Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: semi-empirical *via* ψ scan (Sheldrick, 1995)
$T_{\min} = 0.117$, $T_{\max} = 0.358$
6305 measured reflections
6047 independent reflections
4398 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.032$
$\theta_{\max} = 30.01°$
$h = -15 \rightarrow 16$
$k = -9 \rightarrow 12$
$l = -26 \rightarrow 26$
3 standard reflections every 97 reflections intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.098$
$S = 0.922$
6047 reflections
197 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.085$ e Å^{-3}
$\Delta\rho_{\min} = -1.159$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.00113 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I1—C1	2.074 (4)	Si1—C8	1.849 (4)
I2—C6	2.067 (3)	Si2—C3	1.852 (4)
C5—C1—I1	125.3 (3)	C10—C6—I2	125.2 (3)
C2—C1—I1	125.5 (3)	Fe1—C6—I2	129.2 (2)
C2—C3—Si2	127.0 (3)	C9—C8—Si1	126.8 (3)
C4—C3—Si2	126.6 (3)	C7—C8—Si1	127.5 (3)
Si2—C3—Fe1	129.5 (2)	Si1—C8—Fe1	127.8 (2)
C7—C6—I2	125.7 (2)		

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1467). Services for accessing these data are described at the back of the journal.

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Hexaaquametal(II) 4-styrenesulfonates of manganese, cobalt and nickel

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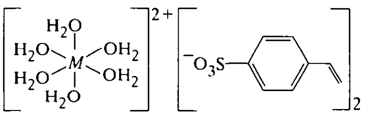
Abstract

The title compounds form an isomorphous series of the general formula $[M(H_2O)_6](C_8H_7SO_3)_2$, where M = Mn {hexaaquamanganese(II) bis(4-styrenesulfonate), $[Mn(H_2O)_6](C_8H_7SO_3)_2$}, Co {hexaaquacobalt(II) bis(4-styrenesulfonate), $[Co(H_2O)_6](C_8H_7SO_3)_2$} or Ni {hexaaquanickel(II) bis(4-styrenesulfonate), $[Ni(H_2O)_6](C_8H_7SO_3)_2$}. The three compounds share a structure built of alternating layers of hexaaquametal(II) cations and 4-styrenesulfonate anions. The coordination environments of the metal cations are octahedral, with only minor deviations from ideal geometries [Mn—O 2.126 (3)–2.176 (5) Å, O—Mn—O 84.6 (1)–89.9 (2)°; Co—O 2.052 (2)–2.087 (4) Å, O—Co—O 86.4 (1)–89.5 (1)°; Ni—O 2.021 (3)–2.041 (5) Å, O—Ni—O 87.8 (2)–89.6 (2)°]. The 4-styrenesulfonate layers contain alternating rows of anions, with the sulfonate groups directed towards opposite faces of the layer. The layers are held together by a two-dimensional array of O—H···O hydrogen bonds between the coordinated water molecules and sulfonate O atoms [O···O 2.717 (6)–2.816 (5) Å]. Similarities with the structures of other divalent metal arenesulfonate salts are described.

Comment

Previous studies have shown that the first-row transition metal cations tend to crystallize as hexaaqua complexes in the presence of a variety of organosulfonate anions (Aquino *et al.*, 1995; Couldwell *et al.*, 1978; Gunderman *et al.*, 1997; Henderson & Nicholson, 1995; Shakeri & Haussuhl, 1992). These structures have alternating layers of hexaaquametal cations and organosulfonate anions. The latter usually have anions whose SO_3^- groups are directed towards one face of the layer, interleaved with anions of the opposite orientation, so that both faces of the layer are negatively charged. Double layers of anions in opposite orientations have also been observed (Shubnell *et al.*, 1994). In either case, the layers are held together by a strong network of O—H···O hydrogen bonds between the coordinated water molecules and the sulfonate O atoms. The isomorphous 4-styrenesulfonate salts reported here, of manganese, (I), cobalt, (II), and nickel, (III), represent other members of this family of structurally related compounds.



(I) M = Mn
(II) M = Co
(III) M = Ni

As shown in Fig. 1, the metal ion lies on a center of inversion and is octahedrally coordinated to six water molecules. The M—O distances (Tables 2, 5 and 8) follow the expected trend based on the ionic radii of the cations, and are within the reported ranges for $[M(H_2O)_6]^{2+}$ complexes (Cotton *et al.*, 1993). In each case, M—O4 is notably shorter than both M—O5 and M—O6, though the cause of this phenomenon is unclear. It does not appear to correlate with the strengths of the hydrogen-bonding interactions of the water H atoms, *i.e.* the H atoms of O4, which has the shortest M—O bond, do not have the longest and therefore weakest H···O interactions.

