

## The Structures of $[\text{Ni}(\text{C}_{18}\text{H}_{34}\text{N}_6)](\text{ClO}_4)_2$ and $[\{\text{Ni}(\text{C}_{18}\text{H}_{34}\text{N}_6)\}_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ . Complexes of a [16]Tetraene $\text{N}_4(\text{N}_2)$ Macrocyclic Produced by a Schiff-Base-Type Condensation

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### Abstract

$[\text{NiL}](\text{ClO}_4)_2$  ( $L$  is 3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-2,4,6,16-tetraene),  $M_r = 592.12$ , crystallizes in space group  $P\bar{1}$ , with  $a = 13.415$  (6),  $b = 10.609$  (6),  $c = 11.764$  (6) Å,  $\alpha = 118.41$  (1),  $\beta = 61.77$  (1),  $\gamma = 96.57$  (1)°,  $V = 1284.2$  Å<sup>3</sup>,  $Z = 2$ ;  $D_m$  (floatation in  $\text{CHCl}_3/\text{CHBr}_3$ ) = 1.53,  $D_c = 1.531$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.02$  mm<sup>-1</sup>. The structure was determined from X-ray diffraction data (2517 counter-measured reflexions with  $I > 2.3\sigma_I$ ) and refined by least squares to a final  $R = 0.066$ . The Ni atom is coordinated by four N atoms of the macrocycle in an approximate square-planar arrangement with a significant tetrahedral distortion. The distances from Ni to the amine and imine N atoms are equal [average 1.907 (2) Å]. The oxalate adduct,  $[\{\text{NiL}\}_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $M_r = 1109.40$ , crystallizes in space group  $P2_1/n$ , with  $a = 13.642$  (4),  $b = 9.406$  (4),  $c = 20.454$  (6) Å,  $\beta = 102.32$  (3)°,  $V = 2564.1$  Å<sup>3</sup>,  $Z = 2$ ;  $D_m$  (floatation in  $\text{CHCl}_3/\text{C}_6\text{H}_5\text{NO}_2$ ) = 1.42,  $D_c = 1.437$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.91$  mm<sup>-1</sup>. The X-ray structure analysis (2004 reflexions with  $I > 2.3\sigma_I$ ) converged to  $R = 0.060$ . The two halves of the dimer are related by a crystallographic centre of symmetry. The Ni atom is six-coordinate: an edge-on bonded oxalate occupies two adjacent sites [Ni–O = 2.089 and 2.120 (4) Å] while the macrocycle folds to allow the ligating N atoms to occupy the remaining four positions [Ni–N = 2.131 and 2.109 (6) Å *trans* to the oxalate and 2.072 and 2.094 (5) Å].

### Introduction

The previous paper (Davis, Einstein & Willis, 1982) reported the conformation and configuration of the tetradentate ligand 3,5,5,10,10,12-hexamethyl-1,2,6,9,13,14-hexaazatetradeca-2,12-diene,  $L1$ , in two nickel(II) complexes. In  $[\text{Ni}(L1)(\text{NCS})_2] \cdot \text{H}_2\text{O}$  the four

ligating N atoms of the ligand occupied the equatorial sites of the six-coordinate Ni atom but in  $[\text{Ni}(L1)(\text{NO}_2)]\text{ClO}_4$  the ligand was folded.

When condensed with 2,4-butanedione, the dihydrazone  $[\text{Ni}(L1)](\text{ClO}_4)_2$  yields the macrocyclic complex  $[\text{Ni}(L2)](\text{ClO}_4)_2$ , where  $L2 = 3,4,7,9,9,14,14,16$ -octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-2,4,6,16-tetraene (Curtis, 1980). This complex (I) can be isolated as salmon-red crystals. In solution it reacts with 0.5 mol oxalate to give royal-blue crystals of  $[\{\text{Ni}(L2)\}_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (II).

A structural investigation of these compounds was undertaken to confirm the presence of the novel, seven-membered di-imine chelate ring that results from the condensation and to examine the conformations of this ring as well as the rest of the macrocycle in both planar and folded configurations.

