Structure of Bis(N-methylimidazole)copper(I) Tetrafluoroborate

By G. O. Tan and K. O. Hodgson

Department of Chemistry, Stanford University, Stanford, CA 94305, USA

B. Hedman

Stanford Synchrotron Radiation Laboratory, Stanford University, SLAC, Bin 69, Stanford, CA 94309, USA

G. R. Clark

Department of Chemistry, University of Auckland, Auckland, New Zealand

and M. L. Garrity and T. N. Sorrell

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA

Abstract. $[Cu(C_4H_6N_2)_2]^+ \cdot [BF_4]^-$, $M_r = 314 \cdot 56$, triclinic, $P\bar{1}$, $a = 7 \cdot 811$ (2), $b = 8 \cdot 993$ (3), $c = 10 \cdot 136$ (3) Å, $\alpha = 77 \cdot 95$ (2), $\beta = 77 \cdot 91$ (2), $\gamma = 72 \cdot 11$ (2)°, $V = 654 \cdot 5$ (3) Å^3, $Z = 2$, $D_x = 1 \cdot 60$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = $0 \cdot 71073$ Å, μ(Mo $K\bar{\alpha}$) = $17 \cdot 71$ cm^{-1}, $F(000) = 316$, $T = 293$ K, $R(F) = 0 \cdot 060$ for 1163 [$I > 3\sigma(I)$] reflections. The copper atom is linearly coordinated to the imidazole nitrogen donors [Cu—N $1 \cdot 863$ (7), $1 \cdot 855$ (7) Å; N—Cu—N $173 \cdot 6$ (3)°]. The approximately planar cations stack in pairs to create weakly bound dimers with Cu···Cu separations of $3 \cdot 198$ (2) Å.

Introduction. Complexes containing coordinatively unsaturated copper(I) atoms and nitrogen heterocyclic ligands are of interest as possible models for deoxyhemocyanin (Sorrell, 1989). An intriguing feature of this protein is that its binuclear active site binds just one molecule of CO, despite the apparent availability of further coordination sites (Volbeda & Hol, 1989). Sorrell & Jameson (1983) have prepared a number of copper(I) complexes using imidazole, pyrazole and pyridine derivatives and studied their reactivity towards CO binding. They carried out structural studies of Cu(1,3,5-trimethylpyrazole)$_2^+ \cdot$BF$_4^-$, which is inert towards CO, and Cu(1-methylpyrazole)$_2^+ \cdot$BF$_4^-$, which absorbs CO. The overall cation structure is similar in both complexes, but the latter forms dimeric units in the solid state whereas the former does not. All of their imidazole complexes are inert towards CO. In order to augment the structural data available on two-coordinate copper(I) complexes, especially those having imidazole ligands, we have determined the single-crystal X-ray structure of Cu(N-methylimidazole)$_2^+ \cdot$BF$_4^-$.

Experimental. The complex was prepared under an inert atmosphere according to the literature method (Sorrell & Jameson, 1983). Colorless parallelepipeds were obtained by slow cooling of a hot ethanol solution of the complex. The density was not measured because of extreme sensitivity to oxygen. A crystal measuring approximately $0 \cdot 50 \times 0 \cdot 25 \times 0 \cdot 15$ mm was mounted in a glass capillary and employed to collect X-ray intensity data on a Nicolet $P2_1$ diffractometer, using graphite-monochromated Mo $K\bar{\alpha}$ radiation. Unit-cell dimensions were from 50 reflections, $2 \cdot 9 < \theta < 18 \cdot 6°$; no systematic absences, space group $P\bar{1}$ by intensity statistics and satisfactory structure solution and refinement; 2796 unique reflections, $1 \cdot 0 < \theta < 27 \cdot 5°$; [(sin$\theta$)/$\lambda$]$_{max}$ $0 \cdot 6497$ Å^{-1}; 1163 with $I > 3\sigma(I)$, $-10 \le h \le 10$, $-9 \le k \le 9$, $-11 \le l \le 11$; three intensity standards checked every 50 reflections showed a small decline in intensity (maximum decline 6%) during data collection; the data were scaled accordingly, Lorentz and polarization corrections were applied, but no absorption corrections were made. The copper atom was located from a Patterson map. All other non-hydrogen atoms were located from a subsequent difference Fourier map. Hydrogen atoms were included in calculated positions (C—H $0 \cdot 96$ Å). The program used for F_{obs} refinement was *SHELX76* (Sheldrick, 1976). Final refinement values were $w = 1 \cdot 0/[\sigma^2(F) + 2 \cdot 05 \times 10^{-4}F^2]$ (for 165 parameters), $R = 0 \cdot 060$, $wR = 0 \cdot 056$, $S = 2 \cdot 437$, $\Delta_{max}/\sigma = 0 \cdot 03$ for non-hydrogen atoms; max. $\Delta\rho$ excursion in final difference map $0 \cdot 62$ e Å^{-3} (near [BF$_4$]$^-$), min. $\Delta\rho = -0 \cdot 41$ e Å^{-3}; calculations were performed on a MicroVAX 3600 computer. Diagrams were produced using *ORTEP*II (Johnson, 1976). Atomic scattering factors used were those of

