Sterically Hindered Co-ordination Sites in Metal Complexes. Part 2.[1] Structural Characterisation of Two Ligand Conformations in the Nickel(II) Complex of the 'Fly-over' Ligand 2,2'-Tetramethylenedioxydi(8-*N*-salicylideneiminonaphthalene)

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The crystal and molecular structure of the title complex has been determined at 295 K from three-dimensional *X*-ray diffraction data measured by counter techniques. The complex crystallises in the monoclinic space group $P2_1/c$ with a = 18.631(1), b = 35.524(2), c = 9.756(1) Å, β = 111.21(1)°, U = 6 019.6 Å^3, and Z = 8. The structure has been solved by conventional Patterson and Fourier techniques and refined by block-diagonal least squares to final residuals of R = 0.043, R' = 0.058 for 7 179 independent reflections with $I/\sigma(I) \geqslant 3.0$. The *trans*-planar 'capped' structure proposed in Part 1 is confirmed (Ni–O, mean 1.820 Å; Ni–N, mean 1.910 Å) although it emerges that the dimensions and shape of the cavity are markedly sensitive to which of two conformations is adopted by the polymethylene bridging group. The details of the structures of the two independent molecules are discussed with respect to the potential of Schiff-base compounds of this type to serve as possible models for oxygen carriers in biological systems.

THE active sites of naturally occurring oxygen carriers such as haemoglobin are known to contain a metal atom situated in a hydrophobic cavity which is appropriately shaped to discourage the ingress of molecules other than dioxygen. The synthesis of new but smaller molecules which might also bind dioxygen in a reversible manner and hence replicate the transport of dioxygen in biological systems is currently exciting much interest.

In the previous paper [1] we have described the design and synthesis of a series of transition-metal–Schiff base complexes in which the *trans*-ligating nitrogen atoms are linked by a 'fly-over' bridge consisting of two naphthyl groups orthogonal to the MN_2O_2 co-ordination plane joined by a polymethylene diether moiety. This stereochemical arrangement produces a cavity between the metal centre and the 'bridge' whose dimensions may be controlled by varying the number of methylene groups in the bridge. In order to verify that the metal complex has the desired stereochemistry, and to determine the dimensions of the cavity, we have initially undertaken the *X*-ray structural analysis of the title crystalline nickel(II) complex with a tetramethylene bridge, [NiL^4].

EXPERIMENTAL

(*a*) *Collection and Reduction of* X-*Ray Data*.—A suitable single crystal of the title compound was mounted on a quartz fibre with an epoxy-cement. Preliminary *X*-ray photographic examination established the crystal class as monoclinic, the systematic absences $l = 2n + 1$ for $h0l$ data and $k = 2n + 1$ for $0k0$ data uniquely defining the space group as $P2_1/c$. Reflection intensities were collected on a Picker FACS-I computer-controlled four-circle diffractometer. Accurate unit-cell dimensions and the crystal-orientation matrix were obtained from the least-squares refinement of the 2θ, ω, χ, and φ setting angles of 12 carefully centred high-angle reflections ($81 \leqslant 2\theta \leqslant 108°$, graphite-crystal monochromated Cu-$K_{\alpha 1}$ radiation, λ = 1.540 51 Å, take-off angle 1.5°). Crystal data are given in Table 1.

The essential details of data collection are given in Table 2, both data collection and reduction following methods and formulae described elsewhere.[2] Reflection data were rejected if the individual background counts differed significantly [*i.e.* $|b_1 - b_2|/(b_1 + b_2)^{\frac{1}{2}} \geqslant 5.0$]. Equivalent reflection forms were averaged and reflections with $I/\sigma(I) < 3.0$ were regarded as unobserved and were excluded from the data set.

TABLE 1

Crystal data

Formula	$C_{38}H_{30}N_2NiO_4$
M	637.4
Crystal class	Monoclinic
Cell dimensions (22 ± 1 °C)	
a/Å	18.631(1) [a]
b/Å	35.525(2)
c/Å	9.756(1)
α/°	90.0
β/°	111.21(1)
γ/°	90.0
U/Å^3	6 019.6
D_m/g cm^{-3}	1.405
D_c/g cm^{-3}	1.406
Z	8
Space group	$P2_1/c$
Crystal dimensions (cm) [b]	{100}, 0.0215 {010}, 0.0150 {01$\bar{1}$}, 0.0200
μ(Cu-K_α)/cm^{-1}	12.51

[a] Estimated standard deviations (in parentheses) in this and subsequent Tables, and in the text, refer to the last significant digit(s). [b] Crystal dimensions are quoted as the perpendicular distance between faces of the form {*hkl*}.

(*b*) *Solution and Refinement of the Structure*.—The observed density indicated that there were eight formula units in the unit cell, requiring an asymmetric unit comprised of two independent complex molecules or a bimetallic complex of formula [Ni$_2$L$^4_2$]. A three-dimensional Patterson synthesis was readily solved for the positions of the two Ni atoms and subsequent Fourier syntheses located all non-hydrogen atoms revealing two independent symmetry-unrelated NiL^4 molecules in the unit cell. A detailed description of the course of refinement is given in Table 3. Atomic scattering factors for non-hydrogen atoms were taken from ref. 3 and were corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[4] The scattering curve for

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TABLE 2

Details of data collection

Radiation	Cu-K_α
λ(Cu-K_α)/Å	1.5418
Take-off angle (°)	3
Monochromator	Graphite crystal
2θ/°	26.5
Scan technique	θ—2θ moving crystal/counter
Scan speed/° min^{-1}	2
Individual scan range [a]	$(2\theta_{\alpha_1} - 0.8)$ to $(2\theta_{\alpha_1} + 0.8 + \Delta)$
2θ Range/°	3—125 for ($hk \pm l$)
Total background count time/s	20
Standard reflections monitoring	3 every 100
indices	(4 0 4), (0 16 0), (2 0 −4)
Crystal stability	Small linear decrease in intensities of standards (1.1%). No correction applied
Data collected	10 469
Unique data $I/\sigma(I) \geqslant 3.0$	7 179
ρ^2	0.002
R_s [b]	0.025

[a] The reflection scan range is asymmetric; the term Δ is the 2θ angular separation of the K_{α_1} and K_{α_2} components of the diffracted beam. [b] The statistical R factor is defined as $\Sigma\sigma_s(F_o)/\Sigma|F_o|$ where $\sigma_s(F_o) = \sigma(I)/C_{LP}(2|F_o|)$ and C_{LP} is the Lorentz-polarisation correction.

