metal-organic compounds

catena-Poly[[bis(quinoxaline-κN)cobalt(II)]-di-μ-dicyanamido-κ²N¹:N⁵] and *catena*-poly[[bis(quinoxaline-κN)copper(II)]-di-μ-dicyanamido-κ²N¹:N⁵]

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Two new complexes, $[Co(C_2N_3)_2(C_8H_6N_2)_2]$, (I), and $[Cu(C_2N_3)_2(C_8H_6N_2)_2]$, (II), are reported. They are essentially isomorphous. Complex (I) displays distorted octahedral geometry, with the Co atom coordinated by four dicyanamide nitrile N atoms [Co—N = 2.098 (3) and 2.104 (3) Å] in the basal plane, along with two monodentate quinoxaline N atoms [Co—N = 2.257 (2) Å] in the apical positions. In complex (II), the Cu atom is surrounded by four dicyanamide nitrile N atoms [Cu—N = 2.003 (3) and 2.005 (3) Å] in the equatorial plane and two monodentate quinoxaline N atoms [Cu—N = 2.479 (3) Å] in the axial sites, to form a distorted tetragonal–bipyramidal geometry. The metal atoms reside on twofold axes of rotation. Neighbouring metal atoms are connected *via* double dicyanamide bridges to form one-dimensional infinite chains. Adjacent chains are then linked by π–π stacking interactions of the quinoxaline molecules, resulting in the formation of a three-dimensional structure.

Comment

Dicyanamide coordination polymers have attracted considerable interest because of their novel structural characteristics (Manson *et al.*, 1998; Batten *et al.*, 1999) and fascinating magnetic properties (Manson *et al.*, 1999; Batten *et al.*, 1998). Previous results indicate that the introduction of N-containing conjugated rigid co-ligands, such as pyridine (Luo *et al.*, 2002), 2,2′-bipyridine (Vangdal *et al.*, 2002), 4,4′-bipyridine (Jensen *et al.*, 2002), pyrimidine (Manson *et al.*, 2003), 2,2′-bipyrimidine (Triki *et al.*, 2001) and pyrazine (Jensen *et al.*, 2001), to binary transition metal dicyanamide systems can not only modify the structuresz but also adjust the magnetic properties. For example, the binary complex $[Mn(C_2N_3)_2]$ shows a rutile-like structure and weak ferromagnetic ordering below 16 K, while the corresponding pyrazine (pyz) adduct α-$[Mn(C_2N_3)_2(pyz)]$ displays an interpenetrating three-dimensional α-Po-related network structure and behaves as an ordered antiferromagnet at temperatures below 2.7 K (Jensen *et al.*, 2001). To the best of our knowledge, no dicyanamide complex with quinoxaline as co-ligand has been reported to date. In order to gain insight into the influence of the nature of co-ligands on the structures and properties of dicyanamide-type complexes, we report here the syntheses and crystal structures of two new complexes, (I) and (II).

(I) $M = $Co
(II) $M = $Cu
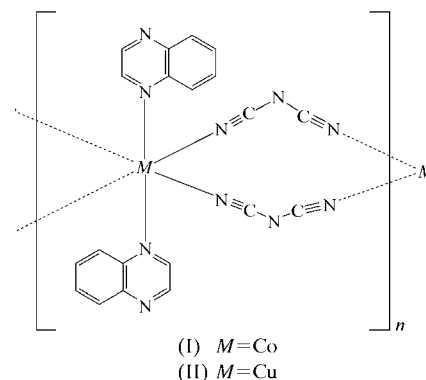
In (I) (Fig. 1), the Co^{II} ion is coordinated to four dicyanamide anions and two quinoxaline ligands to give a distorted octahedral geometry, in which the basal plane is formed by four nitrile N atoms (atoms N3, N3[i], N5[ii] and N5[iii]) of the dicyanamide anions and the apical positions are occupied by two N atoms (N1 and N1[i]) from two monodentate quinoxaline molecules [symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, y - 1, z$; (iii) $-x, y - 1, \frac{1}{2} - z$]. The Co^{II} ions are linked by double dicyanamide anion bridges to form a one-dimensional infinite chain, and π–π stacking interactions between quinoxaline ligands in adjacent chains result in the formation of a three-dimensional structure (Fig. 2).

In (II), the Cu^{II} ion is in essentially the same coordination environment as the Co atom in (I), with the only notable difference being the Jahn–Teller distortion of the former. As observed in (I), the Cu^{II} ions are joined by double dicyanamide-anion bridges to form a one-dimensional chain, and a similar three-dimensional structure (Fig. 3) is also generated *via* quinoxaline π–π interactions between adjacent chains.

In (I), the Co—N(quinoxaline) distances [2.257 (2) Å] are slightly longer than the Co—N(dicyanamide) distances [2.098 (3)–2.104 (3) Å; Table 1]. These values are similar to the corresponding distances observed in other cobalt–dicyanamide complexes (Jensen *et al.*, 2002, 2001).