### X-ray data collection

Samples of (I) and (II) were kindly supplied by Professor Neil Curtis. Well formed single crystals were selected and mounted on glass fibres with their longest dimensions parallel to the fibre axes. Weissenberg and precession X-ray photographs were taken using Cu  $K\alpha$  radiation and gave approximate unit-cell parameters. (I) is triclinic, space group  $P1$  or  $P\bar{1}$ . (II) is monoclinic with systematic absences  $h0l: h + l = 2n + 1$  and  $0k0: k = 2n + 1$  uniquely determining the space group as  $P2_1/n$ .

The crystals were then mounted on a Picker FACS-I four-circle automated diffractometer employing graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.70926$  Å). Accurate cell dimensions were determined from the setting angles of 12 reflexions with  $2\theta > 25^\circ$  for (I) [23 with  $2\theta > 19^\circ$  for (II)] which had been centred on the diffractometer counter.

Intensity data were collected under the conditions listed in Table 1. In each case two standard reflexions were monitored at frequent intervals but showed no evidence of sample decomposition. Intensities were

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Table 1. Measurement of data

	(I)	(II)
Crystal size (mm)	0.5 × 0.1 × 0.1	0.17 × 0.19 × 0.47
2θ range	3–45°	3–40°
Scan type	θ–2θ	θ–2θ
Scan speed	2° min <sup>-1</sup>	2° min <sup>-1</sup>
Scan width	$\begin{cases} 2\theta < 30^\circ \\ 2\theta > 30^\circ \end{cases}$	$\begin{cases} 1.7^\circ \\ 1.3^\circ \end{cases}$
Background count time	20 s	0.4 × scan time
on each side of scan*	10 s	0.4 × scan time
Number of unique reflections	3317	2392
Number of observed reflections†	2517	2004

\* Stationary-crystal stationary-counter.

†  $I > 2.3\sigma_I$ ;  $\sigma_I = [T + (t_s/t_b)^2(B_1 + B_2) + (0.03I)^2]^{1/2}$  where  $T$  is the total count,  $B_1$  and  $B_2$  are the background counts,  $t_s$  is the scan time,  $t_b$  is the background time, and  $I$  is the net count.

corrected for Lorentz and polarization effects, but not for absorption.

### Solution and refinement

The structure of (I) was solved by heavy-atom methods assuming space group  $P\bar{1}$ . All non-hydrogen atoms were quickly located. Successful refinement of the structure confirms this choice of space group. In one perchlorate group three of the O atoms were found to be disordered over sites of half-occupancy. These atoms were refined throughout with isotropic temperature factors whilst the other non-hydrogen atoms were refined anisotropically.

(II) was also solved by heavy-atom procedures. Anisotropic temperature factors were used only for Ni, the CO<sub>4</sub> group, O(3) and three peripheral C atoms, all of which had shown indications of anisotropic motion in difference maps.

In both structures most of the H atoms were located in inner-data difference maps and the remainder were calculated. In (I) all H atoms were given  $B = 5.0 \text{ \AA}^2$ ; in (II) each H atom was assigned the  $B_{\text{eq}}$  of the atom to which it was attached. H-atom scattering contributions were included in all further calculations, but the parameters were not refined. Refinement was continued until all shift-to-error ratios were  $< 0.1$ . The final agreement factors, for (I) and (II), respectively, are  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.066$  and  $0.060$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2} = 0.075$  and  $0.069$  for 314 and 188 variables. The final difference maps were generally featureless, with the largest peaks  $[0.4$  (1) e  $\text{\AA}^{-3}]$  being in the vicinity of the Ni atoms in both cases.

Full-matrix least-squares calculations minimizing the function  $\sum w(|F_o| - |F_c|)^2$  were used to refine both structures; the weights,  $w$ , were initially set at unity, but in later stages  $1/\sigma_F^2$  was used. The average of  $w(|F_o| - |F_c|)^2$  did not vary systematically with  $F_o$  or  $(\sin \theta)/\lambda$ . Neutral scattering factors were employed for all atoms and anomalous-dispersion corrections applied for Ni

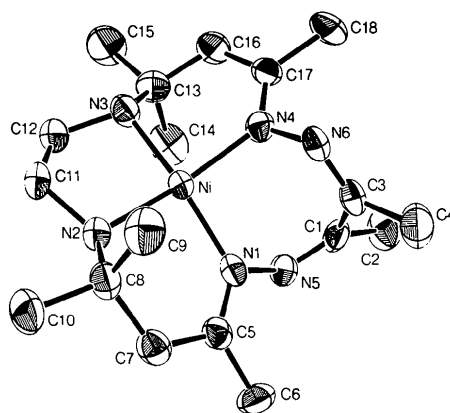


Fig. 1. A perspective view of the [Ni(L2)]<sup>2+</sup> molecule showing atomic labelling. H atoms have been deleted for clarity. Thermal ellipsoids show 50% probability levels.

