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Bis{2,6-bis[3-(2,4,6-trimethylphenyl)pyrazol-1-yl-κN^2]pyridine-κN}zinc(II) diperchlorate bis(nitromethane) solvate

Malcolm A. Halcrow,* Colin A. Kilner and Mark Thornton-Pett

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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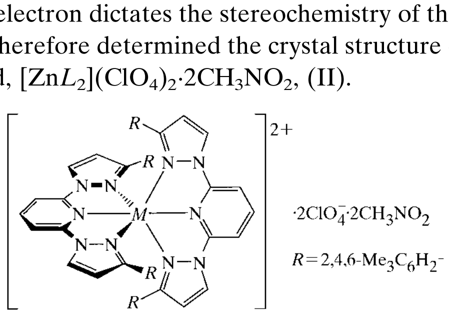
The title compound, $[Zn(C_{29}H_{29}N_5)_2](ClO_4)_2\cdot 2CH_3NO_2$, contains a Zn^{II} ion showing only small deviations from local D_{2d} symmetry. The lower rhombicity exhibited by this complex compared with that of its Cu^{II} congener suggests that the highly rhombic stereochemistry exhibited by the latter is largely imposed by the stereoelectronic preferences of the Cu^{II} ion.

Comment

We have recently described the complex $[CuL_2](ClO_4)_2\cdot 2CH_3NO_2$, (I) {*L* is 2,6-bis[3-(2,4,6-trimethylphenyl)pyrazol-1-yl]pyridine}, which exhibits a rhombic six-coordinate stereochemistry in the crystal (Solanki *et al.*, 1998). This complex exhibits an unusual $\{d_{z^2}\}^1$ electronic ground state, which is imposed by intramolecular steric repulsions at the metal ion between the mesityl substituents of one ligand and the pyridine ring of the other (Solanki *et al.*, 1998; Bridgeman *et al.*, 1999). We were interested in comparing the molecular structure of (I) with an analogue containing a metal ion with a spherical *d* shell, to determine the extent to which the $\{d_{z^2}\}^1$ unpaired electron dictates the stereochemistry of the Cu^{II} ion. We have therefore determined the crystal structure of the title compound, $[ZnL_2](ClO_4)_2\cdot 2CH_3NO_2$, (II).



(I) *M* = Cu
(II) *M* = Zn

Compound (II) is isomorphous with its Cu^{II} congener (Solanki *et al.*, 1998), also crystallizing in space group $P2_1/c$. The asymmetric unit contains one formula unit, with the cation and all anions and solvent molecules in general positions. The Zn^{II} ion adopts a rhombic coordination geometry, with the Zn—N$_{\rm pyrazole}$ bonds to one ligand (Zn1—N9 and Zn1—N23) being shorter than the corresponding bonds to the other ligand (Zn1—N43 and Zn1—N57) by 0.027 (3)–0.037 (3) Å. This is a lower rhombicity than is exhibited by the Cu^{II} complex, however, where the Cu—N$_{\rm pyrazole}$ bonds to one ligand are 0.091 (8)–0.114 (8) Å shorter than those to the other. Interestingly, although one ligand (N2–C35) is bound symmetrically to the Zn^{II} ion, the other (N36–C69) is slightly asymmetrically coordinated, with Zn1—N43 being 0.018 (3) Å shorter than Zn1—N57. Since space-filling models show no steric contacts that could impose these small distortions from ideal D_{2d} symmetry, both the rhombicity of the coordination sphere and the asymmetric binding of ligand N36–C69 are probably imposed by the local lattice environment. Overall, the coordination geometry in this complex closely resembles those of stereochemically similar Zn^{II} complexes containing two terpyridyl derivatives as ligands (Whittle *et al.*, 1998; Alcock *et al.*, 2000). The small rhombicity exhibited by (II) suggests that the more rhombic stereochemistry adopted by (I) is largely driven by the electronic preferences of the Cu^{II} ion.

The mesityl rings of each ligand in (II) sandwich the pyridine ring of the coligand, forming two perpendicular triple π–π stacks. The metric parameters for these π–π interactions are given in Table 2. For comparison, the Cu—N$_{\rm pyrazole}$ bonds in (I) range from 2.136 (6)–2.256 (6) Å, while the π–π interplanar distances are in the range 3.5–3.7 Å and the dihedral angles in the range 2.0 (2)–13.2 (2)° (Solanki *et al.*, 1998). The small horizontal offsets of these interacting rings are consistent with these being electrostatically repulsive π–π interactions (Hunter & Sanders, 1990). There are no close intermolecular contacts within the crystal lattice.

