

catena-Poly[[bis(1*H*-benzotriazole- κ N³)cobalt(II)]-di- μ -tricyanomethanido- κ^2 N:N'] and catena-poly[[bis(3,5-dimethyl-1*H*-pyrazole- κ N²)manganese(II)]-di- μ -tricyanomethanido- κ^2 N:N']

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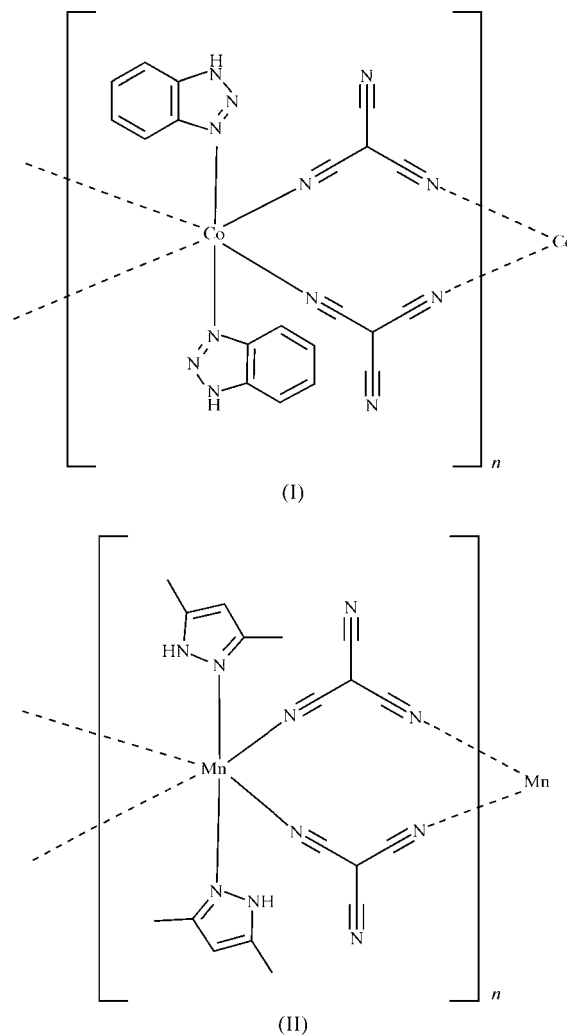
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Two new one-dimensional coordination polymers, *viz.* the title compounds, $[\text{Co}\{\text{C}(\text{CN})_3\}_2(\text{C}_6\text{H}_5\text{N}_3)_2]_n$, (I), and $[\text{Mn}\{\text{C}(\text{CN})_3\}_2(\text{C}_5\text{H}_8\text{N}_2)_2]_n$, (II), have been synthesized and characterized by X-ray diffraction. Both complexes consist of linear chains with double 1,5-tricyanomethanide bridges between neighbouring divalent metal ions. The Co and Mn atoms are located on centres of inversion. In (I), the coordination environment of the Co^{II} atom is that of an elongated octahedron. The Co^{II} atom is coordinated in the equatorial plane by four nitrile N atoms of four bridging tricyanomethanide ions, with Co–N distances of 2.106 (2) and 2.110 (2) Å, and in the apical positions by two N atoms from the benzotriazole ligands, with a Co–N distance of 2.149 (2) Å. The $[\text{Co}\{\text{C}(\text{CN})_3\}_2(\text{C}_6\text{H}_5\text{N}_3)_2]$ units form infinite chains extending along the *a* axis. These chains are crosslinked *via* a hydrogen bond between the uncoordinated nitrile N atom of a tricyanomethanide anion and the H atom on the uncoordinated N atom of a benzotriazole ligand from an adjacent chain, thus forming a three-dimensional network structure. In (II), the Mn^{II} atom also adopts a slightly distorted octahedral geometry, with four nitrile N atoms of tricyanomethanide ligands [Mn–N = 2.226 (2) and 2.227 (2) Å] in equatorial positions and two N atoms of the monodentate 3,5-dimethylpyrazole ligands [Mn–N = 2.231 (2) Å] in the axial sites. In (II), one-dimensional polymeric chains extending along the *b* axis are formed, with tricyanomethanide anions acting as bidentate bridging ligands. A hydrogen bond between the uncoordinated nitrile N atom of the tricyanomethanide ligand and the H atom on the uncoordinated N atom of a 3,5-dimethylpyrazole group from a neighbouring chain links the molecule into a two-dimensional layered structure.

