Par contre, la géométrie obtenue pour l'alaninate de cadmium est très proche de celle observé dans le di-α-aminoisobutyrate de nickel tétrahydraté (Noguchi, 1962).

La molécule d'eau O(7), non seulement participe à la coordination du cadmium, mais contribue également à la cohésion du cristal en reliant entre elles trois molécules (L-α-Ala)$_2$Cd.2H$_2$O (Fig. 1) par l'intermédiaire de deux liaisons hydrogène échangées avec des atomes d'oxygène carboxylique; il est remarquable que les atomes d'hydrogène de la molécule d'eau O(7)H$_2$ sont pratiquement sur ces liaisons puisque l'angle $O(6^{vi})_{100}$—O(7)—$O(5)_{\bar{1}\bar{1}0}$ vaut 106,4(4)°. Une liaison hydrogène plus faible entre l'azote de la fonction amine et un oxygène carboxylique [N(1)—$O(6)_{\bar{1}\bar{1}0}$ = 3,178 (7) Å] vient renforcer cette cohésion. Cet assemblage conduit à la formation de feuillets parallèles au plan (001) équidistants de $z = \frac{1}{3}$. Ces plans (001) sont les plans de clivage des monocristaux. La cohésion entre ces feuillets est assurée par les molécules d'eau O(8)H$_2$ dont le rôle est également double: elles échangent des liaisons hydrogène (*a*) avec deux atomes d'oxygène O(6) [$O(8^{ii})_{10\bar{1}}$—O(6) = $O(8^{ii})_{10\bar{1}}$—$O(6^{v})_{210}$ = 2,766 (8) Å (Fig. 2)] en utilisant les atomes d'hydrogène de la molécule d'eau [O(6)—$O(8^{ii})_{10\bar{1}}$—$O(6^{v})_{210}$ = 105,9 (4)°]; et (*b*) avec deux atomes d'azote N(1) [$O(8^{ii})_{10\bar{1}}$—N(1) = $O(8^{ii})_{10\bar{1}}$—$N(1^{v})_{100}$ = 3,092 (9) Å]. Un atome d'azote échange donc deux liaisons hydrogène, l'une intrafeuillet et l'autre interfeuillet, les atomes d'hydrogène de la fonction amine sont vraisemblablement très proches de ces liaisons, en effet: $O(8^{ii})_{00\bar{1}}$—N(1)—$O(6)_{\bar{1}\bar{1}0}$ = 112,1(4)°, de plus C(2)—N(1)—$O(6)_{\bar{1}\bar{1}0}$ = 114,2(6)° et C(2)—N(1)—$O(8^{ii})_{00\bar{1}}$ = 95,9 (6)°. L'alaninate de cadmium contient donc deux types de molécules d'eau qui remplissent un rôle totalement différent; il est remarquable que, dans ces conditions, le départ des deux types de molécules ne puisse être discerné par analyse thermogravimétrique et par analyse thermique différentielle (Démaret & Mercier, 1983).

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Bicyclic Nickel(II) Cyclidene Complexes Bridged by Cyclohexane and Bis(phenoxy)butane Groups

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(*Received* 8 *April* 1987; *accepted* 23 *June* 1987)

Abstract. Complex (1): (2,12,14,20-tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,12,14,19,21,26-hexaene-κ^4N)nickel(II) hexafluorophosphate; nickel[*cis*-1,3-bis(methylene)cyclohexane-[16]cyclidene-N$_4$] hexafluorophosphate; [Ni(C$_{26}$H$_{42}$N$_6$)]$^{2+}$.2[PF$_6$]$^-$, M_r = 787·3, orthorhombic, *Pnma*, a = 16·752 (2), b = 11·258 (2), c = 17·604 (3) Å, U = 3320 (1) Å^3, Z = 4, D_x = 1·57, D_m = 1·57 (1) g cm^{-3},

