Table 3. *Selected bond distances (Å) and angles (°) for the two title compounds*

cis-[$PtBr_2$(dmso)$_2$]		*trans*-[PtI_2(dmso)$_2$]	
Pt—Br(1)	2.441 (1)	Pt—I	2.6111 (9)
Pt—Br(2)	2.447 (2)		
Pt—S(1)	2.254 (2)	Pt—S	2.289 (2)
Pt—S(2)	2.245 (2)		
S(1)—O(1)	1.463 (6)	S—O	1.482 (6)
S(1)—C(1)	1.793 (9)	S—C(1)	1.78 (1)
S(1)—C(2)	1.783 (10)	S—C(2)	1.79 (1)
S(2)—O(2)	1.455 (7)		
S(2)—C(3)	1.789 (9)		
S(2)—C(4)	1.780 (9)		
Br(1)—Pt—Br(2)	87.02 (4)		
Br(1)—Pt—S(1)	173.03 (6)	I—Pt—S	93.36 (6)
Br(1)—Pt—S(2)	89.39 (6)		
Br(2)—Pt—S(1)	93.11 (6)		
Br(2)—Pt—S(2)	176.38 (6)		
S(1)—Pt—S(2)	90.50 (8)		
Pt—S(1)—O(1)	112.7 (3)	Pt—S—O	114.8 (3)
Pt—S(1)—C(1)	115.1 (3)	Pt—S—C(1)	116.3 (3)
Pt—S(1)—C(2)	113.2 (4)	Pt—S—C(2)	108.4 (4)
O(1)—S(1)—C(1)	105.9 (5)	O—S—C(1)	106.5 (4)
O(1)—S(1)—C(2)	109.2 (4)	O—S—C(2)	109.9 (4)
Pt—S(2)—O(2)	117.4 (3)		
Pt—S(2)—C(3)	112.3 (4)		
Pt—S(2)—C(4)	108.6 (3)		
O(2)—S(2)—C(3)	107.3 (5)		
O(2)—S(2)—C(4)	107.8 (5)		

The structure of *cis*-[$PtCl_2$(dmso)$_2$] has previously been determined by Melanson & Rochon (1975) and Shibaeva (1983). The characterization of the chloro compound was therefore made by comparing the unit-cell parameters only. The position of the Pt atom in the bromo complex was found by the Patterson method and in *trans*-[PtI_2(dmso)$_2$], the Pt atom was placed on the origin. Difference-Fourier calculations revealed the rest of both structures, which were refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. The H atoms could not be located in the difference-Fourier maps and were not included in the calculations. The high max./min. residuals due to the presence of heavy elements are situated 1.56/0.86 Å and 1.03/0.81 Å from the Pt atom in the bromo and iodo complexes, respectively.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *DETTH* (Enraf–Nonius, 1989); data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN LS*; software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1349). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three Metal (1,4,8,11-Tetraazacyclotetradecane) Halide Salts

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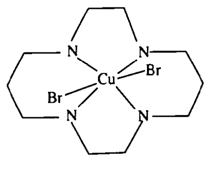
Abstract

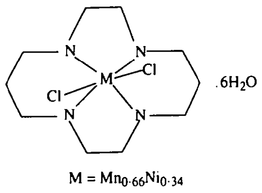
Attempts to synthesize [M([14]aneN$_4$)][$M'X_4$] chain systems (M,M' = divalent metal ion, [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane, X = Cl, Br) yielded three M([14]aneN$_4$)X_2.xH$_2$O salts. The structures of these three salts, dibromo(1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)copper(II), $[CuBr_2(C_{10}H_{24}N_4)]$, dichloro-(1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)manganese(II)–dichloro(1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)nickel(II)–water (0.66/0.34/6), $[Mn_{0.66}Ni_{0.34}Cl_2(C_{10}H_{24}N_4)].6H_2O$, and dichloro(1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)cobalt(III)–dichloro(1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)manganese(II)–chloride–water (0.5/0.5/0.5/5.5), $[Co_{0.5}Mn_{0.5}Cl_2(C_{10}H_{24}N_4)]Cl_{0.5}.5.5H_2O$, are described.

