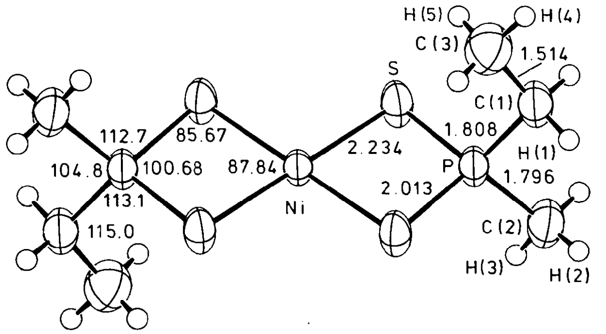

Fig. 1. Molecule of $[Ni(C_3H_8PS_2)_2]$ in arbitrary crystallographic orientation with thermal ellipsoids at 50% probability (*ORTEP* II; Johnson, 1976), bond lengths (Å), and bond angles (°). Values not given are related by the point symmetry $2/m$ of the molecule. H atoms are shown with radii of 1·0 Å^2. The e.s.d.'s are: Ni—S, S—P 0·001; P—C 0·003; C—C 0·005 Å; angles in the four-membered ring 0·02–0·03; other angles 0·1–0·2°.

acid (Arora, Hayes & Fernando, 1978). The P atom is 0·1 Å out of the NiS_4 plane and reduces the distance between Ni and the ethyl group. The tetrahedral configuration around the P atom is distorted (Fig. 1). The ethyl group shows the expected staggered conformation.

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{2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II) Monohydrate Diperchlorate (β Form)

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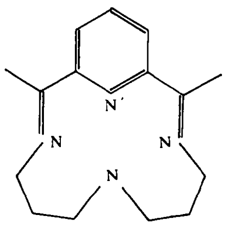
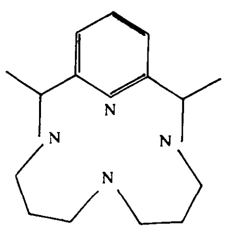
Abstract. $C_{15}H_{26}N_4Ni^{2+}.2ClO_4^-.H_2O$, $[Ni(C_{15}H_{26}N_4)](ClO_4)_2.H_2O$, M_r = 538, triclinic, $P\bar{1}$, a = 9·230 (8), b = 8·768 (9), c = 14·734 (13) Å, α = 112·5 (1), β = 87·7 (1), γ = 93·7 (1)°, U = 1099 Å^3, Z = 2, D_m = 1·61 (2), D_c = 1·62 Mg m^{-3}, $F(000)$ = 560. Mo $K\alpha$ radiation λ = 0·7107 Å, μ = 1·18 mm^{-1}. The Ni atom in the complex occupies an approximately square-planar environment [Ni—N 1·95 (1), 1·82 (1), 1·95 (1), 1·95 (1) Å]. In axial positions there are two perchlorate O atoms at 2·78 (2) and 3·29 (2) Å. 2306 independent reflections above background have been refined to R = 0·077.

Introduction. The condensation of 2,6-diacetylpyridine with 3,3′-diaminopropylamine in the presence of nickel(II) salts produces the macrocyclic complex $[NiL^1]^{2+}$ which was first isolated as the perchlorate salt (Curry & Busch, 1964). Reduction of $[NiL^1]^{2+}$ under mild conditions gave rise to $[NiL^2]^{2+}$ (Karn & Busch, 1969). Two forms of this latter cation were isolated, namely a red β form and a yellow α form in the ratio of *ca* 10:1. Stereochemical considerations and the properties of the derivatives formed indicated that the β form had the *meso* structure. The structure of the α form has



L^1



L^2

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† Deceased.

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been determined (Dewar & Fleischer, 1969) and shows the methyl groups on opposite sides of the ring (racemic form). Here we present the structure of the red β form.

