

(1,2-Bis[[3-(2-pyridyl)pyrazol-1-yl]methyl]-benzene)perchloratosodium

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In the title compound, $[\text{Na}(\text{ClO}_4)(\text{C}_{24}\text{H}_{20}\text{N}_6)]$, the sodium cation is in a square-pyramidal geometry, which is distorted from the ideal ($\tau = 0.19$), with the four N-donor atoms of the bis-bidentate chelating units from the ligand arranged equatorially, and with the perchlorate anion at the apical site.

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Key indicators

Single-crystal X-ray study

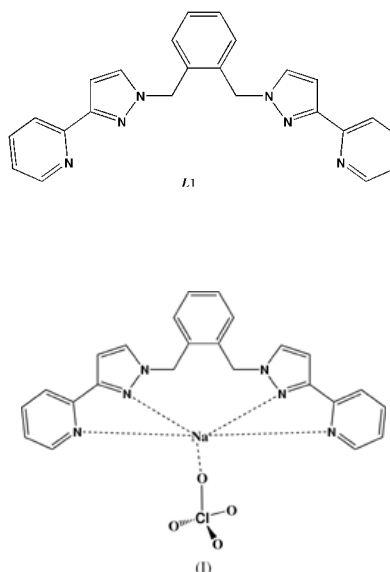
 $T = 173 \text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ R factor = 0.042 wR factor = 0.112

Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The coordination chemistry of the ligand *L1* has been well documented for the first-row transition metals; it forms tetrahedral cages and open-chain dinuclear structures (Fleming *et al.*, 1998; Paul *et al.*, 2002). Several complexes of alkali metals with N-donor ligands are observed in the literature, although they usually employ highly preorganized ligands, where the cavity size is comparable to that of the alkali metal ion and the coordination geometry is particularly unsuited to a transition metal. Examples include ligands such as torands (Bell *et al.*, 1992, 1993), macrocycles (Constable *et al.*, 1988) and cryptands (Lehn & DeVains, 1992). However, a helical structure containing K^+ ions has been reported, based on a hexadentate N-donor ligand which consists of two terdentate binding domains (Psillakis *et al.*, 1997).



The molecular structure of the title compound, (I), is shown in Fig. 1. It is a relatively unusual example of an alkali metal complex with an open-chain N-donor chelating ligand. The sodium cation is surrounded by four nitrogen donors from *L1* and a single perchlorate anion, thus yielding a neutral complex. The average Na–N bond length is 2.487 Å, which is comparable to the average Na–N bond length found in six-

coordinate chelate complexes with the bidentate phen unit (Qian *et al.*, 1994). Although there are many sodium complexes reported with cryptands (Echegoyen *et al.*, 1991; McKee *et al.*, 1992), the comparison of bond lengths can be complex, since it is thought that they are, in part, dependent on the rigidity of the ligand and the coordination number of the Na⁺ ion (Caron *et al.*, 1985). The N atoms of the ligand unit are not bound to the sodium ion in a plane. One of the pyrazole–pyridine units is approximately planar, but the other has an angle of 17.1 (2)° between the rings. The approximate angle between the bidentate arms is 131.9 (14)°, thus enabling the perchlorate anion to coordinate comfortably to the Na⁺ ion in the apical position. The Na–O bond length is 2.3359 (18) Å.

For a five-coordinate geometry, there is a structural continuum between the ideal square-pyramidal (SP) and trigonal-bipyramidal (TBP) extremes. The structural index parameter τ (degree of trigonality) can be defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest and smallest angles, respectively, at the central atom. τ is equal to zero for a perfect SP geometry, and equal to unity for a perfect TBP geometry (Addison *et al.*, 1984). For the title compound, $\tau = 0.19$, indicating that the coordination geometry of sodium is closer to, but distorted from, ideal square pyramidal.

Experimental

Crystals of the title compound were obtained *via* a serendipitous route upon reaction of (CH₃CO₂)₃Mn·2H₂O and L1 in a 2:3 ratio in methanol. An aqueous solution of NaClO₄ was added, to afford a white precipitate, which was collected by filtration. The title compound was isolated upon recrystallization of the precipitate from MeCN/Et₂O.

Crystal data

[Na(ClO ₄)(C ₂₄ H ₂₀ N ₆)]	Z = 2
$M_r = 514.90$	$D_x = 1.471 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.353 (4) \text{ \AA}$	Cell parameters from 54 reflections
$b = 10.558 (3) \text{ \AA}$	$\theta = 0.8\text{--}1.0^\circ$
$c = 12.794 (4) \text{ \AA}$	$\mu = 0.23 \text{ mm}^{-1}$
$\alpha = 100.26 (3)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 107.64 (3)^\circ$	Block, colourless
$\gamma = 97.33 (3)^\circ$	$0.20 \times 0.15 \times 0.12 \text{ mm}$
$V = 1162.3 (8) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	5304 independent reflections
Narrow-frame ω scans	3677 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.824$, $T_{\text{max}} = 0.970$	$\theta_{\text{max}} = 27.5^\circ$
12 525 measured reflections	$h = -12 \rightarrow 12$
	$k = -13 \rightarrow 13$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2]$
$wR(F^2) = 0.112$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5304 reflections	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
325 parameters	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$

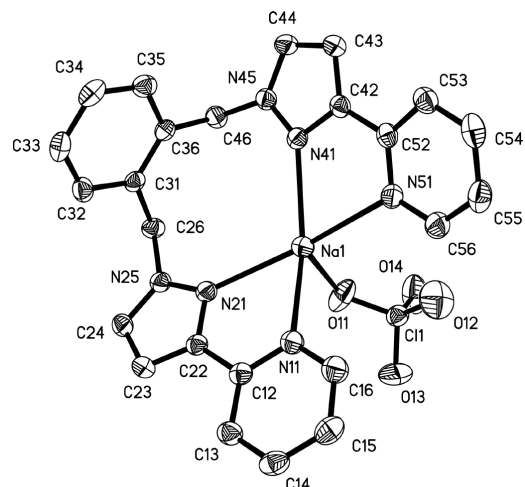


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Table 1

Selected geometric parameters (Å, °).

Na1—O11	2.3359 (18)	Na1—N41	2.499 (2)
Na1—N11	2.462 (2)	Na1—N51	2.5046 (19)
Na1—N21	2.4805 (18)		
O11—Na1—N11	90.60 (7)	N21—Na1—N41	111.12 (7)
O11—Na1—N21	92.44 (6)	O11—Na1—N51	103.64 (6)
N11—Na1—N21	68.75 (6)	N11—Na1—N51	103.28 (7)
O11—Na1—N41	117.95 (6)	N21—Na1—N51	162.31 (6)
N11—Na1—N41	151.16 (6)	N41—Na1—N51	67.84 (6)

All H atoms were constrained to ideal geometries, with C–H distances of 0.93 and 0.97 Å, and assigned isotropic displacement parameters equal to $1.2U_{\text{eq}}$ of their parent C atoms.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT and SHELXTL (Bruker, 1998); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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