TABLE 3

Details of refinement [a]

	R	R'
(*i*) Course of refinement		
(1) All non-hydrogen atoms, isotropic temperature factors (t.f.), equal (unit) reflection weights	0.109	0.107
(2) All non-hydrogen atoms with anisotropic t.f., individual reflection weights	0.071	0.108
(3) Hydrogen atoms included at calculated positions [b] with isotropic t.f. Reflection data corrected for absorption effects [c]	0.044	0.059
(4) In addition, isotropic extinction parameter (c) refined [d]	0.043	0.058

(*ii*) Final parameters

Standard deviation of an observation of unit weight [e]	1.73
Secondary extinction parameter	$0.39(2) \times 10^{-4}$
Maximum (parameter shift/e.s.d.) in last cycle	0.54 for C(219) and C(220), all others <0.15
Maxima and minima in final difference electron-density map	0.59 to −0.40 e Å^{-3}

[a] Refinement was by block-diagonal least-squares minimising the function $\Sigma w(|F_o| - |F_c|)^2$. The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The refinement indices are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where F_o and F_c are the observed and calculated structure-factor amplitudes respectively and w is the weight. Individual reflection weights were of the form $[\sigma(F_o)]^{-2}$. [b] Hydrogen atom positions were recalculated before each cycle of refinement using a C–H distance of 0.95 Å, and isotropic temperature factors were assigned the value of equivalent isotropic t.f. of the carbon atom to which the hydrogen is bonded. [c] An analytical absorption correction was applied; the transmission factors ranged from 0.882 to 0.922. [d] The secondary extinction correction, applied to F_c, was of the form $(1 + c\beta I_o)^{-1}$ where c is the refined extinction parameter, β is the Zachariesen beta factor, and I_o the observed intensity. [e] Defined as $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$ where m is the number of observations (7 179) and n the number of refined parameters (812).

hydrogen was taken from ref. 5. The final atomic parameters are given in Table 4, together with their estimated standard deviations derived from inversion of the block-diagonal matrices. The anisotropic thermal parameters, calculated hydrogen-atom positions, and the final observed and calculated structure factors are available as Supplementary Publication No. SUP 22526 (52 pp.).* The atom-labelling is defined in Figure 1. All calculations were performed on a UNIVAC-1108 computer at the Australian National University Computer Centre using programs which have been described elsewhere.[6]

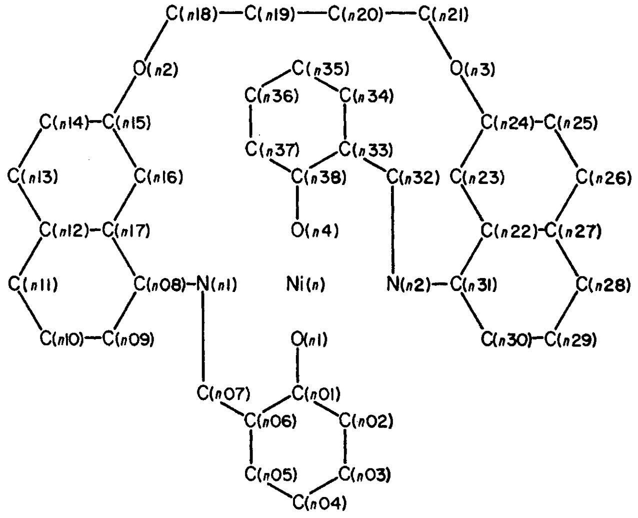

FIGURE 1 Atom-labelling scheme. Hydrogen atoms (not shown) have the same numerical subscript as the atoms to which they are bonded. The value of *n* is related to the molecule number

RESULTS AND DISCUSSION

Selected bond lengths, interbond angles, and intra- and inter-molecular contacts are presented in Tables 5 and 6. Average bond lengths and angles in the chemically unique part of the ligand are given in Figure 2. Torsion angles in the tetramethylene carbon chains are given in Table 7 and the least-squares planes are presented in Table 8.

The crystal structure of [NiL^4] contains two crystallographically independent discrete molecules of the title complex. Both molecules possess the stereochemistry intended, *viz. trans*-N_2O_2 square-planar co-ordination of the metal atom with the tetramethylene diether functionality, which links the naphthyl groups, forming a 'fly-over' bridge above the metal (Figure 3), and differ essentially only in the conformation of the $[CH_2]_4$ chain and the consequent effect on the orientation of the naphthyl groups [Figure 3(*c*) and (*d*)]. There are no unusually short intermolecular contacts; the packing of the molecules in the unit cell is illustrated in Figure 4.

The co-ordination of the nickel atoms in the two molecules can be described as square planar. The average Ni–O and Ni–N distances, 1.820 and 1.910 Å respectively, are in good agreement with corresponding distances of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

Table 4

Atom fractional co-ordinates

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni(1)	0.817 02(3)	0.100 50(1)	0.679 28(5)
O(11)	0.869 83(12)	0.117 21(7)	0.864 62(23)
O(12)	0.701 50(16)	0.227 42(7)	0.339 15(26)
O(13)	0.915 07(16)	0.220 84(7)	0.510 26(31)
O(14)	0.763 71(11)	0.080 75(6)	0.498 57(22)
N(11)	0.719 23(13)	0.113 88(7)	0.686 75(25)
N(12)	0.914 22(13)	0.087 43(6)	0.669 27(24)
C(101)	0.844 32(18)	0.122 36(9)	0.971 24(33)
C(102)	0.898 30(22)	0.125 57(13)	1.115 91(37)
C(103)	0.874 06(25)	0.131 39(14)	1.231 77(39)
C(104)	0.798 09(25)	0.133 47(12)	1.212 19(39)
C(105)	0.744 18(21)	0.130 39(11)	1.072 75(37)
C(106)	0.766 28(18)	0.124 24(8)	0.951 11(32)
C(107)	0.708 26(18)	0.121 71(8)	0.808 44(34)
C(108)	0.651 49(16)	0.110 35(8)	0.556 47(32)
C(109)	0.602 74(18)	0.080 68(10)	0.544 54(36)
C(110)	0.540 38(18)	0.074 25(10)	0.413 13(38)
C(111)	0.528 08(18)	0.097 04(10)	0.295 90(37)
C(112)	0.575 11(17)	0.128 96(9)	0.305 87(33)
C(113)	0.561 13(20)	0.154 87(11)	0.189 80(34)
C(114)	0.603 04(22)	0.186 26(10)	0.202 39(37)
C(115)	0.664 73(20)	0.194 33(9)	0.337 62(36)
C(116)	0.681 85(18)	0.169 65(9)	0.452 96(33)
C(117)	0.637 79(16)	0.136 46(8)	0.440 04(32)
C(118)	0.750 38(24)	0.241 70(11)	0.476 07(44)
C(119)	0.786 07(28)	0.278 26(11)	0.449 48(52)
C(120)	0.849 42(30)	0.274 84(11)	0.388 40(49)
C(121)	0.924 11(26)	0.260 65(11)	0.495 97(52)
C(122)	0.999 90(17)	0.142 23(8)	0.752 71(32)
C(123)	0.949 01(18)	0.165 06(9)	0.641 58(34)
C(124)	0.968 20(21)	0.201 40(9)	0.623 02(41)
C(125)	1.039 03(23)	0.216 57(10)	0.716 95(49)
C(126)	1.087 61(21)	0.195 08(11)	0.827 70(46)
C(127)	1.070 52(19)	0.157 45(10)	0.849 13(37)
C(128)	1.121 95(19)	0.134 62(11)	0.959 33(39)
C(129)	1.105 48(10)	0.097 99(11)	0.973 46(39)
C(130)	1.036 57(18)	0.082 43(10)	0.876 75(35)
C(131)	0.984 98(16)	0.103 71(8)	0.769 94(31)
C(132)	0.922 89(16)	0.062 65(8)	0.578 46(31)
C(133)	0.862 72(17)	0.043 67(8)	0.465 06(30)
C(134)	0.881 69(19)	0.015 72(9)	0.381 94(35)
C(135)	0.825 45(21)	−0.002 34(10)	0.270 16(35)
C(136)	0.748 44(20)	0.007 80(10)	0.237 33(34)
C(137)	0.729 48(18)	0.035 52(9)	0.312 56(32)
C(138)	0.785 53(17)	0.054 20(8)	0.430 03(30)
Ni(2)	0.363 13(3)	0.101 54(1)	0.404 67(5)
O(21)	0.311 66(13)	0.091 53(6)	0.211 23(21)
O(22)	0.153 73(17)	0.210 46(8)	0.457 14(37)
O(23)	0.071 32(13)	0.070 00(7)	0.429 76(28)
O(24)	0.413 97(14)	0.111 14(6)	0.599 53(21)
N(21)	0.385 58(14)	0.152 29(6)	0.366 21(24)
N(22)	0.348 49(13)	0.049 77(6)	0.439 07(24)
C(201)	0.320 82(17)	0.107 72(8)	0.098 32(31)
C(202)	0.299 55(20)	0.087 97(9)	−0.036 04(33)
C(203)	0.307 51(21)	0.103 35(10)	−0.155 23(34)
C(204)	0.334 75(23)	0.140 01(11)	−0.152 94(35)
C(205)	0.335 08(21)	0.160 32(10)	−0.024 59(34)
C(206)	0.351 14(17)	0.144 18(8)	0.103 85(30)
C(207)	0.379 65(18)	0.164 47(8)	0.238 06(32)
C(208)	0.416 10(18)	0.178 46(8)	0.486 32(31)
C(209)	0.492 79(21)	0.184 45(10)	0.549 12(39)
C(210)	0.522 69(25)	0.208 95(11)	0.672 97(47)
C(211)	0.472 67(28)	0.225 22(10)	0.728 64(41)
C(212)	0.393 39(24)	0.220 22(9)	0.663 65(36)
C(213)	0.338 71(29)	0.237 62(10)	0.717 67(44)
C(214)	0.261 38(29)	0.233 19(11)	0.645 53(52)
C(215)	0.232 24(25)	0.211 71(10)	0.518 29(46)
C(216)	0.282 59(21)	0.193 69(8)	0.466 91(36)
C(217)	0.363 16(20)	0.197 25(8)	0.538 03(32)
C(218)	0.118 12(26)	0.184 91(13)	0.336 80(59)
C(219)	0.124 01(41)	0.144 64(17)	0.384 77(62)
C(220)	0.112 03(43)	0.133 63(17)	0.504 08(58)
C(221)	0.113 84(22)	0.094 22(11)	0.546 35(43)
C(222)	0.216 88(17)	0.027 14(8)	0.301 46(30)
C(223)	0.185 92(17)	0.050 01(9)	0.383 62(33)
C(224)	0.108 33(19)	0.049 64(10)	0.354 65(37)
C(225)	0.059 01(19)	0.026 99(11)	0.240 02(39)
C(226)	0.089 14(21)	0.004 52(10)	0.161 81(37)
C(227)	0.167 72(20)	0.003 30(9)	0.187 76(32)
C(228)	0.199 52(22)	−0.020 11(9)	0.108 37(34)
C(229)	0.275 33(24)	−0.020 09(10)	0.135 45(37)
C(230)	0.324 32(21)	0.003 56(9)	0.244 10(35)
C(231)	0.296 35(17)	0.026 13(8)	0.325 28(30)
C(232)	0.388 06(17)	0.031 97(8)	0.558 24(31)
C(233)	0.443 27(16)	0.047 48(8)	0.686 05(30)
C(234)	0.486 74(20)	0.024 44(9)	0.800 79(35)
C(235)	0.540 38(21)	0.038 87(11)	0.927 84(36)
C(236)	0.549 71(19)	0.077 14(10)	0.940 95(33)
C(237)	0.508 00(20)	0.101 35(9)	0.833 66(33)
C(238)	0.453 34(17)	0.087 37(9)	0.700 81(30)

