

One-dimensional zinc-based coordination polymers incorporating cyanate anions

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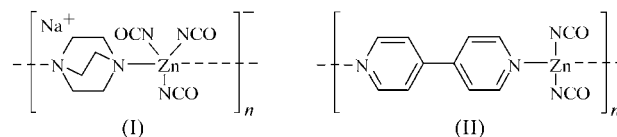
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Two one-dimensional zinc-based coordination polymers containing cyanate anions are reported. *catena*-Poly[sodium [[tricyanatozinc(II)]- μ -1,4-diazabicyclo[2.2.2]octane- κ^2 N:N']], $\{\text{Na}[\text{Zn}(\text{NCO})_3(\text{C}_6\text{H}_{12}\text{N}_2)]\}_n$, consists of linear [tricyanatozinc(II)]- μ -1,4-diazabicyclo[2.2.2]octane strands in which the Zn^{2+} cations adopt trigonal-bipyramidal coordination on sites of $\bar{6}m2$ point symmetry. Na^+ cations lie between the strands on sites of $\bar{3}m$ point symmetry, coordinated in a distorted octahedral geometry by six O atoms of the cyanate anions. *catena*-Poly[[dicyanatozinc(II)]- μ -4,4'-bipyridine- κ^2 N:N']], $[\text{Zn}(\text{NCO})_2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$, crystallizes in the space group $P2_1/n$ with $Z' = 5$. The structure consists of zigzag strands formed by Zn^{2+} cations linked *via* 4,4'-bipyridine. Each Zn^{2+} cation adopts a tetrahedral coordination, with two sites occupied by 4,4'-bipyridine and two cyanate anions completing the coordination sphere. The structure is closely comparable with the thiocyanate and halide analogues $[\text{Zn}X_2(\text{C}_{10}\text{H}_8\text{N}_2)]$ ($X = \text{NCS}, \text{Cl}$ or Br).

Comment

1,4-Diazabicyclo[2.2.2]octane (DABCO) and 4,4'-bipyridine (bipy) are commonly employed as 'spacer' ligands for the construction of metal-organic frameworks (MOFs). With Zn^{II} , the latter ligand in particular has been included in MOFs with three-dimensional (for example, Wang *et al.*, 2004; Tao *et al.*, 2000) and two-dimensional (Gable *et al.*, 1990; Ng, 2003) architectures, and also in numerous one-dimensional coordination polymers (Kondo *et al.*, 1999; Pan *et al.*, 1999; Sampanthar & Vittal, 1999; Ma *et al.*, 2000). MOFs incorporating DABCO are less prevalent, but two-dimensional (He *et al.*, 2002) and three-dimensional (Dybtsev *et al.*, 2004) frameworks have been reported in which DABCO is present in combination with terephthalic acid. Zn-DABCO complexes that incorporate monodentate or chelating ligands have been observed as discrete units (for example, Fronczek *et al.*, 1990; Petrusenko *et al.*, 1997) and as one-dimensional coordination

polymers, with both linear (Petrusenko *et al.*, 1997) and zigzag (Huang *et al.* 1996; Ng, 1999; Braga *et al.*, 2004) geometries. Structures incorporating cyanate anions bonded to Zn^{II} are rather more rare; only three examples (Choi *et al.*, 1999; Secondo *et al.*, 2000; Soldatov *et al.*, 1999) exist in the Cambridge Structural Database (CSD; Version of November 2004, plus three updates; Allen, 2002), and there are no examples in the Inorganic Crystal Structure Database (ICSD, 2005).



In the first complex, $\text{Na}[\text{Zn}(\text{NCO})_3(\text{DABCO})]$, (I) (Fig. 1), one-dimensional linear strands are formed from Zn^{2+} cations linked *via* DABCO moieties. The coordination geometry of the Zn^{2+} cation is trigonal-bipyramidal, with three cyanate anions, coordinated through N, lying in the equatorial plane. The anionic $[\text{Zn}(\text{NCO})_3(\text{DABCO})]^-$ strands adopt a trigonal arrangement, with the cyanate anions lying in mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. Na^+ cations (at $z = 0$ and $\frac{1}{2}$) lie between the mirror planes (Fig. 2) and are coordinated by the O atoms of the cyanate anions. The single symmetry-independent cyanate anion in the structure is modelled as disordered, with one orientation (atoms C1 and O1) lying along the twofold rotation axis that passes through atoms Zn1 and N1, and a second orientation (atoms C1A and O1A) displaced slightly from the twofold axis. The disordered description was deemed to be