The geometrical data for the anion are normal and consistent with those found in similar sulfonates (Gunderman *et al.*, 1997). The displacement parameters of the vinyl C atoms are indicative of substantial thermal motion or positional disorder, which is consistent with the lack of strong interactions in the hydrophobic portion of the structure. In contrast, the water molecules and sulfonate groups are linked by a network of hydrogen bonds in the *ab* plane, as summarized in Tables 3, 6 and 9. Each water H atom in the Ni and Co salts is involved in one nearly linear hydrogen bond; the larger deviations from linearity for the hydrogen bonds in the Mn compound presumably arise from discrepancies in the H-atom positions obtained from the difference maps. This pattern is essentially the same as that found in similar transition metal sulfonate salts. Indeed, if one compares the structures of $[M(H_2O)_6](RSO_3)_2$, where $R = C_6H_5$ (Kosnic *et al.*, 1996), $H_2NC_6H_4$ (Shakeri & Haussuhl, 1992), $CH_3(NH_2)C_6H_3$ (Gunderman *et al.*, 1997), and $CH_2CHC_6H_4$ (this study), one finds that they all crystallize in space group 14 ($P2_1/c$ or $P2_1/n$), with nearly the same a and b cell parameters. Thus, these structures are fundamentally the same in how the metal–water–sulfonate framework repeats along these directions. However, the structures differ in how the layers stack in the perpendicular direction. Taking account of small variations in the β angle, there is a progressive increase in the interlayer spacing [calculated as $\frac{1}{2}(c\sin\beta)$ = 11.21, 12.08, 12.24, 13.41 Å], which corresponds to the increasing length of the R group. So far,

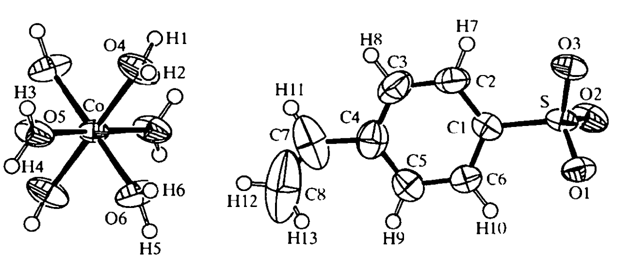


Fig. 1. An *ORTEP*II diagram (Johnson, 1976) showing the 4-styrenesulfonate anion, the coordination sphere around the Co atom, and the atom-labeling scheme. The displacement ellipsoids of non-H atoms are shown at the 50% probability level. The Mn and Ni analogues are isostructural.

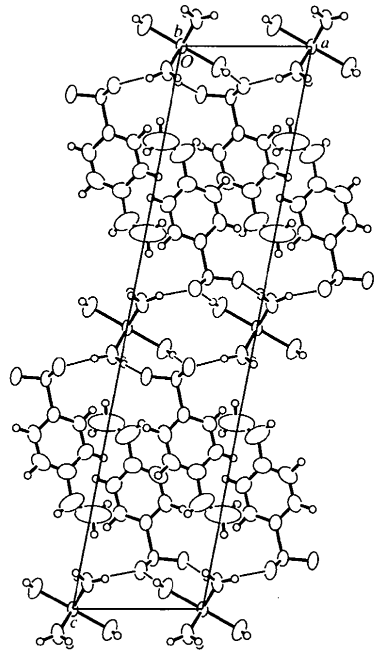


Fig. 2. An *ORTEP*II diagram (Johnson, 1976) showing the crystal packing as viewed down the *b* axis. Hydrogen bonds are shown by narrow lines. The displacement ellipsoids of non-H atoms are shown at the 50% probability level.

this shows that small changes in the size and shape of the organic group do not greatly affect the electrostatically driven packing in these arenesulfonate salts. Such behavior has been observed previously for a series of metal alkylphosphonates (Cao *et al.*, 1988). It would be of interest to test the limits of this phenomenon in the arenesulfonate system.

Experimental

All three title compounds were prepared by a similar route. A stoichiometric amount of the metal sulfate or acetate salt in water (15 ml) was combined with sodium 4-styrenesulfonate (4.0 g) in water (20 ml). The resulting solution was heated to *ca* 308 K and methanol (80 ml) was added, causing precipitation of the sodium sulfate or acetate. The mixture was filtered and the filtrate allowed to sit at room temperature. X-ray quality crystals grew upon slow evaporation of the solvent. The compounds were conveniently prepared in powder form by a metathesis reaction of concentrated aqueous solutions of the metal nitrate or chloride salt and sodium 4-styrenesulfonate.