1.825 and 1.908 Å in bis(*N*-phenylsalicylaldiminato)-nickel(II).[7] There are small deviations of the in-plane atoms from the NiN_2O_2 plane. In molecule 1, the oxygen atoms are displaced by 0.05 and 0.06 Å both away from the 'fly-over' bridge, and in molecule 2 the nitrogen atoms are both displaced by 0.08 Å, again away from the bridge. This is also reflected in decreased angles O(11)–Ni(1)–O(14), 176.3°, and N(21)–Ni(2)–Ni(22), 175.0°, compared with the other *trans* angles of 179.2°. It is also pertinent to note the close intramolecular Ni(1) • • • H(123) contact distance of 2.88 Å. Although H(123) does not occupy the apical co-ordination site above the metal [*e.g.* N(12)–Ni(1)–H(123) 60.2°], the distance is similar to Ni • • • H contacts of 2.89 Å in $[Ni(S_2CNPr^i_2)_2]$,[8] 2.86 Å in $[Ni(S_2CNH_2)_2]$,[9] and 2.79 Å in bis(pyrrolidinyldithiocarbamato)nickel(II),[10] which have been ascribed [11] to weak metal–hydrogen bonding. However, in the present structure, it is undoubtedly due to the steric constraints of the ligand. For example, in molecule 2 where the conformation of the $[CH_2]_4$ bridge has increased the distance between the naphthyl groups relative to molecule 1 (see below) the Ni(2) • • • H(223) distance has increased to 3.19 Å.

The average bond lengths in the salicylaldimine groups (Figure 2) are in good agreement with previously observed values.[12,13] As usual, the three C–C bonds at the back of the C_6 ring (mean 1.370 Å) are significantly shorter than the remaining C–C bonds (mean 1.407 Å). The C_6 rings are planar with a maximum atom deviation over the four groups of 0.022 Å. In general, the planarity extends over the entire salicylaldimine moiety and, with the exception of atoms C(207) and N(21), the maximum deviation is 0.090 Å. The latter two atoms are respectively 0.133 and 0.291 Å out of the C_6 plane. The metal atoms are significantly non-planar with their respective salicylaldimine ligands, with deviations ranging from 0.391 to 0.539 Å. This results in an unbrella-shaped configuration of the salicylaldimine groups about the metal with the ligands bending away from the bridged side of the nickel co-ordination plane [Figure 3(*c*) and (*d*)].

The naphthyl groups are approximately orthogonal to the NiN_2O_2 plane with dihedral angles of 80.0 and 81.5° for molecule 1, with the naphthyl groups inclining toward each other [Figure 3(*c*)], and corresponding angles of 88.5 and 89.4° for molecule 2. This is the usual

TABLE 5

Bond distances (Å) and interbond angles (°)