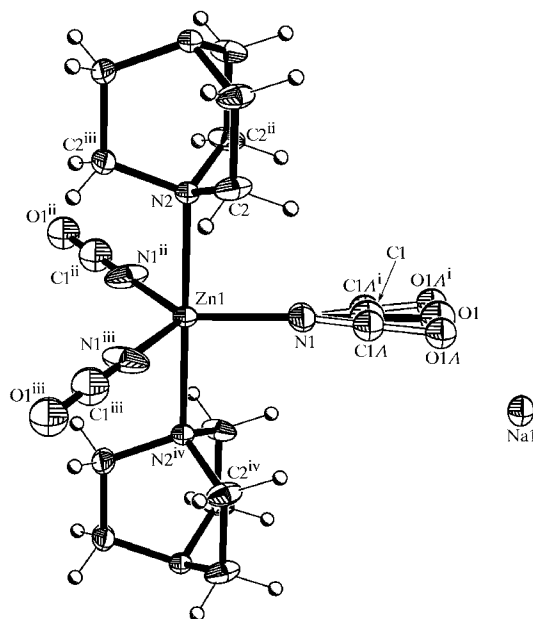


Figure 1

The coordination environment of atom Zn1 in (I), showing displacement ellipsoids at the 50% probability level. The disorder of the cyanate moiety is shown for only one ligand. [Symmetry codes: (i) $x, x - y, z$; (ii) $1 - y, x - y, z$; (iii) $1 - x + y, 1 - x, z$; (iv) $x, y, \frac{1}{2} - z$.]

more satisfactory than an ordered description incorporating displacement ellipsoids that are grossly distorted in the direction perpendicular to the twofold axis. On the basis of the O-atom sites lying on the twofold axes, the coordination geometry around Na^+ may be described as distorted octahedral, the distortion being parallel to the threefold axis of the octahedron (the crystallographic c axis). Incorporation of Na^+ at this coordination site must be consistent with the $\text{Zn} \cdots \text{Zn}$ separation imposed by the DABCO moiety. That is, the perpendicular separation of 3.54 Å between the mirror planes containing the Zn^{2+} cations and cyanate anions is consistent with an $\text{Na}-\text{O1}$ distance of 2.377 (6) Å. Inclusion of a larger spacer ligand such as bipy in a similar structure would provide a coordination site between the cyanate anions that is too large to accommodate Na^+ efficiently.

The second compound, $[\text{Zn}(\text{NCO})_2(\text{DABCO})]$, (II) (Fig. 3), crystallizes in space group $P2_1/n$ with $Z' = 5$. This is relatively unusual; only 32 examples exist at present in the CSD of structures in space group $P2_1/c$ (or equivalent) with $Z' \geq 5$. The structure of (II) comprises neutral one-dimensional

strands in which the coordination geometry around Zn^{2+} is tetrahedral. The environment of atom Zn1 closely resembles that in the comparable mononuclear complex $[\text{Zn}(\text{NCO})_2[4-(N,N'\text{-dimethylamino})\text{pyridine}]_2]$ (Secondo *et al.*, 2000). The strands in (II) adopt a zigzag geometry and can be envisaged as lying in layers parallel to the bc plane at $x = \frac{1}{4}$ and $\frac{3}{4}$. Similar layered arrangements are observed in the thiocyanate and halide analogues $[\text{Zn}X_2(\text{DABCO})]$, where $X = \text{NCS}$ (Kondo *et al.*, 1999; Pan *et al.*, 1999), Cl or Br (Hu & Englert, 2001), the Cl derivative having been observed to be dimorphic (Fu *et al.*, 2001). In each of these structures, the layers display regular planar geometry, having mirror or twofold rotation symmetry. In (II), the layers are rather more distorted, and the Zn^{2+} cations in adjacent strands are not strictly coplanar. This distortion appears to be driven to some extent by differing coordination arrangements of the cyanate ligands: on each of the five symmetry-independent Zn^{2+} cations, one cyanate ligand adopts a $\text{Zn}-\text{NCO}$ geometry that is closer to linear [the $\text{Zn}-\text{N}-\text{C}$ angle falls in the range 158.4 (14)–177.3 (17)°], while the other is more bent at the N atom [the $\text{Zn}-\text{N}-\text{C}$ angle falls in the range 140.2 (14)–146.3 (11)°]. Within the layers, the Zn^{2+} cations in adjacent strands along the c direction lie alternately above and below the mean plane through all Zn^{2+} cations, apparently to optimize the packing arrangement of the cyanate moieties. The layers are stacked one upon the other with an offset that enables the cyanate moieties to project between the pyridine rings of the bipy units in adjacent layers.

