

The Ni^{II}, Hg^{II} and Cu^{II} complexes of 12-membered-ring mixed-donor macrocycles

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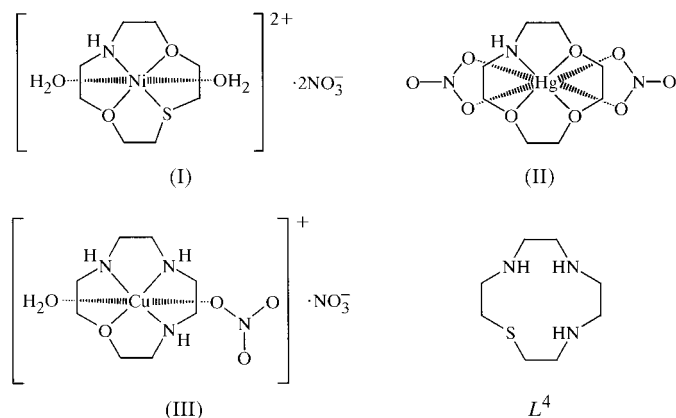
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The structures of diaqua(1,7-dioxa-4-thia-10-azacyclododecane)nickel dinitrate, $[\text{Ni}(\text{C}_8\text{H}_{17}\text{NO}_2\text{S})(\text{H}_2\text{O})_2](\text{NO}_3)_2$, (I), bis(nitrato-*O,O'*)(1,4,7-trioxa-10-azacyclododecane)mercury, $[\text{Hg}(\text{NO}_3)_2(\text{C}_8\text{H}_{17}\text{NO}_3)]$, (II), and aqua(nitrato-*O*)(1-oxa-4,7,10-triazacyclododecane)copper nitrate, $[\text{Cu}(\text{NO}_3)(\text{C}_8\text{H}_{19}\text{N}_3\text{O})(\text{H}_2\text{O})]\text{NO}_3$, (III), reveal each macrocycle binding in a tetradentate manner. The conformations of the ligands in (I) and (III) are the same and distinct from that identified for (II). These differences are in agreement with molecular-mechanics predictions of ligand conformation as a function of metal-ion size.

Comment

The coordination chemistry of 12-membered macrocycles has been dominated by the symmetrical N₄ (cyclen) and O₄ (12-crown-4) ligands. Mixed-donor macrocycles have been much less extensively studied, due in part to the greater complexity of their syntheses. There are a number of possible combinations of N-, O- and S-donor atoms in a 12-membered macrocyclic ring (substituted at the 1,4,7,10 positions), and it has



been found that judicious replacement of heteroatoms by either harder or softer donors can have a marked effect on the thermodynamic stability, and hence metal-ion selectivity, of

the macrocycle (Byriel *et al.*, 1993; Afshar *et al.*, 1999; Marcus *et al.*, 1999). In this paper, we report the crystal structures of the Ni^{II}, Hg^{II} and Cu^{II} complexes of three different mixed-donor macrocycles comprising NO₂S, NO₃ and N₃O donor sets, respectively.

The crystal structure of $[\text{Ni}L^1(\text{OH}_2)_2](\text{NO}_3)_2$ ($L^1 = 1,7$ -dioxo-4-thia-10-azacyclododecane) (Fig. 1) comprises separate complex cations with neither anion bound to the metal. The Flack (1983) parameter [0.00 (2)] establishes unequivocally that the space group $P6_5$ is correct and not the enantiomorphic $P6_1$ space group. The complex cation is six-coordinate, with the macrocycle adopting a non-planar *cis* conformation. The two aqua ligands are thus forced to occupy *cis* coordination sites. The aqua ligands exhibit the shortest coordinate bonds (Table 1), the ether and amine donors display slightly longer bond lengths, while the Ni—S bond is the longest, as expected. There are a number of hydrogen bonds involving both the aqua ligands and the amine-H atoms as donors (Table 2). The macrocycle adopts an asymmetric [2424] conformation (Buschmann, 1987). This conformation has also been observed in the structures of $[\text{Ni}L^4(\text{OH}_2)(\text{ONO}_2)]\text{NO}_3$ and the dimer $[\{\text{Cu}L^4(\text{OH})\}_2](\text{ClO}_4)_2$, where L^4 is the N₃S analogue of L^1 (Marcus *et al.*, 1999). The Hg^{II} complex of L^1 (Byriel *et al.*, 1993) finds the ligand in the [3333] conformation, where the four donor atoms are approximately coplanar and the metal ion is displaced well above this plane, in contrast to the present structure.