	n	
(*a*) Bond distances	1	2
Ni(*n*)–O(*n*1)	1.817(2)	1.816(2)
Ni(*n*)–O(*n*4)	1.822(2)	1.824(2)
Ni(*n*)–N(*n*1)	1.910(3)	1.918(3)
Ni(*n*)–N(*n*2)	1.906(3)	1.907(3)
O(*n*1)–C(*n*01)	1.304(5)	1.308(4)
C(*n*01)–C(*n*02)	1.411(4)	1.411(4)
C(*n*02)–C(*n*03)	1.376(6)	1.341(5)
C(*n*03)–C(*n*04)	1.360(7)	1.395(6)
C(*n*04)–C(*n*05)	1.372(5)	1.374(5)
C(*n*05)–C(*n*06)	1.407(6)	1.404(5)
C(*n*06)–C(*n*01)	1.397(5)	1.406(4)
C(*n*06)–C(*n*07)	1.423(4)	1.419(4)
C(*n*07)–N(*n*1)	1.305(5)	1.290(4)
N(*n*1)–C(*n*08)	1.437(3)	1.442(4)
C(*n*08)–C(*n*09)	1.369(5)	1.352(5)
C(*n*09)–C(*n*10)	1.403(4)	1.429(5)
C(*n*10)–C(*n*11)	1.352(5)	1.365(7)
C(*n*11)–C(*n*12)	1.415(5)	1.392(6)
C(*n*12)–C(*n*13)	1.409(5)	1.444(7)
C(*n*13)–C(*n*14)	1.341(5)	1.365(7)
C(*n*14)–C(*n*15)	1.431(4)	1.389(6)
C(*n*15)–C(*n*16)	1.370(5)	1.372(6)
C(*n*16)–C(*n*17)	1.416(4)	1.413(5)
C(*n*17)–C(*n*12)	1.429(4)	1.409(4)
C(*n*17)–C(*n*08)	1.417(4)	1.426(5)
C(*n*15)–O(*n*2)	1.358(4)	1.366(5)
O(*n*2)–C(*n*18)	1.411(4)	1.442(6)
C(*n*18)–C(*n*19)	1.524(6)	1.497(8)
C(*n*19)–C(*n*20)	1.507(9)	1.321(10)
C(*n*20)–C(*n*21)	1.495(6)	1.457(7)
C(*n*21)–O(*n*3)	1.437(5)	1.418(4)
O(*n*3)–C(*n*24)	1.371(4)	1.379(5)
C(*n*22)–C(*n*23)	1.410(4)	1.403(5)
C(*n*23)–C(*n*24)	1.369(5)	1.369(5)
C(*n*24)–C(*n*25)	1.413(5)	1.414(5)
C(*n*25)–C(*n*26)	1.364(5)	1.358(6)
C(*n*26)–C(*n*27)	1.407(5)	1.393(5)
C(*n*27)–C(*n*28)	1.409(5)	1.405(5)
C(*n*27)–C(*n*22)	1.419(4)	1.432(4)
C(*n*28)–C(*n*29)	1.355(6)	1.340(6)
C(*n*29)–C(*n*30)	1.403(4)	1.401(4)
C(*n*30)–C(*n*31)	1.363(4)	1.357(5)
C(*n*31)–C(*n*22)	1.419(4)	1.414(5)
C(*n*31)–N(*n*2)	1.449(3)	1.450(3)
N(*n*2)–C(*n*32)	1.300(4)	1.294(3)
C(*n*32)–C(*n*33)	1.428(4)	1.417(4)
C(*n*33)–C(*n*34)	1.406(5)	1.397(4)
C(*n*34)–C(*n*35)	1.368(4)	1.379(4)
C(*n*35)–C(*n*36)	1.399(5)	1.371(5)
C(*n*36)–C(*n*37)	1.349(5)	1.360(4)
C(*n*37)–C(*n*38)	1.407(4)	1.417(4)
C(*n*38)–C(*n*33)	1.403(4)	1.412(4)
C(*n*38)–O(*n*4)	1.303(4)	1.305(3)
(*b*) Interbond angles		
O(*n*1)–Ni(*n*)–N(*n*1)	93.5(1)	92.9(1)
O(*n*1)–Ni(*n*)–O(*n*4)	176.3(1)	179.2(1)
O(*n*1)–Ni(*n*)–N(*n*2)	87.0(1)	86.5(1)
N(*n*1)–Ni(*n*)–O(*n*4)	86.5(1)	87.7(1)
N(*n*1)–Ni(*n*)–N(*n*2)	179.2(1)	175.0(1)
O(*n*4)–Ni(*n*)–N(*n*2)	93.0(1)	92.9(1)
Ni(*n*)–O(*n*1)–C(*n*01)	128.1(2)	127.5(2)
Ni(*n*)–O(*n*4)–C(*n*38)	127.8(2)	127.3(2)
Ni(*n*)–N(*n*1)–C(*n*07)	123.6(2)	123.8(2)
Ni(*n*)–N(*n*1)–C(*n*08)	119.3(2)	119.8(2)
Ni(*n*)–N(*n*2)–C(*n*32)	123.7(2)	123.9(2)
Ni(*n*)–N(*n*2)–C(*n*31)	121.1(2)	121.5(2)
O(*n*1)–C(*n*01)–C(*n*06)	123.8(3)	123.1(3)
O(*n*1)–C(*n*01)–C(*n*02)	118.4(3)	119.0(3)
C(*n*06)–C(*n*01)–C(*n*02)	117.8(3)	117.9(3)
C(*n*01)–C(*n*02)–C(*n*03)	120.5(4)	121.4(3)
C(*n*02)–C(*n*03)–C(*n*05)	121.8(3)	121.4(3)
C(*n*03)–C(*n*04)–C(*n*05)	119.1(4)	118.9(3)
C(*n*04)–C(*n*05)–C(*n*06)	121.1(4)	120.8(3)
C(*n*05)–C(*n*06)–C(*n*01)	119.8(3)	119.5(3)
C(*n*05)–C(*n*06)–C(*n*07)	119.0(3)	119.5(3)
C(*n*01)–C(*n*06)–C(*n*07)	121.2(3)	121.0(3)
C(*n*06)–C(*n*07)–N(*n*1)	126.1(3)	126.6(3)
C(*n*07)–N(*n*1)–C(*n*08)	116.5(3)	116.2(2)
N(*n*1)–C(*n*08)–C(*n*09)	119.1(3)	120.7(3)
N(*n*1)–C(*n*08)–C(*n*17)	119.9(3)	118.0(3)
C(*n*17)–C(*n*08)–C(*n*09)	121.0(2)	121.2(2)
C(*n*08)–C(*n*09)–C(*n*10)	120.5(3)	120.3(4)
C(*n*09)–C(*n*10)–C(*n*11)	120.4(3)	118.8(4)
C(*n*10)–C(*n*11)–C(*n*12)	120.7(3)	122.0(3)
C(*n*11)–C(*n*12)–C(*n*17)	119.5(3)	119.6(4)
C(*n*11)–C(*n*12)–C(*n*13)	122.6(3)	123.5(3)
C(*n*17)–C(*n*12)–C(*n*13)	117.8(3)	116.9(4)
C(*n*12)–C(*n*13)–C(*n*14)	122.5(3)	121.0(4)
C(*n*13)–C(*n*14)–C(*n*15)	119.9(3)	121.5(5)
C(*n*14)–C(*n*15)–C(*n*16)	120.0(3)	119.0(4)
C(*n*14)–C(*n*15)–O(*n*2)	114.7(3)	114.7(4)
C(*n*16)–C(*n*15)–O(*n*2)	125.3(3)	126.2(3)
C(*n*15)–C(*n*16)–C(*n*17)	120.3(3)	121.6(3)
C(*n*16)–C(*n*17)–C(*n*12)	119.5(3)	119.9(4)
C(*n*16)–C(*n*17)–C(*n*08)	122.9(2)	122.2(3)
C(*n*08)–C(*n*17)–C(*n*12)	117.6(3)	118.0(3)
C(*n*15)–O(*n*2)–C(*n*18)	118.2(3)	118.7(4)
O(*n*2)–C(*n*18)–C(*n*19)	108.5(3)	112.8(4)
C(*n*18)–C(*n*19)–C(*n*20)	116.8(4)	122.8(6)
C(*n*19)–C(*n*20)–C(*n*21)	114.4(4)	122.7(6)
C(*n*20)–C(*n*21)–O(*n*3)	106.7(3)	114.0(3)
C(*n*21)–O(*n*3)–C(*n*24)	119.8(3)	120.2(3)
O(*n*3)–C(*n*24)–C(*n*23)	115.7(3)	125.4(3)
O(*n*3)–C(*n*24)–C(*n*25)	124.2(3)	114.3(3)
C(*n*22)–C(*n*23)–C(*n*24)	120.6(3)	119.9(3)
C(*n*23)–C(*n*24)–C(*n*25)	120.1(3)	120.3(4)
C(*n*24)–C(*n*25)–C(*n*26)	119.8(3)	119.8(3)
C(*n*25)–C(*n*26)–C(*n*27)	121.9(3)	122.5(3)
C(*n*26)–C(*n*27)–C(*n*22)	118.0(3)	117.2(3)
C(*n*26)–C(*n*27)–C(*n*28)	122.1(3)	122.9(3)
C(*n*22)–C(*n*27)–C(*n*28)	119.9(3)	119.9(3)
C(*n*27)–C(*n*28)–C(*n*29)	120.9(3)	121.0(3)
C(*n*28)–C(*n*29)–C(*n*30)	119.7(3)	120.1(4)
C(*n*29)–C(*n*30)–C(*n*31)	121.1(3)	120.9(4)
C(*n*30)–C(*n*31)–N(*n*2)	120.9(3)	119.8(3)
C(*n*30)–C(*n*31)–C(*n*22)	120.8(3)	121.3(3)
N(*n*2)–C(*n*31)–C(*n*22)	118.3(2)	118.9(3)
C(*n*31)–C(*n*22)–C(*n*23)	122.7(2)	122.9(2)
C(*n*31)–C(*n*22)–C(*n*27)	119.7(3)	116.8(3)
C(*n*23)–C(*n*22)–C(*n*27)	117.6(2)	120.3(3)
C(*n*31)–N(*n*2)–C(*n*32)	115.2(3)	114.3(2)
N(*n*2)–C(*n*32)–C(*n*33)	126.3(3)	126.2(3)
C(*n*32)–C(*n*33)–C(*n*34)	119.3(3)	119.4(3)
C(*n*32)–C(*n*33)–C(*n*38)	120.7(3)	121.0(2)
C(*n*38)–C(*n*33)–C(*n*34)	119.8(2)	119.6(2)
C(*n*33)–C(*n*34)–C(*n*35)	120.7(3)	121.3(3)
C(*n*34)–C(*n*35)–C(*n*36)	119.2(3)	118.6(3)
C(*n*35)–C(*n*26)–C(*n*37)	120.8(3)	122.5(3)
C(*n*36)–C(*n*37)–C(*n*38)	121.6(3)	120.2(3)
C(*n*37)–C(*n*38)–C(*n*33)	117.8(3)	117.7(3)
C(*n*37)–C(*n*38)–O(*n*4)	118.8(3)	119.1(3)
C(*n*33)–C(*n*38)–O(*n*4)	123.4(2)	123.1(2)