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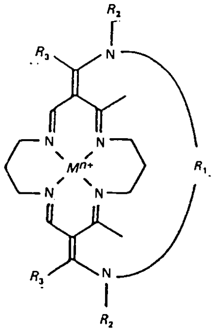
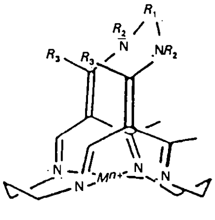
$\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 7{\cdot}75$ cm^{-1}, $F(000) = 1624$, $T = 293$ K, $R = 0{\cdot}082$ for 1958 observed $[I/\sigma(I) \geq 2{\cdot}5]$ reflections. Complex (2): (2,3,22,23,25,31-hexamethyl-10,15-dioxa-3,22,26,30,33,37-hexaazatetracyclo[22.7.7.1^{5,9}.1^{16,20}]tetraconta-1,5,7,9 (39),16,18,20(40),23,25,30,32,37-dodecaene-κ^4N)nickel(II) hexafluorophosphate; nickel[1,4-butanebis(phenoxy-3-methylene)[16]cyclidene-N_4] hexafluorophosphate; $[Ni(C_{38}H_{52}N_6O_2)]^{2+}.2[PF_6]^-.0{\cdot}5(C_2H_3N)$, $M_r = 994{\cdot}02$, orthorhombic, $Pn2_1a$, $a = 18{\cdot}529$ (6), $b = 22{\cdot}631$ (11), $c = 11{\cdot}049$ (2) Å, $U = 4633$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}42$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}7$ cm^{-1}, $F(000) = 2060$, $T = 290$ K, $R = 0{\cdot}104$ for 1251 unique observed $[I/\sigma(I) \geq 3{\cdot}0]$ reflections. For (1) the synthesis of both *cis*- and *trans*-isomers of the cyclohexyl bridging groups is reported; crystal structure analysis of the *cis*-isomer shows it to adopt the 'lid-on' geometry. For (2), the butylbisphenoxy bridging group approaches the 'lid-on' geometry, but with a very much wider cavity than for (1).

Introduction. A family of totally synthetic lacunar cyclidene complexes (structures 3*a* and 3*b*) has been developed to model certain features of the active-site environments of such heme proteins as hemoglobin and the monoxygenase metalloenzymes, *e.g.* cytochromes p-450 (Busch, 1980).



(3*a*)



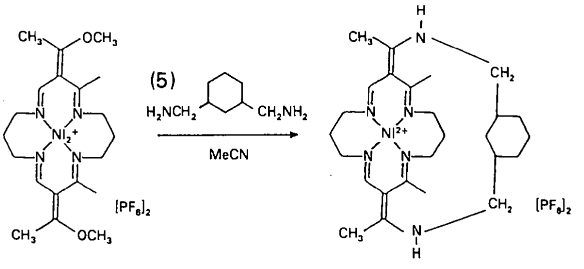
(3*b*)

(1) $R_1 = -CH_2C_6H_8CH_2-$ $R_2 = H; R_3 = CH_3$

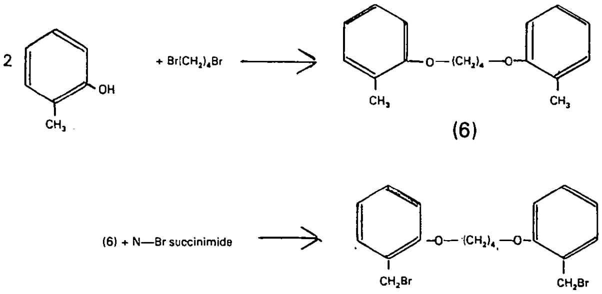
(2) $R_1 = -CH_2C_6H_4O(CH_2)_4OC_6H_4CH_2-$ $R_2 = R_3 = CH_3$

These complexes contain bulky bridges, designed to provide hydrophobic cavities that will protect bound O_2 or, for the larger cavities, bind organic substrates by guest–host interactions. Following earlier studies of *m*-xylene bridges [(3), $R_3 = -CH_2C_6H_4CH_2-$] the complex (1) containing a cyclohexyl bridge was synthesized; it was hoped that the saturated ring might reduce the susceptibility to autoxidation in oxygen adducts of the complex containing Fe^{II}. It should also increase the hydrophobic character of the cavity. Similarly, in an effort to increase the binding constants of aromatic guest molecules, complexes containing phenyl ether groups in the bridge have been prepared. (2) is typical of these. We report the structural characterization by X-ray methods of (1) and (2).