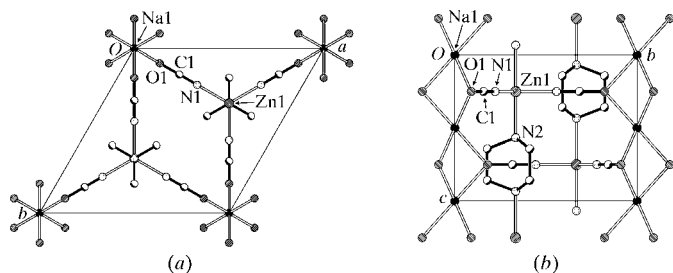


Figure 2
The structure of (I), viewed (a) along the c direction and (b) along the a direction. For the cyanate anions, only the disordered components lying on the twofold axes are shown.

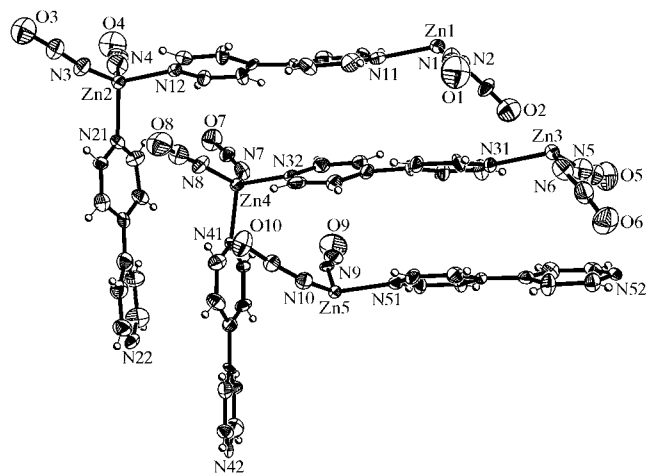


Figure 3
The asymmetric unit in (II), showing displacement ellipsoids at the 50% probability level. For clarity, C atoms are not labelled. The tetrahedral geometry around Zn is shown most clearly for atom Zn4, and the differing coordination modes of the cyanate anions are illustrated most clearly by N8 (linear) and N7 (bent).

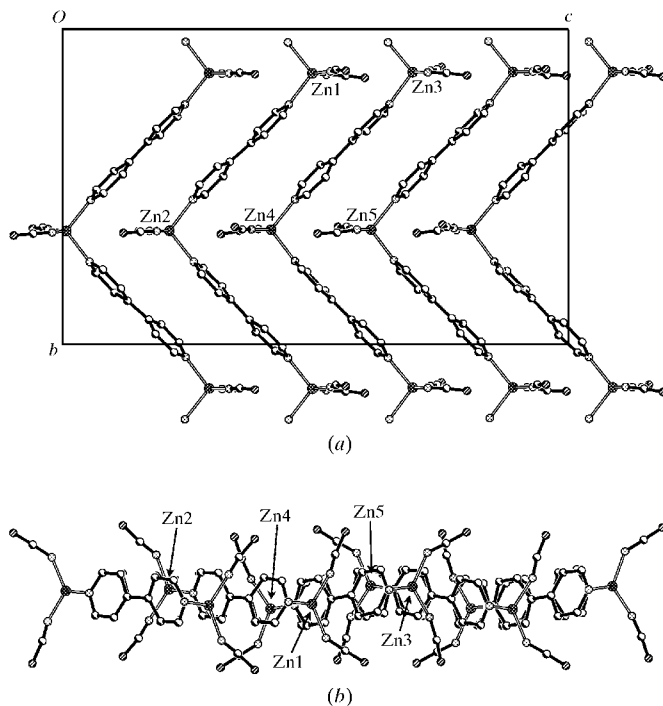


Figure 4
A single layer in (II), viewed (a) along the a direction (perpendicular to the layer plane) and (b) along the b direction, showing Zn^{2+} cations lying above and below the mean plane of the layer.