Cromer & Mann (1968) (F, O, N, C, B); *International Tables for X-ray Crystallography* (1974) (Cu, H); Cromer & Liberman (1970).

Discussion. Atomic positions are given in Table 1.* The molecular geometry and atomic numbering are depicted in Fig. 1.

Within each cation, the copper atom is nearly linearly coordinated to the two nitrogen donors of the two imidazole groups, with Cu—N(1) 1·863 (7), Cu—N(3) 1·855 (7) Å and N(1)—Cu—N(3) 173·6 (3)°. The imidazole rings are disposed such that the two methyl substituents project to the same side of the molecule, rather than adopting the alternative centrosymmetric arrangement. Bond lengths and angles are given in Table 2.

The above geometry contrasts with that of tetrahedral tetrakis(N-methylimidazole)copper(I) perchlorate (Clegg, Acott & Garner, 1984), where Cu—N is 2·054 (2) Å, but compares closely with that found for Cu(1-methylpyrazole)$_2^+$ and Cu(1,3,5-trimethyl-pyrazole)$_2^+$, where Cu—N and N—Cu—N are 1·873 (3), 1·879 (3) Å, 178·2 (2)° and 1·878 (3), 1·863 (4) Å, 173·8 (2)° respectively (Sorrell & Jameson, 1983), and with Cu(2,4-dimethylpyridine)$_2^+$, where Cu—N and N—Cu—N are 1·86 (1) Å and 170 (1)° respectively (Engelhardt, Pakawatchai, White & Healy, 1985). However, the degree of aggregation in the solid state is different for each of the four complexes. In Cu(1,3,5-trimethylpyrazole)$_2^+$, there are no long-range interactions involving the copper atoms; in Cu(1-methylpyrazole)$_2^+$, weak interactions between copper and the outer carbon atoms of a neighboring pyrazole ring give a weak dimeric structure [Cu···C(2a) 3·15 Å and a pseudo three-coordinate copper]; in the present complex there is a much more pronounced dimeric unit with a Cu···Cu distance of 3·198 (2) Å and overlapping stacked imidazole rings (see Fig. 2); and in Cu(2,4-dimethylpyridine)$_2^+$, there is a weak interaction with