Experimental. Complex (1) was prepared according to Scheme 1, starting from (4) (Schammel, Zimmer & Busch, 1980). For complex (2), the preparative route was similar, but the final ring closure involved the condensation of a dibromide (Scheme 2) with an aminocyclidene. Full preparative details are included in the supplementary material.*



Scheme 1



Scheme 2

Experimental details for the crystal structure analyses are in Table 1. Both (1) and (2) showed weak diffraction, especially above 35–40° (2θ). For (2), data were collected from two separate crystals, in the second case including two octants, to examine any departures from orthorhombic symmetry (which was finally accepted). Scan speeds were chosen according to the intensity of a 2s pre-scan; backgrounds were measured at each end of the scan. The density of (1) was measured by flotation. Reflections were processed using profile analysis, and those considered observed (Table 1) were used in subsequent calculations. An Lp correction was applied, but absorption effects were neglected.

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* Preparative details for (1) and (2), centrosymmetric refinement results for (2), lists of structure factors, anisotropic thermal parameters and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44177 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Data-collection details*

	(1)	(2)
Diffractometer	Syntex *P*1	Syntex $P2_1$
$2\theta_{\max}$(°)	50	45
Scan range (°) about α_1–α_2 position	−1·0 + 1·2	±1·1
Scan speed (° $\min^{-1}$)	2–24	2–29
Background time (fraction of scan)	2 × 0·5	2 × 0·25
Standards	Six every 100 refls	Three every 200 refls
Decay	None	Slight (corrected by point-to-point rescaling)
2θ range for unit-cell det.	16–29	18–20
Octants examined	$+h$ $+k$ $+l$	(*a*) $+h+k+l$ (*b*) $+h+k\pm l$
Reflections: unique	3101	3406
observed	1958	1251
[criterion $I \geq n\sigma(I)$]: *n*	2·5	3·0
Crystal dimensions (mm)	0·17 × 0·24 × 0·50	(*a*) 0·22 × 0·25 × 0·85 (*b*) 0·15 × 0·45 × 0·6
Absorption correction	None	None
Final refinement parameters	229	304
Max. on *F* map (e Å^{-3})	±0·3	±0·6
Weight scheme	$1/\sigma^2(F)$	Unity
Final *R*	0·082	0·104
Final *wR*	0·073	0·104
Max. Δ/σ	0·2	0·2
Computer	Amdahl 470/V6	Data General DG30
Programs	*XRAY*76 (Stewart, 1976)	*SHELXTL* (Sheldrick, 1983)

For both crystals, systematic absences $0kl$, $k+l\neq 2n$; $hk0$, $h\neq 2n$ indicated either space groups *Pnma*, with the molecule on a special position of *m* symmetry, or $Pn2_1a$ (a non-standard setting of $Pna2_1$). For (1) the former was assumed and gave a successful refinement, with no disorder to suggest the lower symmetry. The Ni atom was located by Patterson methods and the light atoms from successive Fourier syntheses. All non-hydrogen atoms were refined with anisotropic temperature factors. H atoms were given a fixed isotropic $U = 0{\cdot}063$ Å^2 and not refined; H-atom positions were taken from a difference Fourier synthesis, with a few included at calculated positions. Final refinement on *F* was by least-squares methods using large blocks. The relatively high final *R* is understandable in view of the weak diffraction.