Experimental

For the preparation of compound (I), sodium cyanate (0.26 g, 4 mmol) in water (4 ml) and 1,4-diazabicyclo[2.2.2]octane (0.234 g, 2 mmol) in methanol (1 ml) were added to a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 g, 0.5 mmol) and concentrated nitric acid (14 M, 0.07 ml, 1 mmol) in methanol (3 ml). Crystals of (I) were deposited from the colourless solution over a period of several hours (yield 62 mg, 37%). IR $\nu(\text{NCO})$: 2239, 2170 cm^{-1} . For the preparation of compound (II), sodium cyanate (0.26 g, 4 mmol) in water (4 ml) and 4,4'-bipyridine (0.082 g, 0.53 mmol) in methanol (8 ml) were added to a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (154 mg, 0.52 mmol) and concentrated nitric acid (14 M, 0.07 ml, 1 mmol) in methanol (3 ml). Crystals of (II) were deposited from the colourless solution over a period of several hours (yield 71 mg, 45%). IR $\nu(\text{NCO})$: 2227 cm^{-1} .

Compound (I)

Crystal data

$\text{Na}[\text{Zn}(\text{NCO})_3(\text{C}_6\text{H}_{12}\text{N}_2)]$
 $M_r = 326.60$
 Hexagonal, $P6_3/mmc$
 $a = 10.2345$ (2) Å
 $c = 7.0799$ (3) Å
 $V = 642.23$ (3) Å³
 $Z = 2$
 $D_x = 1.689$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 3837 reflections
 $\theta = 2.3$ – 30.1°
 $\mu = 1.96$ mm⁻¹
 $T = 180$ (2) K
 Block, colourless
 $0.35 \times 0.25 \times 0.20$ mm

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.580$, $T_{\max} = 0.675$
 6400 measured reflections

407 independent reflections
 388 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 30.6^\circ$
 $h = -10 \rightarrow 14$
 $k = -12 \rightarrow 10$
 $l = -9 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.076$
 $S = 1.11$
 407 reflections
 30 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.743P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.64$ e Å⁻³
 Extinction correction: SHELXTL (Sheldrick, 2000)
 Extinction coefficient: 0.014 (3)

Compound (II)

Crystal data

$[\text{Zn}(\text{NCO})_2(\text{C}_{10}\text{H}_8\text{N}_2)]$
 $M_r = 305.59$
 Monoclinic, $P2_1/n$
 $a = 14.388$ (1) Å
 $b = 16.483$ (2) Å
 $c = 26.438$ (3) Å
 $\beta = 90.024$ (6) $^\circ$
 $V = 6270.0$ (11) Å³
 $Z = 20$

$D_x = 1.619$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1757 reflections
 $\theta = 3.2$ – 22.8°
 $\mu = 1.96$ mm⁻¹
 $T = 180$ (2) K
 Block, colourless
 $0.25 \times 0.10 \times 0.10$ mm

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.423$, $T_{\max} = 0.828$
 34766 measured reflections

12763 independent reflections
 5045 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.130$
 $\theta_{\text{max}} = 26.4^\circ$
 $h = -17 \rightarrow 17$
 $k = -20 \rightarrow 13$
 $l = -33 \rightarrow 33$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.221$
 $S = 0.89$
 12763 reflections
 857 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.90$ e Å⁻³

The disorder of the cyanate ligand in (I) was modelled with two pairs of C and O atoms. One pair (C1 and O1) lie exactly on the twofold axis that passes through atoms Zn1 and N1, and the other pair (C1A and O1A) are displaced from it. Both pairs lie in the mirror plane at $z = \frac{1}{4}$. The N–C, C–O and N...O distances within each component were restrained to equivalent refined values, with standard uncertainties of 0.01 Å. Initially, the atomic displacement parameters were fixed at 0.04 Å² and the site-occupancy factors (s.o.f.) were refined with s.o.f.(C1/O1) + s.o.f.(C1A/O1A) = 0.25 (to account for the multiplicity of the atomic sites). The site-occupancy factors were subsequently constrained to the refined values (C1 = O1 = 0.05, C1A = O1A = 0.20), and two isotropic displacement parameters were refined, one common to both atoms in each component. The crystal of (II) is monoclinic with β ca 90 $^\circ$, and was twinned to appear orthorhombic: twin law (100, 0 $\bar{1}$ 0, 00 $\bar{1}$), refined BASF = 0.497 (3). Diffraction was relatively weak, with less than 50% of the data observed at the $2\sigma(I)$ level. The resulting structure is of relatively low precision. The anisotropic displacement parameters of the C, N and O atoms were restrained to be approximately isotropic with a standard uncertainty of 0.01 Å². The largest peak and deepest hole in the residual electron density are associated with atoms Zn2 and Zn3, respectively. For both structures, H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C–H = 0.99 Å for the methylene group in the DABCO moiety in (I) and 0.95 Å for the bipy moieties in (II). In both cases, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: APEX2 (Bruker–Nonius, 2004); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; 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: FG1873). Services for accessing these data are described at the back of the journal.

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