The crystal structure of $[\text{Hg}L^2(\text{O}_2\text{NO})_2]$ ($L^2 = 1,4,7$ -trioxa-10-azacyclododecane) (Fig. 2) comprises the tetradentate coordinated ligand in the [3333] conformation and two nitrate ligands. In contrast with the structure of $[\text{Ni}L^1(\text{OH}_2)_2]^{2+}$, there is a large difference between the macrocyclic Hg—N and Hg—O bond lengths (Table 3), with the former being *ca.* 0.4 Å shorter. This reflects the preference of Hg for amines compared with harder ether donors. Both nitrate ligands coordinate asymmetrically, with unequal Hg—O bond lengths. Moreover, one nitrate ligand is bound more tightly [Hg1—O4 2.166 (5) and Hg1—O5 2.698 (6) Å] than the other [Hg1—O8 2.541 (5) and Hg1—O9 2.906 (6) Å]. The sole hydrogen-bond donor (the amine-H atom) forms an intermolecular hydrogen bond with the non-coordinated O atom of one nitrate ligand (Table 4). The only other report of a crystal structure of L^2 is the complex $[\text{Na}(L^2)_2]\text{I}$, where both ligands exhibit the [3333]

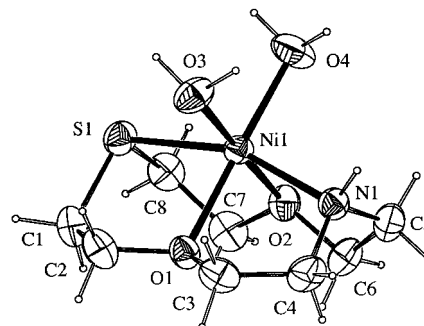


Figure 1
View of $[\text{Ni}L^1(\text{OH}_2)_2]^{2+}$ showing 30% probability ellipsoids.

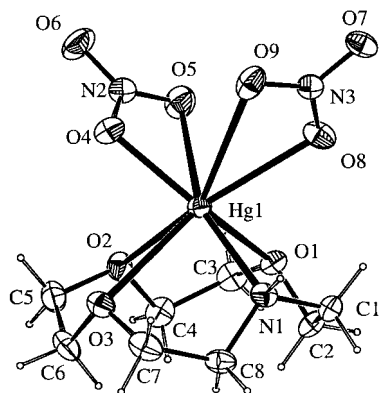


Figure 2
View of $[\text{HgL}^2(\text{ONO}_2)_2]$ showing 30% probability ellipsoids.

conformation (White *et al.*, 1987). More common are structural reports of N-functionalized derivatives of L^2 (so-called lariat ethers; Schultz *et al.*, 1985).

The structure of $[\text{CuL}^3(\text{OH}_2)(\text{ONO}_2)]\text{NO}_3$ ($L^3 = 1\text{-oxa-4,7,10-triazacyclododecane}$) (Fig. 3) defines a six-coordinate, distorted octahedral complex cation, comprising one weakly bound nitrate ligand, and one free nitrate anion both on general sites. The macrocycle adopts a folded [2424] conformation as seen in the $[\text{NiL}^1(\text{OH}_2)_2]^{2+}$ structure. The electronic preference of Cu^{II} for axially elongated five- and six-coordinate geometries is evident from the significantly longer axial $\text{Cu}-\text{O}2$ and $\text{Cu}-\text{O}5$ bond lengths (Table 5) compared with the equatorial bonds involving the N-donors and aqua ligand. Numerous hydrogen bonds are formed involving the aqua ligands and the amine-H atoms as donors (Table 6). This structure is closely related to $[\text{CuL}^3\text{Br}]\text{PF}_6$ (Felix *et al.*, 1994), where a bromo ligand replaces the aqua ligand in the present structure. The other structural report of an L^3 complex is that of $[\text{MnL}^3(\text{NCS})_2]$ (Zhang *et al.*, 1992).

It has been established that 12-membered macrocycles are too small to encircle a metal ion, and either *cis*-octahedral coordination or square-based pyramidal structures are found. In no case is the metal coplanar with the four donor atoms. We have reported recently a molecular-mechanics analysis of the

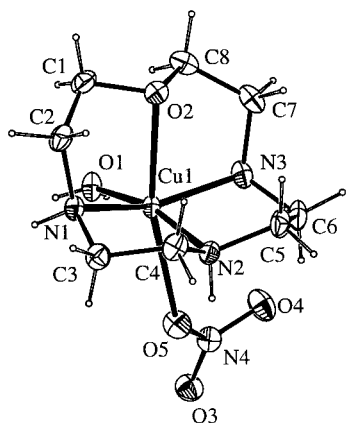


Figure 3
View of $[\text{CuL}^3(\text{OH}_2)(\text{ONO}_2)]^+$ showing 30% probability ellipsoids.

conformational preference of the 12-membered N_3S macrocyclic relative of L^1 for metal ions of various sizes (Marcus *et al.*, 1999). The conclusions of this analysis were that the [3333] conformation of ligands of this class will be dominant when the metal–ligand bond lengths are large ($>2.25 \text{ \AA}$), and the crystal structures observed so far are in agreement with this.