Crystals of the title compound were prepared following the method of Karn & Busch (1969) and recrystallized from water. A crystal of approximate size 0·33 × 0·5 × 1·2 mm was mounted with the b^* axis parallel to the axis of a General Electric XRD-5 diffractometer. 2816 independent reflections with $2\theta < 45°$ were measured by the stationary-crystal–stationary-counter method using 10 s counts. Of these, 2306 with $I > 2\sigma(I)$ were used in subsequent calculations. The positions of the Ni atoms were located from the Patterson map and those of all other atoms except H were obtained from Fourier maps. The Ni, Cl, O, N and C atoms were refined anisotropically. The H atoms were fixed in trigonal or tetrahedral positions but their thermal parameters were refined successfully. The methyl H atoms on C(21) were located as a rigid group and their thermal parameter was refined but those on C(17) could not be located. The final R was 0·077. The weighting scheme used was $w^{1/2} = 1$ for $F_o < 100$ and $100/F_o$ for $F_o > 100$. This gave satisfactory values of $w\Delta^2$ over groups of F_o and $\sin\theta/\lambda$. The calculations were carried out on a CDC 7600 computer at the University of London Computer Centre using *SHELX* 76 (Sheldrick, 1976). Atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final atomic positions are given in Table 1, bond lengths and angles in Table 2.*

Table 1. *Atomic coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

	x	y	z
Ni	2328 (2)	226 (3)	2537 (2)
Cl(1)	4173 (5)	−3020 (5)	3272 (3)
O(11)	3743 (17)	−4121 (18)	3736 (12)
O(12)	4942 (22)	−1620 (22)	3958 (14)
O(13)	4986 (23)	−3743 (23)	2429 (14)
O(14)	2967 (19)	−2412 (24)	3036 (16)
Cl(2)	−228 (6)	3095 (7)	1939 (4)
O(21)	612 (23)	3542 (26)	2787 (15)
O(22)	−1418 (26)	4098 (26)	2091 (18)
O(23)	−770 (26)	1529 (24)	1644 (24)
O(24)	505 (23)	3516 (40)	1240 (18)
N(3)	1113 (15)	−1385 (16)	1524 (10)
C(4)	−104 (20)	−2049 (21)	1981 (13)
C(5)	−420 (18)	−732 (20)	2982 (13)
N(6)	752 (14)	328 (15)	3339 (10)
C(7)	699 (18)	1525 (20)	4234 (12)
C(8)	2146 (20)	2450 (21)	4524 (13)
N(9)	3022 (13)	2189 (15)	3639 (10)
C(10)	4615 (19)	2361 (24)	3873 (14)
C(11)	5547 (19)	2274 (24)	3015 (15)
C(12)	5437 (20)	662 (25)	2208 (16)
N(13)	4020 (16)	224 (18)	1704 (11)
C(14)	4263 (23)	−1313 (31)	857 (16)
C(15)	2932 (24)	−1991 (32)	214 (15)
C(16)	1737 (21)	−2741 (25)	700 (14)
C(17)	−1483 (21)	−2597 (26)	1313 (16)
C(18)	−1688 (18)	−559 (25)	3516 (15)
C(19)	−1745 (20)	687 (25)	4433 (15)
C(20)	−553 (18)	1758 (21)	4795 (14)
C(21)	2026 (27)	4278 (25)	5185 (16)
O(1)	−3589 (18)	−3043 (21)	8919 (12)

Table 2. *Molecular dimensions: distances* (Å) *and angles* (°)

