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catena-Poly[[dithiocyanatomanganese(II)]-di-μ-4,4′-methylenebis(3,5-dimethylpyrazole)]

Wei Han, Ling Li, Wen Gu, Zhan-Quan Liu, Shi-Ping Yan,* Peng Cheng, Dai-Zheng Liao, Zong-Hui Jiang and Pan-Wen Shen

Department of Chemistry, Nankai University, Tianjin, 300071, People's Republic of China

Correspondence e-mail: yansp@nankai.edu.cn

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.103
Data-to-parameter ratio = 16.9

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

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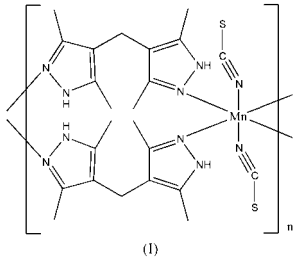
A novel Mn(II) one-dimensional coordination polymer with the bridging ligand 4,4′-methylenebis(3,5-dimethylpyrazole), (H_2mbdpz), has been isolated. It is composed of $[Mn(C_{11}H_{16}N_4)_2(SCN)_2]$ units. The crystal structure determination shows that an infinite chain is composed of alternating manganese ions and H_2mbdpz ligands. The Mn(II) ion lies on a twofold axis.

Comment

The design and synthesis of polymeric coordination complexes has attracted increasing interest over the last decade because of their interesting structures. The dimensionality of the network depends on the number of translations of the coordination pattern in different directions of space. Thus, a one-dimensional coordination network is generated by a single translation of the coordination pattern. Interest in one-dimensional chain structures arises partly because these structures are expected to play a crucial role as precursors in the formation of two- and three-dimensional structures (Neeraj *et al.*, 1999). In the past, the majority of one-dimensional coordination networks were composed of bis-monodentate tectons (Yaghi *et al.*, 1998; Hennigar *et al.*, 1997), while few examples of complexes with bis-bidentate (Veltan & Rehahn, 1996; Kaes *et al.*, 1998), and bis-tridentate tectons (Constable & Cargill Thompson, 1992; Neels *et al.*, 1997; Loi *et al.*, 1999) were published.



(I)

Here we report a one-dimensional chain complex bridged by the bis-bidentate organic tecton 4,4′-methylene-bis(3,5-dimethylpyrazole). The structure of the title compound, (I), is shown in Fig. 1. The Mn atom, on a twofold axis, is octahedrally coordinated by two thiocyanate groups in a *trans* arrangement and four H_2mbdpz ligands. The octahedral geometry is slightly distorted, with all angles at Mn deviating from the ideal; values range from 81.73 (11) to 94.11 (8)°, and 175.01 (8) to 179.90 (12)°.

The average Mn—$N_{pyrazole}$ bond distance [2.31 (4) Å] is longer than the Mn—N_{SCN} bond length [2.219 (2) Å]. These values are similar to those in other octahedral manganese complexes (Dalai *et al.*, 2002; Han *et al.*, 2000).

The alternating manganese ions and H_2mbdpz ligands form an infinite one-dimensional chain, the dihedral angle between the two pyrazole rings within one ligand being 81.1 (1)°, which is slightly smaller than that in the free ligand. This suggests that the two pyrazole rings underwent a slight rotation in the course of formation of the coordination polymer. The Mn···Mn non-bonding distance between adjacent metal ions is 9.723 (4) Å.

Experimental

H_2mbdpz (204 mg, 1 mmol) in ethanol (10 ml) was added to a solution of $Mn(ClO_4)_2{\cdot}6H_2O$ (366 mg, 1 mmol) in H_2O (10 ml). After dissolution was complete, an aqueous solution of NH_4SCN (152 mg, 2 mmol) was added. The mixture was refluxed for a further 2 h with stirring, yielding a brown precipitate. The solution was then filtered to remove the precipitate, which was subsequently washed with water, methanol and acetone, and finally dried. The solid was dissolved in DMF, producing a clear solution, which was allowed to stand undisturbed at room temperature for a few weeks. Pale red crystals were obtained.

Crystal data

$[Mn(C_{11}H_{16}N_4)_2(SCN)_2]$
M_r = 579.66
Monoclinic, $C2/c$
a = 21.258 (10) Å
b = 9.723 (4) Å
c = 17.253 (7) Å
β = 126.610 (14)°
V = 2863 (2) Å^3
Z = 4
D_x = 1.345 Mg m^{-3}
D_m = 1.322 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 713 reflections
θ = 2.4–25.1°
μ = 0.64 mm^{-1}
T = 293 (2) K
Prism, pale red
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.831, T_{max} = 0.883
7826 measured reflections
2899 independent reflections
1972 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 26.4°
$h = -26 \rightarrow 26$
$k = -11 \rightarrow 12$
$l = -21 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.103
S = 1.02
2899 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 1.465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

H atoms were refined with a riding model (C—H 0.96, N—H 0.86 Å; U_{iso} = 1.2 or 1.5 U_{eq} of the parent atom). The methyl groups were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

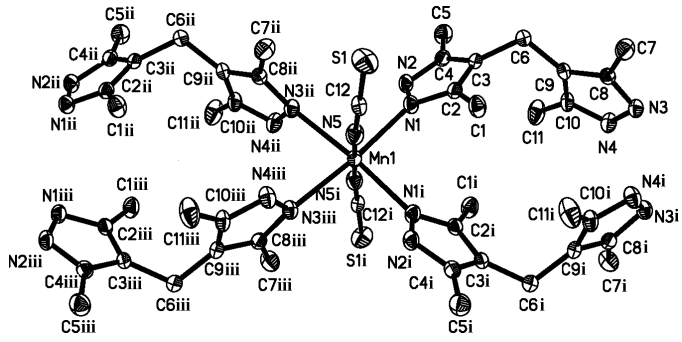


Figure 1
A view of a segment of the structurer structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x+1$, y, $-z+\frac{1}{2}$; (ii) x, $y-1$, z; (iii) $-x+1$, $y-1$, $-z+\frac{1}{2}$.]

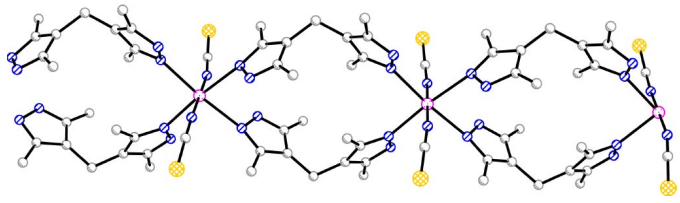


Figure 2
View of the one-dimensional chain architecture. H atoms have been omitted for clarity. Colour code: C black, N blue, Mn magenta, S yellow.

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