CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1976). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MENTZEN, B. F., PUAUX, J. P. & SAUTEREAU, H. (1978). *Acta Cryst.* B**34**, 1846–1849.
NAHRINGBAUER, I. (1978). *Acta Cryst.* B**34**, 315–318.
NISHIGAKI, S., YOSHIOKA, H. & NAKATSU, K. (1978). *Acta Cryst.* B**34**, 875–879.
SIMMONS, C. J., LUNDEEN, M. & SEFF, K. (1978). *Inorg. Chem.* **17**, 1429–1435.
SIMMONS, C. J., SEFF, K., CLIFFORD, F. & HATHAWAY, B. J. (1983). *Acta Cryst.* C**39**, 1360–1367.
STEWART, J. M. (1976). Editor. The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1983). C**39**, 1646–1648

The Structure of (4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.5]tricosane-$N,N',O^4,O^{13},O^{16},O^{21}$)nickel(II) Nitrate, $[Ni(C_{16}H_{32}N_2O_5)].(NO_3)_2$

BY S. B. LARSON, J. N. RAMSDEN, S. H. SIMONSEN AND J. J. LAGOWSKI

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, *USA*

(*Received* 2 *June* 1983; *accepted* 30 *August* 1983)

Abstract. $M_r = 515{\cdot}16$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}374\,(2)$, $b = 13{\cdot}862\,(2)$, $c = 16{\cdot}442\,(2)$ Å, $V = 2136{\cdot}8\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}601$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}79$ cm^{-1}, $F(000) = 1088$, 163 K, $R = 0{\cdot}042$ for 2139 ($I \geq 3\sigma_I$) of 3533 unique reflections. The Ni^{2+} ion resides inside the cryptand cavity but is coordinated to only six of the seven potential donor atoms. The Ni—O distances are 2·054 (4), 2·072 (3), 2·093 (3) and 2·106 (4) Å. The Ni—N distances are 2·114 (4) and 2·180 (5) Å. The nitrate ions are not bound to the nickel.

Introduction. Diazapolyoxamacrobicyclic ligands (a type of cryptand) have been shown by X-ray crystallography to encapsulate transition-metal ions in only four cases (Mathieu & Weiss, 1973; Hart, Hursthouse, Malik & Moorhouse, 1978; Ciampolini, Dapporto & Nardi, 1979; Burns, 1979) although there is considerable evidence for complexation in solution (for example, Arnaud-Neu, Spiess & Schwing-Weill, 1977; Cox, Firman & Schneider, 1982). The cavity of the cryptand *C*221 is approximately the correct size to accommodate divalent first-row transition-metal ions inside the cavity without gross distortion. Therefore, as part of our survey of the binding of polyether ligands to first-row transition-metal ions, we prepared the complex Ni(*C*221)$(NO_3)_2$ for which a single-crystal X-ray diffraction study is presented.

Experimental. Prepared by addition of cryptand *C*221 to a solution of $Ni(EtOH)_6(NO_3)_2$ in a mixture of ethanol and triethyl orthoformate; yellowish brown crystalline blocks formed, sensitive to atmospheric moisture. Single crystal mounted in Lindemann capillary; details of data collection and structure refinement appear in Table 1; systematic absences $h00$, h odd; $0k0$, k odd; $00l$, l odd; data corrected for Lorentz and polarization effects, absorption and decay. Ni atom located by Patterson methods. *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) gave same Ni position but also two sets of peaks related by a mirror plane. Ni-phased heavy-atom map produced a similarly mirrored set of peaks attributed to the presence of both enantiomorphs. Location of remaining non-hydrogen atoms required careful selection of peaks from several subsequent difference maps so as to enhance only one enantiomorph. Hydrogen atoms located in a difference map as peaks of 0·3–0·6 e Å^{-3}, but idealized positions [d(C—H) = 1·0 Å] used in model with U fixed at 0·038 Å^2; non-hydrogen positions and anisotropic thermal parameters refined, $R = 0{\cdot}0423$.* Refinement of enantiomorph gave $R = 0{\cdot}051$; Hamilton's test (Hamilton, 1965) suggests that this configuration can be rejected at the 99·5% confidence level; hydrogen scattering factors from Stewart, Davidson & Simpson (1965); other scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Principal computer programs given by Riley & Davis (1976); parameter and geometry tables generated by *FUER* by S. B. Larson.