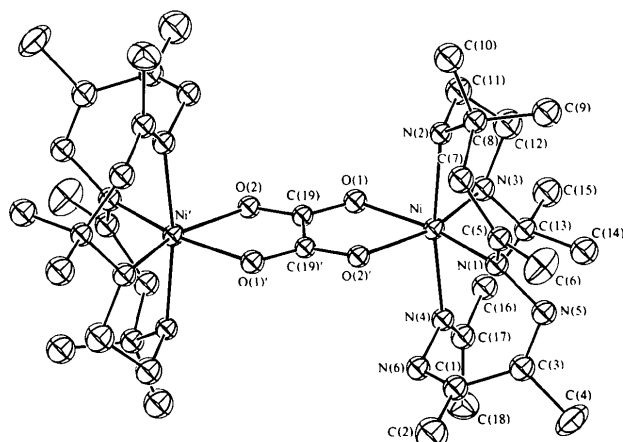


Fig. 2. A projected view of the [Ni(L2)]<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>2+</sup> dimer showing atomic labelling and 25% probability thermal ellipsoids.

and Cl (*International Tables for X-ray Crystallography*, 1974).

Figs. 1 and 2 show the atom-labelling schemes of (I) and (II) respectively. The final atomic coordinates for the non-hydrogen atoms are listed in Table 2 and bond-lengths and angles in Table 3.\*

Computer programs (Einstein & Jones, 1972; Gabe, Larsen, Lee & Wang, 1979) were run on an in-house PDP-8e computer and on the IBM 370/155 computer of this university.

\* For both compounds, lists of structure factors, anisotropic thermal parameters, H-atom coordinates, angles for the perchlorate groups and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36327 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic coordinates ( $\times 10^4$ ,  $\times 10^5$  for Ni) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) of the non-hydrogen atoms for (I) and (II) with e.s.d.'s in parentheses