configuration in chelated *N*-arylsalicylaldimines {*e.g.* the dihedral angle of 81.6° in bis(*N*-phenylsalicylaldiminato)-nickel(II),[7] 75.0° in *trans*-bis[*N*-(2-biphenylyl)salicylaldiminato]bis(pyridine)nickel(II) [14]}. The four naphthyl groups are essentially planar (maximum deviation of in-plane atom, 0.066 Å) with the planarity extending to the ether oxygen and the first carbon atom of the methylene chain. Only in the naphthalene moiety C(108)—C(117) is the methylene carbon, C(118), a substantial distance (0.50 Å) out of the plane. There

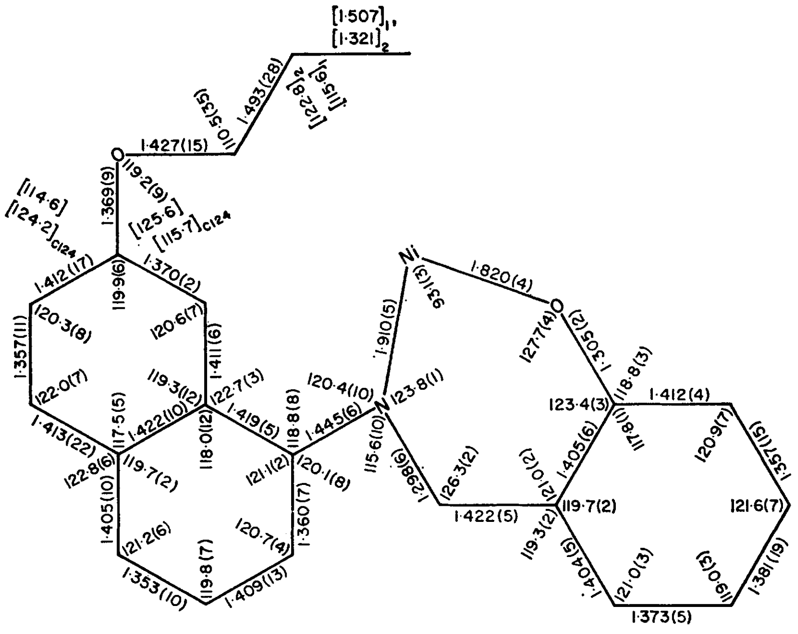

FIGURE 2 Average bond lengths and angles in the unique part of the ligand. Standard deviations (in parentheses) are calculated from $\sigma = [\sum_{1}^{n}(x_n - \bar{x})^2/(n - 1)]^{\frac{1}{2}}$ where $\bar{x}$ is the mean value. Where an individual value is significantly different from the mean, the value is quoted in square brackets with a subscript denoting the atom or molecule concerned

are no unusual features in the bonding geometry of the naphthalene molecules.

TABLE 6

Selected intra- and inter-molecular contacts (Å) *

(*a*) Intramolecular

Ni(1) ··· H(123)	2.88	Ni(2) ··· H(223)	3.19
Ni(1) ··· H(116)	3.18	Ni(2) ··· H(216)	3.27
O(12) ··· O(13)	3.724(4)	O(22) ··· O(23)	5.199(4)
H(116) ··· H(123)	3.27	H(216) ··· H(223)	4.21

(*b*) Intermolecular involving hydrogen atoms

Ni(2) ··· H(110)	3.16	C(217) ··· H(213^{VIII})	2.86
O(11) ··· H(120A^{I})	2.98	C(217) ··· H(204^{V})	2.89
O(14) ··· H(104^{II})	2.93	C(226) ··· H(226^{IV})	2.91
O(23) ··· H(132^{III})	2.82	C(226) ··· H(130^{V})	2.97
O(24) ··· H(204^{V})	2.83	C(229) ··· H(109^{IV})	2.97
C(112) ··· H(209)	2.91	C(230) ··· H(109^{V})	2.79
C(117) ··· H(209)	2.72	C(234) ··· H(230^{IV})	2.97
C(131) ··· H(221A^{VI})	2.90	C(234) ··· H(235^{V})	3.00
C(201) ··· H(111)	2.95	C(218) ··· H(125^{VI})	2.97
C(201) ··· H(128^{VII})	2.97		
C(203) ··· H(221B^{II})	3.00	H(120) ··· H(226^{IV})	2.30
C(205) ··· H(113)	2.90	H(132) ··· H(221^{XII})	2.47
C(208) ··· H(213^{VII})	3.00	H(136) ··· H(202^{XIII})	2.42
C(212) ··· H(204^{V})	2.95	H(203) ··· H(221B^{II})	2.38
C(213) ··· H(207^{I})	2.78	H(207) ··· H(213^{VIII})	2.37

(*c*) Intermolecular <3.5 Å involving only non-hydrogen atoms

Ni(2) ··· C(110)	3.414(4)	C(106) ··· C(119^{I})	3.484(5)
O(23) ··· C(134^{IV})	3.500(4)	C(134) ··· C(224^{IV})	3.418(5)
O(24) ··· C(204^{V})	3.412(5)		