Ni–N(3)	1·949 (12)	N(3)–Ni–N(6)	84·5 (6)
Ni–N(6)	1·822 (14)	N(3)–Ni–N(9)	163·1 (6)
Ni–N(9)	1·952 (11)	N(3)–Ni–N(13)	97·2 (6)
Ni–N(13)	1·947 (15)	N(6)–Ni–N(9)	83·5 (5)
		N(6)–Ni–N(13)	177·5 (6)
		N(9)–Ni–N(13)	94·4 (5)
N(3)–C(4)	1·49 (2)	C(8)–C(21)	1·53 (2)
N(3)–C(16)	1·47 (2)	N(9)–C(10)	1·51 (2)
C(4)–C(5)	1·52 (2)	C(10)–C(11)	1·48 (3)
C(4)–C(17)	1·57 (3)	C(11)–C(12)	1·46 (2)
C(5)–N(6)	1·36 (2)	C(12)–N(13)	1·48 (2)
C(5)–C(18)	1·37 (2)	C(14)–N(13)	1·47 (2)
C(7)–N(6)	1·34 (2)	C(14)–C(15)	1·53 (3)
C(7)–C(8)	1·51 (2)	C(15)–C(16)	1·54 (3)
C(7)–C(20)	1·37 (2)	C(18)–C(19)	1·38 (2)
C(8)–N(9)	1·46 (2)	C(19)–C(20)	1·38 (2)
Ni–N(3)–C(4)	110·2 (10)	C(5)–N(6)–C(7)	120·5 (14)
Ni–N(3)–C(16)	121·6 (11)	Ni–N(6)–C(7)	120·2 (11)
C(4)–N(3)–C(16)	109·6 (13)	Ni–N(6)–C(5)	119·1 (10)
N(3)–C(4)–C(5)	107·5 (13)	N(6)–C(7)–C(8)	111·9 (14)
N(3)–C(4)–C(17)	112·1 (17)	N(6)–C(7)–C(20)	120·9 (14)
C(5)–C(4)–C(17)	112·3 (15)	C(8)–C(7)–C(20)	127·1 (13)
C(4)–C(5)–N(6)	111·9 (14)	C(7)–C(8)–C(21)	113·6 (16)
C(4)–C(5)–C(18)	127·3 (15)	C(7)–C(8)–N(9)	108·7 (13)
N(6)–C(5)–C(18)	120·8 (14)	N(9)–C(8)–C(21)	113·5 (17)
Ni–N(9)–C(10)	117·8 (9)	Ni–N(9)–C(8)	111·8 (10)
C(8)–N(9)–C(10)	110·2 (14)	N(13)–C(14)–C(15)	113·4 (18)
N(9)–C(10)–C(11)	112·0 (16)	C(14)–C(15)–C(16)	112·7 (20)
C(10)–C(11)–C(12)	113·1 (18)	C(15)–C(16)–N(3)	107·9 (16)
C(11)–C(12)–N(13)	115·3 (16)	C(5)–C(18)–C(19)	118·6 (16)
C(12)–N(13)–C(14)	104·2 (14)	C(18)–C(19)–C(20)	120·5 (17)
Ni–N(13)–C(12)	115·7 (13)	C(19)–C(20)–C(7)	118·7 (15)
Ni–N(13)–C(14)	117·0 (12)		
Cl(1)–O(11)	1·41 (2)	Cl(2)–O(21)	1·41 (2)
Cl(1)–O(12)	1·42 (2)	Cl(2)–O(22)	1·41 (2)
Cl(1)–O(13)	1·38 (2)	Cl(2)–O(23)	1·34 (2)
Cl(1)–O(14)	1·38 (2)	Cl(2)–O(24)	1·36 (3)
O(11)–Cl(1)–O(12)	108·7 (11)	O(21)–Cl(2)–O(22)	112·1 (13)
O(11)–Cl(1)–O(13)	113·0 (11)	O(21)–Cl(2)–O(23)	111·9 (18)
O(11)–Cl(1)–O(14)	109·8 (12)	O(21)–Cl(2)–O(24)	110·6 (14)
O(12)–Cl(1)–O(13)	111·2 (12)	O(22)–Cl(2)–O(23)	106·8 (14)
O(12)–Cl(1)–O(14)	105·4 (12)	O(22)–Cl(2)–O(24)	98·8 (18)
O(13)–Cl(1)–O(14)	108·4 (14)	O(23)–Cl(2)–O(24)	115·9 (19)

Discussion. The molecule is shown in Fig. 1, together with the atomic-numbering scheme. The Ni atom is in an approximately square-planar environment with the maximum deviation of an atom from the NiN_4 plane being 0·11 Å (Table 3). Bond lengths are Ni–N(3) 1·95 (1), Ni–N(6) 1·82 (1), Ni–N(9) 1·95 (1), Ni–N(13) 1·95 (1) Å. These values are slightly longer

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* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34967 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

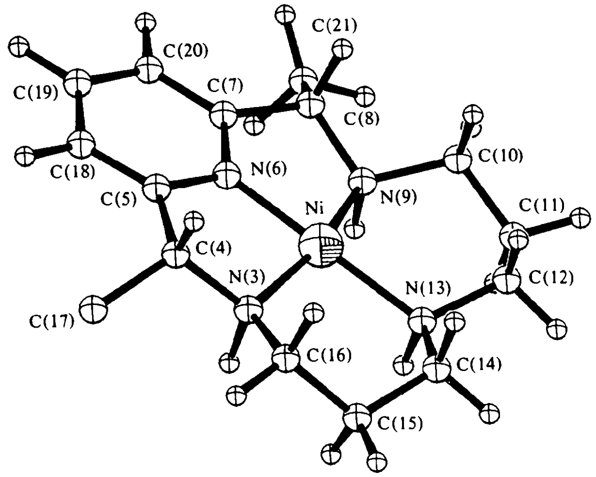

Fig. 1. View of the molecule showing the atom numbering.