---

* Lists of anisotropic thermal parameters, H-atom calculated positions, miscellaneous interatomic distances, least-squares planes and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38784 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/121646-03$01.50

Table 1. *Summary of data collection and structure refinement for* $\mathrm{Ni}(C221)(\mathrm{NO_3})_2$

A. Data collection (163 K)*†	
Mode	ω scan
Scan range	Symmetrically over 1·2° about $K\alpha_{1,2}$ maximum
Background	Offset 1·0 and −1·0° in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min^{-1})	3·0–6·0
Exposure time (h)	52·6
Stability analysis†	
Computed *s*, *t*	0·000124, −0·000003
Max. correction (on *I*)(%)	0·2
2θ range (°)	4·0–60·0
Range in *hkl*, min.	000
max.	13,19,23
Total reflections measured	3533
Data crystal dimensions (mm)	0·45 × 0·32 × 0·22
Data crystal volume (mm^3)	0·0296
Data crystal faces	$(0\bar{1}\bar{1})$,(011),(012),(100),$(\bar{1}00)$, and fragmentary faces
Transmission factor range	0·662–0·806
B. Structure refinement‡	
Ignorance factor *p*	0·04
Reflections used, $I \geq 3{\cdot}0\,\sigma_I$	2139
Number of variables	289
Goodness of fit	1·189
R, R_w	0·0423, 0·0427
R for all data	0·0899
Max. shift/e.s.d. (non-H)	0·02
Max. peak in $\Delta\rho$ map (e Å^{-3})	0·47 [near nitrate(2)]
Min. density in $\Delta\rho$ map (e Å^{-3})	−0·33

* Unit-cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with $25 < 2\theta < 29°$.

† Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of 4 check reflections after every 96 reflections. These data were analyzed as detailed in Henslee & Davis (1975).

‡ Function minimized was $\sum w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$.

Table 2. *Positional parameters in fractional coordinates and* $U_{\rm eq}$ *for non-hydrogen atoms in* $\mathrm{Ni}(C221)(\mathrm{NO_3})_2$

$U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct-space unit-cell vectors.