* Lists of structure factors, thermal parameters and hydrogen coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52871 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positions and equivalent isotropic displacement factors for non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\Sigma_{ij}U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Cu	0·1703 (1)	0·0643 (1)	0·4235 (1)	0·102
N(1)	0·0437 (9)	0·2167 (9)	0·2968 (7)	0·082
N(2)	−0·1326 (8)	0·4415 (9)	0·2112 (8)	0·080
N(3)	0·3097 (8)	−0·0711 (9)	0·5503 (8)	0·087
N(4)	0·4342 (11)	−0·1530 (13)	0·7377 (8)	0·103
C(1)	−0·0493 (12)	0·3618 (13)	0·3174 (8)	0·079
C(2)	0·0156 (12)	0·2049 (12)	0·1705 (10)	0·086
C(3)	−0·0930 (1)	0·3421 (12)	0·1183 (8)	0·079
C(4)	−0·2550 (12)	0·6043 (11)	0·2016 (10)	0·135
C(5)	0·3180 (13)	−0·0372 (12)	0·6705 (12)	0·105
C(6)	0·4255 (13)	−0·2189 (13)	0·5434 (10)	0·100
C(7)	0·5023 (12)	−0·2683 (13)	0·6585 (13)	0·113
C(8)	0·4742 (15)	−0·1580 (15)	0·8736 (10)	0·160
B	−0·1821 (21)	0·2783 (17)	0·7621 (14)	0·119
F(1)	−0·2734 (8)	0·3991 (7)	0·8329 (6)	0·149
F(2)	−0·0535 (8)	0·1837 (8)	0·8450 (8)	0·194
F(3)	−0·2916 (8)	0·1832 (7)	0·7634 (6)	0·167
F(4)	−0·1087 (16)	0·3192 (12)	0·6448 (7)	0·274

Table 2. *Bond lengths (Å) and angles (°)*

Cu—N(1)	1·863 (7)	N(4)—C(5)	1·325 (11)
Cu—N(3)	1·855 (7)	N(4)—C(7)	1·354 (11)
N(1)—C(1)	1·320 (9)	N(4)—C(8)	1·463 (11)
N(1)—C(2)	1·374 (10)	C(2)—C(3)	1·340 (10)
N(2)—C(1)	1·334 (9)	C(6)—C(7)	1·353 (11)
N(2)—C(3)	1·357 (10)	B—F(1)	1·356 (14)
N(2)—C(4)	1·478 (10)	B—F(2)	1·404 (12)
N(3)—C(5)	1·334 (11)	B—F(3)	1·379 (14)
N(3)—C(6)	1·365 (10)	B—F(4)	1·240 (14)
N(1)—Cu—N(3)	173·6 (3)	N(1)—C(1)—N(2)	111·2 (8)
Cu—N(1)—C(1)	124·6 (7)	N(1)—C(2)—C(3)	109·3 (8)
Cu—N(1)—C(2)	129·9 (8)	N(2)—C(3)—C(2)	106·9 (7)
C(1)—N(1)—C(2)	105·3 (7)	N(3)—C(5)—N(4)	111·8 (9)
C(1)—N(2)—C(3)	107·2 (7)	N(3)—C(6)—C(7)	108·2 (9)
C(1)—N(2)—C(4)	126·0 (9)	N(4)—C(7)—C(6)	108·1 (9)
C(3)—N(2)—C(4)	126·7 (8)	F(1)—B—F(2)	103·0 (9)
Cu—N(3)—C(5)	124·7 (8)	F(1)—B—F(3)	110·8 (12)
Cu—N(3)—C(6)	129·8 (8)	F(1)—B—F(4)	114·7 (12)
C(5)—N(3)—C(6)	105·5 (8)	F(2)—B—F(3)	103·8 (10)
C(5)—N(4)—C(7)	106·4 (8)	F(2)—B—F(4)	111·8 (14)
C(5)—N(4)—C(8)	126·7 (12)	F(3)—B—F(4)	112·0 (11)
C(7)—N(4)—C(8)	126·9 (11)		

Fig. 1. Molecular geometry and atomic numbering. Anisotropic ellipsoids represent 33% probability boundaries.
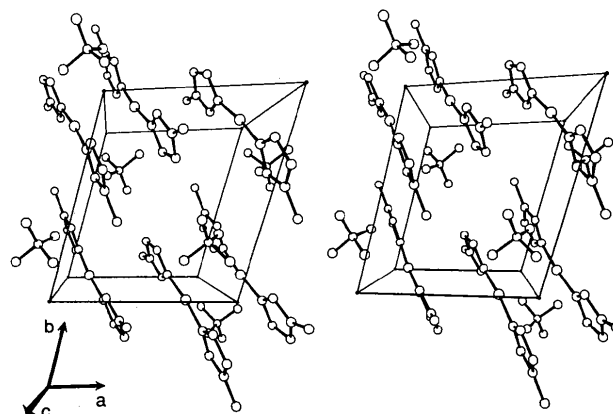

Fig. 2. Stereographic projection of the unit-cell contents.

the perchlorate counterion [Cu···O 2·72 (4) Å] to form a pseudo three-coordinate structure.