Table 3. *Distances of atoms from least-squares planes* (Å)

Atoms marked with an asterisk do not contribute to the plane.

Plane (1): Ni −0·09 (2), N(3) 0·11 (2), N(6) −0·08 (2), N(9) 0·11 (2), N(13) −0·05 (2), C(17)* 0·47 (2), C(21)* 0·72 (2)
Plane (2): Ni, N(3), N(13) 0·00, C(14)* 0·65 (2), C(15)* 0·15 (2), C(16)* 0·67 (2)
Plane (3): Ni, N(9), N(13) 0·00, C(10)* 0·86 (2), C(11)* 0·53 (2), C(12)* 0·85 (2)

Values in the α form are: Plane (1) −0·06, 0·17, −0·17, 0·18, 0·13, 0·62, −1·35; Plane (2) 0·49, −0·04, 0·53; Plane (3) 1·08, 1·35, 1·22, respectively.

Table 4. *Torsion angles* (°) *in the macrocycle*

	β Form	αForm*
C(7)–C(8)–N(9)–C(10)	−153 (1)	−125
C(21)–C(8)–N(9)–C(10)	79 (1)	133
C(8)–N(9)–C(10)–C(11)	−174 (1)	−170
N(9)–C(10)–C(11)–C(12)	−65 (1)	−49
C(10)–C(11)–C(12)–N(13)	68 (1)	52
C(11)–C(12)–N(13)–C(14)	172 (1)	163
C(12)–N(13)–C(14)–C(15)	−179 (1)	78
N(13)–C(14)–C(15)–C(16)	−73 (1)	68
C(14)–C(15)–C(16)–N(3)	70 (1)	−68
C(15)–C(16)–N(3)–C(4)	177 (1)	180
C(16)–N(3)–C(4)–C(17)	−72 (1)	78
C(16)–N(3)–C(4)–C(5)	164 (1)	−161
N(3)–C(4)–C(5)–N(6)	−24 (1)	19
N(6)–C(7)–C(8)–N(9)	20 (1)	1

* Values calculated from published coordinates. Atoms have been renumbered to conform with the β form.

than those found in the α form (1·84, 1·88, 1·90, 1·90 Å) but in both structures the Ni—N(pyridine) bond is the shortest.

As expected, the two methyl groups, C(17) and C(21), are on the same side of the equatorial NiN_4 plane; thus the β form is the *meso* isomer. Indeed, as indicated by the torsion angles (Table 4), the molecule has approximate C_s symmetry. In addition to the differences in the methyl positions of the two structures, the ring conformations differ considerably, particularly around N(13).

It has been argued (Karn & Busch, 1969) that the mechanism of hydrogenation of L^1 causes the *meso* isomer to be produced in yields far exceeding that of the racemic form. This seems likely as there are no differences in the two structures sufficient to cause any structural instability. However, the two six-membered rings are considerably strained in that their conformations differ markedly from the ideal chair form, as shown in Table 3, planes (2) and (3). In the β form both pairs of central C atoms are much closer to the NiN_2 plane than in an unstrained chair. In the α form, while one ring has the unstrained chair conformation, the other is also very flattened.

In the β form, the axial positions are occupied by two perchlorate O atoms, O(14) and O(21), at 2·78 (2) and 3·29 (2) Å, but these distances are too long to suggest any bond formation. In the α form the axial positions are also occupied by perchlorate O atoms at 2·64 and 2·85 Å. The water molecule in the structure is not strongly hydrogen bonded, the shortest distances being 3·00 to N(13), 2·89 to O(24) and 3·00 Å to O(13). There are no contacts shorter than the sums of van der Waals radii between adjacent molecules.

We are at present investigating the structure of the β form of L^2 in molecules of the type $[NiL^2(L\text{–}L)]^{2+}$ where $L\text{–}L$ represents a bidentate ligand. Models indicate that the β form can fold to leave two vacant sites while the α form cannot assume such an unstrained non-planar conformation.

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