For (2), initial attempts at structure solution by simple Patterson and Fourier methods with both the first and second data sets failed, then both sets were merged ($R_{\text{int}} = 0{\cdot}10$). This merging may have improved the data precision sufficiently for the structure to be solved, though this can equally be attributed to the different strategy adopted. The Patterson interpretation section of *SHELXTL* (Sheldrick, 1983) located possible Ni and P positions in space group $Pn2_1a$ and the *FIND* routine revealed parts of PF_6 groups and the macrocycle around Ni. After further refinement it became clear that the molecule conformed, at least approximately, to *Pnma*. A molecule of CH_3CN was also located, on the mirror plane. Refinement proceeded reasonably well in *Pnma* (202 parameters) but converged at $R = 0{\cdot}127$, with anisotropic temperature factors for N, Ni, P, F, O, N (except solvent). Four atoms with fractional occupancy were needed to approximate half of the $(CH_2)_4$ chain; H atoms were included in calculated positions for CH, and CH_2 groups apart from those on this chain. The structure was then transferred to $Pn2_1a$ with the addition of atoms in the symmetry-related positions, but omitting one C_6H_4O group and the $(CH_2)_4$ chain. These atoms were found from Fourier syntheses; only Ni,P,F were given anisotropic temperature factors and the C_6 rings were held rigid (304 parameters); all CH and CH_2 hydrogen atoms were included in calculated positions with a fixed isotropic $U = 0{\cdot}07$ Å^2. The refinement was damped and Ni—N distances were also loosely constrained (to 1·873 Å, the value found in the centrosymmetric refinement), to prevent alternating long and short bonds. The solvent was also constrained to lie in the pseudo-mirror plane.

The choice of a disordered centrosymmetric or ordered non-centrosymmetric refinement is always difficult, and the weak diffraction of these crystals compounded the problem. However, despite the necessity to constrain the non-centrosymmetric refinement this is strongly preferred: it shows an ordered $(CH_2)_4$ chain, and also clearly visible differences between the inclinations of the phenyl rings to the pseudo-mirror plane. Although the final *R* is poor this is understandable in view of the weak diffraction and the pseudosymmetry/disorder. No attempt was made to define the hand of the crystals chosen. Final refinement was on *F* by cascaded least-squares methods. Unit weights were deemed satisfactory from an analysis of variance.

Deposited material includes full bond lengths and angles from both refinements and the centrosymmetric coordinates; these may be more reliable for the section near to Ni, which undoubtedly conforms closely to mirror symmetry. For both (1) and (2) scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 2, and selected bond lengths in Table 3.*

Discussion. Figs. 1 and 2 show views of the two complexes from two directions. The prominent saddle shapes of the ligands are apparent, as are the cavities enclosed by this saddle and the bridging groups. The saturated portions of the macrocycle adopt the chair–boat conformation commonly observed for these complexes. The Ni atoms have almost square-planar environments [deviations from the mean N_4 planes 0·10 (2) and 0·06 (2) Å]. The Ni—N bond lengths are similar to those observed in other complexes of this type.

The bond lengths in the unsaturated chelate rings of (1) show that considerable delocalization is present, with the C(3)—C(4) and C(4)—C(5) distances almost

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* See deposition footnote.

Table 2. *Fractional atom coordinates of non-hydrogen atoms* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

(1)

	x	y	z	U_{eq}*
Ni	2522 (1)	2500	5493 (1)	47 (1)
P(1)	4563 (2)	2500	8152 (2)	62 (2)
P(2)	5100 (2)	2500	3157 (2)	61 (2)
F(11)	5437 (4)	2500	8499 (4)	101 (6)
F(12)	3706 (4)	2500	7783 (4)	101 (6)
F(13)	4300 (3)	1494 (5)	8737 (3)	108 (4)
F(14)	4835 (3)	1502 (4)	7567 (3)	89 (4)
F(21)	6040 (4)	2500	3117 (6)	123 (7)
F(22)	4188 (4)	2500	3287 (6)	130 (7)
F(23)	5058 (4)	1482 (7)	2588 (4)	172 (7)
F(24)	5172 (3)	1514 (6)	3787 (4)	141 (6)
N(1)	1734 (3)	1322 (5)	5428 (3)	49 (3)
N(2)	3282 (3)	1313 (5)	5669 (3)	47 (4)
N(3)	1583 (3)	231 (5)	7619 (3)	50 (4)
C(1)	1215 (7)	2500	4370 (6)	70 (8)
C(2)	1109 (4)	1378 (8)	4837 (4)	69 (5)
C(3)	1682 (4)	534 (6)	5961 (4)	47 (4)
C(4)	2349 (4)	341 (6)	6483 (4)	45 (4)
C(5)	3143 (4)	531 (6)	6184 (4)	48 (4)
C(6)	4100 (4)	1378 (8)	5352 (4)	59 (5)
C(7)	4509 (6)	2500	5590 (6)	70 (9)
C(8)	986 (5)	334 (7)	5997 (4)	70 (5)
C(9)	2276 (4)	35 (6)	7258 (4)	48 (5)
C(10)	2957 (5)	450 (7)	7688 (4)	67 (6)
C(11)	1507 (5)	269 (7)	8456 (4)	54 (5)
C(12)	1892 (5)	1374 (6)	8780 (4)	51 (4)
C(13)	1880 (5)	1385 (8)	9631 (4)	67 (6)
C(14)	2269 (7)	2500	9951 (7)	70 (9)
C(15)	1518 (6)	2500	8443 (5)	45 (6)