Despite the similar Cu—N distances among these structurally characterized pyrazole, pyridine and imidazole complexes, only the two-coordinate copper imidazole complexes are inert towards CO in solution, supporting the contention that the Cu–imidazole interaction is a particularly strong one which stabilizes the observed linear structure.

References

CLEGG, W., ACOTT, S. R. & GARNER, C. D. (1984). *Acta Cryst.* C40, 768–769.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
ENGELHARDT, L. M., PAKAWATCHAI, C., WHITE, A. H. & HEALY, P. C. (1985). *J. Chem. Soc. Dalton Trans.* pp. 117–123.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
SORRELL, T. N. (1989). *Tetrahedron,* 45, 3–68.
SORRELL, T. N. & JAMESON, D. L. (1983). *J. Am. Chem. Soc.* 105, 6013–6018.
VOLBEDA, A. & HOL, W. G. J. (1989). *J. Mol. Biol.* 209, 249–279.

Structure of a Copper(II) Kinetin Complex

BY MASOOD PARVEZ*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

AND WILLIAM J. BIRDSALL

Department of Chemistry, Albright College, Reading, PA 19603, USA

Abstract. Tris(ethylamine)bis[N-(2-furylmethyl)-1H-purin-6-aminato]copper(II)–diaquabis(ethylamine)-bis[N-(2-furylmethyl)-1H-purin-6-aminato]copper(II), [Cu(C$_{10}$H$_9$N$_5$O)$_2$(C$_2$H$_7$N)$_3$][Cu(C$_{10}$H$_9$N$_5$O)$_2$(C$_2$H$_7$N)$_2$(H$_2$O)$_2$], $M_r = 1249·40$, monoclinic, $P2_1$, $a = 12·280$ (3), $b = 11·972$ (11), $c = 21·565$ (9) Å, $\beta = 106·64$ (3)°, $V = 2961·4$ Å^3, $Z = 2$, $D_x = 1·401$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·786$ mm^{-1}, $F(000) = 1312$, $T = 293$ (1) K, $R = 0·064$ for 2390 observed reflections with $I > 3\sigma(I)$. The crystal structure consists of two types of molecules, Cu(kin)$_2$(EtNH$_2$)$_2$(H$_2$O)$_2$ (*A*) and Cu(kin)$_2$-(EtNH$_2$)$_3$ (*B*) which are separated by normal van der Waals distances. The coordination of the Cu atom in *A* is distorted octahedral while in *B* it is trigonal bipyramidal.

Introduction. Kinetin (kin) is a representative of a class of compounds known as cytokinins which promote cell division in plants. Cytokinins are N(6)-substituted adenines in their free base as well as their nucleoside and nucleotide forms. Few studies have

been undertaken on kinetin–metal ion complexes; Cabras & Zoroddu (1987) have recently reported two copper adducts, Cu(kin)$_2$(ClO$_4$)$_2$.H$_2$O and Cu-(kin)$_2$.4H$_2$O. Although several structures have been reported for other purine derivatives containing metal ions, no crystal structures have been reported for metal complexes of kinetin to date. Various bonding modes are possible in these complexes, with the site and stereochemistry of metal coordination influenced by, for example, substituent and pH effects.

Cu^{II}–adenine and Cu^{II}–6-hydroxypurine adducts have been shown to be dimeric with the bidentate purine ligand bridging copper centers *via* N(3) and N(9) coordination (Sletten, 1969; De Meester & Skapski, 1971; Sletten, 1970). A Cu^{II}–purine structure has been determined which involves N(7), N(9) bridging between metal centers resulting in polymer formation (Vestues & Sletten, 1981), while a Cu^{II} chloride derivative of guanine consists of a dimer with Cu—N(9) bonding and copper bridging by Cl atoms (Carrabine & Sundaralingam, 1970). In addition, structures of monomeric complexes are known; for example, a theophylline–copper chloride

---