cis-Bis(dicyanamido)bis(1,10-phenanthroline)manganese(II) and *cis*-bis-(dicyanamido)bis(1,10-phenanthroline)zinc(II)

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cis-Bis(dicyanamido)bis(1,10-phenan-throline)manganese(II) and cis-bis-(dicyanamido)bis(1,10-phenanthro-line)zinc(II)

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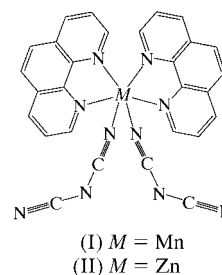
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The title compounds are isomorphous, comprised of neutral monomeric [M(phen)$_2$(dca)$_2$] [(I): M = Mn, (II): M = Zn; phen is 1,10-phenanthroline, $C_{12}H_8N_2$; dca is dicyanamide, C_2N_3] molecules. In the molecule, the divalent metal ion is in a distorted octahedral coordination environment formed by six N atoms from the phen and dca ligands. The Mn—N [2.144 (2)–2.319 (2) Å] and Zn—N [2.075 (2)–2.245 (2) Å] distances are in agreement with the difference in size of the two divalent ions.

Comment

Recently, dicyanamide has been used to construct many transition metal complexes with unusual coordination chemistry and physical properties (Manson *et al.*, 1998, 1999; Kurmoo & Kepert, 1998; Batten *et al.*, 1999). Although many complexes with extended one-dimensional, two-dimensional or three-dimensional structures have been structurally characterized, the reports on monomeric dca complexes, as far as we know, are few and limited to some copper complexes (Dunaj-Jurco *et al.*, 1996; Potocnak *et al.*, 1995, 1996) only. During our systematic investigation of transition metal complexes with dicyanamide (dca), we isolated the two title compounds, (I) and (II). They are isomorphous and their structures are reported here.

Both crystal structures consist of neutral monomeric [M(phen)$_2$(dca)$_2$] [(I): M = Mn, (II): M = Zn; phen is 1,10-phenanthroline; dca is dicyanamide] molecules. The metal ions are sixfold coordinated by four N atoms from two phen ligands and two terminal N atoms from two dca anions, in a distorted octahedral environment. The two phen ligands are in *cis* positions similar to the analogous [Cu(phen)$_2$(dca)$_2$] (Potocnak *et al.*, 1995) and [Mn(phen)$_2$(NCS)$_2$] compounds

(Holleman *et al.*, 1994).

(I) M = Mn
(II) M = Zn

In complex (I), the two shorter Mn—N(dca) distances [2.144 (2) and 2.151 (2) Å] are comparable to the Mn—N(NCS) distances in the monomeric complexes [Mn(phen)$_2$(NCS)$_2$] (Holleman *et al.*, 1994) and [Mn(2,2′-bipy)$_2$(NCS)$_2$] (Veidis *et al.*, 1981), while typically *ca* 0.05 Å shorter than those Mn—N(dca) distances in Mn—dca complexes with an extended structure, such as [Mn(dca)$_2L$] [L is a pyridine-type ligand; 2.187 (6)–2.258 (3) Å; Manson *et al.*, 1999] and [Mn(dca)$_2L_2$] [L = DMF, CH$_3$CH$_2$OH *etc.*; 2.179 (2)–2.233 (2) Å; Batten *et al.*, 1999], in which dca acts as a bridging ligand to connect two Mn cations. The four Mn—N(phen) distances [2.257 (2)–2.319 (2) Å] are similar to the corresponding distances in [Mn(phen)$_2$(NCS)$_2$] (Holleman *et al.*, 1994), [Mn(2,2′-bipy)$_2$(NCS)$_2$] (Veidis *et al.*, 1981) and [Mn(dca)$_2$(2,2′-bipy)] (Manson *et al.*, 1999). But unlike [Mn(phen)$_2$(NCS)$_2$] (Holleman *et al.*, 1994), in which the four Mn—N(phen) bond distances show no significant difference, in (I), the four Mn—N(phen) bonds can be obviously divided into two groups, *i.e.* 2.257 (2)/2.259 (2) Å and 2.293 (2)/2.319 (2) Å. The two longer Mn—N(phen) bonds are *trans* to the dca ligands. In *cis*-[Mn(2,2′-bpy)$_2$(NCS)$_2$] (Veidis *et al.*, 1981) and *cis*-[Mn(2,2′-bipy)$_2$Cl$_2$] (Lumme & Lindell, 1988), the same effect is observed. The zinc complex, (II), shows a similar case. The Zn—N(phen) distances [2.148 (2)–2.245 (2) Å] are comparable to the corresponding Zn—N distances in [Zn(phen)$_3$](TCNQ)$_2$ [2.135 (5)–2.225 (4) Å; Bencini *et al.*, 1989], [Zn(2,2′-bipy)$_3$](ClO$_4$)$_2$ [2.135 (2)–2.172 (3) Å; Chen *et al.*, 1995] and [Zn(phen)$_2$]$_2$[V$_4$O$_{12}$] [2.117 (4)–2.229 (4) Å; Zhang *et al.*, 1997]. The two short Zn—N(dca) distances [2.075 (2) and 2.081 (2) Å] are close to that found in [Zn(pbp)$_2$] (ClO$_4$)$_2$ [2.070 (6)–2.123 (6) Å; Liu *et al.*, 1996], in which the inter-ligand repulsion effect is less due to the ligand structure. So in both (I) and (II), the dca ligand with less steric hindrance gives shorter metal–N bonds, while the reverse is observed in Cu complexes [Cu(phen)$_2$(dca)$_2$] (Potocnak *et al.*, 1995) and [Cu(2,2′-bipy)(add)(dca)] (Dunaj-Jurco *et al.*, 1996). The Zn—N distances in (II) are about 0.08 Å shorter than the corresponding Mn—N distances in (I). This is in agreement with the difference between the Zn and Mn ionic radii (0.74 and 0.80 Å, respectively). The steric constraints of the phen ligand make the N—Mn—N angles in the range 72.48 (7)–102.40 (7)°, N—Zn—N angles in the range 75.75 (7)–99.12 (9)°, with the ideal value being 90°, and a range of 157.54 (7)–165.73 (7)° for N—Mn—N angles and 161.14 (8)–169.30 (9)° for N—Zn—N angles, with the ideal

