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Bis[μ-3{5}-(2-pyridyl)pyrazolido]bis[(acetonitrile)copper(II)] diperchlorate

Matthew J. Hallam, Colin A. Kilner and Malcolm A. Halcrow*

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, England
Correspondence e-mail: m.a.halcrow@chem.leeds.ac.uk

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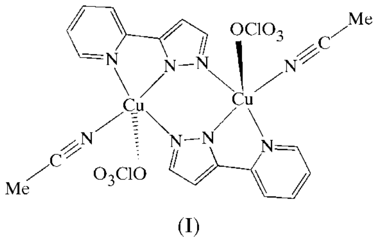
The title compound, $[Cu_2(C_8H_6N_3)_2(C_2H_3N)_2](ClO_4)_2$, contains a centrosymmetric dinuclear dication, with square-pyramidal Cu^{II} centres linked by two 1,2-pyrazolide bridging groups. There is a weak apical interaction between each Cu ion and a perchlorate O atom.

Comment

Several polydentate ligands derived from 3-(2-pyridyl)-pyrazol-1-yl moieties linked by a monoatomic spacer have been prepared by McCleverty and Ward (Ward *et al.*, 2001). Of particular use have been the compounds $R_2BH_2^-$ (Bardwell *et al.*, 1997; Jones *et al.*, 1997; Fleming, Psillakis, Couchman *et al.*, 1998; Armaroli *et al.*, 1999), R_2CH_2 (Mann *et al.*, 1998), $R_2PO_2^-$ (Psillakis *et al.*, 1997) and $R_2P\{O\}\{S\}^-$ (Fleming, Psillakis, Jeffrey *et al.*, 1998), where *R* is 3-(2-pyridyl)pyrazol-1-yl. These ligands have afforded several luminescent lanthanide complexes (Bardwell *et al.*, 1997; Armaroli *et al.*, 1999), as well as a variety of high nuclearity coordination arrays (Jones *et al.*, 1997; Psillakis *et al.*, 1997). We have been employing bis(pyrazol-1-yl) ketone derivatives as organic synthetic intermediates, and so decided to investigate the complex chemistry of the new derivative bis[3-(2-pyridyl)pyrazol-1-yl] ketone (*i.e.* $R_2C{=}O$; *L*). Unfortunately, we have found that the sensitivity of the bis(pyrazol-1-yl) ketone moiety towards hydrolysis is increased upon coordination to transition ions, so that reaction of *L* with metal salts most often yields products containing 3{5}-(2-pyridyl)pyrazole (HL') as ligand. We report here the crystal structure of one such product, (I), which we isolated from the reaction of *L* with $Cu(ClO_4)_2{\cdot}6H_2O$. Two other, tetrameric Cu^{II} complexes of L'^- have been reported previously (Jeffrey *et al.*, 1997; Mann *et al.*, 1999), while two dimeric complexes closely related to (I), containing methylated derivatives of L'^-, have also been structurally characterized (Singh *et al.*, 1998; Satake *et al.*, 2000).

The asymmetric unit of (I) contains half a dimeric dication lying across the crystallographic inversion centre and a perchlorate anion on a general position (Fig. 1). The $[Cu_2(\mu\text{-}L')_2]^{2+}$ portion of the molecule is almost perfectly planar. The acetonitrile ligand is coordinated in an almost perfectly linear fashion [Cu—N1*C*—C2*C* = 176.0 (2)°], but is displaced by 19.38 (8)° from the least-squares plane formed by the atoms of the $[CuL']^+$ unit. This distortion is a consequence of the close intramolecular contacts N1*C*···H6*B* = 2.57 Å and N1*C*···H3*A*^{i} = 2.63 Å [symmetry code: (i) $1-x, 1-y, 1-z$]. These values are slightly shorter than the sum of the van der Waals radii of H (1.2 Å) and N (1.5 Å; Pauling, 1960). There is a long apical interaction between the Cu ion and O1 of the perchlorate anion, leading to a distorted square-pyramidal geometry at the Cu ion. The τ index of Addison and Reedijk for (I) is 0.32, which is closer to the ideal value of 0 for a square pyramid than to the value of 1 expected for a trigonal bipyramid (Addison *et al.*, 1984). The Cu···Cu^{i} distance is 3.9247 (6) Å.



(I)

The molecules in the crystal are arranged into stacks by translational symmetry parallel to the crystallographic *a* direction. Neighbouring molecules in the stacks are coplanar by symmetry, separated by 3.374 (6) Å, and aligned such that a pyridine ring of one molecule overlies the five-membered Cu—N—C—C—N chelate ring of its neighbour. The offset of the centroids of the two overlying L'^- ligands is 0.884 (9) Å, while the centroids of the pyridine rings of the two interacting ligands are offset by 2.775 (9) Å. This latter parameter, and the intermolecular spacing, are typical values for an attractive π–π interaction (Hunter & Sanders, 1990). There are no other noteworthy intermolecular contacts in the lattice.

