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[2,6-Bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine]iodocopper(I) dichloromethane solvate

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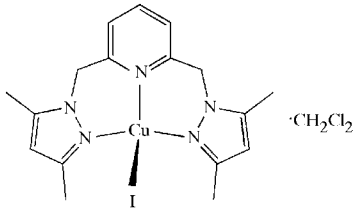
The title compound, $[CuI(C_{17}H_{21}N_5)]\cdot CH_2Cl_2$, contains a tetracoordinate Cu^I centre with an unusual distorted tetrahedral stereochemistry, which has also been observed in other Cu^I complexes containing this tridentate ligand. This distortion is probably a result of intermolecular steric contacts between the I^- ligand and a neighbouring CH_2Cl_2 molecule.

Comment

Perhaps more than for any other type of metalloprotein, synthetic model chemistry has led to great advances in the understanding of the small-molecule chemistry that occurs at the active sites of type 2 and type 3 Cu/O proteins. Much of this synthetic chemistry has been carried out using facially or meridionally coordinating tridentate ligands, such as 1,4,7-triazacyclononane (Tolman, 1997) and *N*-alkyl-bis[2-(2-pyridyl)ethyl]amine (Blain *et al.*, 2001) derivatives, to mimic the tris-histidine ligation to Cu in these proteins. We have been studying the stereochemistry of Cu complexes of meridional tris-imine ligands in order to define more rigorously the solution structures of complexes of this type (Foster *et al.*, 2002; Solanki *et al.*, 2002), and have prepared the title compound, (I), in the course of our studies.



(I)

The crystal of (I) contains one molecule of the complex and one CH_2Cl_2 solvent molecule per asymmetric unit, each lying on a general position. The four-coordinate Cu^I ion has the expected N_3I donor set, with all four Cu–ligand bond lengths lying within the usual ranges (Orpen *et al.*, 1989). The disposition of ligand donor atoms about Cu1 reflects a rather distorted tetrahedral stereochemistry. Unusually, this irregular structure does not reflect a distortion from an ideal tetrahedron towards a more planar coordination geometry, which is a common structural type for Cu^I complexes of chelating imine ligands (Halcrow *et al.*, 1997, and references therein). Rather, the I^- ligand is displaced out of its 'ideal' position, towards the N10 donor atom. This is evidenced by the N18—Cu1—I24 angle being larger than N10—Cu1—I24 (Table 2). Concomitantly, the Cu1—N18 bond is shorter than Cu1—N10 (Table 2), possibly as a result of steric interactions between atoms N10 and I24.

In common with many known complexes of 2,6-bis(pyrazol-1-ylmethyl)pyridine derivatives (Watson *et al.*, 1987; Mahapatra *et al.*, 1993; Manikandan *et al.*, 1996, 1998, 2000*a*,*b*; Lal *et al.*, 1999; Foster *et al.*, 2002), the $Cu—N_{pyridine}$ bond (Cu1—N2) is substantially longer than the two $Cu1—N_{pyrazole}$ bonds, by an average of 0.112 (5) Å. This is inconsistent with the greater basicity of a pyridine compared with a pyrazole *N*-donor, and presumably originates from conformational strain within the ligand chelate backbone. The two six-membered chelate rings in the complex both have a chair-like conformation.

An identical pattern of distortion away from an ideal tetrahedral geometry is exhibited by three of the four other known Cu^I complexes of 2,6-bis[(3,5-dimethylpyrazol-1-yl)-methyl]pyridine, hereinafter *L*, in the crystal (Table 2), namely $[CuL(NCMe)]BF_4$, (II) (Foster *et al.*, 2002), $[CuL(PPh_3)]ClO_4$, (III) (Manikandan *et al.*, 1996), and $[(CuL)_2(\mu\text{-}Ph_2PC_2H_4PPh_2)](ClO_4)_2$, (IV) (Manikandan *et al.*, 1998). In contrast, $[CuL(OClO_3)]$, (V) (Manikandan *et al.*, 1996), shows a more regular tetrahedral stereochemistry (Table 2). The pattern of distortion away from an idealized tetrahedron is the same in (I)–(IV). However, the magnitude of the displacement of the monodentate ligand towards one pyrazole ring and the degree of lengthening of the corresponding Cu—N bond vary markedly between these four structures (Table 2). There is no apparent correlation of the degree of distortion with the identity of the exogenous ligand *X*24 in Table 2, or with any of the bond lengths to Cu1. In particular, the Cu1—N2 distance shows some variation between these compounds, from being the same magnitude as the $Cu—N_{pyrazole}$ bonds in (III) to being substantially longer in (I). However, this variation does not correlate with the degree of distortion (Table 2). The apparent lack of a systematic trend makes it unlikely that the structural distortions in (I)–(IV) are caused by the electronic structure at Cu.

