)
C(28)	6522 (25)	4449 (19)	4715 (11)	9·7 (13)
C(29)	6814 (19)	3799 (21)	5021 (9)	8·2 (11)
N(20)	7003 (15)	3003 (15)	4799 (7)	7·3 (8)
N(31)	6346 (12)	2637 (11)	2447 (6)	4·6 (5)
C(32)	6801 (15)	1870 (14)	2602 (7)	4·2 (7)
C(33)	7263 (14)	1962 (13)	3050 (6)	3·7 (6)
C(34)	6573 (12)	2044 (14)	3408 (6)	3·1 (6)
N(35)	6948 (12)	2112 (12)	3847 (5)	4·5 (6)
B(1)	4523 (19)	2814 (25)	659 (8)	6·6 (12)
F(11)	4074 (13)	3242 (13)	344 (6)	10·6 (7)
F(12)	4006 (13)	2390 (15)	884 (6)	12·6 (8)
F(13)	5218 (14)	2429 (19)	502 (7)	15·4 (10)
F(14)	4891 (16)	3438 (16)	923 (7)	14·4 (10)
B(2)	8930 (17)	2739 (19)	1929 (10)	5·5 (10)
F(21)	8449 (11)	2231 (13)	1666 (5)	10·2 (7)
F(22)	9297 (12)	2250 (12)	2244 (5)	10·2 (7)
F(23)	9604 (11)	3138 (12)	1721 (6)	10·1 (7)
F(24)	8355 (11)	3298 (13)	2105 (7)	11·1 (7)
B(3)	7836 (18)	3757 (18)	613 (8)	4·8 (9)
F(31)	7506 (16)	3036 (11)	725 (5)	11·4 (7)
F(32)	8096 (13)	3676 (12)	188 (5)	9·9 (7)
F(33)	7243 (15)	4369 (14)	635 (7)	13·5 (9)
F(34)	8557 (13)	3929 (16)	847 (8)	14·1 (10)
B(4)	2507 (37)	4626 (29)	1599 (16)	11·6 (18)
F(41)	1999 (14)	5166 (13)	1342 (7)	11·8 (8)
F(42)	3348 (17)	4969 (17)	1646 (9)	16·1 (11)
F(43)	2594 (17)	3870 (14)	1393 (8)	14·1 (10)
F(44)	2116 (21)	4530 (18)	1982 (8)	19·8 (14)

*XP*21 (Pavelčík, 1987). The coordinates of the two Cu atoms were found by program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Remaining non-H atoms were located using Fourier synthesis (Sheldrick, 1976). The structure was anisotropically refined by block-diagonal least squares (on F). Scattering factors from *International Tables for X-ray Crystallography* (1962). Positions of H atoms were calculated. All later calculations were performed by *XRC*83 program system (Pavelčík, Kettmann & Majer, 1985). Maximum positive and maximum negative electron density in final difference Fourier synthesis 0·69 and $-0{\cdot}61$ e Å^{-3}. Final $R = 0{\cdot}082$, $wR = 0{\cdot}089$, $w = 1{\cdot}0/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0{\cdot}1$ in final refinement cycle; 424 parameters refined (damped fudge factor = 0·3). Calculations performed using an M4030-1 computer, Slovak Technical University, and an EC-1045 computer, J. A. Komensky University, Bratislava, Czechoslovakia.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for non-*H *atoms*

Cu(1)—N(11)	2·02 (2)	C(27)—C(28)	1·47 (5)
—N(15)	2·04 (2)	C(28)—C(29)	1·45 (4)
—N(16)	2·04 (2)	C(29)—N(20)	1·45 (4)
—N(10)	2·01 (1)	N(31)—C(32)	1·46 (3)
—N(31)	2·23 (2)	C(32)—C(33)	1·54 (3)
Cu(2)—N(21)	2·06 (2)	C(33)—C(34)	1·49 (3)
—N(25)	2·02 (2)	C(34)—N(35)	1·46 (2)
—N(26)	2·01 (2)	B(1)—F(11)	1·35 (3)
—N(20)	2·05 (2)	—F(12)	1·24 (4)
—N(35)	2·25 (2)	—F(13)	1·28 (4)
N(11)—C(12)	1·43 (4)	—F(14)	1·38 (4)
C(12)—C(13)	1·56 (4)	B(2)—F(21)	1·33 (3)
C(13)—C(14)	1·46 (4)	—F(22)	1·35 (3)
C(14)—N(15)	1·43 (3)	—F(23)	1·33 (3)
N(16)—C(17)	1·47 (3)	—F(24)	1·33 (3)
C(17)—C(18)	1·46 (4)	B(3)—F(31)	1·28 (3)
C(18)—C(19)	1·50 (4)	—F(32)	1·36 (3)
C(19)—N(10)	1·48 (3)	—F(33)	1·30 (3)
N(21)—C(22)	1·47 (3)	—F(34)	1·30 (3)
C(22)—C(23)	1·50 (4)	B(4)—F(41)	1·38 (5)
C(23)—C(24)	1·47 (4)	—F(42)	1·35 (6)
C(24)—N(25)	1·46 (3)	—F(43)	1·36 (5)
N(26)—C(27)	1·45 (4)	—F(44)	1·32 (6)