Comment

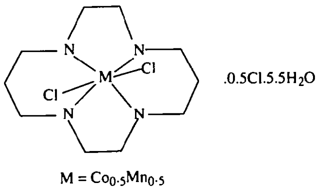
The structures of several $M([14]aneN_4)X_2$ compounds (where $[14]aneN_4$ is 1,4,8,11-tetraazacyclotetradecane) have been reported previously. $[Ni([14]aneN_4)Cl_2]$ is monoclinic, $P2_1/a$, but is not isostructural with any of the above salts. The conformation of the $[14]aneN_4$ ring is the *trans*-(III) conformer (Bosnich, Mason, Pauling, Robertson & Tobe, 1965), as in the three salts reported here, dibromo(1,4,8,11-tetraazacyclotetradecane)copper, (I), dichloro(1,4,8,11-tetraazacyclotetradecane)manganesenickel hexahydrate, (II), and dichloro(1,4,8,11-tetraazacyclotetradecane)manganese-cobalt–chloride–water (1/0.5/5.5), (III). In this conformer, the two N—H bonds in the six-membered chelate rings lie on the same side of the chelate rings. The same conformation of the ligand is found in the Zn^{II} and Ag^{II} perchlorate salts (Mertes, 1978; Ito, Ito & Toriumi, 1981) although a different isomer was also observed for the Ag^{II} salt (Ito, Ito & Toriumi, 1981).



(I)



(II)



(III)

Compound (I), $[Cu([14]aneN_4)Br_2]$, contains discrete molecules in which the Cu^{2+} ion has a tetragonally elongated octahedral geometry. The $[14]aneN_4$ macrocycle girdles the Cu^{2+} ion to yield a centrosymmetric complex [Cu—N = 2.016 (5) and 2.023 (5) Å], with the Br^- ions forming long bonds of 2.952 (2) Å. The six-membered chelate rings assume boat conformations while the five-membered chelate rings are also non-planar with the C—C bond twisted out of the CuN_2 plane.

Compound (II), $[Mn_{0.66}Ni_{0.34}([14]aneN_4)Cl_2].6H_2O$, is a mixed salt for which the Mn/Ni ratio was determined by chemical analysis. The structure contains isolated centrosymmetric *trans*-$M([14]aneN_4)Cl_2$ molecules, with $M = Mn^{II}$ or Ni^{II}. The mean *M*—N distances are 2.027 (5) and 2.032 (4) Å, with *M*—Cl = 2.525 (2) Å. The conformation of the chelate ring is identical to that observed in (I). The lattice water molecules form hydrogen bonds between themselves, the coordinated Cl^- ions and the N atoms of the macrocycle.

Compound (III) has the composition $[Co_{0.5}Mn_{0.5}([14]aneN_4)Cl_2]Cl_{0.5}.5.5H_2O$, with the Mn/Co ratio again determined by chemical analysis. The mean *M*—N distances are 1.974 (9) and 1.969 (11) Å, with *M*—Cl = 2.259 (3) Å. The conformation of the $[14]aneN_4$ species is the same as in (I) and (II). The crystal contains a mixture of Mn^{2+} and Co^{3+} ions, each coordinated meridianally by the $[14]aneN_4$ rings with two Cl^- ions also coordinated to complete the octahedral geometry. Thus, the observed structure consists of a superposition of neutral $[Mn([14]aneN_4)Cl_2]$ complexes and $[Co([14]aneN_4)Cl_2]^+$ cations. To compensate for the excess charge on the complex when $M = Co^{III}$, one lattice water site is partially occupied by a Cl^- ion. The *M*—N and *M*—Cl distances in (III) are substantially shorter (by approximately 0.06 and 0.26 Å, respectively) than those found in (II), as anticipated with the partial replacement of an M^{II} ion by an M^{III} ion.