Comment

The tricyanomethanide anion $[\text{C}(\text{CN})_3]^-$, tcm] has proved to be a versatile ligand for the construction of coordination polymers. It has been found that tcm can coordinate to metal ions in various modes, such as monodentate bonding through a nitrile N atom (Potočňák *et al.*, 1997), bridging through two nitrile N atoms (Hvastijová *et al.*, 1995; Batten *et al.*, 2000), and triple or quadruple coordination through all three terminal N atoms (Chow & Britton, 1975; Manson *et al.*, 1998; Batten *et al.*, 1991, 1999). Therefore, tcm complexes continue to attract considerable interest, especially in the preparation of magnetic materials containing this ligand (Miller & Manson, 2001; Batten & Murray, 2003). Many results indicate that the



network topologies and the magnetic properties of the tcm-containing coordination polymers depend on the co-ligands. For example, the structure of the $\text{Ag}(\text{tcm})$ -type complex changes from two- to three-dimensional with the introduction of the pyrazine co-ligand (Batten *et al.*, 1998). Notably, although metal–tcm coordination polymers with nitrogen-containing co-ligands, such as pyrazole (Kožíšek *et al.*, 1991), 2-methylimidazole (Hvastijová *et al.*, 1995, 1998), bipyridine (Batten *et al.*, 2000) and tetramethylpyrazine (Batten *et al.*, 2001; Abrahams *et al.*, 2003), have been studied extensively, no

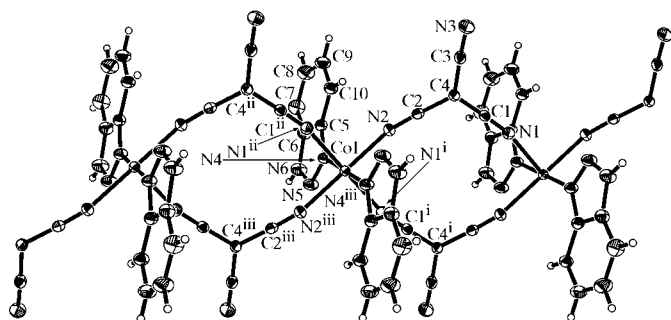


Figure 1

The chain structure of (I), with displacement ellipsoids at the 30% probability level. [Symmetry codes: (i) $x + 1, y, z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $2 - x, 2 - y, 2 - z$.]

tcm complexes with benzotriazole or 3,5-dimethylpyrazole as co-ligands have been characterized crystallographically so far. In order to study further how the nature of the co-ligands affects the structures and properties of tcm complexes, we report here the syntheses and crystal structures of two novel transition-metal-tcm complexes with benzotriazole or 3,5-dimethylpyrazole as co-ligands, namely $[\text{Co}(\text{tcm})_2(\text{benzotriazole})_2]_n$ (I), and $[\text{Mn}(\text{tcm})_2(3,5\text{-dimethylpyrazole})_2]_n$ (II).

Complex (I) is composed of linear chains of Co^{II} ions bridged by tcm ligands and coordinated by benzotriazole ligands (Fig. 1). Each Co^{II} ion is connected to two neighbours by four equatorially bound tcm ligands, which participate in two successive $\text{Co}(\text{tcm})_2\text{Co}$ units. Two nitrile N atoms in one tcm ligand are involved in coordination, so that the tcm ligands act as bridges in a μ -1,5 mode; a similar trend has been observed in $\text{Co}(\text{tcm})_2(\text{H}_2\text{O})_2$ (Batten *et al.*, 2001). The slightly distorted octahedral coordination environment of the Co atoms is completed by the coordination of two N atoms from