Space-filling models of (I) show that there are no intramolecular steric contacts to atom I24 that could account for its displacement towards atom N10. However, there are several close intermolecular interatomic contacts to this atom, namely I24···Cl26 [3.842 (5) Å], I24···H25A^{i} (3.05 Å), I24···H16A^{ii} (3.04 Å), I24···H8B^{iii} (3.12 Å) and I24···H15A^{iii} (3.20 Å) [symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x+1, y, z$; (iii) $x, \frac{1}{2}-y, z+\frac{1}{2}$]. The first two of these are to atoms from the CH_2Cl_2 molecule. For comparison, the sum of the van der Waals radii of Cl and I is 3.95 Å, and of H and I is 3.35 Å (Pauling, 1960). Interestingly, atom H25A^{i} is positioned close to the putative 'ideal' coordination site for atom I24, which would be equidistant from atoms N10 and N18. This is

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apparent from the similar distances from H25A^{i} to these two N atoms, which are N10$\cdots$H25A^{i} 6.53 Å and N18$\cdots$H25A^{i} 6.31 Å.

Hence, it is possible that the distorted coordination geometry in (I) is a result of intermolecular steric repulsion between atom I24 and the solvent molecule at $(1-x, 1-y, 1-z)$, which would prevent I24 from occupying its idealized position in the coordination sphere. In (II), the structural distortions are also probably caused by an intermolecular steric repulsion, between the methyl group of the MeCN ligand and a neighbouring BF_4^- anion (Foster *et al.*, 2002). Hence, while no analysis of intermolecular interactions was carried out for (III)–(V), it seems likely that the unusual coordination geometries adopted by (I)–(IV) in the crystal are a consequence of intermolecular packing interactions, rather than any intrinsic intramolecular electronic factors.

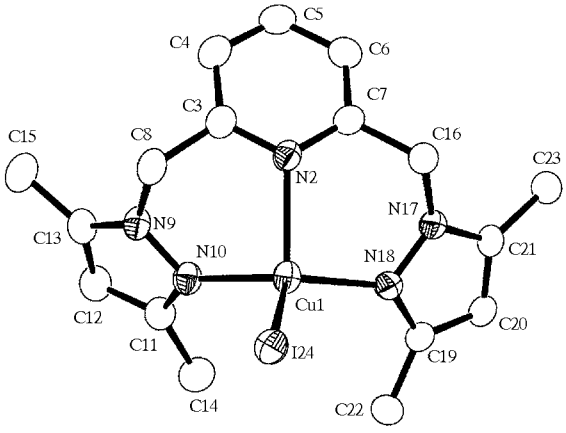

Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed. For clarity, the solvent molecule and all H atoms have been omitted.

Experimental

A mixture of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (0.25 g, 8.4 mmol; Mahapatra *et al.*, 1991) and CuI (0.16 g, 8.4 mmol) in CH_2Cl_2 (25 ml) was stirred under N_2 for 20 min. The resulting yellow solution was filtered, concentrated *in vacuo* to *ca* 5 ml and stored at 253 K overnight. The yellow polycrystalline precipitate was filtered off, washed with pentane and dried *in vacuo* (yield 0.36 g, 88%). Slow diffusion of pentane into a solution of the (sparingly soluble) complex in CH_2Cl_2 yielded yellow blocks of (I). Analysis found: C 38.1, H 4.0, N 12.5%; calculated for $C_{17}H_{21}CuIN_5\cdot CH_2Cl_2$: C 37.9, H 4.1, N 12.3%.

