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Bis[tris(3-isopropylpyrazolyl)methanesulfonato]-manganese(II) dichloromethane disolvate

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Key indicators

Single-crystal X-ray study

T = 120 K

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

R factor = 0.076

wR factor = 0.209

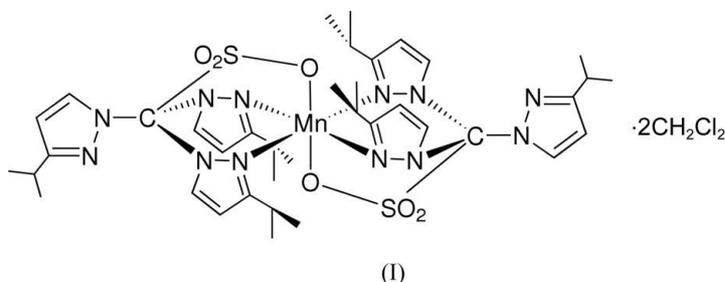
Data-to-parameter ratio = 14.2

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

The title compound, $[\text{Mn}(\text{C}_{19}\text{H}_{27}\text{N}_6\text{O}_3\text{S})_2] \cdot 2\text{CH}_2\text{Cl}_2$ or $[\text{Mn}(\text{Tpms}^{\text{iPr}})_2] \cdot 2\text{CH}_2\text{Cl}_2$, contains a distorted octahedral Mn atom bound to two N atoms and an O atom from each ligand. The Mn atom lies on a center of symmetry. This structure is compared with previously reported octahedral complexes of the same ligand and other octahedral manganese complexes containing N_4O_2 donor sets.

Comment

The tris(3-isopropylpyrazolyl)methanesulfonate (Tpms^{iPr}) ligand has been used as a structural model for histidine and aspartate residues in metalloenzymes (Papish *et al.*, 2006). To complete our studies of late first-row transition metal complexes of this ligand, we prepared an Mn^{II} complex, (I). Again, this ligand prefers to form homoleptic ML_2 complexes with N_2O donated from each ligand. $\text{Mn}(\text{Tpms}^{\text{iPr}})_2$ has an octahedral geometry with an inversion center at the metal. Bond lengths and angles are consistent with the trends we have seen for other $\text{M}(\text{Tpms}^{\text{iPr}})_2$ ($\text{M} = \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}$) complexes (Papish *et al.*, 2006). As for $\text{M} = \text{Zn}, \text{Co}, \text{Ni}$ and Fe , $\text{Mn}(\text{Tpms}^{\text{iPr}})_2$ has an Mn—O bond length of 2.121 (3) Å which is shorter than its Mn—N bond lengths of 2.252 (4) and 2.261 (4) Å. The bond lengths are most similar to the iron complex, which is not surprising given that Fe^{II} and Mn^{II} have similar ionic radii. $\text{Mn}(\text{Tpms}^{\text{iPr}})_2$ shows a relatively large (approximately 10°) distortion from octahedral geometry; similar bond angles were seen for $\text{M}(\text{Tpms}^{\text{iPr}})_2$ complexes where $\text{M} = \text{Fe}, \text{Co}, \text{Zn}$. In contrast, the Cu and Ni complexes have bond angles that show less distortion from an idealized octahedral geometry.



Very few other octahedral MnN_4O_2 complexes of similar structure were found in the literature. One report of a manganese(II) complex (Lumme *et al.*, 1988) had water molecules at 2.148 (3) Å and pyrazole molecules at 2.245 (4) and 2.264 (3) Å from the metal center. These bond distances are very similar to those in the title compound, but the bond angles were much closer to a perfect octahedron. The (2-

hydroxyphenyl)bis(pyrazolyl)methane ligand reported by Higgs *et al.* (1998) forms a trinuclear Mn^{II} complex that contains two octahedral Mn atoms and one five-coordinate Mn. The unique octahedral Mn atom is relevant here because it has an N₄O₂ donor set from pyrazole N atoms and phenolate O atoms. The bond lengths of the octahedral Mn are 2.111 (6) Å for Mn–O and 2.227 (9) and 2.257 (9) Å for Mn–N. In comparing these values with Mn(Tpms^{iPr})₂, the Mn–O distances are within experimental error of each other, and the Mn–N distances are similar. We should expect some differences between these structures because the complex of Higgs *et al.* (1998) has the O atoms *cis*, whereas Mn(Tpms^{iPr})₂ has *trans* O atoms. Also, the ligand frameworks are different and Mn(Tpms^{iPr})₂ has more steric bulk near the metal.