In (II), the axial Cu—N(quinoxaline) distances [2.479 (3) Å] are noticeably longer than the basal Cu—N(dicyanamide) distances [2.003 (3)–2.005 (3) Å; Table 2]. This situation is quite different from that found in $[Cu(C_2N_3)_2(ampym)_2]$ (ampym is 2-aminopyrimidine) and $\{[Cu(C_2N_3)_2(pm)]\cdot CH_3CN\}_n$ (pm is pyrimidine) (van Albada *et al.*, 2000; Riggio *et al.*, 2001), in which the Cu atoms are coordinated by the N atoms of the neutral rigid co-ligands in the basal plane, and the apical sites are totally occupied by dicyanamide nitrile N atoms.

In (I), the N—Co—N angles (two neighbouring N atoms) are in the range 86.76 (14)–93.83 (9)°. Analogous to (I), the corresponding N—Cu—N angles in (II) are in the range 86.84 (9)–93.72 (10)°, indicating that the distortion of the geometry in (I) and (II) is not serious.

In both complexes, the bond distances and angles of the quinoxaline ring [1.299 (4)–1.420 (4) Å and 114.9 (3)–123.4 (3)°, respectively] are in the normal ranges observed in
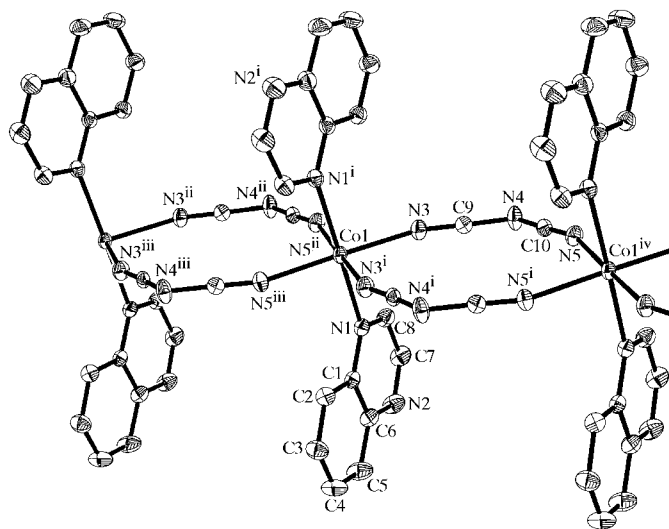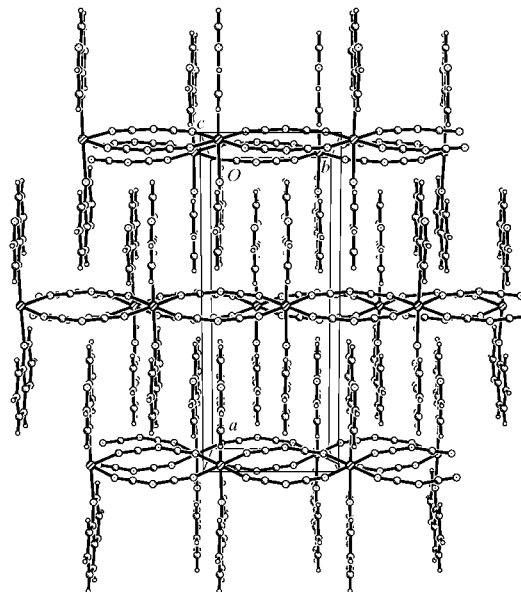

Figure 1
A view of the one-dimensional chain in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity [symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, y - 1, z$; (iii) $-x, y - 1, \frac{1}{2} - z$; (iv) $x, 1 + y, z$]. Compound (II) is essentially isomorphous.
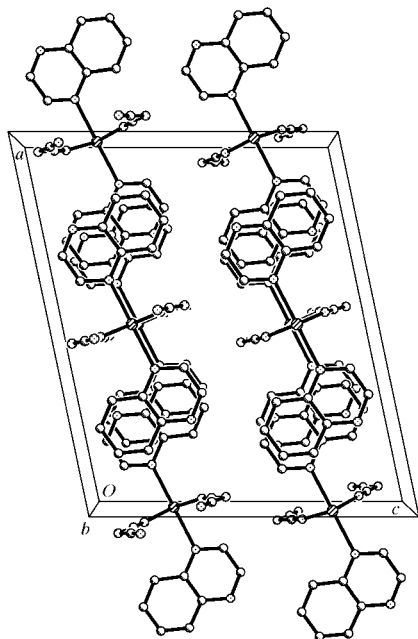
Figure 2
The three-dimensional network formed *via* quinoxaline π–π interactions, viewed along the *b* axis.

Figure 3
A view along the *c* axis, emphasizing the quinoxaline π–π interactions.

phenazine-containing complexes (Kutasi *et al.*, 2002). Each dicyanamide moiety is almost planar. Two different bond distances and angles are found: C≡N triple-bond distances [1.140 (4)–1.148 (3) Å] and C—N single-bond distances [1.300 (4)–1.301 (4) Å], together with C—N—C angles [119.9 (2)–120.2 (2)°] and N—C—N angles [173.7 (3)–175.6 (3)°]. These values are in good agreement with those found in other dicyanamide complexes (Luo *et al.*, 2002; Vangdal *et al.*, 2002; Manson *et al.*, 2003).