Experimental

The title complexes were crystallized from methanolic solutions containing equimolar amounts of the corresponding metal(II) nitrate and ligand L^1 (Byriel *et al.*, 1993), L^2 (Calverley & Dale, 1981) or L^3 (Thöm *et al.*, 1986).

Compound (I)

Crystal data

$[\text{Ni}(\text{C}_8\text{H}_{17}\text{NO}_2\text{S})(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 $M_r = 410.05$
 Hexagonal, $P6_3$
 $a = 8.7242(3) \text{ \AA}$
 $V = 2445.6(2) \text{ \AA}^3$
 $Z = 6$
 $D_x = 1.671 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation

Cell parameters from 25 reflections
 $\theta = 10\text{--}14^\circ$
 $\mu = 1.372 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Prism, blue
 $0.40 \times 0.40 \times 0.40 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.529$, $T_{\text{max}} = 0.578$
 4648 measured reflections
 1459 independent reflections
 1208 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 24.98^\circ$
 $h = -10 \rightarrow 8$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 44$
 3 standard reflections
 frequency: 120 min
 intensity decay: $<5\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.078$
 $S = 1.055$
 1459 reflections
 209 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.4947P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0010 (4)
 Absolute structure: Flack (1983)
 Flack parameter = 0.00 (2)

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Ni1—O4	2.028 (5)	Ni1—N1	2.082 (5)
Ni1—O3	2.029 (5)	Ni1—O1	2.082 (4)
Ni1—O2	2.073 (4)	Ni1—S1	2.4185 (17)
O4—Ni1—O3	91.9 (2)	O2—Ni1—O1	91.66 (17)
O4—Ni1—O2	87.0 (2)	N1—Ni1—O1	80.19 (17)
O3—Ni1—O2	178.8 (2)	O4—Ni1—S1	98.07 (15)
O4—Ni1—N1	99.1 (2)	O3—Ni1—S1	95.33 (15)
O3—Ni1—N1	98.0 (2)	O2—Ni1—S1	84.27 (12)
O2—Ni1—N1	82.75 (18)	N1—Ni1—S1	157.83 (14)
O4—Ni1—O1	178.5 (2)	O1—Ni1—S1	82.31 (12)
O3—Ni1—O1	89.45 (19)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O7	0.91	2.44	3.177 (9)	139
N1—H1...O8	0.91	2.56	3.180 (9)	126
O3—H31...O8	0.96	2.02	2.779 (8)	134
O3—H31...O9	0.96	2.65	3.244 (10)	121
O3—H32...O5 ⁱ	0.96	2.00	2.734 (7)	132
O3—H32...O7 ⁱ	0.96	2.40	3.347 (9)	171
O3—H32...N2 ⁱ	0.96	2.55	3.465 (8)	160
O4—H41...O6	0.96	1.99	2.763 (9)	136
O4—H41...O7	0.96	2.32	3.174 (10)	149
O4—H41...N2	0.96	2.49	3.380 (8)	154
O4—H42...O10 ⁱⁱ	0.96	2.14	2.704 (8)	116

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

Compound (II)

Crystal data

[Hg(NO₃)₂(C₈H₁₇NO₃)]
M_r = 499.84
 Monoclinic, *P*₂₁/*n*
a = 8.245 (3) Å
b = 11.927 (2) Å
c = 14.272 (5) Å
 β = 96.60 (2)°
V = 1394.2 (7) Å³
Z = 4
D_x = 2.381 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10–14°
 μ = 11.090 mm⁻¹
T = 275 (2) K
 Prism, colourless
 0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω–2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.055, *T_{max}* = 0.109
 2623 measured reflections
 2444 independent reflections
 2082 reflections with *I* > 2σ(*I*)
R_{int} = 0.024
θ_{max} = 24.97°
h = 0 → 9
k = 0 → 14
l = –16 → 16
 3 standard reflections
 frequency: 120 min
 intensity decay: <5%

Table 3
Selected geometric parameters (Å, °) for (II).