	x	*y*	*z*	$U_{\rm eq}$(Å^2)
$\mathrm{Ni^{2+}}$	−0·00920 (7)	−0·04278 (4)	0·06283 (4)	0·01992 (15)
N(1)	0·1484 (4)	0·0586 (3)	0·0967 (3)	0·0253 (14)
C(2)	0·0727 (6)	0·1452 (4)	0·1261 (3)	0·029 (2)
C(3)	−0·0447 (5)	0·1732 (3)	0·0669 (4)	0·027 (2)
O(4)	−0·1155 (3)	0·0860 (2)	0·0422 (2)	0·0222 (10)
C(5)	−0·2573 (5)	0·0999 (4)	0·0073 (3)	0·024 (2)
C(6)	−0·3661 (6)	0·1228 (4)	0·0711 (4)	0·033 (2)
O(7)	−0·3831 (4)	0·0466 (3)	0·1279 (2)	0·0344 (12)
C(8)	0·2837 (6)	0·0464 (5)	0·1929 (3)	0·033 (2)
C(9)	0·2299 (6)	−0·0539 (4)	0·2135 (3)	0·033 (2)
N(10)	−0·1620 (5)	−0·1101 (4)	0·1451 (3)	0·0254 (14)
C(11)	−0·2797 (6)	−0·1508 (4)	0·0942 (3)	0·032 (2)
C(12)	−0·2227 (6)	−0·1945 (4)	0·0164 (4)	0·034 (2)
O(13)	0·1330 (4)	0·1199 (3)	−0·0172 (2)	0·0273 (12)
C(14)	−0·0638 (7)	0·1469 (4)	−0·0914 (3)	0·035 (2)
C(15)	0·0184 (7)	−0·0593 (4)	−0·1162 (3)	0·040 (2)
O(16)	0·1031 (4)	−0·0325 (3)	−0·0469 (2)	0·0290 (11)
C(17)	0·1662 (6)	0·0629 (4)	0·0550 (4)	0·035 (2)
C(18)	0·2396 (6)	0·0817 (5)	0·0240 (4)	0·030 (2)
C(19)	0·2397 (6)	0·0149 (4)	0·1612 (3)	0·032 (2)
C(20)	0·2668 (6)	0·0891 (4)	0·1368 (3)	0·032 (2)
O(21)	0·1308 (4)	0·1368 (3)	0·1241 (2)	0·0281 (12)
C(22)	0·0684 (7)	−0·1671 (4)	0·2013 (4)	0·036 (2)
C(23)	0·0834 (7)	0·1929 (4)	0·1810 (4)	0·033 (2)
N(*N*1)	0·4569 (5)	0·2592 (3)	0·1994 (3)	0·032 (2)
O(*N*1)*A*	0·4012 (5)	0·2826 (3)	0·1341 (2)	0·0441 (15)
O(*N*1)*B*	0·5794 (5)	0·2858 (4)	0·2159 (3)	0·066 (2)
O(*N*1)*C*	0·3908 (6)	0·2061 (3)	0·2471 (3)	0·057 (2)
N(*N*2)	−0·0032 (6)	0·0480 (4)	0·3858 (3)	0·043 (2)
O(*N*2)*A*	0·0080 (5)	0·0420 (4)	0·3792 (3)	0·062 (2)
O(*N*2)*B*	0·0232 (5)	0·0872 (3)	0·4508 (2)	0·051 (2)
O(*N*2)*C*	0·0487 (10)	0·0942 (4)	0·3291 (3)	0·140 (4)

Table 3. $\mathrm{Ni^{2+}}$ *to cryptand distances* (Å) *and angles* (°) *about* $\mathrm{Ni^{2+}}$

1	2	3	1–2	∠1–2–3
N(1)	$\mathrm{Ni^{2+}}$	O(4)	2·114 (4)	78·8 (2)
N(1)	$\mathrm{Ni^{2+}}$	N(10)		125·5 (2)
N(1)	$\mathrm{Ni^{2+}}$	0(13)		155·4 (2)
N(1)	$\mathrm{Ni^{2+}}$	O(16)		80·23 (15)
O(4)	$\mathrm{Ni^{2+}}$	N(10)	2·072 (3)	98·9 (2)
O(4)	$\mathrm{Ni^{2+}}$	O(13)		94·10 (14)
O(4)	$\mathrm{Ni^{2+}}$	O(16)		92·43 (14)
O(4)	$\mathrm{Ni^{2+}}$	O(21)		155·65 (14)
N(10)	$\mathrm{Ni^{2+}}$	O(13)	2·180 (5)	78·7 (2)
N(10)	$\mathrm{Ni^{2+}}$	O(16)		153·4 (2)
N(10)	$\mathrm{Ni^{2+}}$	O(21)		81·2 (2)
O(13)	$\mathrm{Ni^{2+}}$	O(16)	2·054 (4)	76·55 (14)
O(13)	$\mathrm{Ni^{2+}}$	O(21)		109·7 (2)
O(16)	$\mathrm{Ni^{2+}}$	O(21)	2·093 (3)	98·10 (14)
O(21)	$\mathrm{Ni^{2+}}$	N(1)	2·106 (4)	81·4 (2)