Compound (I)

Crystal data

$[Mn(H_2O)_6](C_8H_7SO_3)_2$
$M_r = 529.43$
Monoclinic
$P2_1/c$
$a = 6.290\ (2)$ Å
$b = 7.040\ (3)$ Å
$c = 27.479\ (4)$ Å
$\beta = 100.83\ (3)°$
$V = 1195.1\ (6)$ Å^3
$Z = 2$
$D_x = 1.471$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 23 reflections
$\theta = 10.4–15.8°$
$\mu = 0.750$ mm^{-1}
$T = 296$ K
Plate
0.30 × 0.24 × 0.22 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: empirical *via* ψ scans of 3 reflections (North *et al.*, 1968)
$T_{min} = 0.780$, $T_{max} = 0.848$
2517 measured reflections
2294 independent reflections

2101 reflections with $I > 0$
$R_{int} = 0.042$
$\theta_{max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = -32 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: −1.50%

Refinement

Refinement on F^2
$R(F) = 0.083$
$wR(F^2) = 0.091$
$S = 1.48$
2101 reflections
142 parameters
H atoms not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.036$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn	0	0	0	0.0424 (3)
S	0.5495 (2)	0.0003 (4)	0.40573 (4)	0.0459 (3)
O1	0.4698 (8)	0.1731 (6)	0.4254 (2)	0.057 (2)
O2	0.4719 (8)	−0.1700 (6)	0.4267 (2)	0.058 (2)
O3	0.7838 (4)	0.0003 (7)	0.4093 (1)	0.0583 (10)
O4	0.3221 (4)	0.0014 (7)	0.0411 (1)	0.073 (1)
O5	0.0839 (7)	0.2238 (6)	−0.0475 (2)	0.066 (2)
O6	−0.0887 (7)	0.2329 (6)	0.0443 (2)	0.071 (2)
C1	0.4365 (6)	−0.007 (1)	0.3418 (2)	0.044 (1)
C2	0.5526 (8)	−0.0697 (8)	0.3075 (2)	0.065 (2)
C3	0.457 (1)	−0.0746 (8)	0.2582 (2)	0.072 (2)
C4	0.2462 (9)	−0.015 (1)	0.2423 (2)	0.065 (2)
C5	0.1305 (8)	0.046 (1)	0.2770 (2)	0.072 (2)
C6	0.2250 (8)	0.0543 (8)	0.3262 (2)	0.061 (2)
C7	0.159 (1)	−0.027 (2)	0.1888 (3)	0.099 (3)
C8	−0.026 (2)	0.036 (2)	0.1681 (3)	0.145 (4)

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

Mn—O4	2.126 (3)	S—O2	1.454 (4)
Mn—O5	2.173 (4)	S—O3	1.458 (3)
Mn—O6	2.176 (5)	S—C1	1.769 (4)
S—O1	1.458 (4)		
O4—Mn—O5	90.1 (2)	O1—S—C1	106.9 (3)
O4—Mn—O6	91.1 (2)	O2—S—O3	112.5 (3)
O5—Mn—O6	84.6 (1)	O2—S—C1	105.6 (3)
O1—S—O2	112.1 (2)	O3—S—C1	106.3 (2)
O1—S—O3	112.9 (3)		

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1···O1^{i}	0.92	1.82	2.729 (6)	169
O4—H2···O2^{ii}	0.85	2.02	2.717 (6)	138
O5—H3···O1^{iii}	0.92	1.93	2.766 (6)	149
O5—H4···O3^{iv}	0.80	2.02	2.811 (5)	172
O6—H5···O2^{v}	0.81	2.21	2.763 (7)	126
O6—H6···O3^{ii}	1.09	1.75	2.816 (5)	166

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

Compound (II)

Crystal data

$[Co(H_2O)_6](C_8H_7SO_3)_2$
$M_r = 533.43$
Monoclinic
$P2_1/c$
$a = 6.298\ (2)$ Å
$b = 6.987\ (3)$ Å
$c = 27.309\ (4)$ Å
$\beta = 100.86\ (4)°$
$V = 1180.2\ (7)$ Å^3
$Z = 2$
$D_x = 1.501$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 18 reflections
$\theta = 16.4–19.1°$
$\mu = 0.947$ mm^{-1}
$T = 296$ K
Rectangular plate
0.28 × 0.24 × 0.20 mm
Pink

