Structure of Tetrakis(*N*-methylimidazole-*N'*)copper(I) Perchlorate, [Cu(C₄H₆N₂)₄].[ClO₄]

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Abstract. $M_r = 491.4$, tetragonal, $I\bar{4}$, $a = 12.952$ (1), $c = 6.617$ (1) Å, $V = 1110.0$ (2) Å³, $Z = 2$, $D_x = 1.470$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.14$ mm⁻¹, $F(000) = 508$, $T = 291$ K, $R = 0.044$ for 1347 reflections. The Cu atom, with S_4 site symmetry, is tetrahedrally coordinated, with Cu–N = 2.054 (2) Å and N–Cu–N = 108.1 (1) and 112.2 (1)°. The perchlorate anion is disordered. The cation is ordered except for the methyl substituent on the imidazole ligand. This appears to be the first reported structure determination of a simple monodentate–imidazole Cu^I complex.

Introduction. In the course of research into complexes of copper with imidazole ligands, we have attempted to prepare complexes in which thiolate ligands (RS^-) are also present. Reaction of a slurry of the polymeric [Cu(SC₆H₄Cl)]$_n$.n[ClO₄] with excess *N*-methylimidazole (Meim) in methyl cyanide solution at room temperature under an inert atmosphere, followed by concentration of the solution, removal of excess Meim by vacuum sublimation, addition of tetrahydrofuran (THF), and cooling to 253 K afforded pale yellow, air-sensitive crystals of [Cu(Meim)₄].[ClO₄], identified and characterized by crystal structure determination.

Experimental. Crystal of size 0.45 × 0.55 × 0.35 mm, sealed in capillary, Stoe–Siemens AED diffractometer, unit-cell parameters refined from 2θ values of 60 reflections centred at $\pm\omega(20 < 2\theta < 25°)$, 5622 reflections with $2\theta < 60°$ and $k \geq 0$ (hemisphere of data, some repeated), profile analysis (Clegg, 1981), no significant intensity variation for 3 standard reflections, no absorption corrections, 1613 unique reflections (Friedel's law not applied), 1347 with $F > 4\sigma(F)$, $R_{int} = 0.053$; Cu atom on special position, other atoms from difference syntheses, blocked-cascade refinement on F, anisotropic thermal parameters for non-H atoms, ring H atoms on external-angle bisectors with C–H = 0.96 Å, methyl H atoms twofold disordered with C–H = 0.96 Å, H–C–H = 109.5° within each component and a 60° torsional transformation of each component into the other, $U(H) = 1.2U_{eq}(C)$, occupancy factor = 0.5, scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974), absolute assignment of the x and y axes by refinement of $\eta = +1.00$ (3) (Rogers, 1981), 87 parameters, $R = 0.044$, $wR = 0.039$, $w^{-1} = \sigma^2(F) + 0.00009F^2$, slope of normal probability plot = 1.45, mean $\Delta/\sigma = 0.38$, max. = 3.0–3.5 [oscillation of U_{ij} parameters for O(1)], largest peak in final difference map = 0.88 e Å⁻³, largest hole = −0.41 e Å⁻³; programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles for the cation in Table 2.* The anion is disordered, as is commonly observed for perchlorate. The best simple fit of parameters to the data was obtained by displacing the Cl atom from the special position 0.5,0,0.75 and refining freely the position of this and two O atoms in general positions, with fixed occupancy factors of 0.25 for Cl and 0.5 for O; no attempt was made to interpret these parameters in terms of anion geometry. The high thermal parameters indicate that the disorder is actually more complex, and, consistent with chemical analytical data, it is possible that the perchlorate may be partially substituted by other oxochloroanions, presumably generated as a consequence of redox reactions with the thiol.

The cation is ordered (except for a twofold torsional disorder of the methyl group of the Meim ligand; this is not surprising for a methyl group attached to a planar ring). The Cu atom is coordinated by four chemically

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* Tables of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39162 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$)

$U = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U
Cu	5000	5000	5000	626 (2)
N(1)	6208 (1)	5523 (1)	6732 (3)	562 (6)
C(2)	6185 (2)	6096 (2)	8367 (4)	564 (7)
N(3)	7116 (1)	6188 (2)	9219 (3)	587 (6)
C(31)	7358 (3)	6775 (3)	11057 (5)	885 (11)
C(4)	7786 (2)	5645 (2)	8047 (4)	662 (8)
C(5)	7229 (2)	5245 (2)	6522 (4)	641 (7)
Cl	5042 (17)	−183 (5)	7704 (29)	924 (40)
O(1)	5112 (8)	430 (10)	5798 (15)	2046 (76)
O(2)	4624 (5)	1161 (5)	7544 (17)	1572 (38)

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

Cu–N(1)	2·054 (2)	N(1)–C(2)	1·312 (3)
C(2)–N(3)	1·337 (3)	N(3)–C(4)	1·360 (3)
C(4)–C(5)	1·345 (4)	C(5)–N(1)	1·378 (3)
N(3)–C(31)	1·468 (4)		