(2) (non-centrosymmetric refinement)

	x	y	z	U_{eq} or U
Ni	7487 (2)	2500	5422 (3)	105 (2)†
P(1)	6755 (5)	−962 (7)	5447 (8)	90 (4)†
F(11)	6541 (12)	−906 (17)	4100 (17)	186 (8)†
F(12)	6876 (16)	−926 (18)	6858 (16)	209 (9)†
F(13)	6049 (12)	−740 (18)	5791 (18)	185 (8)†
F(14)	7545 (14)	−1219 (14)	5100 (19)	166 (9)†
F(15)	7056 (18)	−318 (16)	5246 (25)	203 (10)†
F(16)	6453 (23)	−1554 (15)	5677 (30)	218 (10)†
P(2)	6735 (8)	5881 (9)	5451 (11)	146 (6)†
F(21)	6597 (15)	5945 (16)	4021 (17)	188 (9)†
F(12)	6904 (15)	5951 (19)	6745 (20)	224 (9)†
F(13)	5957 (15)	5594 (17)	5702 (25)	162 (9)†
F(14)	7408 (15)	6146 (20)	5085 (31)	248 (10)†
F(15)	7071 (17)	5312 (15)	5422 (28)	183 (10)†
F(16)	6460 (31)	6506 (17)	5252 (33)	252 (10)†
N(1)	6990 (17)	1968 (12)	4491 (25)	71 (9)
N(2)	7869 (24)	1988 (16)	6473 (33)	137 (13)
N(3)	5729 (15)	823 (13)	6634 (23)	66 (8)
N(4)	7070 (17)	3139 (11)	4544 (24)	62 (8)
N(5)	7868 (10)	3100 (9)	6371 (15)	15 (4)
N(6)	5516 (22)	3943 (18)	6503 (35)	136 (12)
O(1)	5200 (19)	1372 (17)	11169 (31)	158 (12)
O(2)	4897 (16)	3498 (15)	10779 (27)	131 (10)
N(001)	837 (26)	2500	7074 (43)	273 (15)
C(001)	1215 (23)	2500	6335 (38)	170 (13)
C(002)	1749 (25)	2500	5525 (42)	172 (14)
C(1)	6819 (22)	1465 (19)	4710 (36)	99 (11)
C(2)	6347 (15)	1006 (14)	4172 (23)	51 (8)
C(3)	6808 (15)	1394 (15)	6205 (25)	53 (8)
C(4)	7613 (23)	1324 (21)	6723 (33)	116 (12)
C(5)	8623 (29)	2095 (19)	6847 (42)	130 (14)
C(6)	8678 (15)	2636 (15)	7593 (25)	80 (9)