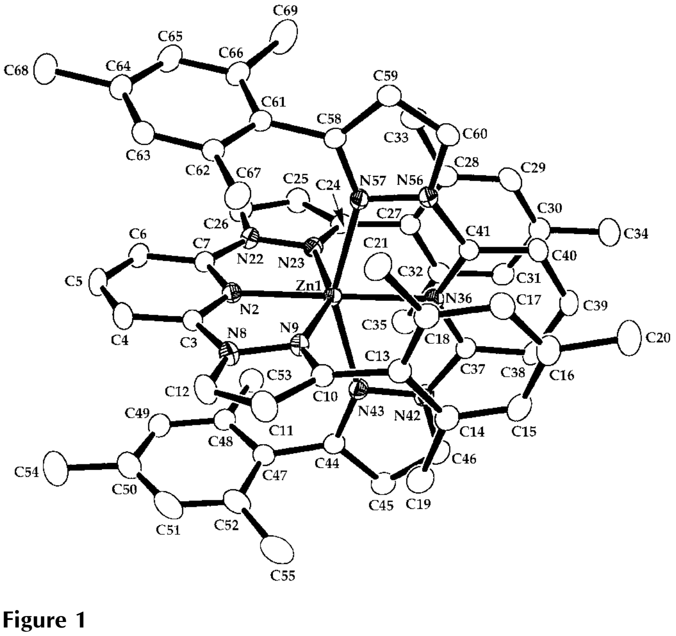


Figure 1
The molecular structure of the cation of (II) showing 35% probability displacement ellipsoids and the atom-numbering scheme employed. For clarity, H atoms have been removed.

Experimental

Complexation of $Zn(ClO_4)_2·6H_2O$ by 2 molar equivalents of *L* (Solanki *et al.*, 1998) in CH_3NO_2 yielded a pale-yellow solution, which was filtered and concentrated *in vacuo*. Vapour diffusion of Et_2O into this solution afforded colourless blocks of (II) of diffraction quality. Elemental analysis, found: C 65.1, H 6.6, N 7.5%; calculated for $C_{58}H_{58}Cl_2N_{10}O_4Zn·2CH_3NO_2$: C 65.3, H 6.6, N 7.6%.

Crystal data

$[Zn(C_{29}H_{29}N_5)_2](ClO_4)_2·2CH_3NO_2$
$M_r = 1281.50$
Monoclinic, $P2_1/c$
$a = 11.9913$ (2) Å
$b = 19.8605$ (3) Å
$c = 25.1833$ (3) Å
$\beta = 100.0240$ (9)°
$V = 5905.93$ (15) Å^3
$Z = 4$

$D_x = 1.441$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 86 756 reflections
$\theta = 1.64–27.47°$
$\mu = 0.581$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.54 × 0.42 × 0.28 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.745$, $T_{max} = 0.854$
86 756 measured reflections

13 519 independent reflections
9275 reflections with $I > 2\sigma(I)$
$R_{int} = 0.100$
$\theta_{max} = 27.47°$
$h = -15 \rightarrow 15$
$k = -25 \rightarrow 25$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.136$
$S = 1.039$
13 519 reflections
784 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2 + 1.2064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	2.0607 (19)	Zn1—N36	2.0497 (19)
Zn1—N9	2.176 (2)	Zn1—N43	2.195 (2)
Zn1—N23	2.168 (2)	Zn1—N57	2.2130 (19)
N2—Zn1—N9	76.01 (8)	N9—Zn1—N57	93.47 (7)
N2—Zn1—N23	75.65 (8)	N23—Zn1—N36	103.65 (8)
N2—Zn1—N36	179.25 (8)	N23—Zn1—N43	95.29 (7)
N2—Zn1—N43	104.16 (7)	N23—Zn1—N57	91.79 (7)
N2—Zn1—N57	104.02 (7)	N36—Zn1—N43	75.57 (7)
N9—Zn1—N23	151.62 (7)	N36—Zn1—N57	76.25 (7)
N9—Zn1—N36	104.69 (8)	N43—Zn1—N57	151.82 (7)
N9—Zn1—N43	93.12 (7)		

Table 2
Mean interplanar spacings (Å), dihedral angles between the least-squares planes of the interacting arenes (°) and centroid offsets (Å) for the intramolecular π–π interactions within the complex dication of (II).

Ring *A*	Ring *B*	Interplanar spacing	Dihedral angle	Offset
N2–C7	C47–C52	3.56	8.2 (2)	1.2
N2–C7	C61–C66	3.89	14.4 (2)	0.7
N36–C41	C13–C18	3.47	5.6 (2)	1.0
N36–C41	C27–C32	3.52	2.8 (2)	0.6

Methyl H atoms were located in difference Fourier syntheses, while *sp*^{2} H atoms were placed geometrically. All *sp*^{2} H atoms were refined with C—H = 0.925 Å and $U_{iso} = 1.2U_{eq}$(C), while for methyl groups the corresponding values were 0.98 Å and $1.5U_{eq}$(C). The slightly high R_{int} value for the structure reflects a very large data set containing a great deal of redundancy, collected from a sample of only moderate quality.

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: *SHELXL*97 and local software.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1431). Services for accessing these data are described at the back of the journal.

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