Data collection

Rigaku AFC-6*S* diffractometer

2060 reflections with $I > 0$

ω scans
Absorption correction: empirical *via* ψ scans of 3 reflections (North *et al.*, 1968)
$T_{min} = 0.798$, $T_{max} = 0.868$
2471 measured reflections
2253 independent reflections
$R_{int} = 0.032$
$\theta_{max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = -32 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: 0.29%

Refinement

Refinement on F^2
$R(F) = 0.068$
$wR(F^2) = 0.088$
$S = 1.93$
2060 reflections
142 parameters
H atoms not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.021$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0	0	0	0.0382 (2)
S	0.5444 (1)	0.0001 (3)	0.40972 (4)	0.0430 (3)
O1	0.4645 (6)	0.1739 (5)	0.4295 (2)	0.052 (2)
O2	0.4663 (6)	−0.1718 (5)	0.4309 (2)	0.056 (2)
O3	0.7789 (4)	−0.0007 (6)	0.41402 (10)	0.0534 (8)
O4	0.3155 (4)	0.0011 (6)	0.0369 (1)	0.0646 (9)
O5	0.0748 (6)	0.2131 (5)	−0.0475 (2)	0.061 (2)
O6	−0.0780 (6)	0.2211 (5)	0.0443 (2)	0.065 (2)
C1	0.4340 (6)	−0.004 (1)	0.3451 (2)	0.044 (1)
C2	0.5534 (7)	−0.0665 (7)	0.3111 (2)	0.061 (2)
C3	0.459 (1)	−0.0719 (8)	0.2613 (2)	0.071 (2)
C4	0.2488 (9)	−0.014 (1)	0.2444 (2)	0.065 (2)
C5	0.1312 (8)	0.0497 (9)	0.2790 (2)	0.071 (2)
C6	0.2235 (8)	0.0547 (8)	0.3294 (2)	0.064 (2)
C7	0.164 (1)	−0.024 (2)	0.1903 (3)	0.102 (3)
C8	−0.016 (2)	0.035 (1)	0.1690 (3)	0.169 (5)

Table 5. *Selected geometric parameters (Å, °) for (II)*

Co—O4	2.052 (2)	S—O2	1.458 (4)
Co—O5	2.087 (4)	S—O3	1.459 (2)
Co—O6	2.077 (4)	S—C1	1.772 (4)
S—O1	1.456 (4)		
O4—Co—O5	89.5 (1)	O1—S—C1	106.5 (3)
O4—Co—O6	91.4 (1)	O2—S—O3	112.1 (2)
O5—Co—O6	86.4 (1)	O2—S—C1	106.5 (3)
O1—S—O2	111.9 (2)	O3—S—C1	106.3 (2)
O1—S—O3	112.9 (2)		

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1···O1^{i}	0.92	1.82	2.741 (5)	178
O4—H2···O2^{ii}	0.85	1.88	2.726 (5)	178
O5—H3···O1^{iii}	0.91	1.85	2.761 (5)	176
O5—H4···O3^{iv}	0.96	1.85	2.807 (5)	170
O6—H5···O2^{v}	0.94	1.83	2.762 (5)	167
O6—H6···O3^{ii}	0.92	1.87	2.795 (5)	175

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

Compound (III)

Crystal data

[$Ni(H_2O)_6](C_8H_7SO_3)_2$
$M_r = 533.19$
Monoclinic
$P2_1/c$
$a = 6.292$ (2) Å
$b = 6.934$ (5) Å
$c = 27.315$ (5) Å
$\beta = 100.68$ (4)°
$V = 1171$ (1) Å^3
$Z = 2$
$D_x = 1.512$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 16.1–19.2°$
$\mu = 1.056$ mm^{-1}
$T = 296$ K
Slab
0.30 × 0.30 × 0.20 mm
Pale green

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: empirical *via* ψ scans of 3 reflections (North *et al.*, 1968)
$T_{min} = 0.756$, $T_{max} = 0.810$
2454 measured reflections
2238 independent reflections
2045 reflections with $I > 0$
$R_{int} = 0.032$
$\theta_{max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = -32 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: −0.20%