(I), (II) and (III) were prepared as part of our attempt to prepare analogous compounds to the one-dimensional alternating binuclear magnetic system of the type $Cu(TIM)MX_4$ (where TIM = 2,3,12,13-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-tetraenetetradecane) and *M* = Cu, Co or Mn (Wang, 1993; Wang & Willett, 1993; Vasilevesky, Rose, Stenkamp & Willett, 1991; Willett, Wang, Molnar, Brewer, Landee, Turnbull & Zhang, 1993). In these compounds, the MX_4^{2-} anions

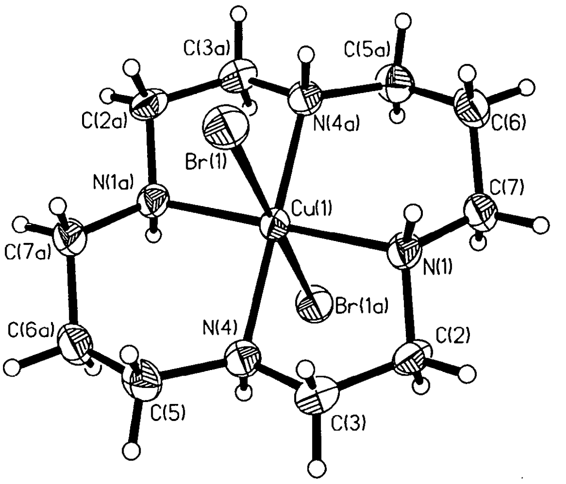


Fig. 1. A view of the $[Cu([14]aneN_4)Br_2]$ molecule in (I). Ellipsoids are shown at the 50% probability level for non-H atoms.

bridge adjacent Cu(TIM)$^{2+}$ cations through the formation of long Cu$\cdots X$ bonds. With the [14]aneN$_4$ ligand, the Cu([14]aneN$_4$)CuX_4 salts form similar chain systems (Studer, Reisen & Kaden, 1989; Chen, Willett, Molnar & Brewer, 1996), but synthetic attempts with other metal ions have yielded different compounds. Interestingly, when ethylenediamine is used as a ligand, the compound Cu(en)$_2M$Cl$_4$ is obtained (Chiari, Cinti, Piovesana & Zanazzi, 1995). In this compound, the MnCl$_4^{2-}$ anions again act as bridging groups between the Cu(en)$_2^{2+}$ cations.

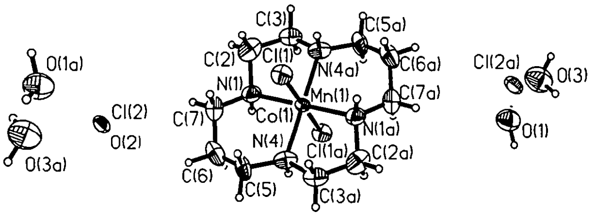


Fig. 2. A view of the formula unit for (III). Ellipsoids are shown at the 50% probability level.

Experimental

The title compounds were prepared following the method described by Chen, Willett, Molnar & Brewer (1996).

Compound (I)

Crystal data

[CuBr$_2$(C$_{10}$H$_{24}$N$_4$)]
$M_r = 419.7$
Monoclinic
$P2_1/c$
$a = 7.101\ (2)$ Å
$b = 12.521\ (3)$ Å
$c = 8.877\ (2)$ Å
$\beta = 110.60\ (3)°$
$V = 738.8$ Å^3
$Z = 2$
$D_x = 1.886$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 3$–$15°$
$\mu = 6.87$ mm^{-1}
$T = 295$ K
Chunk
0.3 × 0.25 × 0.2 mm
Brown

Data collection

Syntex $P2_1$ diffractometer upgraded to Siemens $P4$
ω scans
Absorption correction: ψ scan (*XEMP* in *SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.674$, $T_{\max} = 1.000$
2905 measured reflections
2102 independent reflections

1369 observed reflections [$|F| > 3\sigma(F)$]
$R_{\rm int} = 0.041$
$\theta_{\max} = 30°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 17$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.057$
$wR = 0.053$
$S = 1.13$
1369 reflections
92 parameters
Only H-atom U's refined with a riding model
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.98$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: $F^* = F[1 + 0.002\chi \times F^2/\sin(2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.0009\ (2)$
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br(1)	−0.2273 (1)	0.4733 (1)	0.2193 (1)	0.036 (1)
Cu(1)	0	1/2	0	0.026 (1)
N(4)	0.2682 (7)	0.4714 (4)	0.1735 (6)	0.028 (2)
N(1)	0.0416 (7)	0.6525 (4)	0.0802 (6)	0.027 (2)
C(7)	−0.0261 (8)	0.7379 (5)	−0.0412 (8)	0.032 (2)
C(3)	0.3137 (9)	0.5629 (5)	0.2858 (8)	0.033 (2)
C(2)	0.2540 (8)	0.6629 (5)	0.1845 (7)	0.030 (2)
C(6)	−0.2488 (10)	0.7260 (5)	−0.1445 (9)	0.036 (3)
C(5)	0.2967 (10)	0.3676 (5)	0.2607 (8)	0.034 (2)