Crystal data

$[CuI(C_{17}H_{21}N_5)]\cdot CH_2Cl_2$	D_x = 1.721 Mg m^{-3}
M_r = 570.75	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 307 reflections
a = 8.4293 (2) Å	θ = 1.8–27.5°
b = 18.8330 (3) Å	μ = 2.65 mm^{-1}
c = 13.9401 (3) Å	T = 150 (2) K
β = 95.4144 (9)°	Block, yellow
V = 2203.10 (8) Å^3	0.17 × 0.11 × 0.11 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	5028 independent reflections
Area-detector scans	4154 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	R_{int} = 0.054
T_{min} = 0.662, T_{max} = 0.759	θ_{max} = 27.5°
25 307 measured reflections	$h = -10 \rightarrow 10$
	$k = -22 \rightarrow 24$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = [\sigma^2(F_o^2) + (0.038P)^2 + 2.411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.088	$\Delta\rho_{max}$ = 1.06 e Å^{-3}
S = 1.02	$\Delta\rho_{min}$ = −0.78 e Å^{-3}
5027 reflections	
249 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	2.148 (3)	Cu1—N18	2.020 (3)
Cu1—N10	2.052 (3)	Cu1—I24	2.6157 (5)
N18—Cu1—N10	129.10 (11)	N18—Cu1—I24	114.25 (8)
N18—Cu1—N2	95.23 (11)	N10—Cu1—I24	108.62 (8)
N10—Cu1—N2	92.11 (10)	N2—Cu1—I24	113.02 (7)

Table 2
Structural distortions in Cu^I complexes of 2,6-bis[(3,5-dimethylpyrazol-1-yl)methyl]pyridine (Å, °).

Compound†	X	Cu1—N2‡	(Cu1—N10) − (Cu1—N18)	(N18—Cu1—X24) − (N10—Cu1—X24)
(I)	I	2.148 (3)	0.032 (4)	5.63 (11)
(II)	N	2.1198 (12)	0.1122 (18)	17.77 (8)
(III)	P	2.097 (4)	0.068 (6)	11.5 (2)
(IV)	P	2.111 (4)	0.039 (6)	6.19 (17)
(V)	O	2.131 (2)	0.000 (3)	0.40 (13)

† The compound numbers, and the references describing them, are defined in the *Comment*. ‡ The atom numbers used to define the parameters listed are based on those in Fig. 1.

All H atoms were placed in calculated positions and refined using a riding model. The constraints employed for the final refinement were C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for all sp^2 H atoms, C—H = 0.99 Å and U_{iso}(H) = 1.3U_{eq}(C) for the methylene and solvent CH_2 groups, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms. The highest residual Fourier peak lies 0.93 Å from the solvent atom C25. Attempts to incorporate this peak into a disorder model for the solvent molecule were unsuccessful.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1500). Services for accessing these data are described at the back of the journal.

References

Blain, I., Pierrot, M., Giorgi, M. & Réglier, M. (2001). *C. R. Acad. Sci. Paris Ser. IIC*, **4**, 1–10.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Foster, C. L., Kilner, C. A., Thornton-Pett, M. & Halcrow, M. A. (2002). *Polyhedron*, **21**, 1031–1041.

Halcrow, M. A., Cromhout, N. L. & Raithby, P. R. (1997). *Polyhedron*, **16**, 4257–4264.

Lal, T. K., Gupta, R., Mahapatra, S. & Mukherjee, R. (1999). *Polyhedron*, **18**, 1743–1750.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Mahapatra, S., Butcher, R. J. & Mukherjee, R. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3723–3726.

Mahapatra, S., Gupta, N. & Mukherjee, R. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2911–2915.

Manikandan, P., Justin Thomas, K. R. & Manoharan, P. T. (2000*b*). *Acta Cryst.* C**56**, 308–309.

Manikandan, P., Subramoni, M., Varghese, B. & Manoharan, P. T. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3219–3225.

Manikandan, P., Thomas, K. R. J. & Manoharan, P. T. (2000*a*). *J. Chem. Soc. Dalton Trans.* pp. 2779–2785.

Manikandan, P., Varghese, B. & Manoharan, P. T. (1996). *J. Chem. Soc. Dalton Trans.* pp. 371–376.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Orpen, G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Solanki, N. K., McInnes, E. J. L., Collison, D., Kilner, C. A., Davies, J. E. & Halcrow, M. A. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1625–1630.

Tolman, W. B. (1997). *Acc. Chem. Res.* **30**, 227–237.

Watson, A. A., House, D. A. & Steel, P. J. (1987). *Inorg. Chim. Acta*, **130**, 167–176.