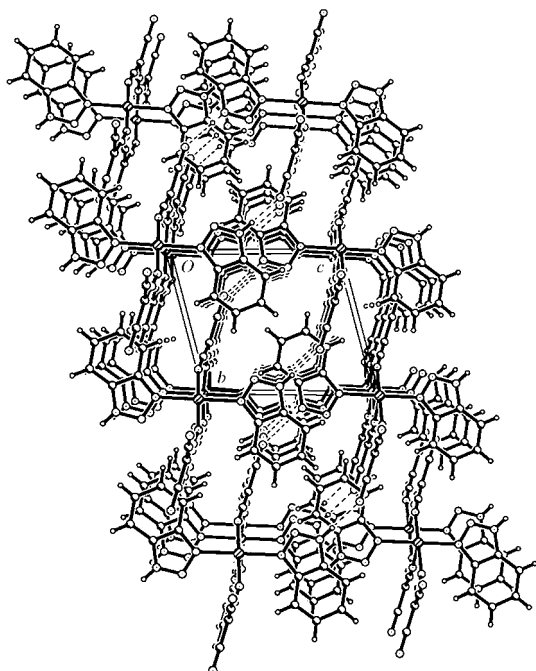


Figure 2

The three-dimensional network of (I), crosslinked *via* hydrogen-bonding interactions (dashed lines), viewed along the *a* axis.

trans benzotriazole ligands, which act as monodentate ligands. The $\text{Co}-\text{N}_{\text{tcm}}$ equatorial distances [2.106 (2) and 2.110 (2) Å; mean 2.108 (2) Å] are slightly shorter than the $\text{Co}-\text{N}(\text{benzotriazole})$ axial lengths [2.149 (2) Å]; these distances are comparable to those in $\text{Co}(\text{tcm})_2(2\text{-methylimidazole})_2$ (Hvastijová *et al.*, 1995). The CoN_6 octahedron is only slightly distorted, as shown by the values (near 90°) of the *cis* $\text{N}-\text{Co}-\text{N}'$ angles, which range from 88.37 (9) to 91.16 (9) $^\circ$ (Table 1).

The polymeric one-dimensional chains lie along the *a* axis and are crosslinked by a hydrogen-bonding interaction between one H atom on an uncoordinated N atom (3-position) of a benzotriazole ligand and the uncoordinated nitrile N atom of a bridging tcm ligand from an adjacent chain (Table 2), thus forming a three-dimensional structure (Fig. 2). The shortest $\text{Co}\cdots\text{Co}$ intrachain length [7.287 (2) Å] is very similar to that in $\text{Co}(\text{tcm})_2(\text{H}_2\text{O})_2$ (7.308 Å; Batten *et al.*, 2001) and the shortest $\text{Co}\cdots\text{Co}$ interchain distance [7.962 (3) Å] in (I) is shorter than that in $\text{Co}(\text{tcm})_2(2\text{-methylimidazole})_2$ (Hvastijová *et al.*, 1995). As the adjacent chains are not staggered, there are no π - π interactions between adjacent benzotriazole rings. It is only the hydrogen bonds that hold the crystal in the three-dimensional structure.

The structure of (II) also consists of polymeric one-dimensional chains, in this case formed by $\{\text{Mn}(3,5\text{-dimethylpyrazole})_2\}^{2+}$ cations linked together by two bridging tcm anions (Fig. 3). The Mn^{II} atom is pseudo-octahedrally coordinated by four tcm nitrile atoms [N1, N1^{vi}, N2^{vii} and N1^{viii}; symmetry codes: (vi) $2 - x, 1 - y, 1 - z$; (vii) $x, y - 1, z$; (viii) $2 - x, -y, 1 - z$] in the equatorial plane and two N atoms (N4 and N4^{viii}) from the two *trans* monodentate 3,5-dimethylpyrazole ligands in the axial positions. In (II), the equatorial $\text{Mn}-\text{N}_{\text{tcm}}$ bond lengths (Table 3) are in the normal range and are comparable to the $\text{Mn}-\text{N}$ bond lengths in $\text{Mn}(\text{tcm})_2$ (Manson *et al.*, 1998), while the axial $\text{Mn}-\text{N}(3,5\text{-dimethylpyrazole})$ distance is a little shorter than those observed in $\text{Mn}(\text{pydazine})_2(\text{dca})_2$ (Escuer *et al.*, 2002) and $\text{Mn}(2,5\text{-Me}_2\text{pyz})_2(\text{dca})_2(\text{H}_2\text{O})_2$ (2,5-Me₂pyz is 2,5-dimethylpyrazine; Manson *et al.*, 2001).