Refinement

Refinement on F^2
$R(F) = 0.081$
$wR(F^2) = 0.104$
$S = 2.27$
2045 reflections
143 parameters
H atoms not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.045$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}
Extinction correction: type 2 Gaussian isotropic (Zachariasen, 1968)
Extinction coefficient: 1.85×10^{-6}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0	0	0	0.0393 (3)
S	0.5414 (2)	0.0003 (4)	0.41110 (5)	0.0441 (4)
O1	0.4620 (7)	0.1741 (7)	0.4311 (2)	0.051 (2)
O2	0.4631 (8)	−0.1739 (7)	0.4315 (2)	0.061 (2)
O3	0.7757 (4)	0.0004 (7)	0.4153 (1)	0.055 (1)
O4	0.3131 (4)	0.0002 (7)	0.0346 (1)	0.062 (1)
O5	0.0690 (7)	0.2077 (6)	−0.0476 (2)	0.068 (2)
O6	−0.0709 (7)	0.2159 (7)	0.0450 (2)	0.076 (3)
C1	0.4317 (7)	−0.002 (1)	0.3465 (2)	0.045 (1)
C2	0.5522 (9)	−0.0639 (9)	0.3127 (2)	0.062 (2)
C3	0.462 (1)	−0.0676 (10)	0.2624 (3)	0.075 (3)
C4	0.249 (1)	−0.011 (1)	0.2460 (2)	0.066 (2)
C5	0.1290 (10)	0.049 (1)	0.2808 (2)	0.075 (3)
C6	0.2203 (9)	0.054 (1)	0.3304 (2)	0.067 (2)
C7	0.170 (2)	−0.024 (2)	0.1905 (4)	0.120 (4)
C8	−0.013 (2)	0.036 (2)	0.1718 (4)	0.187 (7)

Table 8. *Selected geometric parameters (Å, °) for (III)*

Ni—O4	2.021 (3)	S—O2	1.453 (5)
Ni—O5	2.041 (5)	S—O3	1.457 (3)
Ni—O6	2.038 (5)	S—C1	1.771 (5)
S—O1	1.449 (5)		
O4—Ni—O5	90.4 (2)	O1—S—C1	106.5 (3)
O4—Ni—O6	91.2 (2)	O2—S—O3	112.3 (3)
O5—Ni—O6	87.8 (2)	O2—S—C1	106.0 (4)
O1—S—O2	112.5 (2)	O3—S—C1	106.3 (2)
O1—S—O3	112.6 (3)		

Table 9. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1···O1^{i}	0.98	1.79	2.739 (6)	164
O4—H2···O2^{ii}	0.91	1.83	2.732 (6)	175
O5—H3···O1^{iii}	0.98	1.79	2.767 (6)	177
O5—H4···O3^{iv}	1.03	1.80	2.799 (6)	161
O6—H5···O2^{v}	0.95	1.82	2.771 (7)	174
O6—H6···O3^{ii}	1.09	1.72	2.787 (6)	164

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

For the three title compounds, phenyl C—C distances were in the range 1.367 (7)–1.391 (7) Å, C4—C7 in the range 1.471 (8)–1.51 (1) Å, and C7—C8 in the range 1.24 (1)–1.28 (1) Å. The short double bond and the irregular displacement parameters are indicative of disorder involving C7 and C8, however, no additional peaks of electron density leading to such a model could be found. H atoms were either located on difference electron-density maps (O—H) or placed in calculated positions (C—H) with isotropic *B* values equal to 1.2 times those of the attached atoms at the time of their inclusion.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1487). Services for accessing these data are described at the back of the journal.

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[1,5-Bis(2-pyridylmethyl-*N*)-1,5-diazacyclooctane-*N*,*N*′]chloronickel(II) perchlorate

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Abstract

The structure of the title compound, $[NiCl(C_{18}H_{24}N_4)]ClO_4$, is comprised of discrete $[NiCl(C_{18}H_{24}N_4)]^+$ cations and perchlorate anions. The Ni^{II} atom is five-coordinated by the four nitrogen donors of the new mini-ring macrocyclic ligand 1,5-bis(2-pyridylmethyl)-1,5-diazacyclooctane [Ni—N 2.074 (3)–2.108 (3) Å], and by a chloride anion in the apical site [Ni—Cl 2.302 (1) Å]. The coordination geometry of the complex could be considered as intermediate between square-pyramidal and trigonal-bipyramidal. The mini-ring macrocyclic ligand has a boat–chair conformation and the two pyridyl pendants are not coplanar.

Comment

The coordination properties toward metal ions of macrocycles bearing pendant donor groups have recently attracted much interest as models for protein–metal binding sites and multi-electron catalysis (Alexander, 1995; Norante *et al.*, 1990). Recently, we found that functionalized aza-macrocycles containing pendant pyridine groups can form stable complexes with transition metals and that these complexes exhibit interesting properties (Bu *et al.*, 1997). In order to extend our studies and to obtain some non-octahedral transition metal complexes possessing good catalytic functions, we synthesized a new mini-ring macrocyclic ligand, 1,5-