Compound (I)	x	y	z	$U_{\text{eq}}$ or $U_{\text{iso}}$
Ni	22708 (7)	1783 (8)	3267 (8)	33.3 (6)*
N(1)	2574 (4)	-1723 (5)	-1272 (5)	37 (3)*
N(2)	1728 (5)	-563 (5)	1676 (5)	42 (3)*
N(3)	1576 (4)	2057 (5)	1973 (5)	35 (3)*
N(4)	3192 (4)	997 (5)	-909 (5)	36 (3)*
N(5)	2436 (5)	-1750 (5)	-2422 (5)	39 (3)*
N(6)	4300 (4)	166 (6)	-2030 (5)	40 (3)*
C(1)	3241 (6)	-1396 (6)	-3276 (7)	34 (4)*
C(2)	3182 (7)	-1318 (8)	-4463 (7)	52 (5)*
C(3)	4291 (6)	-978 (7)	-3112 (7)	44 (5)*
C(4)	5397 (6)	-1978 (8)	-4294 (7)	61 (5)*
C(5)	2665 (6)	-2948 (7)	-1356 (7)	39 (4)*
C(6)	2722 (7)	-4337 (7)	-2622 (8)	58 (5)*
C(7)	2663 (6)	-3058 (7)	-130 (8)	51 (5)*
C(8)	2609 (7)	-1707 (7)	1199 (7)	50 (5)*
C(9)	3770 (7)	-1146 (8)	795 (9)	67 (6)*
C(10)	2321 (8)	-2071 (8)	2408 (9)	76 (7)*
C(11)	1344 (6)	687 (7)	3179 (7)	50 (4)*
C(12)	764 (6)	1876 (7)	3269 (7)	50 (4)*
C(13)	1072 (6)	2912 (7)	1590 (7)	41 (4)*
C(14)	397 (6)	1957 (8)	822 (7)	53 (5)*
C(15)	289 (6)	4272 (7)	2970 (7)	59 (4)*
C(16)	2074 (6)	3363 (7)	571 (7)	41 (4)*
C(17)	3090 (6)	2308 (7)	-664 (7)	35 (4)*
C(18)	4015 (6)	2867 (7)	-1568 (7)	51 (5)*
Cl(1)	3695 (2)	4462 (2)	2898 (2)	60 (1)*
O(11)	3610 (6)	2985 (7)	2394 (8)	117 (6)*
O(12)	4127 (7)	4712 (9)	1713 (8)	71 (6)*
O(13)	2613 (6)	5116 (8)	3891 (8)	222 (7)*
O(14)	4438 (6)	4893 (7)	3517 (7)	110 (6)*
Cl(2)	1076 (2)	2231 (2)	-2745 (2)	62 (1)*
O(21)	2061 (6)	2322 (7)	-2534 (7)	100 (5)*
O(22A)†	1580 (15)	2431 (18)	-4002 (18)	108 (6)
O(22B)†	1089 (14)	2779 (17)	-3653 (17)	89 (5)
O(23A)†	261 (13)	3498 (17)	-1478 (17)	97 (5)
O(23B)†	65 (15)	2876 (19)	-1474 (19)	110 (6)
O(24A)†	661 (12)	991 (16)	-2645 (17)	79 (4)
O(24B)†	906 (10)	740 (13)	-3562 (14)	106 (5)
Compound (II)				
Ni	41672 (6)	38388 (9)	59859 (4)	28.9 (7)*
N(1)	4270 (4)	1696 (6)	6332 (3)	35 (2)
N(2)	5339 (4)	4434 (6)	6777 (2)	31 (2)
N(3)	3283 (4)	5110 (6)	6484 (3)	35 (2)
N(4)	2874 (4)	3189 (6)	5326 (2)	33 (2)
N(5)	3419 (4)	796 (6)	6308 (3)	39 (2)
N(6)	3082 (4)	2169 (6)	4869 (3)	38 (2)
C(1)	2942 (5)	490 (8)	5728 (4)	44 (2)
C(2)	1990 (7)	-399 (10)	5689 (5)	84 (7)*
C(3)	3174 (5)	897 (7)	5086 (3)	39 (2)
C(4)	3486 (7)	-224 (10)	4667 (4)	72 (3)
C(5)	5109 (5)	1137 (8)	6639 (3)	37 (2)
C(6)	5194 (6)	-390 (9)	6845 (4)	68 (6)*
C(7)	6028 (5)	2033 (8)	6797 (3)	43 (2)
C(8)	5926 (5)	3327 (7)	7234 (3)	38 (2)
C(9)	6984 (6)	3903 (8)	7547 (4)	56 (2)
C(10)	5425 (6)	2912 (8)	7801 (4)	54 (2)
C(11)	4968 (5)	5642 (8)	7111 (4)	46 (2)
C(12)	3880 (6)	5412 (9)	7158 (4)	57 (2)
C(13)	2187 (5)	4833 (7)	6432 (3)	33 (2)
C(14)	1679 (6)	6020 (8)	6742 (4)	53 (2)

Table 2 (cont.)

	x	y	z	$U_{\text{eq}}$ or $U_{\text{iso}}$
C(15)	2042 (5)	3454 (8)	6777 (4)	49 (2)
C(16)	1706 (5)	4798 (8)	5678 (3)	43 (2)
C(17)	1970 (5)	3624 (7)	5251 (3)	39 (2)
C(18)	1133 (5)	3096 (9)	4713 (4)	62 (6)*
C(19)	4765 (4)	5724 (7)	5041 (3)	28 (2)
O(1)	4266 (3)	5795 (5)	5488 (2)	36 (1)
O(2)	4903 (3)	6715 (4)	4663 (2)	32 (1)
O(3)	1915 (4)	-872 (6)	1205 (3)	81 (4)*
Cl	3876 (2)	2153 (3)	1075 (1)	70 (2)*
O(11)	2941 (6)	1618 (8)	714 (4)	126 (7)*
O(12)	4366 (7)	1259 (13)	1539 (5)	204 (10)*
O(13)	4431 (7)	2316 (15)	611 (5)	209 (11)*
O(14)	3670 (8)	3345 (15)	1342 (6)	259 (12)*

\*  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ .  
 † Disordered. Occupancy 0.5.