value being 180°. Hence, the distortion of the ZnN_6 moiety from the ideal octahedron is less than the MnN_6 moiety.

The phen ligands are all planar in the two compounds, with the largest deviation of atoms from their mean plane less than 0.07 Å. The dihedral angle between the mean planes of the two phen is 79.67 (4)° in (I) and 80.79 (4)° in (II). The bond distances and angles in phen [1.323 (3)–1.448 (4) Å and 116.4 (3)–124.7 (3)°, respectively] are all normal (Potocnak *et al.*, 1996; Holleman *et al.*, 1994). The dca ligands are also planar and the largest deviation of atoms from their mean planes are less than 0.02 Å. All N—C distances of dca ligands, *i.e.* 1.125 (3)–1.140 (3) Å for N—C triple bonds and 1.277 (4)–1.308 (4) Å for N—C double bonds, together with the C—N—C angles of 123.0 (3)–124.9 (3)° and N—C—N angles of 171.6 (3)–173.1 (3)°, are all comparable with values found in other dca complexes (Manson *et al.*, 1998, 1999; Kurmoo & Kepert, 1998; Batten *et al.*, 1999; Potocnak *et al.*, 1996, 1995). The bonding mode of dca to metal ions is angular as the metal—N—C angles range from 164.5 (2) to 166.7 (2)° (Potocnak *et al.*, 1996).

Experimental

[Mn(phen)₂(dca)₂]: a 4 ml ethanol solution containing phenanthroline ($C_{12}H_8N_2 \cdot H_2O$, 59.5 mg, 0.30 mmol) and a 4 ml ethanol solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ (73.5 mg, 0.30 mmol) were mixed and stirred for 5 min, then a 2 ml aqueous solution of $NaN(CN)_2$ (26.7 mg, 0.30 mmol) was added to the above solution and stirred for another 5 min. The clear-brown solution was filtered. Brown block-shaped crystals were obtained after slow evaporation of the filtrate for one week. Yield 16%. Analysis calculated for $C_{28}H_{16}N_{10}Mn$: C 61.43, H 2.95, N 25.59, Mn 10.04%; found: C 60.02, H 3.11, N 25.44, Mn 11.4% (by ICP). [Zn(phen)₂(dca)₂]: the colourless block-shaped crystals of the Zn complex were obtained by the same route, using $Zn(CH_3COO)_2 \cdot 2H_2O$ (65.9 mg, 0.30 mmol) instead of $Mn(CH_3COO)_2 \cdot 4H_2O$. Yield 15%. Analysis calculated for $C_{28}H_{16}N_{10}Zn$: C 60.28, H 2.89, N 25.11, Zn 11.72%; found: C 58.91, H 3.00, N 23.85, Mn 13.8% (by ICP).

Compound (I)

Crystal data

[Mn(C₁₂H₈N₂)₂(C₂N₃)₂]	$D_x = 1.441$ Mg m⁻³
$M_r = 547.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 46192
$a = 9.7989$ (2) Å	reflections
$b = 15.0160$ (5) Å	$\theta = 3.46$–27.87°
$c = 17.7189$ (5) Å	$\mu = 0.562$ mm⁻¹
$\beta = 104.5946$ (16)°	$T = 293$ (2) K
$V = 2523.04$ (12) Å³	Block, brown
$Z = 4$	$0.33 \times 0.30 \times 0.15$ mm