Experimental

Lithium tris(3-isopropylpyrazolyl)methanesulfonate (0.310 g, 0.727 mmol) was mixed with an excess of MnCl₂ (0.244 g, 1.94 mmol) in CH₂Cl₂ (10 ml). After stirring for 1 h, the solution was filtered in an inert atmosphere. Impurities were removed by recrystallization from CH₂Cl₂ followed by filtration and washing with cold CH₂Cl₂. The resulting white solid was dried under vacuum to yield Mn(Tpms^{iPr})₂ (0.094 g, 0.105 mmol) in 29% yield. Colorless crystals for single-crystal X-ray diffraction were grown by slow evaporation of a CH₂Cl₂ solution.

Crystal data

[Mn(C ₁₉ H ₂₇ N ₆ O ₃ S) ₂] ₂ ·2CH ₂ Cl ₂	<i>Z</i> = 2
<i>M</i> _r = 1063.84	<i>D</i> _x = 1.441 Mg m ⁻³
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 10.437 (6) Å	<i>μ</i> = 0.63 mm ⁻¹
<i>b</i> = 21.860 (8) Å	<i>T</i> = 120 (2) K
<i>c</i> = 11.341 (6) Å	Block, colorless
<i>β</i> = 108.626 (7)°	0.20 × 0.10 × 0.05 mm
<i>V</i> = 2452 (2) Å ³	

Data collection

Bruker APEX diffractometer	11367 measured reflections
<i>ω</i> scans	4285 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	3243 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.884, <i>T</i> _{max} = 0.969	<i>R</i> _{int} = 0.092
	<i>θ</i> _{max} = 25.0°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.1003P)^2 + 2.0495P]$
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.076	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> (<i>F</i> ²) = 0.209	(Δ/σ) _{max} = 0.002
<i>S</i> = 1.05	Δρ _{max} = 1.64 e Å ⁻³
4285 reflections	Δρ _{min} = -1.11 e Å ⁻³
301 parameters	
H-atom parameters constrained	

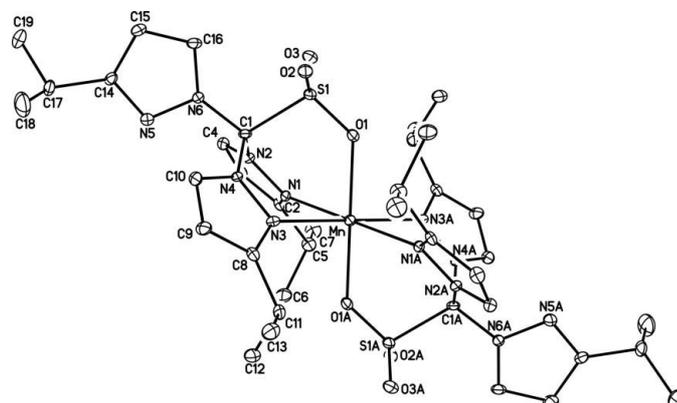


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. The solvent molecules and the H atoms have been omitted for clarity.

The molecule is located at an inversion center. The equivalent isotropic parameters of the atoms on the free pyrazolyl arm are higher than those of the coordinated arms suggesting higher thermal motion. Consequently, C–C bond precision is low. Apparently high thermal motion of the Cl atoms in the cocrystallized dichloromethane solvent molecule has a coincident pivotal C-atom position, resulting in a lower *U*_{eq} for C20 compared with the Cl atoms. H atoms were assigned calculated positions (C–H = 0.95–1.00 Å) with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C). The highest unassigned peak is located 0.97 Å from atom Cl2. The deepest electron density hole is located 0.84 Å from atom Cl2.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*, Sheldrick (2001); software used to prepare material for publication: *SHELXTL*.

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