### Description and discussion

(I) crystallizes as the simple perchlorate salt. The structure confirms that the condensation reaction has produced the predicted [16]macrocycle with a considerably twisted seven-membered bis-diazine chelate ring. The  $[\text{Ni}(L2)]^{2+}$  cation contains an approximately square-planar coordinated metal ion with no suggestions of axial interactions with adjacent cations or anions (all distances  $> 3.5 \text{ \AA}$ ). An approximate (non-crystallographic) twofold axis bisects the C(1)–C(3) and C(11)–C(12) bonds and passes through Ni. The macrocycle is *N-rac* (*i.e.* the amine N atoms have the same chirality). The Ni–N distances are equal within experimental error [mean  $1.907(2) \text{ \AA}$ ]. As with the complexes of the parent dihydrazone (Davis *et al.*, 1982), there is no differentiation between Ni–N(imine) and Ni–N(amine) bond lengths. The four coordinating N atoms show a tetrahedral distortion from ideal square-planar geometry, alternating above and below the least-squares plane defined by these atoms plus Ni by about  $0.26 \text{ \AA}$ . A similar tetrahedral distortion (displacements of  $\pm \sim 0.30 \text{ \AA}$ ) is also observed for the four-coordinated  $\text{Cu}^{\text{II}}$  complex of  $\text{Me}_4\text{C}_6\text{H}_{10}[15]$ diene  $\text{N}_4(\text{N}_2)$  (Curtis, de Courcey & Waters, 1979). It should be noted that the N electron lone pairs would be closer to in-plane than their respective N atoms in both the Cu complex and (I).

In (II) the Ni atom has an irregular octahedral environment. Two adjacent sites are occupied by O atoms of an edge-on bonded oxalate group which forms a five- rather than a four-membered chelate ring with the Ni atom. The other edge of the oxalate is bonded to a further Ni(L2) moiety to form a dimer, the two halves of the dimer being related by a crystallographic centre of symmetry situated half-way between the C atoms of the oxalate group. The four remaining (non-planar) sites about the Ni atom are occupied by the ligating N

Table 3. Selected interatomic distances (Å) and angles (°)