	x	y	z	U
C(7)	8655 (18)	3126 (14)	6881 (26)	54 (9)
C(8)	7460 (14)	3499 (12)	6703 (18)	25 (6)
C(9)	6858 (17)	3908 (16)	6202 (27)	68 (9)
C(10)	6717 (16)	3631 (14)	5003 (23)	50 (8)
C(11)	6469 (23)	4187 (21)	4091 (36)	116 (12)
C(12)	7147 (20)	2903 (15)	3149 (29)	96 (11)
C(13)	7455 (15)	2364 (15)	2819 (22)	70 (8)
C(14)	7046 (14)	1779 (12)	3169 (20)	40 (7)
C(15)	6490 (21)	983 (18)	6873 (32)	97 (11)
C(16)	6707 (19)	494 (17)	7736 (31)	89 (10)
C(17)	5222 (18)	1229 (17)	5956 (29)	81 (10)
C(18)	5158 (16)	348 (14)	7253 (25)	65 (9)
C(19)	4804 (13)	569 (11)	8442 (18)	108 (12)
C(20)	4091	392	8633	88 (10)
C(21)	3729	565	9681	75 (9)
C(22)	4079	916	10538	93 (11)
C(23)	4791	1093	10347	71 (9)
C(24)	5154	919	9299	108 (12)
C(25)	4883 (27)	1753 (21)	12160 (41)	134 (14)
C(26)	4803 (34)	2244 (24)	12273 (47)	184 (17)
C(27)	4703 (30)	2731 (27)	11514 (45)	198 (16)
C(28)	4364 (22)	3265 (18)	11712 (34)	109 (12)
C(29)	4612 (15)	3943 (11)	10002 (21)	104 (12)
C(30)	3997	4290	10172	94 (11)
C(31)	3817	4723	9326	137 (14)
C(32)	4251	4809	8310	199 (17)
C(33)	4865	4462	8139	105 (12)
C(34)	5045	4029	8985	111 (12)
C(35)	5440 (27)	4478 (20)	7012 (40)	168 (15)
C(36)	5318 (19)	3452 (18)	6173 (31)	93 (11)
C(37)	6340 (18)	4183 (16)	6855 (26)	66 (9)
C(38)	6716 (22)	4597 (18)	7871 (35)	109 (12)

* Average of principal U_{ij} values.

† Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

equal to C(4)—C(9), rather than having the formal single- and double-bond character indicated by the bond scheme of (3). The distances in this part of (2) are not reliable, because of the correlations caused by the pseudosymmetry; this is probably also responsible for the differences between the two sides of the molecule. The cavities in (1) and (2) are clearly defined, however, and have very different shapes. (1) is much narrower [N(3)—N(3′), 5·11 (1), C(9)—C(9′) 5·51 (1) Å] compared to (2) [N(3)—N(6) 7·07 (3), C(15)—C(37) 7·25 (3) Å]. This is clearly a consequence of the length of the bridging group in (2), with the tetramethylene chain taking up an extended conformation; the phenyl rings are rotated towards a face-to-face alignment, but the dihedral angle between them is still large [98 (1)°]. A final consequence of the length of the bridge is that the cyclic bonds to N(3) and N(6) point outwards, causing the methyl groups on these atoms to rotate inwards, giving a C(17)—C(36) distance of only 5·04 (3) Å.

Table 3. *Principal bond lengths* (Å)

(1)

Ni—N(1)	1·874 (6)	C(3)—C(4)	1·463 (9)
Ni—N(2)	1·872 (5)	C(4)—C(5)	1·446 (9)
N(1)—C(3)	1·294 (9)	C(4)—C(9)	1·412 (10)
N(2)—C(5)	1·285 (9)	C(9)—N(3)	1·342 (8)

(2) (centrosymmetric values in brackets)

Ni—N(1)	1·83 (3)	[1·89 (2)]	C(1)—C(3)	1·66 (5)	[1·50 (3)]
Ni—N(2)	1·79 (4)	[1·82 (2)]	C(4)—C(3)	1·61 (5)	[1·46 (3)]
Ni—N(3)	1·91 (3)		C(8)—C(9)	1·55 (4)	
Ni—N(4)	1·86 (2)		C(10)—C(9)	1·49 (4)	
N(1)—C(1)	1·21 (5)	[1·27 (3)]	C(9)—C(37)	1·35 (5)	
N(2)—C(4)	1·61 (6)	[1·37 (3)]	C(15)—N(3)	1·48 (5)	[1·38 (3)]
N(4)—C(10)	1·39 (4)		C(37)—N(6)	1·67 (5)	
N(5)—C(8)	1·23 (3)				