Table 4. *Distances* (Å), *angles* (°) *and torsion angles* (°) *in cryptand*

1	2	3	4	1–2	∠1–2–3	∠1–2–3–4
N(1)	C(2)	C(3)	O(4)	1·476 (7)	110·2 (4)	42·7 (6)
C(2)	C(3)	O(4)	C(5)	1·520 (8)	107·4 (4)	161·0 (4)
C(3)	O(4)	C(5)	C(6)	1·438 (6)	114·8 (4)	−75·1 (5)
O(4)	C(5)	C(6)	O(7)	1·461 (6)	111·9 (4)	−62·5 (6)
C(5)	C(6)	O(7)	C(8)	1·497 (8)	112·3 (4)	84·5 (6)
C(6)	O(7)	C(8)	C(9)	1·419 (7)	115·1 (4)	−138·7 (5)
O(7)	C(8)	C(9)	N(10)	1·418 (7)	112·9 (5)	56·3 (6)
C(8)	C(9)	N(10)	C(11)	1·517 (9)	116·5 (4)	−79·3 (6)
C(9)	N(10)	C(11)	C(12)	1·510 (7)	107·5 (4)	170·7 (4)
N(10)	C(11)	C(12)	O(13)	1·494 (7)	111·3 (5)	−50·5 (6)
C(11)	C(12)	O(13)	C(14)	1·513 (8)	104·0 (4)	178·5 (4)
C(12)	O(13)	C(14)	C(15)	1·443 (7)	113·7 (4)	178·3 (4)
O(13)	C(14)	C(15)	O(16)	1·432 (7)	104·6 (4)	52·7 (6)
C(14)	C(15)	O(16)	C(17)	1·495 (9)	106·2 (4)	−167·7 (4)
C(15)	O(16)	C(17)	C(18)	1·438 (6)	112·7 (4)	175·6 (4)
O(16)	C(17)	C(18)	N(1)	1·455 (7)	105·4 (5)	−47·2 (6)
C(17)	C(18)	N(1)	C(19)	1·493 (8)	113·1 (4)	141·9 (5)
C(18)	N(1)	C(19)	C(20)	1·504 (7)	109·0 (4)	−77·2 (5)
N(1)	C(19)	C(20)	O(21)	1·492 (7)	107·1 (4)	−55·2 (5)
C(19)	C(20)	O(21)	C(22)	1·518 (8)	108·8 (5)	−80·9 (5)
C(20)	O(21)	C(22)	C(23)	1·452 (7)	110·9 (4)	167·0 (4)
O(21)	C(22)	C(23)	N(10)	1·460 (7)	104·7 (5)	−58·9 (6)
C(22)	C(23)	N(10)	C(11)	1·505 (9)	112·0 (5)	154·7 (5)
C(23)	N(10)	C(11)	C(12)	1·486 (8)	107·3 (4)	−73·2 (5)
C(22)	C(23)	N(10)	C(9)			89·6 (6)
C(23)	N(10)	C(9)	C(8)		108·1 (4)	165·2 (5)
C(17)	C(18)	N(1)	C(2)			−94·3 (6)
C(18)	N(1)	C(2)	C(3)		111·2 (4)	71·5 (5)
C(2)	N(1)	C(19)	C(20)		111·9 (4)	159·4 (4)
C(3)	C(2)	N(1)	C(19)			−166·3 (4)

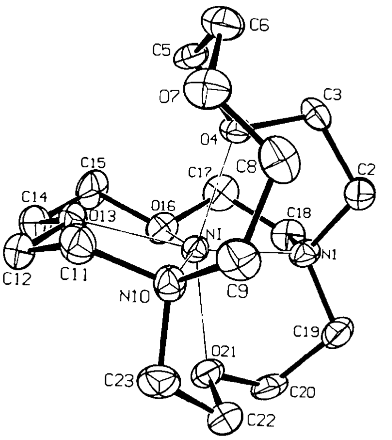

Fig. 1. View of $\mathrm{Ni}(C221)^{2+}$ illustrating atom labeling and the highly distorted octahedral coordination.

Discussion. Atomic parameters are in Table 2, distances, angles and torsion angles in Tables 3 and 4 and atom numbering in Fig. 1. The nickel ion lies in the cavity of the cryptand, as was found in the case of $[Co(C221)][Co(NCS)_4]$ (Mathieu & Weiss, 1973). In the case of nickel, however, only six of the seven available macrobicyclic donor atoms are bonded, giving rise to a distorted octahedral coordination around the cryptated ion. The nitrate ions do not enter the nickel coordination sphere.