In (II), the polymeric one-dimensional chains are generated parallel to the *b* axis. An intermolecular hydrogen-bonding interaction between the uncoordinated terminal N atom of the tcm ligand and the H atom of the 3,5-dimethylpyrazole ligand

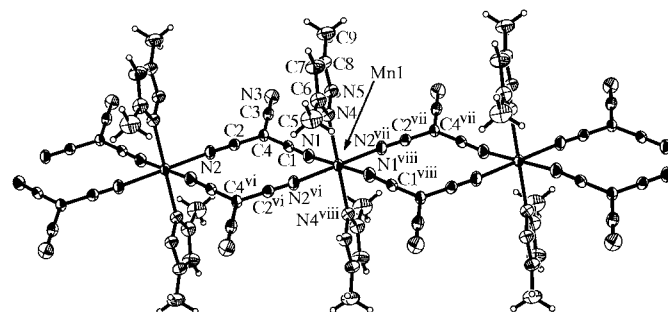


Figure 3

The chain structure of (II), with displacement ellipsoids at the 30% probability level. [Symmetry codes: (vi) $2 - x, 1 - y, 1 - z$; (vii) $x, y - 1, z$; (viii) $2 - x, -y, 1 - z$.]

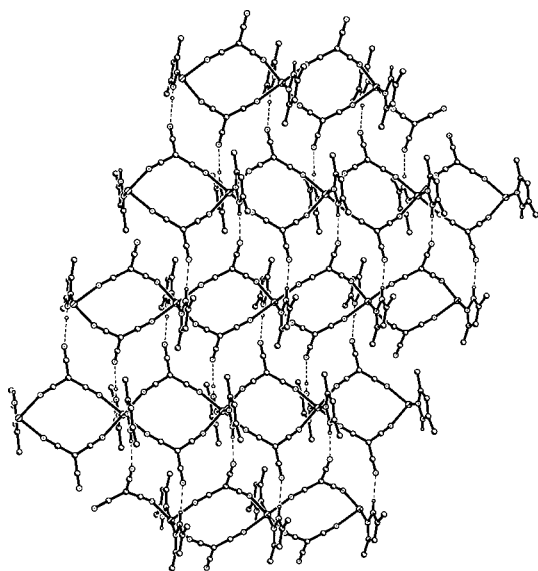


Figure 4
Part of the infinite two-dimensional network formed in (II) by hydrogen-bonding interactions (dashed lines).

in an adjacent chain (Table 4) results in the formation of a two-dimensional network (Fig. 4). The interchain Mn···Mn distance [8.053 (5) Å] is slightly longer than the intrachain Mn···Mn distance [7.547 (4) Å].

In (I) and (II), each tcm group is almost planar [the largest deviation of atoms from the mean plane is 0.026 (5) Å], and the bond lengths and angles of the tcm ions are in the normal range (Potočňák *et al.*, 1997). The benzotriazole and 3,5-dimethylpyrazole ligands are also almost planar [the largest deviations of atoms from the mean planes are 0.031 (5) and 0.002 (7) Å, respectively].

Experimental

An aqueous solution (2 ml) of potassium tricyanomethanide (0.60 mmol, 77.4 mg) and an ethanol solution (4 ml) of benzotriazole (0.60 mmol, 71.4 mg) were mixed and stirred for 5 min; the resulting solution was colourless. To the mixture was added slowly an aqueous solution (2 ml) of cobalt nitrate (0.30 mmol, 87.3 mg). After stirred for another 5 min, the solution was filtered and the filtrate was evaporated slowly in air. After two weeks, pink block-shaped crystals of (I) were isolated in 35% yield. Complex (II) was prepared in a similar manner (40% yield).