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

Cu(1)—N(4)	2.016 (4)	Cu(1)—N(1)	2.023 (5)
Cu(1)—N(4$^{\rm i}$)	2.016 (4)	Cu(1)—N(1$^{\rm i}$)	2.023 (5)
Cu(1)—Br(1)	2.952 (2)	N(4)—C(5)	1.490 (8)
N(4)—C(3)	1.478 (8)	N(1)—C(2)	1.472 (7)
N(1)—C(7)	1.474 (8)	C(3)—C(2)	1.512 (9)
C(7)—C(6)	1.531 (8)	C(5)—C(6$^{\rm i}$)	1.519 (9)
C(6)—C(5$^{\rm i}$)	1.519 (9)		
N(4)—Cu(1)—N(1)	85.2 (2)	N(4)—C(5)—C(6$^{\rm i}$)	111.4 (5)
N(1)—Cu(1)—Br(1)	85.4 (1)	N(4)—Cu(1)—N(4$^{\rm i}$)	180.0 (1)
N(4)—Cu(1)—Br(1)	93.7 (1)	N(4)—Cu(1)—N(1$^{\rm i}$)	94.8 (2)
N(1)—Cu(1)—N(4$^{\rm i}$)	94.8 (2)	N(4$^{\rm i}$)—Cu(1)—N(1$^{\rm i}$)	85.2 (2)
N(1)—Cu(1)—N(1$^{\rm i}$)	180.0 (1)	Cu(1)—N(4)—C(5)	118.1 (4)
Cu(1)—N(4)—C(3)	107.5 (3)	Cu(1)—N(1)—C(7)	117.3 (4)
C(3)—N(4)—C(5)	111.7 (5)	C(7)—N(1)—C(2)	113.2 (5)
Cu(1)—N(1)—C(2)	107.2 (4)	N(4)—C(3)—C(2)	107.0 (5)
N(1)—C(7)—C(6)	111.7 (5)	C(7)—C(6)—C(5$^{\rm i}$)	114.8 (6)
N(1)—C(2)—C(3)	108.2 (5)		

Symmetry code: (i) $-x, 1-y, -z$.

Compound (II)

Crystal data

[Mn$_{0.66}$Ni$_{0.34}$Cl$_2$(C$_{10}$H$_{24}$N$_4$)].6H$_2$O
$M_r = 435.5$
Monoclinic
$P2_1/c$
$a = 9.892\ (2)$ Å
$b = 6.508\ (2)$ Å
$c = 16.648\ (3)$ Å
$\beta = 107.16\ (3)°$
$V = 1024.0\ (4)$ Å^3
$Z = 2$
$D_x = 1.41$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14$–$15°$
$\mu = 1.04$ mm^{-1}
$T = 295$ K
Rectangular plate
0.35 × 0.25 × 0.1 mm
Dark green

Data collection

Syntex $P2_1$ diffractometer upgraded to Siemens $P4$

1794 observed reflections [$|F| > 4\sigma(F)$]

ω scans
Absorption correction: ψ scan (*XEMP* in *SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.275$, $T_{\max} = 0.322$
3418 measured reflections
2316 independent reflections

$R_{\rm int} = 0.262$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 8$
$l = -21 \rightarrow 20$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.077$
$wR = 0.130$
$S = 1.20$
1794 reflections
109 parameters
Coordinates of H atoms refined using a riding model, except for H atoms bonded to N atoms