* Transformations of the asymmetric unit (x,y,z) are defined by Roman numeral superscripts:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $x, y, z - 1$
III $x - 1, y, z$
IV $1 - x, \bar{y}, 1 - z$
V $x, y, 1 + z$
VI $1 + x, 1 + y, z$
VII $x - 1, y, z - 1$
VIII $x, \frac{1}{2} - y, z - \frac{1}{2}$
IX $\bar{x}, \bar{y}, \bar{z}$
X $1 - x, \bar{y}, 2 - z$
XI $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$
XII $1 + x, y, z$
XIII $1 - x, \bar{y}, \bar{z}$

TABLE 7

Torsion angles (°) in the $O[CH_2]_4O$ chain for the two independent molecules of [NiL^4]

Atom				Torsion angles *	
(1)	(2)	(3)	(4)	$n = 1$	$n = 2$
C(n15)	O(n2)	C(n18)	C(n19)	178.8(4)	72.9(6)
O(n2)	C(n18)	C(n19)	C(n20)	−75.2(4)	43.1(8)
C(n18)	C(n19)	C(n20)	C(n21)	−72.8(5)	176.7(5)
C(n19)	C(n20)	C(n21)	O(n3)	75.8(5)	−47.1(8)
C(n20)	C(n21)	O(n3)	C(n24)	−166.7(4)	98.3(5)

* A torsion angle is defined as positive, if, when viewed from atom 2 to atom 3, a clockwise rotation of atom 1 would superimpose it on atom 4.

The essential difference between the two independent molecules of [NiL^4] lies in the conformation of the bridging tetramethylene diether group which is reflected in the torsion angles (Table 7). In molecule 1 the $[CH_2]_4$ chain adopts a ' raised ' conformation [Figure 3(*a*)] with torsion angles of 178.8 and −166.7° at the O(12)–C(118) and C(121)–O(13) bonds directing the chain away from the nickel atom. This also results in drawing the naphthyl groups closer together as evidenced by O(12) ··· O(13) 3.724 Å, compared with the equivalent contact in molecule 2, O(22) ··· O(23) 5.199 Å. In the second molecule [Figure 3(*b*)] the methylene carbon atoms are all approximately the same height as the ether oxygen atoms above the nickel co-ordination plane, the torsion angles at the O(22)–C(218) and C(221)–O(23) bonds being 72.9 and 83.3°, respectively. The C(219)–C(220) bond length [1.321(10)Å] coupled with a torsion angle of 176.7(5)° might suggest that this was a C=C double bond. However, consideration of the high degree of anisotropic thermal motion [maximum root-mean-square (r.m.s.) amplitudes of vibration, 0.525(9)

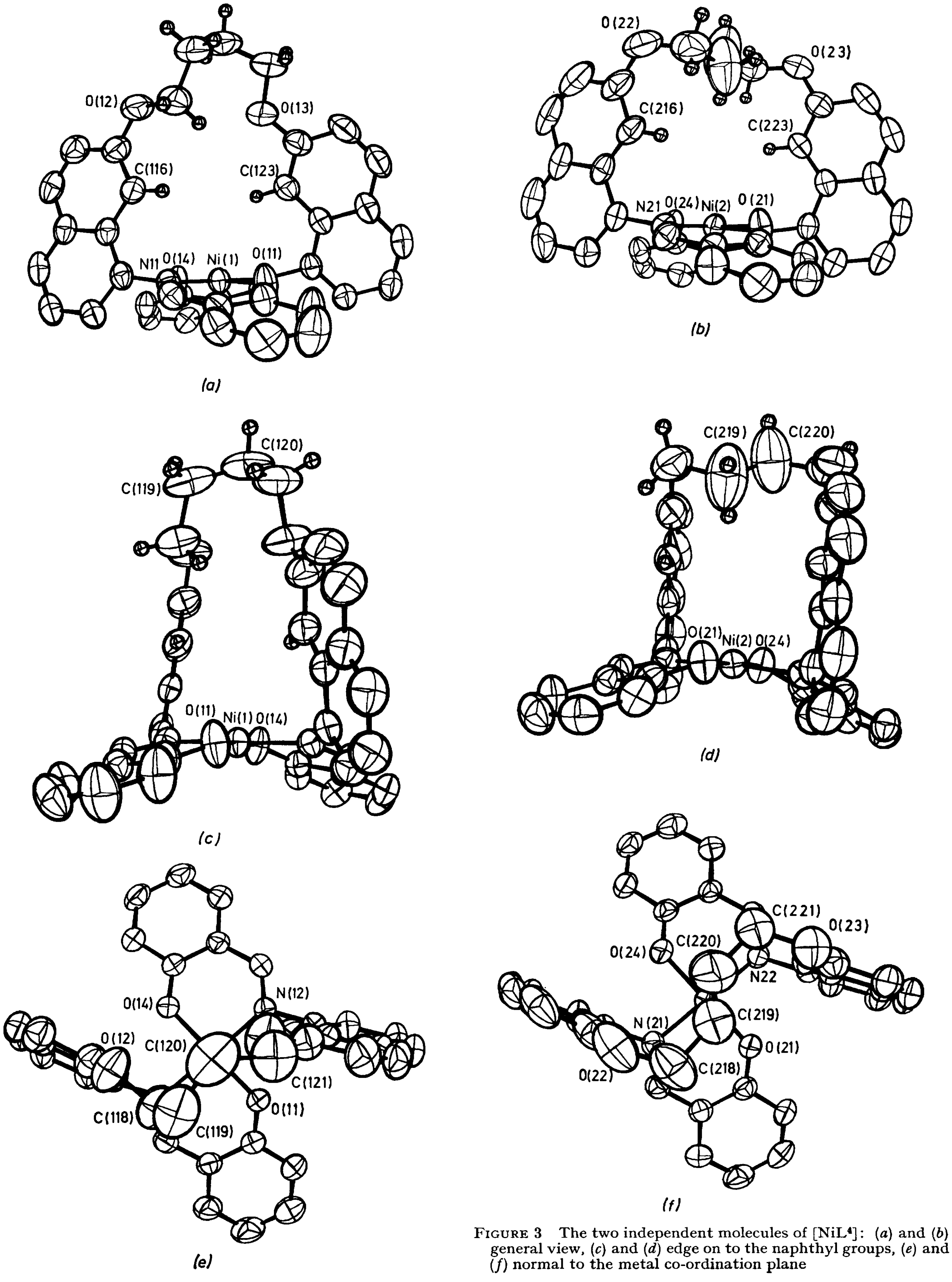

FIGURE 3 The two independent molecules of $[\mathrm{NiL}^4]$: (*a*) and (*b*) general view, (*c*) and (*d*) edge on to the naphthyl groups, (*e*) and (*f*) normal to the metal co-ordination plane

TABLE 8

Weighted least-squares planes [a]