	(I)	(II)		(I)	(II)
Ni—N(1)	1.904 (5)	2.131 (6)	Ni—N(4)	1.911 (5)	2.072 (5)
Ni—N(2)	1.906 (5)	2.094 (5)	Ni—N(3)	1.908 (5)	2.109 (5)
Ni—O(1)		2.120 (4)	Ni—O(2 <sup>i</sup> )		2.089 (4)
C(2)—C(1)	1.476 (9)	1.532 (10)	C(4)—C(3)	1.505 (8)	1.478 (10)
C(1)—N(5)	1.248 (8)	1.259 (8)	C(3)—N(6)	1.278 (8)	1.273 (8)
N(5)—N(1)	1.437 (6)	1.429 (7)	N(6)—N(4)	1.438 (7)	1.410 (7)
N(1)—C(5)	1.272 (7)	1.295 (8)	N(4)—C(17)	1.289 (7)	1.277 (8)
C(5)—C(6)	1.492 (9)	1.495 (10)	C(17)—C(18)	1.485 (8)	1.492 (9)
C(5)—C(7)	1.500 (9)	1.488 (10)	C(17)—C(16)	1.466 (8)	1.499 (9)
C(7)—C(8)	1.512 (9)	1.534 (9)	C(16)—C(13)	1.532 (8)	1.541 (9)
C(8)—C(9)	1.538 (10)	1.547 (10)	C(13)—C(14)	1.534 (9)	1.521 (10)
C(8)—C(10)	1.514 (9)	1.519 (10)	C(13)—C(15)	1.525 (8)	1.510 (9)
C(8)—N(2)	1.496 (8)	1.510 (8)	C(13)—N(3)	1.517 (8)	1.499 (8)
N(2)—C(11)	1.489 (7)	1.470 (8)	N(3)—C(12)	1.486 (8)	1.471 (9)
C(11)—C(12)	1.493 (10)	1.523 (10)	C(1)—C(3)	1.500 (9)	1.465 (9)
O(1)—C(19)		1.253 (7)	O(2)—C(19)		1.251 (7)
C(19)—C(19 <sup>h</sup> )		1.531 (12)			
Cl—O(11)	1.400 (7)	1.422 (7)	Cl(2)—O(21)	1.441 (10)	
Cl—O(12)	1.379 (11)	1.336 (8)	Cl(2)—O(22)	1.42, 1.43 (2)*	
Cl—O(13)	1.345 (7)	1.343 (9)	Cl(2)—O(23)	1.45, 1.37 (2)*	
Cl—O(14)	1.414 (10)	1.304 (10)	Cl(2)—O(24)	1.40, 1.47 (2)*	
N(1)—Ni—N(2)	90.8 (2)	90.6 (2)	N(3)—Ni—N(4)	91.2 (2)	89.2 (2)
N(1)—Ni—N(3)	164.9 (2)	112.3 (2)	N(2)—Ni—N(4)	162.8 (3)	170.4 (2)
N(1)—Ni—N(4)	94.2 (2)	85.6 (2)	N(2)—Ni—N(3)	88.1 (2)	84.0 (2)
N(1)—Ni—O(1)		166.8 (2)	N(4)—Ni—O(1)		94.4 (2)
N(1)—Ni—O(2 <sup>i</sup> )		88.2 (2)	N(4)—Ni—O(2 <sup>i</sup> )		93.5 (2)
N(2)—Ni—O(1)		91.3 (2)	N(3)—Ni—O(1)		80.9 (2)
N(2)—Ni—O(2 <sup>i</sup> )		95.2 (2)	N(3)—Ni—O(2 <sup>i</sup> )		159.4 (2)
O(1)—Ni—O(2 <sup>i</sup> )		78.6 (2)			
Ni—N(1)—N(5)	112.9 (3)	123.6 (4)	Ni—N(4)—N(6)	113.8 (4)	111.7 (4)
Ni—N(1)—C(5)	130.1 (5)	122.3 (5)	Ni—N(4)—C(17)	128.8 (4)	130.5 (5)
N(5)—N(1)—C(5)	115.5 (5)	113.8 (5)	N(6)—N(4)—C(17)	114.9 (5)	117.7 (5)
Ni—N(2)—C(8)	110.4 (4)	120.7 (4)	Ni—N(3)—C(13)	109.9 (3)	122.2 (4)
Ni—N(2)—C(11)	107.9 (4)	106.5 (4)	Ni—N(3)—C(12)	108.0 (4)	107.6 (4)
C(8)—N(2)—C(11)	115.5 (5)	115.8 (5)	C(13)—N(3)—C(12)	115.8 (5)	116.4 (5)
C(1)—N(5)—N(1)	116.0 (6)	114.9 (6)	C(3)—N(6)—N(4)	114.2 (6)	115.2 (5)
Ni—O(1)—C(19)		113.9 (4)	Ni—O(2 <sup>i</sup> )—C(19 <sup>h</sup> )		113.5 (4)
C(3)—C(1)—N(5)	121.8 (7)	128.1 (7)	C(1)—C(3)—N(6)	124.0 (5)	122.3 (6)
C(2)—C(1)—C(3)	117.0 (6)	116.1 (6)	C(1)—C(3)—C(4)	117.6 (6)	118.5 (7)
N(5)—C(1)—C(2)	121.2 (6)	115.8 (7)	N(6)—C(3)—C(4)	118.3 (7)	119.1 (6)
N(1)—C(5)—C(7)	120.9 (6)	119.5 (6)	N(4)—C(17)—C(16)	121.9 (6)	120.8 (6)
N(1)—C(5)—C(6)	122.6 (6)	122.3 (6)	N(4)—C(17)—C(18)	122.2 (6)	123.3 (6)
C(6)—C(5)—C(7)	116.4 (6)	118.2 (6)	C(18)—C(17)—C(16)	115.7 (5)	115.7 (6)
C(5)—C(7)—C(8)	120.1 (5)	113.5 (6)	C(13)—C(16)—C(17)	120.3 (5)	119.7 (6)
C(7)—C(8)—N(2)	108.8 (6)	106.8 (5)	C(16)—C(13)—N(3)	107.1 (5)	106.2 (5)
C(7)—C(8)—C(9)	110.0 (6)	109.1 (6)	C(16)—C(13)—C(14)	111.1 (5)	107.3 (5)
C(7)—C(8)—C(10)	108.8 (6)	110.7 (6)	C(16)—C(13)—C(15)	108.7 (5)	112.2 (6)
N(2)—C(8)—C(9)	108.4 (5)	109.8 (5)	N(3)—C(13)—C(14)	109.4 (5)	112.3 (5)
N(2)—C(8)—C(10)	111.5 (6)	112.6 (5)	N(3)—C(13)—C(15)	110.8 (5)	110.1 (5)
C(9)—C(8)—C(10)	109.3 (6)	107.8 (6)	C(14)—C(13)—C(15)	109.8 (6)	108.6 (5)
N(2)—C(11)—C(12)	106.9 (5)	110.9 (6)	N(3)—C(12)—C(11)	106.1 (5)	108.8 (6)
O(1)—C(18)—C(19 <sup>h</sup> )		115.7 (7)	O(2)—C(19)—C(19 <sup>h</sup> )		118.2 (7)
O(1)—C(19)—O(2)		126.1 (6)			