N(11)—Cu(1)—N(15)	89·6 (8)	Cu(1)—N(11)—C(12)	123 (2)
—N(16)	88·7 (8)	N(11)—C(12)—C(13)	112 (2)
—N(10)	165·3 (8)	C(12)—C(13)—C(14)	113 (2)
—N(31)	95·4 (8)	C(13)—C(14)—N(15)	114 (2)
N(15)—Cu(1)—N(16)	158·2 (8)	Cu(1)—N(15)—C(14)	119 (2)
—N(10)	86·7 (8)	Cu(1)—N(16)—C(17)	122 (2)
—N(31)	95·3 (7)	N(16)—C(17)—C(18)	113 (2)
N(16)—Cu(1)—N(10)	89·5 (8)	C(17)—C(18)—C(19)	115 (2)
—N(31)	106·5 (7)	C(18)—C(19)—N(10)	112 (2)
N(10)—Cu(1)—N(31)	99·1 (7)	Cu(1)—N(10)—C(19)	121 (1)
		Cu(2)—N(21)—C(22)	120 (2)
N(21)—Cu(2)—N(25)	87·4 (8)	N(21)—C(22)—C(23)	113 (2)
—N(26)	89·7 (8)	C(22)—C(23)—C(24)	115 (2)
—N(20)	149·7 (8)	C(23)—C(24)—N(25)	111 (2)
—N(35)	112·6 (7)	Cu(2)—N(25)—C(24)	119 (2)
N(25)—Cu(2)—N(26)	173·9 (8)	Cu(2)—N(26)—C(27)	117 (2)
—N(20)	91·0 (9)	N(26)—C(27)—C(28)	111 (2)
—N(35)	92·0 (7)	C(27)—C(28)—C(29)	118 (3)
N(26)—Cu(2)—N(20)	88·7 (8)	C(28)—C(29)—N(20)	111 (2)
—N(35)	94·1 (7)	Cu(2)—N(20)—C(29)	120 (2)
N(20)—Cu(2)—N(35)	97·7 (8)	Cu(1)—N(31)—C(32)	124 (1)
		N(31)—C(32)—C(33)	114 (2)
		C(32)—C(33)—C(34)	112 (2)
		C(33)—C(34)—N(35)	116 (2)
		Cu(2)—N(35)—C(34)	120 (1)

F(11)—B(1)—F(12)	112 (3)	F(31)—B(3)—F(32)	106 (2)
—F(13)	111 (3)	—F(33)	113 (2)
—F(14)	105 (2)	—F(34)	110 (2)
F(12)—B(1)—F(13)	116 (3)	F(32)—B(3)—F(33)	108 (2)
—F(14)	107 (3)	—F(34)	109 (2)
F(13)—B(1)—F(14)	105 (3)	F(33)—B(3)—F(34)	111 (2)
F(21)—B(2)—F(22)	107 (2)	F(41)—B(4)—F(42)	108 (4)
—F(23)	112 (2)	—F(43)	109 (4)
—F(24)	108 (2)	—F(44)	110 (4)
F(22)—B(2)—F(23)	109 (2)	F(42)—B(4)—F(43)	109 (4)
—F(24)	110 (2)	—F(44)	110 (4)
F(23)—B(2)—F(24)	110 (2)	F(43)—B(4)—F(44)	111 (4)

Discussion. The atom coordinates are in Table 1.* Bond distances and bond angles are given in Table 2. The structure is depicted in Fig. 1 (all BF_4^- ions are omitted). Four tn groups are chelated to two Cu atoms, each in the characteristic chair conformation. The fifth tn molecule is bonded through N atoms to both Cu atoms (Fig. 1). The Cu(1)—Cu(2) distance

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51997 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