Hg1—O4	2.166 (5)	Hg1—O2	2.644 (5)
Hg1—N1	2.184 (5)	Hg1—O3	2.659 (5)
Hg1—O8	2.541 (5)	Hg1—O5	2.698 (6)
Hg1—O1	2.543 (5)	Hg1—O9	2.906 (6)
O4—Hg1—N1	157.7 (2)	O2—Hg1—O3	64.61 (16)
O4—Hg1—O8	108.29 (19)	O4—Hg1—O5	51.21 (18)
N1—Hg1—O8	84.87 (19)	N1—Hg1—O5	151.11 (19)
O4—Hg1—O1	126.29 (17)	O8—Hg1—O5	76.85 (19)
N1—Hg1—O1	73.28 (18)	O1—Hg1—O5	81.04 (17)
O8—Hg1—O1	77.79 (16)	O2—Hg1—O5	73.85 (18)
O4—Hg1—O2	77.63 (18)	O3—Hg1—O5	126.98 (18)
N1—Hg1—O2	105.99 (18)	O4—Hg1—O9	77.50 (17)
O8—Hg1—O2	135.48 (16)	N1—Hg1—O9	101.51 (17)
O1—Hg1—O2	65.19 (15)	O8—Hg1—O9	45.49 (16)
O4—Hg1—O3	87.69 (18)	O1—Hg1—O9	123.06 (15)
N1—Hg1—O3	74.71 (19)	O2—Hg1—O9	152.46 (15)
O8—Hg1—O3	155.73 (18)	O3—Hg1—O9	125.73 (14)
O1—Hg1—O3	107.86 (15)	O5—Hg1—O9	81.42 (18)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O7 ⁱ	0.91	2.10	2.895 (8)	145

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

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.087
S = 1.060
 2444 reflections
 191 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0622*P*)² + 1.3329*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.46 e Å⁻³
 Δρ_{min} = –3.30 e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0018 (3)

Compound (III)

Crystal data

[Cu(NO₃)(C₈H₁₉N₃O)(H₂O)]NO₃
M_r = 378.84
 Triclinic, *P* $\bar{1}$
a = 8.6167 (9) Å
b = 9.3975 (8) Å
c = 10.118 (1) Å
 α = 95.627 (8)°
 β = 112.107 (9)°
 γ = 99.509 (9)°
V = 737.05 (12) Å³
Z = 2
D_x = 1.707 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10–14°
 μ = 1.531 mm⁻¹
T = 295 (2) K
 Prism, blue
 0.60 × 0.60 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω–2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.401, *T_{max}* = 0.632
 2774 measured reflections
 2586 independent reflections
 2392 reflections with *I* > 2σ(*I*)
R_{int} = 0.025
θ_{max} = 24.97°
h = 0 → 10
k = –11 → 11
l = –12 → 11
 3 standard reflections
 frequency: 120 min
 intensity decay: <5%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.068
S = 1.082
 2586 reflections
 200 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0343*P*)² + 0.4836*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.36 e Å⁻³
 Δρ_{min} = –0.27 e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.096 (3)

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

Cu1—O1	1.9663 (15)	Cu1—N3	2.0393 (18)
Cu1—N2	1.9742 (18)	Cu1—O2	2.3465 (16)
Cu1—N1	2.0312 (18)	Cu1—O5	2.7682 (17)
O1—Cu1—N2	163.92 (7)	N1—Cu1—O2	79.83 (7)
O1—Cu1—N1	96.37 (7)	N3—Cu1—O2	79.07 (7)
N2—Cu1—N1	86.73 (7)	O1—Cu1—O5	81.64 (6)
O1—Cu1—N3	96.54 (7)	N2—Cu1—O5	83.03 (6)
N2—Cu1—N3	86.40 (8)	N1—Cu1—O5	118.63 (6)
N1—Cu1—N3	156.15 (8)	N3—Cu1—O5	83.11 (7)
O1—Cu1—O2	95.29 (6)	O2—Cu1—O5	161.46 (5)
N2—Cu1—O2	100.79 (7)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O5 ⁱ	0.91	2.36	3.153 (3)	145
N1—H1...O8 ⁱ	0.91	2.61	3.234 (3)	127
N2—H2...O6	0.91	2.19	2.994 (3)	147
N2—H2...O7	0.91	2.56	3.428 (4)	159
N2—H2...N5	0.91	2.68	3.582 (3)	174
N3—H3...O3 ⁱⁱ	0.91	2.22	3.000 (3)	143
N3—H3...O4	0.91	2.62	3.257 (3)	127
O1—H21...O4 ⁱⁱ	0.79	2.00	2.788 (2)	172
O1—H21...O3 ⁱⁱ	0.79	2.57	3.162 (2)	133
O1—H21...N4 ⁱⁱ	0.79	2.64	3.398 (2)	161
O1—H22...O6 ⁱ	0.73	1.98	2.709 (2)	174

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$.

Ligand-associated H atoms were constrained using a riding model. All water-H atoms were first located from difference maps before being constrained.

For all compounds, data collection: *CAD-4 Manual* (Enraf-Nonius, 1988); cell refinement: *SET4* in *CAD-4 Manual*; data reduction: *Xtal3.2* (Hall *et al.*, 1992); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1589). Services for accessing these data are described at the back of the journal.

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