(*i*) Equations of planes

Plane	Atoms defining plane	Equation
11	C_6 ring; C(101)—C(106)	$0.0753X + 0.9894Y - 0.1245Z = 4.1203$
12	C_6 ring; C(201)—C(206)	$-0.8944X + 0.3618Y - 0.2629Z = -3.8968$
21	C_6 ring; C(133)—C(138)	$0.3429X + 0.6872Y - 0.6404Z = 3.3166$
22	C_6 ring; C(233)—C(238)	$0.9134X - 0.0495Y - 0.4039Z = 2.7244$
31	C_6 ring; C(108)—C(112), C(117)	$0.7616X - 0.5573Y - 0.3306Z = 3.8645$
32	C_6 ring; C(208)—C(212), C(217)	$0.1673X + 0.7799Y - 0.6031Z = 3.3057$
41	C_6 ring; C(112)—C(117)	$0.8013X - 0.4957Y - 0.3348Z = 4.5289$
42	C_6 ring; C(212)—C(217)	$0.2050X + 0.7986Y - 0.5659Z = 3.8343$
51	C_6 ring; C(122)—C(127)	$0.7187X - 0.3083Y - 0.6233Z = 5.6444$
52	C_6 ring; C(222)—C(227)	$0.1314X + 0.7408Y - 0.6588Z = -0.7067$
61	C_6 ring; C(112), C(127)—C(131)	$0.7290X - 0.2584Y - 0.6338Z = 6.0063$
62	C_6 ring; C(222), C(227)—C(231)	$0.1244X + 0.7300Y - 0.6721Z = -0.7642$
71	Naphthalene molecule; C(108)—C(117)	$0.7822X - 0.5255Y - 0.3347Z = 4.1565$
72	Naphthalene molecule; C(208)—C(217)	$0.1886X + 0.7880Y - 0.5860Z = 3.5859$
81	Naphthalene molecule; C(122)—C(131)	$0.7243X - 0.2813Y - 0.6295Z = 5.8688$
82	Naphthalene molecule; C(222)—C(231)	$0.1280X + 0.7352Y - 0.6657Z = -0.7360$
91	Ni(11), O(11), O(14), N(11), N(12)	$0.2104X + 0.8947Y - 0.3940Z = 3.4544$
92	Ni(21), O(21), O(24), N(21), N(22)	$0.9594X - 0.2663Y - 0.0928Z = 3.8240$

(*ii*) Distances (Å) of atoms from best planes

	Plane 1*n*	
Atom	*n* = 1	*n* = 2
C(*n*01)	0.007(3)	0.011(3)
C(*n*02)	−0.006(5)	0.008(4)
C(*n*03)	0.002(5)	−0.018(4)
C(*n*04)	−0.004(4)	0.001(4)
C(*n*05)	0.007(4)	0.022(4)
C(*n*06)	−0.008(3)	−0.022(3)
O(*n*1)	0.012(3)	0.042(3)
C(*n*07)	0.021(3)	−0.133(3)
N(*n*1)	−0.068(2)	−0.291(3)
Ni(*n*)	−0.391(1)	−0.539(1)

	Plane 2*n*	
Atom	*n* = 1	*n* = 2
C(*n*33)	−0.010(3)	0.003(3)
C(*n*34)	0.013(3)	−0.007(4)
C(*n*35)	0.000(3)	0.004(4)
C(*n*36)	−0.014(3)	0.005(4)
C(*n*37)	0.012(3)	−0.008(4)
C(*n*38)	0.000(3)	0.003(3)
O(*n*4)	0.027(2)	−0.010(3)
C(*n*32)	0.040(3)	−0.027(3)
N(*n*2)	−0.049(2)	0.090(3)
Ni(*n*)	−0.422(1)	0.486(1)

	Plane 3*n*	
	n = 1	*n* = 2
C(*n*08)	0.026(3)	−0.019(3)
C(*n*09)	−0.010(4)	0.005(4)
C(*n*10)	−0.019(4)	0.024(4)
C(*n*11)	0.023(4)	−0.019(4)
C(*n*12)	0.001(3)	−0.010(3)
C(*n*17)	−0.022(3)	0.023(3)
C(*n*13)	−0.049(4)	−0.026(4)
C(*n*16)	−0.128(3)	0.105(3)

	Plane 4*n*	
	n = 1	*n* = 2
C(*n*12)	−0.010(3)	0.019(3)
C(*n*13)	0.007(4)	−0.013(4)
C(*n*14)	0.005(4)	−0.011(4)
C(*n*15)	−0.010(4)	0.016(4)
C(*n*16)	0.003(3)	−0.002(3)
C(*n*17)	0.006(3)	−0.010(3)
C(*n*08)	−0.014(3)	−0.038(3)
C(*n*11)	−0.092(4)	0.082(4)

	Plane 5*n*	
	n = 1	*n* = 2
C(*n*22)	0.009(3)	0.006(3)
C(*n*23)	−0.010(3)	0.002(3)
C(*n*24)	0.001(4)	−0.011(3)
C(*n*25)	0.013(5)	0.012(4)
C(*n*26)	−0.010(4)	−0.001(4)
C(*n*27)	−0.003(4)	−0.008(3)
C(*n*28)	0.032(4)	−0.033(3)
C(*n*31)	0.090(3)	0.020(3)

	Plane 6*n*	
	n = 1	*n* = 2
C(*n*22)	−0.007(3)	−0.004(3)
C(*n*27)	0.009(4)	0.009(3)
C(*n*28)	−0.002(4)	−0.005(3)
C(*n*29)	−0.007(4)	−0.006(3)
C(*n*30)	0.006(4)	0.009(3)
C(*n*31)	0.001(3)	−0.003(3)
C(*n*23)	0.019(3)	−0.022(3)
C(*n*26)	0.074(4)	0.028(4)

	Plane 7*n*	
	n = 1	*n* = 2
C(*n*08)	0.048(3)	−0.044(3)
C(*n*09)	−0.040(4)	0.017(4)
C(*n*10)	−0.066(4)	0.065(4)
C(*n*11)	0.010(4)	0.011(4)
C(*n*12)	0.042(3)	−0.018(3)
C(*n*13)	0.028(4)	−0.047(4)
C(*n*14)	−0.020(4)	−0.010(4)
C(*n*15)	−0.057(4)	0.049(4)
C(*n*16)	−0.016(3)	0.030(3)
C(*n*17)	0.036(3)	−0.014(3)
N(*n*1)	0.213(3)	−0.164(2)
O(*n*2)	−0.147(3)	0.105(3)
C(*n*18)	−0.497(4)	−0.014(4)

	Plane 8*n*	
	n = 1	*n* = 2
C(*n*22)	−0.031(3)	0.001(3)
C(*n*23)	−0.025(3)	−0.011(3)
C(*n*24)	0.024(4)	−0.017(3)
C(*n*25)	0.050(5)	0.020(4)
C(*n*26)	0.003(4)	0.014(4)
C(*n*27)	−0.029(4)	0.001(3)
C(*n*28)	−0.019(4)	−0.018(3)
C(*n*29)	0.008(4)	−0.013(3)
C(*n*30)	0.034(4)	0.014(3)
C(*n*31)	0.010(3)	0.009(3)
N(*n*2)	0.052(3)	0.010(2)
O(*n*3)	0.047(3)	−0.062(3)
C(*n*21)	−0.111(4)	−0.087(4)

TABLE 8 (*Continued*)

(*ii*) Distances (Å) of atoms from best planes (*Continued*)

	Plane 9*n*	
	n = 1 [b]	*n* = 2 [c]
Ni(*n*)	0.004(1)	−0.005(1)
O(*n*1)	−0.060(3)	−0.013(3)
N(*n*1)	0.013(2)	0.078(3)
O(*n*4)	−0.051(2)	−0.012(3)
N(*n*2)	0.013(2)	0.077(3)
C(*n*08)	0.199(3)	−0.132(4)
C(*n*31)	0.372(3)	−0.150(4)

(*iii*) Dihedral angles (°) between planes. Values are given in pairs being for *n* = 1 and *n* = 2 respectively