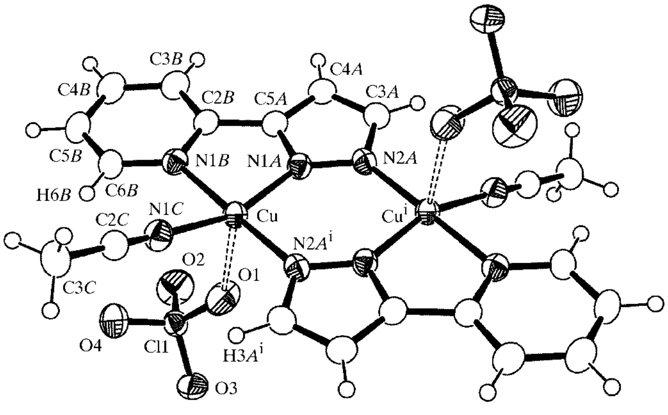


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme employed. H atoms have arbitrary radii and those referred to in the text are labelled. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

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Experimental

Bis[3-(2-pyridyl)pyrazol-1-yl] ketone (*L*) was prepared as follows: a solution of 3{5}-(2-pyridyl)pyrazole (H*L*′; 5 g, 0.034 mol), phosgene (8.4 ml of a 2 *M* solution in toluene) and NEt_3 (3.4 g, 0.034 mol) in tetrahydrofuran (150 ml) was stirred under N_2 at 293 K for 1 h, affording a voluminous white precipitate. The solution was filtered and evaporated to dryness, leaving *L* as a white solid in >98% purity (by NMR). This product was used for the complexation reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 7.27 (*d*, 2.1 Hz), 7.32 (*ddd*; 7.8, 4.8, 0.8 Hz; 2H), 7.80 (*ddd*; 8.0, 7.8, 1.0 Hz; 2H), 8.20 (*ddd*; 8.0, 2.0, 0.8 Hz; 2H), 8.67 (*ddd*; 4.8, 2.0, 1.0 Hz; 2H), 8.82 (*d*, 2.1 Hz, 2H) p.p.m. IR (nujol): 1739 cm^{-1}. EI MS: m/z = 316 $[M]^+$, 172 $[M - L']^+$, 145 $[L'\mathrm{H}]^+$. A solution of *L* (0.25 g, 0.08 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.31 g, 0.08 mmol) in MeOH (30 ml) was stirred at 293 K for 30 min. The solution was filtered and evaporated to dryness. The blue solid residue obtained was extracted with MeCN. Diffusion of Et_2O vapour into the resultant deep-blue solution yielded deep-blue crystals of (I), together with an unidentified sticky white residue.

Crystal data

$[Cu_2(C_8H_6N_3)_2(C_2H_3N)_2](ClO_4)_2$
M_r = 696.40
Monoclinic, $P2_1/c$
a = 7.9977 (3) Å
b = 15.9230 (6) Å
c = 12.1212 (4) Å
β = 124.194 (2)°
V = 1276.77 (8) Å^3
Z = 2

D_x = 1.811 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 294 reflections
θ = 2.9–27.5°
μ = 1.94 mm^{-1}
T = 150 (2) K
Square prism, dark blue
0.21 × 0.20 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Area-detector scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.686, $T_{\max}$ = 0.747
12 294 measured reflections
2913 independent reflections

2563 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.052
$\theta_{\max}$ = 27.5°
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 19$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.094
S = 1.07
2913 reflections
181 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 1.2569P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.49 e Å^{-3}
$\Delta\rho_{\min}$ = −0.63 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1*A*	1.952 (2)	Cu—N1*C*	2.005 (2)
Cu—N2*A*$^{\rm i}$	1.953 (2)	Cu—O1	2.330 (2)
Cu—N1*B*	2.031 (2)		
N1*A*—Cu—N2*A*$^{\rm i}$	97.80 (9)	N1*C*—Cu—N1*B*	89.89 (9)
N1*A*—Cu—N1*C*	160.18 (10)	N1*A*—Cu—O1	97.83 (10)
N2*A*$^{\rm i}$—Cu—N1*C*	90.80 (9)	N2*A*$^{\rm i}$—Cu—O1	91.82 (9)
N1*A*—Cu—N1*B*	81.43 (9)	N1*C*—Cu—O1	99.72 (10)
N2*A*$^{\rm i}$—Cu—N1*B*	179.21 (9)	N1*B*—Cu—O1	88.44 (9)

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

All H atoms were placed in calculated positions and refined using a riding model, except for the acetonitrile H atoms, which were located in a Fourier map and refined as an idealized group based on their initial coordinates. The constraints employed for the final refinement were C—H = 0.95 Å and $U_{\rm iso} = 1.2U_{\rm eq}$(C) for all sp^2 H atoms, and C—H = 0.98 Å and $U_{\rm iso} = 1.5U_{\rm eq}$(C) for the methyl H atoms.

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, 1990); 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: BM1502). Services for accessing these data are described at the back of the journal.

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