Experimental

An aqueous solution (4 ml) of quinoxaline (0.30 mmol, 39.05 mg) was added to an aqueous solution (4 ml) of cobalt nitrate (0.30 mmol, 87.31 mg) and the mixture stirred for 2 min. To the mixed solution was added dropwise an aqueous solution (2 ml) of sodium dicyanamide (0.30 mmol, 26.71 mg). An orange precipitate was immediately formed and the mixture was then warmed slowly until the precipitate had dissolved. One week later, orange block-shaped crystals of (I) were isolated in 57% yield. Analysis calculated for $C_{20}H_{12}CoN_{10}$: C 53.22, H 2.68, N 31.03%; found: C 53.53, H 2.97, N 31.37%. Complex (II) was prepared by a similar method in 21% yield. Analysis calculated for $C_{20}H_{12}CuN_{10}$: C 52.69, H 2.65, N 30.72%; found C 52.94, H 2.87, N 30.95%.

Compound (I)

Crystal data

$[Co(C_2N_3)_2(C_8H_6N_2)_2]$	$D_x = 1.598$ Mg m^{-3}
$M_r = 451.33$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 932
$a = 17.598$ (5) Å	reflections
$b = 7.374$ (2) Å	$\theta = 2.4$–27.1°
$c = 14.771$ (4) Å	$\mu = 0.95$ mm^{-1}
$\beta = 101.894$ (4)°	$T = 293$ (2) K
$V = 1875.7$ (9) Å^3	Block, orange
$Z = 4$	$0.10 \times 0.05 \times 0.02$ mm

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Data collection

Bruker SMART APEX CCD area-detector diffractometer		2036 independent reflections	
		1546 reflections with $I > 2\sigma(I)$	
φ and ω scans		$R_{int} = 0.040$	
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)		$\theta_{max} = 27.0°$	
		$h = -17 \rightarrow 22$	
$T_{min} = 0.911$, $T_{max} = 0.981$		$k = -9 \rightarrow 9$	
4491 measured reflections		$l = -18 \rightarrow 12$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2$	
$R[F^2 > 2\sigma(F^2)] = 0.049$	$\quad + 1.4128P]$	
$wR(F^2) = 0.105$	where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$	
2036 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}	
141 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}	
H-atom parameters constrained		

Table 1
Selected geometric parameters (Å, °) for (I).

Co1—N3	2.098 (3)	Co1—N1	2.257 (2)
Co1—N5^{ii}	2.104 (3)		
N3^{i}—Co1—N3	86.76 (14)	N3—Co1—N1	87.13 (9)
N3—Co1—N5^{ii}	92.73 (10)	N5^{ii}—Co1—N1	87.46 (9)
N3—Co1—N5^{iii}	178.59 (11)	N5^{iii}—Co1—N1	91.60 (9)
N5^{ii}—Co1—N5^{iii}	87.81 (14)	N1^{i}—Co1—N1	178.69 (13)
N3—Co1—N1^{i}	93.83 (9)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, y - 1, z$; (iii) $-x, y - 1, \frac{1}{2} - z$.

Compound (II)

Crystal data

[Cu(C$_2$N$_3$)$_2$(C$_8$H$_6$N$_2$)$_2$]	$D_x = 1.600$ Mg m^{-3}
$M_r = 455.94$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 775 reflections
$a = 18.205$ (4) Å	
$b = 7.2185$ (16) Å	$\theta = 2.8–20.7°$
$c = 14.766$ (3) Å	$\mu = 1.19$ mm^{-1}
$\beta = 102.730$ (4)°	$T = 293$ (2) K
$V = 1892.7$ (7) Å^3	Block, green
$Z = 4$	$0.10 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1843 independent reflections
	1328 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 26.0°$
	$h = -16 \rightarrow 22$
$T_{min} = 0.891$, $T_{max} = 0.943$	$k = -8 \rightarrow 8$
4189 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$\quad + 0.8836P]$
$wR(F^2) = 0.098$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
1843 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
141 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	

In both compounds, all H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1—N3	2.005 (3)	Cu1—N1	2.479 (3)
Cu1—N5^{ii}	2.003 (3)		
N3^{i}—Cu1—N3	87.33 (14)	N3—Cu1—N1	87.44 (10)
N5^{ii}—Cu1—N3	92.39 (10)	N5^{ii}—Cu1—N1	86.84 (9)
N5^{iii}—Cu1—N3	179.37 (11)	N5^{iii}—Cu1—N1	92.01 (9)
N5^{ii}—Cu1—N5^{iii}	87.90 (15)	N1—Cu1—N1^{i}	178.40 (11)
N3—Cu1—N1^{i}	93.72 (10)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, y - 1, z$; (iii) $-x, y - 1, \frac{1}{2} - z$.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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