Plane	2*n*	3*n*	4*n*	5*n*	6*n*	7*n*	8*n*	9*n*
1*n*	38.2, 43.2	63.1, 73.1	67.1, 75.3	80.0, 71.1	83.0, 70.8	65.2, 74.3	81.6, 70.9	18.2, 21.6
2*n*		84.8, 69.0	81.5, 67.9	64.3, 69.6	61.4, 69.6	83.0, 68.3	62.7, 69.6	20.1, 22.0
3*n*			4.2, 3.2	22.3, 4.4	24.7, 5.5	2.2, 1.6	23.6, 5.0	78.0, 89.5
4*n*				20.4, 7.6	22.4, 8.6	2.0, 1.6	21.5, 8.1	81.8, 87.9
5*n*					3.0, 1.1	21.1, 6.0	1.6, 0.6	83.1, 89.4
6*n*						23.3, 7.0	1.4, 0.5	80.1, 89.3
7*n*							22.3, 6.5	80.0, 88.5
8*n*								81.5, 89.4

[a] Planes are defined as $LX + MY + PZ = d$ where (X, Y, Z) are orthogonal co-ordinates (Å) derived from the fractional cell co-ordinates (x, y, z) by $X = 18.631x - 3.529z$, $Y = 35.524y$, $Z = 9.095z$. The in-plane atoms are weighted according to $\omega = 3/[\sigma^2(X) + \sigma^2(Y) + \sigma^2(Z)]$. [b] A positive deviation is toward the 'fly-over' bridge. [c] A negative deviation is toward the 'fly-over' bridge.

and 0.520(9) Å for C(210) and C(220) respectively, approximately normal to the bond vector [*cf.* Figure **3**(*b*), (*d*), and (*f*)] indicates that the observed shortness of the bond was due to either atomic positional disorder or librational shortening as the bond adopts different orientations. No positional disorder was discerned in a difference-Fourier synthesis with contributions of C(219) and C(220) omitted, and so we hold to the latter explanation. A similar observation (*i.e.* on apparent double-bond order for a C–C single bond) was made [15] in the structure of (cyclo-octyne)bis(triphenylphosphine)-platinum. In support of this explanation, a marked increase in the in-plane translational motion of the naphthyl groups in molecule 2 [Figure **3**(*b*), *cf.* Figure **3**(*a*)] should be noted.

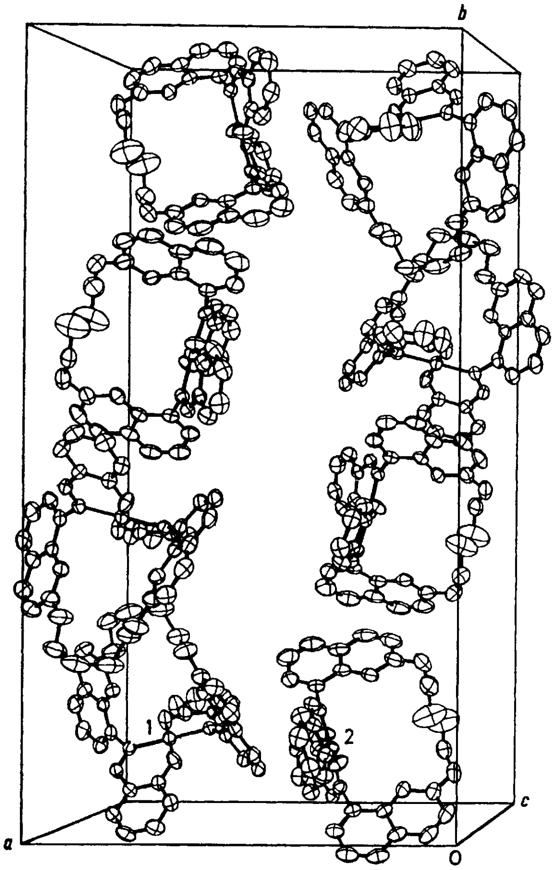

FIGURE 4 Unit-cell molecular packing. The two types of molecule are labelled 1 and 2

One of the principal reasons for undertaking the structural analysis of [NiL^4], apart from the characterisation of this new series of complexes, was to determine the dimensions of the cavity formed above the metal by the 'fly-over' molecular architecture. In particular, it was of interest to ascertain if small molecules such as O_2 could occupy the cavity when co-ordinated to the metal in an end-on fashion, given that the fifth octahedral site was occupied by a suitable basic ligand. It would appear from the crystal structures of [NiL^4] that the cavity is sterically too restrictive, and only in the second ligand conformation is there any possibility of co-ordination of O_2 in this manner. The reasoning is as follows: if bound O_2 is co-ordinated end-on to a metal at an M–O distance of 1.90 Å and in an axial direction with respect to the MN_2O_2 plane, then it is apparent that short intramolecular contacts will ensue, mainly with naphthyl hydrogen atoms. In molecule 1 the calculated distances are O–H(116) 1.97 Å and O–H(123) 1.56 Å which, compared with the sum of the van der Waals radii,[16] 2.6 Å,* would indicate that such non-bonded contacts would inhibit co-ordination of O_2. Reducing the M–O distance to 1.80 Å effects only a small increase in the calculated contact distances (2.01, 1.59 Å). These short contact

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* Recent work [17] would indicate a value closer to 2.4 Å.

distances are only possible in the presence of strong hydrogen bonding (*e.g.* O · · · H 1.66 Å in trichloroacetic acid [18]) but calculated C–H · · · O angles of only 134 and 122° respectively would militate against this possibility. We conclude therefore that the ligand conformation displayed in molecule 1 is not compatible with the co-ordination of O_2.

In molecule 2 there are three hydrogen atoms which project into the cavity, naphthyl protons H(216), H(223), and methylene proton H(219A). Using the same premise as for molecule 1, the hypothetical O · · · H contact distances are 2.26, 2.10, and 1.84 Å respectively for an M–O bond length of 1.90 Å, and 2.28, 2.12, and 1.93 Å for M–O 1.80 Å. It is conceivable that the orientation of the naphthyl hydrogens could be relaxed slightly to give acceptable van der Waals contacts. The H(219A) · · · O distance is potentially a hydrogen-bonded contact especially in view of a predicted angle of 173° at the proton. [It should be noted that some error in the position of H(219A) may exist due to the apparent high thermal motion of C(219).] It may be relevant to note here that in the structure of the iron ' picket fence porphyrin ' dioxygen complex the amide N–H protons are directed towards the co-ordinated O_2 although the estimated O · · · H distance (*ca.* 3.5 Å) is too long for significant hydrogen bonding.[19] Thus end-on co-ordination of O_2 may be sterically possible with the ligand conformation adopted in molecule 2 provided the bound O_2 is not destabilised by the interaction with the bridge methylene proton.

It should also be noted that the ligand conformations characterised in [NiL^4] may be modified by the co-ordination of a ligand in the fifth co-ordination site. In particular, the salicylaldimine groups could be expected to become more coplanar with concomitant reorientation of the groups bonded to the ligating N atoms. This may result in an increased distance between the naphthyl groups and thus potentially different methylene-chain configurations to those observed.

Conclusions.—The *X*-ray crystal structure of [NiL^4] has confirmed that a non-co-ordinating protective group can be constructed perpendicular to the basal plan of a Schiff base with its foundations at the ligand atoms. The presence of two sets of crystallographically independent discrete molecules of [NiL^4] has revealed that the dimensions of the cavity are extremely sensitive to the particular conformation adopted by the polymethylene chain which, in turn, affects the relative inclination of the supporting naphthyl groups. The intrusion of aromatic H atoms into the cavity occurs with both the conformers and indicates that alternative and more rigid capping groups will be required before reversible oxygen binding can be achieved with bioinorganic models of this type.

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