$w = 1/[\sigma^2(F) + 0.0098F^2]$
$(\Delta/\sigma)_{\max} = 0.163$
$\Delta\rho_{\max} = 2.02$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(Mn,Ni)†	0	0	0	0.023 (1)
Cl(1)	0.0832 (2)	0.3091 (2)	−0.0639 (1)	0.033 (1)
N(1)	0.1816 (5)	0.0150 (7)	0.0969 (3)	0.025 (1)
C(5)	−0.0837 (7)	0.1800 (10)	0.1458 (3)	0.037 (2)
C(6)	0.0687 (8)	0.2031 (11)	0.1925 (3)	0.042 (2)
N(4)	−0.1094 (5)	0.1942 (7)	0.0530 (3)	0.025 (1)
C(2)	0.2725 (7)	−0.1592 (10)	0.0866 (4)	0.037 (2)
C(3)	−0.2614 (6)	0.1749 (9)	0.0047 (4)	0.034 (2)
C(7)	0.1665 (8)	0.0250 (9)	0.1828 (3)	0.036 (2)
O(1)	0.5640 (4)	0.8334 (5)	0.3777 (3)	0.029 (1)
O(2)	0.3706 (8)	−0.0047 (13)	−0.2158 (5)	0.093 (4)
O(3)	0.3868 (10)	0.3134 (19)	0.8944 (6)	0.126 (5)

† Site occupancy: Mn/Ni = 0.66/0.34.

Table 4. *Selected geometric parameters (Å, °) for (II)*

(Mn,Ni)—Cl(1)	2.525 (2)	(Mn,Ni)—N(1)	2.032 (4)
(Mn,Ni)—N(4)	2.027 (5)	(Mn,Ni)—Cl(1$^{\rm i}$)	2.525 (2)
(Mn,Ni)—N(1$^{\rm i}$)	2.032 (4)	(Mn,Ni)—N(4$^{\rm i}$)	2.027 (5)
N(1)—C(2)	1.488 (8)	N(1)—C(7)	1.483 (8)
C(5)—C(6)	1.487 (9)	C(5)—N(4)	1.492 (7)
C(6)—C(7)	1.548 (10)	N(4)—C(3)	1.487 (7)
C(2)—C(3$^{\rm i}$)	1.495 (9)	C(3)—C(2$^{\rm i}$)	1.495 (9)
Cl(1)—(Mn,Ni)—N(1)	88.5 (1)	(Mn,Ni)—N(4)—C(3)	107.3 (3)
N(1)—(Mn,Ni)—N(4)	94.9 (2)	C(5)—N(4)—C(3)	112.9 (5)
N(1)—(Mn,Ni)—Cl(1$^{\rm i}$)	91.5 (1)	N(4)—C(3)—C(2)	108.3 (5)
Cl(1)—(Mn,Ni)—N(1$^{\rm i}$)	91.5 (1)	Cl(1)—(Mn,Ni)—N(4)	88.2 (1)
N(4)—(Mn,Ni)—N(1$^{\rm i}$)	85.1 (2)	Cl(1)—(Mn,Ni)—Cl(1$^{\rm i}$)	180.0 (1)
Cl(1)—(Mn,Ni)—N(4$^{\rm i}$)	91.8 (1)	N(4)—(Mn,Ni)—Cl(1$^{\rm i}$)	91.8 (1)
N(4)—(Mn,Ni)—N(4$^{\rm i}$)	180.0 (1)	N(1)—(Mn,Ni)—N(1$^{\rm i}$)	180.0 (1)
N(1$^{\rm i}$)—(Mn,Ni)—N(4$^{\rm i}$)	94.9 (2)	Cl(1$^{\rm i}$)—(Mn,Ni)—N(1$^{\rm i}$)	88.5 (1)
(Mn,Ni)—N(1)—C(2)	107.1 (3)	N(1)—(Mn,Ni)—N(4$^{\rm i}$)	85.1 (2)
(Mn,Ni)—N(1)—C(7)	116.8 (4)	Cl(1$^{\rm i}$)—(Mn,Ni)—N(4$^{\rm i}$)	88.2 (1)
C(2)—N(1)—C(7)	112.4 (4)	N(1)—C(2)—C(3$^{\rm i}$)	107.7 (5)
C(5)—C(6)—C(7)	116.0 (5)	N(1)—C(7)—C(6)	112.2 (4)
(Mn,Ni)—N(4)—C(5)	117.5 (4)		

Symmetry code: (i) $-x, -y, -z$.