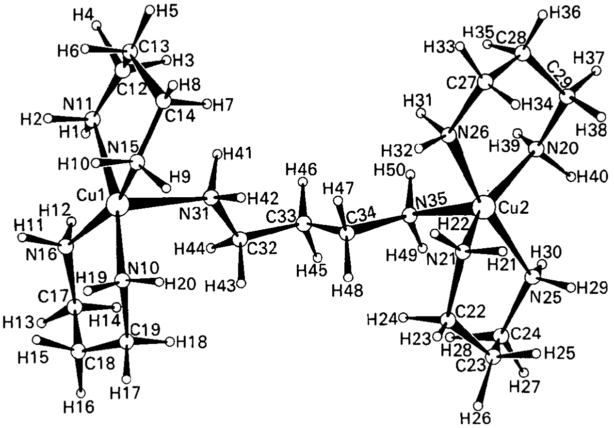

Fig. 1. Structure of the title compound showing the atomic numbering (four BF_4^- groups omitted).

is 8·07 (7) Å, and average Cu—N distances are Cu(1)—N(eq.) 2·03 (2), Cu(1)—N(ax1) 2·23 (2) Å and Cu(2)—N(eq.) 2·04 (2), Cu(2)—N(ax1) 2·25 (2) Å. Coordination around Cu takes the form of a distorted tetragonal pyramid. The dihedral angle between plane (1) [N(11), N(15), N(16), N(10)] and plane (2) [N(21), N(25), N(26), N(20)] is 62·8 (5)°. The distance of Cu(1) from plane (1) is −0·32 (2) Å and that of Cu(2) from plane (2) is +0·31 (2) Å.

It is interesting that, in contrast to the initial assumption, none of the BF_4^- ions are bonded to other atoms in the structure. The shortest intermolecular contacts are F(22)—H(20) 2·09 (2) and (between non-H atoms) F(22)—N(10) 3·00 (2) Å.

Similar crystal structures with several heavy atoms mutually bonded through open tn groups are reported by Vezzosi, Saladini, Battaglia & Corradi (1985), Pajunen & Kivekäs (1979), Näsäkkälä (1977), Kivekäs, Pajunen & Smolander (1977) and Kivekäs (1978).

References

Gažo, J. (1974). *Pure Appl. Chem.* **38**, 279–301.

Gažo, J., Boča, R., Jóna, E., Macášková, Ľ., Šíma, J., Pelikán, P. & Valach, F. (1982). *Coord. Chem. Rev.* **43**, 87–131.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Kivekäs, R. (1978). *Finn. Chem. Lett.* pp. 58–63.

Kivekäs, R., Pajunen, A. & Smolander, K. (1977). *Finn. Chem. Lett.* pp. 256–260.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Näsäkkälä, M. (1977). *Ann, Acad. Sci. Fenn. Ser. A*2, **181**, 3–72.

Pajunen, A. & Kivekäs, R. (1979). *Cryst. Struct. Commun.* **8**, 385–391.

Pavelčík, F. (1987). *XP21. A Computer Program for Syntex P*2$_1$ *Data Reduction.* J. A. Komensky Univ., Czechoslovakia.

Pavelčík, F., Kettmann, V. & Majer, J. (1985). *Chem. Pap.* **39**, 467–472.

Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Sivý, P., Sivý, J. & Koreň, B. (1987). *UB. Automatic Procedure for Unambiguous Choice of Lattice Parameters and Bravais Translation Lattice.* Slovak Technical Univ., Czechoslovakia.

Vezzosi, M., Saladini, M., Battaglia, L. P. & Corradi, A. B. (1985). *Inorg. Chim. Acta,* **100**, 261–266.

Acta Cryst. (1989). C**45**, 1691–1694

Copper 1-Aminocyclohexanecarboxylate Monohydrate [Aquabis(1-aminocyclohexanecarboxylato)copper(II)]; Tetra- and Pentacoordinate Copper

By Helmut M. Haendler

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824-3598, *USA*

(*Received* 31 *January* 1989; *accepted* 7 *March* 1989)

Abstract. $[Cu(C_7H_{12}NO_2)_2(H_2O)]$, $M_r = 365·9$, monoclinic, $P2_1/c$, $a = 10·750$ (3), $b = 13·643$ (4), $c = 22·819$ (5) Å, $\beta = 100·51$ (2)°, $V = 3291$ (1) Å^3, $Z = 8$, $D_x = 1·48$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·40$ mm^{-1}, $F(000) = 1544$, $T = 293$ (1) K, $R = 0·051$ for 4074 reflections. There are two chelated molecules in each of four asymmetric units, with two amino groups and two carboxyl groups coordinated to each Cu atom. The amino groups are in the axial positions of the cyclohexane rings, the carboxyl groups in the equatorial positions. In one molecule the N atoms are in a *trans* position, and the configuration of the Cu atom is intermediate between that of a distorted pentacoordinate trigonal bipyramid and a distorted rectangular pyramid, with the O atom of a water molecule occupying the fifth position. In the second molecule the coordination is planar, with the N atoms in a *cis* position. A second

0108-2701/89/111691-04$03.00