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Methanol{tris[2-(2-pyridylmethyleneamino)ethyl]amino-κ^7N}calcium(II) bis(perchlorate) methanol solvate

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Key indicators

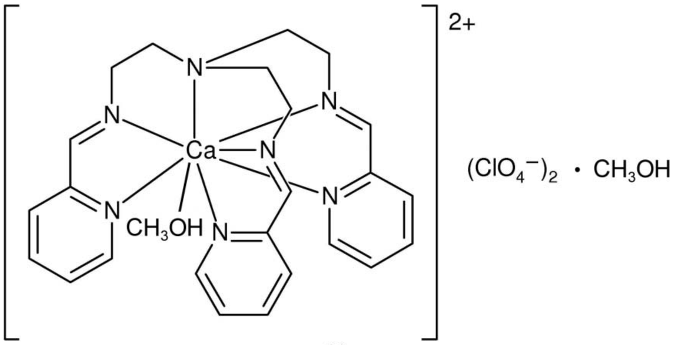
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.054
wR factor = 0.149
Data-to-parameter ratio = 13.3

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

In the title compound, $[Ca(C_{24}H_{27}N_7)(CH_3OH)](ClO_4)_2\cdot CH_3OH$, the Ca^{2+} ion is coordinated by all seven N atoms from the tris[2-(2-pyridylmethyleneamino)ethyl]amine ligand and by the O atom of a methanol molecule, in an approximately square-antiprismatic geometry.

Comment

Tris[2-(2-pyridylmethyleneamino)ethyl]amine (py_3tren) is the condensation product of tris(2-ethylamino)amine (tren) with 2-pyridylcarboxaldehyde. Complexes of py_3tren have been reported with the transition metal cations Mn^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+} (Kirchner *et al.* 1987) and Fe^{2+} (Schultz & Nitschke, 2006; Brewer *et al.*, 2004; Morgenstern-Badarau *et al.*, 2000). In each of these complexes, the metal cation is six-coordinated in a trigonal–antiprismatic environment, with the apical N atom of py_3tren remaining uncoordinated. Each arm of the ligand is twisted to allow the imine and pyridyl N atoms to chelate the metal cation. The extent of the twisting of each leg is dependent on the size of the cation. Previously, we have reported the crystal structures of the Zn^{2+}, Mn^{2+} and Ca^{2+} complexes of the related tren-based tripodal ligand tris[2-(2-thiazolylimino-ethyl)amine] (tatren) and have shown that, while both Zn^{2+} and Mn^{2+} are six-coordinated, the larger Ca^{2+} ion is eight-coordinated (He *et al.*, 2004). We were interested, therefore, in examining whether py_3tren is also able to accommodate larger metal cations, and the crystal structure of the title compound, (I), containing py_3tren with Ca^{2+}, is reported here.



(I)

In compound (I), the Ca^{2+} ion is coordinated by all seven N atoms of the py_3tren ligand and one O atom from a methanol molecule, in an approximately square-antiprismatic geometry (Fig. 1). The orientation of each arm of the ligand differs from that in the complexes with transition metal cations. The dihedral angle between the N4/Ca1/N5 plane and the least-squares plane through atoms Ca1/N5/C11/C12/N12 is

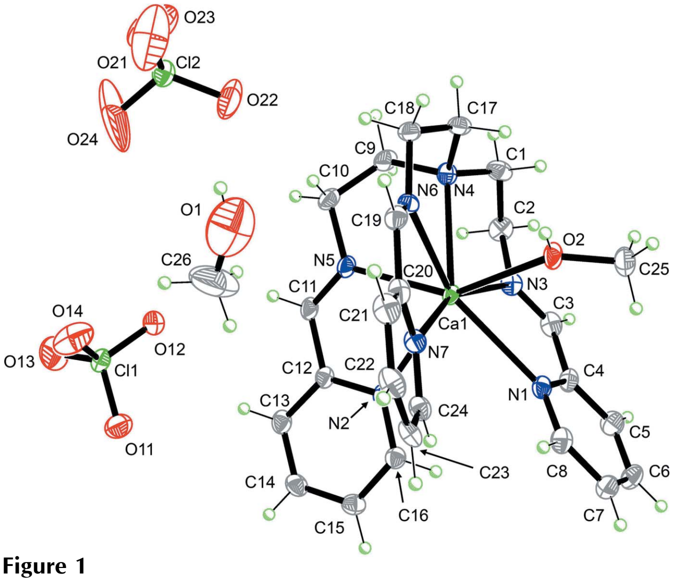


Figure 1
The asymmetric unit of (I), showing displacement ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary radius.

24.7 (2)°, the angle between N4/Ca1/N3 and Ca1/N3/C3/C4/N1 is 19.3 (2)°, and the angle between N4/Ca1/N6 and Ca1/N6/C19/C20/N7 is 2.4 (2)°. The much smaller angle in this last case indicates a lesser degree of twisting for this arm, which is a consequence of the larger size of the Ca^{2+} ion. The coordinated methanol molecule is hydrogen bonded to the O atoms of the perchlorate anion (Table 1).

Experimental

Pyridine-2-carboxaldehyde (0.32 g, 3.0 mmol) dissolved in dried methanol (4 ml) was added with stirring to a solution of tren (0.146 g, 1.0 mmol) dissolved in freshly dried methanol (6 ml). The solution was refluxed for 4 h, and then calcium perchlorate (0.223 g, 1.0 mmol) dissolved in methanol (3 ml) was added dropwise. The mixture was refluxed for a further 2 h and then concentrated by evaporation of the solvent to leave *ca* 5 ml. The resulting solid (0.45 g, yield 69%) was collected by filtration, washed with methanol and dried under vacuum. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex over a period of 2 weeks.

Crystal data

$[Ca(C_{24}H_{27}N_7)(CH_4O)](ClO_4)_2\cdot CH_4O$
$M_r = 716.59$
Orthorhombic, $Pna2_1$
$a = 18.3264\ (5)$ Å
$b = 16.3163\ (4)$ Å
$c = 10.9066\ (2)$ Å
$V = 3261.28\ (13)$ Å^3
$Z = 4$
$D_x = 1.459$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.42$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.30 × 0.25 × 0.23 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.884$, $T_{max} = 0.910$
7131 measured reflections
5546 independent reflections
5077 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.149$
$S = 1.02$
5546 reflections
418 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 3.5065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}
Absolute structure: Flack (1983), with 2509 Friedel pairs
Flack parameter: 0.58 (5)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O23^{i}	0.82	2.09	2.899 (9)	168

Symmetry code: (i) $-x, -y+1, z+\frac{1}{2}$.

The H atoms of the methanol molecules were positioned with O—H = 0.82 Å so as to form reasonable hydrogen bonds to the perchlorate anions. They were refined as riding atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$. The remaining H atoms were positioned geometrically, with C—H = 0.93 (aromatic H), 0.97 (methylene H) or 0.96 Å (methyl H), and refined as riding atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for the methyl groups. The methyl groups were allowed to rotate about their local threefold axes. The refined Flack parameter (Flack, 1983) indicated probable inversion twinning. The highest peak in the residual electron density lies in the vicinity of the methanol solvent molecule, 1.52 Å from O21.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* and *ORTEP-3 for Windows* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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