Compound (III)

Crystal data

$[\rm Co_{0.5}Mn_{0.5}Cl_2(C_{10}H_{24}N_4)]$-$\rm Cl_{0.5}.5.5H_2O$
$M_r = 445.0$
Monoclinic
$P2_1/n$
$a = 6.415$ (2) Å
$b = 7.427$ (2) Å
$c = 21.074$ (4) Å
$\beta = 90.99$ (3)°
$V = 1003.9$ (5) Å^3
$Z = 2$
$D_x = 1.472$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 5$–15°
$\mu = 1.12$ mm^{-1}
$T = 295$ K
Chunk
0.5 × 0.4 × 0.4 mm
Green

Data collection

Syntex $P2_1$ diffractometer upgraded to Siemens $P4$
ω scans
Absorption correction: ψ scan (*XEMP* in *SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.485$, $T_{\max} = 0.701$
1654 measured reflections
939 independent reflections

623 observed reflections $[|F|>3\sigma(F)]$
$R_{\rm int} = 0.0392$
$\theta_{\max} = 20°$
$h = -1 \rightarrow 6$
$k = -1 \rightarrow 7$
$l = -20 \rightarrow 20$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.065$
$wR = 0.073$
$S = 1.23$
623 reflections
115 parameters
Only coordinates of H atoms refined with a riding model

$w = 1/[\sigma^2(F) + 0.0015F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(Co,Mn)†	0	0	0	0.022 (1)
Cl(1)	−0.2611 (5)	−0.2037 (5)	−0.0056 (2)	0.040 (1)
N(1)	0.0042 (15)	0.0206 (16)	−0.0934 (4)	0.042 (4)
N(4)	0.2117 (17)	−0.1919 (15)	0.0000 (5)	0.039 (4)
C(2)	−0.1865 (22)	0.1228 (21)	−0.1129 (6)	0.056 (6)
C(3)	−0.2185 (21)	0.2760 (19)	−0.0639 (7)	0.049 (6)
C(6)	0.2197 (23)	−0.2457 (20)	−0.1136 (7)	0.057 (6)
C(7)	0.0265 (23)	−0.1438 (19)	−0.1322 (6)	0.049 (6)
C(5)	0.2154 (24)	−0.3301 (19)	−0.0508 (6)	0.048 (6)
(Cl,O)‡	0.1759 (9)	−0.2480 (8)	−0.3187 (3)	0.040 (2)
O(1)	0.4852 (15)	1.0773 (14)	0.2424 (5)	0.072 (4)
O(3)	0.1389 (17)	0.9484 (14)	0.3018 (5)	0.089 (5)

† Site occupancy: Co/Mn = 0.50/0.50. ‡ Site occupancy: Cl/O = 0.50/0.50.