Data collection

Nonius KappaCCD diffractometer	3898 reflections with $I > 2\sigma(I)$
CCD scans	$R_{int} = 0.0711$
Absorption correction: empirical	$\theta_{max} = 27.87°$
(Blessing, 1995, 1997)	$h = -12 \rightarrow 12$
$T_{min} = 0.892$, $T_{max} = 0.922$	$k = -19 \rightarrow 19$
46 192 measured reflections	$l = -23 \rightarrow 23$
6007 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.7644P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.008$	$(\Delta/\sigma)_{max} = 0.001$
6007 reflections	$\Delta\rho_{max} = 0.41$ e Å⁻³
417 parameters	$\Delta\rho_{min} = -0.37$ e Å⁻³
All H-atom parameters refined	Extinction correction: *SHELXL*
	Extinction coefficient: 0.0037 (8)

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

Mn1—N5	2.144 (2)	Mn1—N2	2.2588 (17)
Mn1—N8	2.151 (2)	Mn1—N1	2.2927 (17)
Mn1—N4	2.2569 (19)	Mn1—N3	2.3192 (19)
N5—Mn1—N8	98.44 (9)	N2—Mn1—N3	88.60 (6)
N5—Mn1—N4	94.38 (8)	N1—Mn1—N3	85.40 (6)
N8—Mn1—N4	98.78 (7)	C1—N1—Mn1	126.67 (17)
N5—Mn1—N2	102.40 (8)	C12—N1—Mn1	114.61 (13)
N8—Mn1—N2	93.46 (7)	C10—N2—Mn1	125.75 (15)
N4—Mn1—N2	157.54 (7)	C11—N2—Mn1	116.01 (14)
N5—Mn1—N1	88.39 (7)	C13—N3—Mn1	127.57 (17)
N8—Mn1—N1	165.73 (7)	C24—N3—Mn1	114.93 (15)
N4—Mn1—N1	93.13 (6)	C22—N4—Mn1	125.05 (19)
N2—Mn1—N1	72.76 (6)	C23—N4—Mn1	116.77 (15)
N5—Mn1—N3	165.18 (7)	C25—N5—Mn1	164.47 (19)
N8—Mn1—N3	90.68 (8)	C27—N8—Mn1	166.2 (2)
N4—Mn1—N3	72.58 (7)		

Compound (II)

Crystal data

[Zn(C₁₂H₈N₂)₂(C₂N₃)₂]	$D_x = 1.482$ Mg m⁻³
$M_r = 557.88$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 35401
$a = 9.6800$ (3) Å	reflections
$b = 15.0697$ (7) Å	$\theta = 3.47$–27.85°
$c = 17.7166$ (8) Å	$\mu = 1.022$ mm⁻¹
$\beta = 104.628$ (2)°	$T = 293$ (2) K
$V = 2500.64$ (18) Å³	Block, colourless
$Z = 4$	$0.20 \times 0.20 \times 0.18$ mm

Data collection

Nonius KappaCCD diffractometer	3976 reflections with $I > 2\sigma(I)$
CCD scans	$R_{int} = 0.0614$
Absorption correction: empirical	$\theta_{max} = 27.85°$
(Blessing, 1995, 1997)	$h = -12 \rightarrow 12$
$T_{min} = 0.799$, $T_{max} = 0.837$	$k = -19 \rightarrow 19$
35 401 measured reflections	$l = -23 \rightarrow 23$
5913 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 1.5124P]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.027$	$(\Delta/\sigma)_{max} = 0.001$
5913 reflections	$\Delta\rho_{max} = 0.32$ e Å⁻³
417 parameters	$\Delta\rho_{min} = -0.34$ e Å⁻³
All H-atom parameters refined	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0008 (4)

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

Zn1—N5	2.075 (3)	Zn1—N2	2.1498 (19)
Zn1—N8	2.081 (2)	Zn1—N1	2.2217 (19)
Zn1—N4	2.148 (2)	Zn1—N3	2.246 (2)

N5—Zn1—N8	96.76 (9)	N2—Zn1—N3	88.71 (8)
N5—Zn1—N4	95.21 (9)	N1—Zn1—N3	86.07 (7)
N8—Zn1—N4	97.23 (8)	C1—N1—Zn1	128.98 (19)
N5—Zn1—N2	99.12 (9)	C12—N1—Zn1	112.63 (15)
N8—Zn1—N2	93.22 (8)	C10—N2—Zn1	126.31 (17)
N4—Zn1—N2	161.14 (8)	C11—N2—Zn1	115.46 (16)
N5—Zn1—N1	88.79 (8)	C13—N3—Zn1	129.61 (19)
N8—Zn1—N1	168.35 (8)	C24—N3—Zn1	113.29 (17)
N4—Zn1—N1	92.44 (7)	C22—N4—Zn1	125.9 (2)
N2—Zn1—N1	75.75 (7)	C23—N4—Zn1	116.19 (16)
N5—Zn1—N3	169.30 (9)	C25—N5—Zn1	166.2 (2)
N8—Zn1—N3	90.02 (8)	C27—N8—Zn1	166.7 (2)
N4—Zn1—N3	75.67 (8)		

All H atoms were located by difference Fourier synthesis and were refined isotropicaly.

For both compounds, data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *HKL SCALEPAK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *MAXUS* (Mackay *et al.*, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL*97.

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