Previous study of lacunar systems has shown that the conformation at the non-ligand nitrogen atoms [N(3) and N(3′) in (1)] gives rise to two isomers. In the ideal case, the bridging group may either point upwards or across from this nitrogen (Busch, Zimmer, Gryzbowski, Olszanski, Jackels, Callahan & Christoph, 1981), giving the 'lid-on' or 'lid-off' isomers (Fig. 3). The crystal structure of complex (1) confirms that it is the 'lid on' isomer, as originally indicated by NMR (Herron, Nosco & Busch, 1983). In principle the isomers can be interconverted by rotation about the N–C bond [N(3)–C(9) in (1)], but the rigidity of the bridging group makes this unlikely for (1). The cyclohexyl group has the chair form, and the attachment of the rest of the complex simply continues this framework (Fig. 1*b*). For (2), the breadth of the bridging group does not allow the orientation of N(3)/N(6) to correspond to either ideal isomer. It is closer to the 'lid-on' form, with the bonds from the N atoms directed upwards rather than across, but the same rotation that turns the methyl groups [C(17) and C(36)] inwards shifts the bridge away from the ideal position.

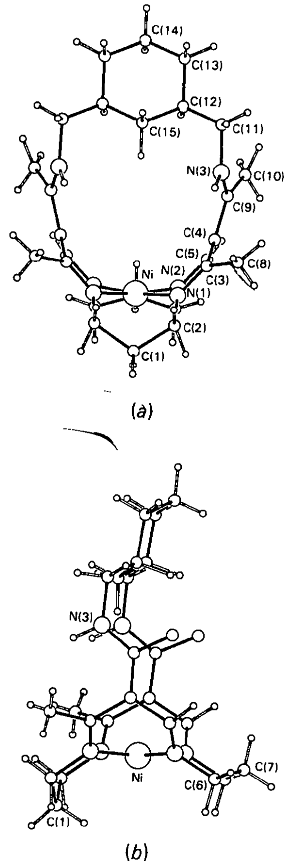

Fig. 1. Views of complex (1). (*a*) Showing the cavity (with atomic numbering). (*b*) Side-on, showing the orientation of the cyclohexyl group. Methyl-group H atoms are omitted.

The isomer formed has a strong influence on the height of the cavity. The 'lid-on' isomer gives the maximum height for a given bridge. In the case of (1), the distance from Ni to the capping carbon atom, C(15), is 5·46 (1) Å, though one of its H atoms points directly down into the cavity, giving a clear Ni–H separation of 4·44 Å. The Ni–C distance is very similar to that in the 'lid-on' *m*-xylyl complex (Busch *et al.*, 1981), but in that complex the aromatic proton points further out of the cavity.

For (2), the much larger bridge gives a height of 8·50 (3) Å [Ni–C(27)]; Ni–C(26) is 9·08 (3) Å. Again, this is reduced for the Ni–H contact, to 7·65 Å,

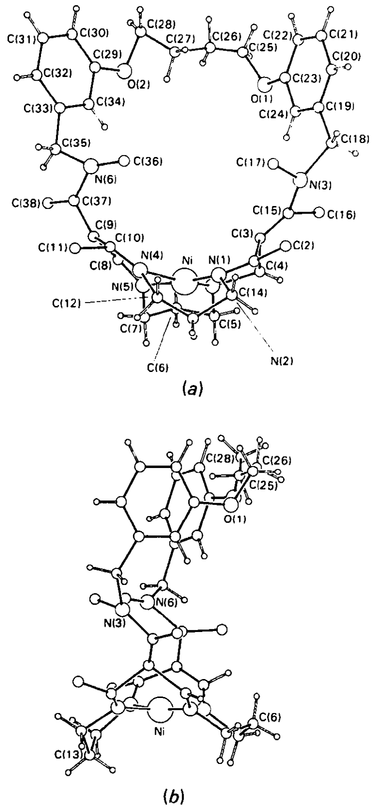

Fig. 2. Views of complex (2), (*a*) and (*b*) as in Fig. 1.