Table 6. *Selected geometric parameters (Å, °) for (III)*

(Co,Mn)—Cl(1)	2.259 (3)	(Co,Mn)—N(1)	1.974 (9)
(Co,Mn)—N(4)	1.969 (11)	(Co,Mn)—Cl(1$^{\rm i}$)	2.259 (3)
(Co,Mn)—N(1$^{\rm i}$)	1.974 (9)	(Co,Mn)—N(4$^{\rm i}$)	1.969 (11)
N(1)—C(2)	1.491 (18)	N(1)—C(7)	1.479 (17)
N(4)—C(5)	1.483 (17)	N(4)—C(3$^{\rm i}$)	1.485 (19)
C(2)—C(3)	1.553 (20)	C(3)—N(4$^{\rm i}$)	1.485 (19)
C(6)—C(7)	1.500 (21)	C(6)—C(5)	1.465 (19)
Cl(1)—(Co,Mn)—N(1)	91.3 (3)	C(5)—N(4)—C(3$^{\rm i}$)	111.3 (10)
N(1)—(Co,Mn)—N(4)	92.0 (5)	C(2)—C(3)—N(4$^{\rm i}$)	107.0 (11)
N(1)—(Co,Mn)—Cl(1$^{\rm i}$)	88.7 (3)	N(1)—C(7)—C(6)	111.0 (11)
Cl(1)—(Co,Mn)—N(1$^{\rm i}$)	88.7 (3)	Cl(1)—(Co,Mn)—N(4)	91.5 (3)
N(4)—(Co,Mn)—N(1$^{\rm i}$)	88.0 (5)	Cl(1)—(Co,Mn)—Cl(1$^{\rm i}$)	180.0 (1)
Cl(1)—(Co,Mn)—N(4$^{\rm i}$)	88.5 (3)	N(4)—(Co,Mn)—Cl(1$^{\rm i}$)	88.5 (3)
N(4)—(Co,Mn)—N(4$^{\rm i}$)	180.0 (1)	N(1)—(Co,Mn)—N(1$^{\rm i}$)	180.0 (1)
N(1$^{\rm i}$)—(Co,Mn)—N(4$^{\rm i}$)	92.0 (5)	Cl(1$^{\rm i}$)—(Co,Mn)—N(1$^{\rm i}$)	91.3 (3)
(Co,Mn$^{\rm i}$)—N(1)—C(2$^{\rm i}$)	106.8 (7)	N(1)—(Co,Mn)—N(4$^{\rm i}$)	88.0 (5)
(Co,Mn)—N(1)—C(7)	119.4 (8)	Cl(1$^{\rm i}$)—(Co,Mn)—N(4$^{\rm i}$)	91.5 (3)
C(2)—N(1)—C(7)	110.7 (10)	N(1$^{\rm i}$)—C(2)—C(3$^{\rm i}$)	107.9 (10)
(Co,Mn)—N(4)—C(5)	121.4 (9)	C(7)—C(6)—C(5)	115.1 (12)
(Co,Mn)—N(4)—C(3$^{\rm i}$)	108.3 (8)	N(4)—C(5)—C(6)	110.9 (11)

Symmetry code: (i) $-x, -y, -z$.

All three structures were solved by direct methods using *SOLV* in *SHELXTL-Plus* (Sheldrick, 1991). Lattice water molecules were identified in each structure. The refinement of (I) was straightforward, with the metal site assumed to be solely occupied by Cu$^{\rm II}$. The metal-site occupancies in (II) and (III) were set equal to the ratio of metal ions found by chemical analyses. For (III), one water-molecule site had excess electron density. It was assumed that the Co$^{\rm II}$ ion had been oxidized to Co$^{\rm III}$ and the following site occupancies were assigned: (Co,Mn) Co 0.5, Mn 0.5; (Cl,O) Cl 0.5, O 0.5. During the final stages of refinement, the displacement parameters of the two metal atoms were constrained have identical values. For the Cl and O atoms occupying the (Cl,O) site, both the positional and displacement parameters were so constrained.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyanoferrocene: a Two-Dimensional Network Generated by Short C—H···N Hydrogen Bonds

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Abstract

In cyanoferrocene, [Fe(C_5H_5)(C_6H_4N)], the N atom acts as a hydrogen-bond acceptor from C—H bonds in two other molecules. Each molecule is thus hydrogen-bonded to four others, forming sheets.

Comment

Simple cyanobenzenes often exhibit intermolecular C—H···N—C hydrogen bonds in the solid state and examples include benzonitrile (C_6H_5CN), where the intermolecular C···N distance across the hydrogen bond is 3.51 (1) Å (Fauvet, Massaux & Chevalier, 1978), 1,4-dicyanobenzene, where the corresponding distance is also 3.51 (1) Å (Guth, Heger & Drück, 1982), 1,3,5-tricyanobenzene in its 1:1 molecular complex with hexamethylbenzene, where the tricyanobenzene forms discrete layers interleaved with layers of hexamethylbenzene and in which there are four intermolecular C···N distances of 3.471 (4) and two of 3.516 (6) Å (Reddy, Goud, Panneerselvam & Desiraju, 1993), and 1,2,4,5-tetracyanobenzene, in which each of the four independent N atoms forms several close intermolecular C···N contacts (Prout & Tickle, 1973), although the precision of this determination, from visually estimated photographic data, is not high. The cyclopentadienyl rings in ferrocene are more electron rich than benzene rings, thus allowing the possibility of a higher negative charge on the N atom of a cyano substituent on the C_5 ring, as compared with the N atom of a cyanobenzene moiety. This in turn opens up the possibility of stronger intramolecular C—H···N—C hydrogen bonds in the ferrocene

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