The superscript (i) indicates the symmetry operation (1 - x, 1 - y, 1 - z).

\* In the disordered perchlorate, the values for orientation A are given prior to those for orientation B.

atoms of the macrocycle. To allow this the macrocycle folds across the N(2)—N(4) diagonal, resulting in angles N(1)—Ni—N(3) and N(2)—Ni—N(4) of 112.3 and 170.4 (2)°, respectively, in comparison with 164.9 and 162.8 (3)° for the same angles in the planar

macrocycle (I). The Ni—N distances range from 2.131 to 2.072 (6) Å with the longest bonds *trans* to the oxalate. All are longer in (II) than in (I) on account of the higher coordination number and different spin state, being more comparable with those found for the



[{Ru(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>]<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)](BF<sub>4</sub>)<sub>2</sub> and by Curtis *et al.* (1973) for [(Ni{NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>})<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)](NO<sub>3</sub>)<sub>2</sub>. The bond lengths within the oxalate group are normal and do not show any asymmetry arising from the unequal Ni—O distances.

The water molecule is hydrogen-bonded to O(11) [3.009 (10) Å *via* H1(O3)], N(2) [2.983 (7) Å *via* H(N2)] and N(6) [2.867 (8) Å, presumably *via* the unlocated H2(O3)] of three different molecules. A consequence of the first-mentioned contact is a reduction in the static disorder and/or the vibrational freedom of O(11), as reflected in its thermal parameters, compared with the other perchlorate O atoms. This causes the observed Cl—O distance to be longer for O(11) than for O(12–14); after application of a Busing & Levy (1964) riding-motion correction, assuming the O atoms to be riding on Cl, all four Cl—O bond lengths lie in the range 1.48 to 1.52 (1) Å.

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## Crystal Structures of Complexes Between Alkali-Metal Salts and Cyclic Polyethers.

### 12.\* The Complex between Sodium Bromide and 2,3-Dimethoxybenzo-15-crown-5 {Bromo(2,3-dimethoxy-6,7,9,10,12,13,15,16-octahydrobenzo[1,4,7,10,13]penta-oxacyclopentadecene)sodium}

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#### Abstract

C<sub>16</sub>H<sub>24</sub>BrNaO<sub>7</sub>, *M<sub>r</sub>* = 431.3, is monoclinic, *P*2<sub>1</sub>/*c*, with *a* = 12.036 (2), *b* = 8.222 (6), *c* = 20.210 (4) Å, β = 102.21 (4)°, *U* = 1954.8 Å<sup>3</sup>, *D<sub>m</sub>* = 1.432, *Z* = 4, *D<sub>c</sub>* = 1.436 Mg m<sup>-3</sup>, μ(Mo *K*α) = 2.13 mm<sup>-1</sup>. The structure was determined by the heavy-atom method and refined by full-matrix least squares to *R* = 0.069 for 1377 observed reflections from measurements on a four-circle X-ray diffractometer. There are discrete molecules consisting of

C<sub>16</sub>H<sub>24</sub>NaO<sub>7</sub><sup>+</sup>.Br<sup>-</sup> ion pairs [Na—Br 2.763 (3) Å] with the Na<sup>+</sup> ion additionally coordinated by the five O atoms of the crown-ether ring [Na—O 2.37 (1) to 2.45 (1) Å]. The *ortho*-dimethoxy groups do not take part in coordination.

#### Introduction

The crown-ether ligand 2,3-dimethoxybenzo-15-crown-5 (1*a*) differs from the parent (1*b*) in being soluble in water. It was synthesized as part of a general study of complexing agents for *d*<sup>0</sup> cations with controlled changes in physical properties and it forms complexes with alkali-metal salts. With sodium iodide

\* Part 11: Owen (1980).

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