N(1)–Cu–N(1ⁱ)	112·2 (1)	N(1)–Cu–N(1ⁱⁱ)	108·1 (1)
Cu–N(1)–C(2)	129·0 (2)	Cu–N(1)–C(5)	126·0 (2)
C(2)–N(1)–C(5)	104·6 (2)	N(1)–C(2)–N(3)	112·2 (2)
C(2)–N(3)–C(31)	126·0 (2)	C(2)–N(3)–C(4)	106·8 (2)
C(31)–N(3)–C(4)	127·2 (2)	N(3)–C(4)–C(5)	106·6 (2)
N(1)–C(5)–C(4)	109·8 (2)		

Symmetry code: (i) $1 - x$, $1 - y$, z; (ii) y, $1 - x$, $1 - z$.

Fig. 1. Structure of the $[Cu(Meim)_4]^+$ cation, without H atoms, showing the atom labelling. Thermal motion is depicted as 50% probability ellipsoids.

and crystallographically equivalent Meim ligands (Fig. 1); the independent N—Cu—N angles do not deviate markedly from regular tetrahedral values: there is a slight flattening of the N_4 tetrahedron along the c axis. The imidazole rings are planar [r.m.s. deviation = 0·003 (1) Å]; the methyl C atom lies insignificantly out of the ring plane [$\Delta = -0·008$ (4) Å], but Cu deviates more markedly from it [$\Delta = +0·198$ (2) Å].

This appears to be the first reported structure of a simple Cu^I–imidazole complex. The Cu—N bond length of 2·054 (2) Å is rather longer than those observed in complexes of Cu^I with multidentate imidazole-containing ligands, where Cu is normally two- or three-coordinate (1·869–1·918 Å) (Dagdigian, McKee & Reed, 1982; Schilstra, Birker, Verschoor & Reedijk, 1982; Hendriks, Birker, van Rijn, Verschoor & Reedijk, 1982), and also longer than in [{(imidazole)$_2$-Cu}$_2$Cl]Cl (1·899 and 1·908 Å) (Clegg, Acott & Garner, 1983), where Cu is also planar three-coordinate. An increase in bond length with co-ordination number is normal, as has been observed, for example, in four- and six-coordinate Zn–imidazole complexes (Bear, Duggan & Freeman, 1975; Sandmark & Bränden, 1967). Cu—N bonds in tetrakis-(imidazole) complexes of Cu^{II} are generally around 2·00 Å (Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983). Ivarsson, Lundberg & Ingri
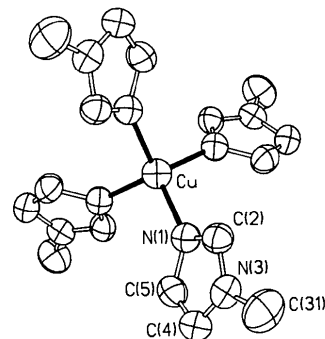
(1972) have discussed such Cu^{II}—N bond lengths, and found a variation with ligand type, especially if some of the ligands are multidentate; a clear pattern did not, however, emerge. Cu^{II}—N(imidazole) bonds as long as 2·058 Å, very similar to the Cu^I—N bond length observed here, have been found in $Cu(imidazole)_2$-(imidazolato)Cl (Lundberg, 1972), where the presence of a deprotonated imidazolato ligand effectively reduces the charge on Cu.

References

BEAR, C. A., DUGGAN, K. A. & FREEMAN, H. C. (1975). *Acta Cryst.* B31, 2713–2715.
BERNARDUCCI, E., BHARADWAJ, P. K., KROGH-JESPERSEN, K., POTENZA, J. A. & SCHUGAR, H. J. (1983). *J. Am. Chem. Soc.* 105, 3860–3866.
CLEGG, W. (1981). *Acta Cryst.* A37, 22–28.
CLEGG, W., ACOTT, S. R. & GARNER, C. D. (1983). *J. Chem. Soc. Dalton Trans.* In the press.
DAGDIGIAN, J. V., McKEE, V. & REED, C. A. (1982). *Inorg. Chem.* 21, 1332–1342.
HENDRIKS, H. M. J., BIRKER, P. J. M. W. L., VAN RIJN, J., VERSCHOOR, G. C. & REEDIJK, J. (1982). *J. Am. Chem. Soc.* 104, 3607–3617.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
IVARSSON, G., LUNDBERG, B. K. S. & INGRI, N. (1972). *Acta Chem. Scand.* 26, 3005–3020.
LUNDBERG, B. K. S. (1972). *Acta Chem. Scand.* 26, 3902–3912.
ROGERS, D. (1981). *Acta Cryst.* A37, 734–741.
SANDMARK, C. & BRÄNDEN, C. I. (1967). *Acta Chem. Scand.* 21, 993–999.
SCHILSTRA, M. J., BIRKER, P. J. M. W. L., VERSCHOOR, G. C. & REEDIJK, J. (1982). *Inorg. Chem.* 21, 2637–2644.
SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.