Lid-on Isomer

Lid-off Isomer

Fig. 3. Schematic view of 'lid-on' and 'lid-off' isomers.

though the greater flexibility of the chain might make this less constricting. It might also be possible, in the presence of a guest molecule, for the bridge to buckle and rotate upwards, increasing its height at the cost of some conformational strain.

Support of the US National Institute of Health is gratefully acknowledged.

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Structure of a Binuclear Nickel(II) Complex of a Pyridine-Containing Tetraaza Macrocycle, Including a Tetradentate Oxalato Bridge, [(*L*)Ni(μ-ox)Ni(*L*)](ClO_4)$_2$*

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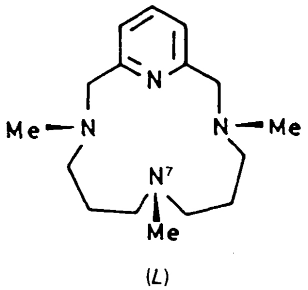
(*Received* 29 *May* 1987; *accepted* 23 *June* 1987)

Abstract. (μ-Oxalato)bis(3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene)-dinickel(II) diperchlorate, [$Ni_2(C_2O_4)(C_{16}H_{28}N_4)_2$]-$(ClO_4)_2$, $M_r = 957{\cdot}1$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}394$ (2), $b = 20{\cdot}270$ (9), $c = 12{\cdot}410$ (3) Å, $\beta = 101{\cdot}22$ (2)°, $U = 2{\cdot}071$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}53$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = 11·09 cm^{-1}, $T = 290$ K, $F(000) = 1004$, $R = 0{\cdot}066$ for 1978 unique observed $[I/\sigma(I) \geq 3{\cdot}0]$ reflections. The tetradentate tetraaza macrocycle adopts a folded conformation, to produce a *cis*-pseudooctahedral geometry at each Ni atom, with the tetradentate bridging oxalate (two five-membered chelate rings) linking the two Ni atoms [Ni—O 2·124 (6) and 2·069 (5) Å; Ni—N(pyridine) 1·989 (7), Ni—N(Me) 2·157 (7), 2·187 (7) and 2·200 (7) Å].

Introduction. We have previously reported the synthesis of the pyridine-containing tetraaza macrocycle (*L*) and its metal complexes of formula [*M*(*L*)][ClO_4]$_2$ (*M* = Ni,Cu,Zn), [Ni(*L*)*X*][ClO_4]$_n$ ($n = 1$, *X* = Cl, NCS, NO_2; $n = 2$, *X* = dimethyl sulfoxide) and [(*L*)Ni(μ-ox)Ni(*L*)][ClO_4]$_2$. Three isomers of the diamagnetic square-planar [Ni(*L*)][ClO_4]$_2$ were observed by ^{13}C NMR in nitromethane solution, and the structure of one of them (the asymmetric isomer) was established by X-ray crystallography. The paramagnetic five-coordinate nickel(II) complexes were found to have square-pyramidal geometries, as shown by crystal structures with *X* = Cl and dimethyl sulfoxide; *X* is coordinated in the basal plane in a *trans* position to the pyridine N atom, and with N^7 at the apex (Alcock, Moore & Omar, 1987). The six-coordinate oxalato complex was assigned a folded *cis* structure, based on an elemental analysis, spectroscopic data, and by comparison with related structures. An X-ray structural investigation was undertaken to establish the structure unequivocally, and to determine the mode of coordination of the bridging oxalate group.



(*L*)

Experimental. The complex [(*L*)Ni(μ-ox)Ni(*L*)]-[ClO_4]$_2$ was prepared as described previously (Alcock, Moore & Omar, 1987). The fast-atom bombardment

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* *L* = 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene; ox = oxalate ion.

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0108-2701/87/112074-03$01.50