Compound (I)

Crystal data

[Co(C₄N₃)₂(C₆H₅N₃)₂]
M_r = 477.33
 Triclinic, *P* $\bar{1}$
a = 7.287 (2) Å
b = 7.962 (3) Å
c = 9.583 (3) Å
 α = 75.643 (4)°
 β = 76.678 (4)°
 γ = 89.697 (4)°
V = 523.4 (3) Å³
Z = 1

D_x = 1.514 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 719 reflections
 θ = 5.6–27.0°
 μ = 0.86 mm⁻¹
T = 298 (2) K
 Block, pink
 0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.847, *T_{max}* = 0.919
 2401 measured reflections
 2008 independent reflections

1943 reflections with *I* > 2σ(*I*)
R_{int} = 0.023
 θ_{\max} = 26.0°
h = -8 → 8
k = -8 → 9
l = -6 → 11

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.051
wR(*F*²) = 0.131
S = 1.05
 2008 reflections
 151 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0926P)^2 + 0.2599P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.88 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

Co1—N1 ⁱ	2.106 (2)	C3—N3	1.143 (4)
Co1—N2	2.110 (2)	C3—C4	1.408 (4)
Co1—N4	2.149 (2)	C4—C1	1.397 (4)
C2—N2	1.143 (4)	C1—N1	1.147 (4)
C2—C4	1.403 (4)		
N1 ⁱ —Co1—N2	91.16 (9)	C1—C4—C3	120.5 (2)
N1 ⁱⁱ —Co1—N4 ⁱⁱⁱ	88.37 (9)	C2—C4—C3	122.2 (2)
N2—Co1—N4 ⁱⁱⁱ	88.84 (9)	C2—N2—Co1	163.6 (2)
N2—C2—C4	176.8 (3)	N1—C1—C4	178.0 (3)
N3—C3—C4	177.5 (3)	C1—N1—Co1 ^{iv}	166.9 (2)
C1—C4—C2	117.3 (2)		

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 - *x*, 2 - *y*, 2 - *z*; (iii) 2 - *x*, 2 - *y*, 2 - *z*; (iv) *x* - 1, *y*, *z*.

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N6—H6···N3 ^v	0.86	1.99	2.849 (4)	179

Symmetry code: (v) 1 + *x*, 1 + *y*, *z* - 1.

Compound (II)

Crystal data

C₁₈H₁₆MnN₁₀
M_r = 427.35
 Orthorhombic, *Pbca*
a = 16.107 (9) Å
b = 7.547 (4) Å
c = 17.437 (10) Å
V = 2120 (2) Å³
Z = 4
D_x = 1.339 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 936 reflections
 θ = 0.7–23.6°
 μ = 0.65 mm⁻¹
T = 298 (2) K
 Block, colourless
 0.25 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.855, *T_{max}* = 0.938
 4692 measured reflections

1853 independent reflections
 1226 reflections with *I* > 2σ(*I*)
R_{int} = 0.029
 θ_{\max} = 25.0°
h = -12 → 19
k = -8 → 8
l = -20 → 12

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.086$
 $S = 0.94$
 1853 reflections
 135 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

Mn1—N2 ^{vi}	2.226 (2)	C2—N2	1.145 (3)
Mn1—N1	2.227 (2)	C2—C4	1.392 (3)
Mn1—N4	2.231 (2)	C3—N3	1.141 (3)
C1—N1	1.149 (3)	C3—C4	1.402 (3)
C1—C4	1.397 (3)		
N2 ^{vii} —Mn1—N1 ^{viii}	86.70 (9)	C2—C4—C1	118.48 (19)
N2 ^{vi} —Mn1—N4 ^{viii}	89.26 (7)	C2—C4—C3	120.9 (2)
N1—Mn1—N4	88.45 (7)	C1—C4—C3	120.4 (2)
N1—C1—C4	178.5 (2)	C1—N1—Mn1	156.8 (2)
N2—C2—C4	178.9 (2)	C2—N2—Mn1 ^{ix}	170.64 (19)
N3—C3—C4	179.2 (3)		

Symmetry codes: (vi) $2-x, 1-y, 1-z$; (vii) $x, y-1, z$; (viii) $2-x, -y, 1-z$; (ix) $x, 1+y, z$.

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5—H5 \cdots N3 ^x	0.86	2.10	2.959 (3)	173

Symmetry code: (x) $\frac{3}{2}-x, y-\frac{1}{2}, z$.

All H atoms were treated using a riding model [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. In (I), H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 \AA and N—H distances of 0.86 \AA . In (II), the positions of the H atoms were constrained to an ideal geometry, with C—H distances in the range 0.93–0.96 \AA and N—H distances of 0.86 \AA .

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1708). Services for accessing these data are described at the back of the journal.

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