The coordination of the nickel can best be described by dividing the donor atoms into two meridional sets consisting of O(21), N(1), O(4) and N(10), O(13), O(16). Each set is in a continguous section of the ligand and the central nickel to ligand bond in each set bisects the angle between the two other bonds of the set. The angle between the planes defined by the donor atoms of each set is 102·5 (1·4)°. There is no obvious pattern in the bond lengths other than that the Ni—N bonds [average 2·147 (5) Å] are longer than the Ni—O bonds [average 2·081 (4) Å]. The lone pairs of the unbound O(7) point out of the cryptand cavity and clearly do not interact with Ni^{2+} [Ni···O(7) = 3·868 (4) Å]. The N atoms are unexpectedly *cis* to one another in the nickel coordination sphere. This is possible because the monocycle containing N(1), O(21), N(10), O(7), O(4) is folded along the O(21)—Ni—O(4) axis and O(7) is not coordinated.

The difference in coordination number of the nickel and cobalt complexes with *C*221, despite their almost identical size (ionic radii in octahedral coordination are 0·69 and 0·72 Å, respectively), may reflect the tendency of divalent nickel to attain pseudo-octahedral coordination in situations where cobalt is seven coordinate (Drew, Nelson & Nelson, 1981; Cairns, McFall, Nelson & Drew, 1979; Nelson, Esho, Drew & Bird, 1979). This has been related to crystal-field effects. However, owing to the irregular coordination environment in the title complex, this argument is very tentative here.

Although the differences are small, it is striking that the C—O distances to the unbound O(7) [1·419 (7), 1·418 (7) Å] are shorter than those of the bound O atoms [average 1·447 (11), shortest 1·432 (7) Å]. We observed a very similar grouping of distances in the equally well resolved structure of $[Ni(18\text{-crown-}6)(EtOH)_3][PF_6]_2$ in which the C—O distances for three bound ether O atoms average 1·448 (2) Å and those for the three unbound ether O atoms average 1·426 (4) Å (Lagowski, Larson, Ramsden & Simonsen, 1983).

We are grateful to the Robert A. Welch Foundation for its support (SBL and SHS grant F-017 and JNR and JJL grant F-081). We express our appreciation to the National Science Foundation for supporting a portion of this investigation and to the Science Research Council (JNR) for a Fellowship.

References

Arnaud-Neu, F., Spiess, B. & Schwing-Weill, M. J. (1977). *Helv. Chim. Acta*, **60**, 2633–2643.

Burns, J. H. (1979). *Inorg. Chem.* **18**, 3044–3047.

Cairns, C., McFall, S. G., Nelson, S. M. & Drew, M. G. B. (1979). *J. Chem. Soc. Dalton Trans.* pp. 446–453.

Ciampolini, M., Dapporto, P. & Nardi, N. (1979). *J. Chem. Soc. Dalton Trans.* pp. 974–977.

Cox, B. G., Firman, P. & Schneider, H. (1982). *Inorg. Chem.* **21**, 2320–2323.

Drew, M. G. B., Nelson, J. & Nelson, S. M. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1691–1696.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Hart, F. A., Hursthouse, M. B., Malik, K. M. A. & Moorhouse, S. (1978). *J. Chem. Soc. Chem. Commun.* pp. 549–550.

Henslee, W. H. & Davis, R. E. (1975). *Acta Cryst.* B**31**, 1511–1519.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–79, 149–150. Birmingham: Kynoch Press.

Lagowski, J. J., Larson, S. B., Ramsden, J. N. & Simonsen, S. H. (1983). Submitted to *Inorg. Chem.*

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mathieu, F. & Weiss, R. (1973). *J. Chem. Soc. Chem. Commun.* p. 816.

Nelson, S. M., Esho, F. S., Drew, M. G. B. & Bird, P. (1979). *J. Chem. Soc. Chem. Commun.* pp. 1035–1037.

Riley, P. E. & Davis, R. E. (1976). *Acta Cryst.* B**32**, 381–386.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.