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Structure of (3,5,5,13,13,15-Hexamethyl-1,2,6,9,12-pentaazacyclopentadeca-2,15-diene)nickel(II) Perchlorate, $C_{16}H_{33}N_5Ni^{2+}.2ClO_4^-$

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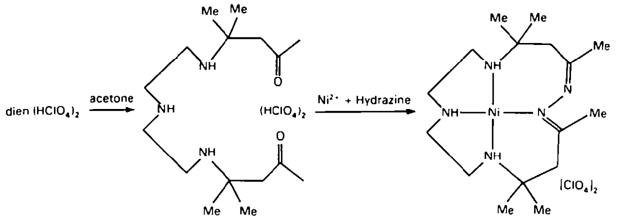
Abstract. $M_r = 553{\cdot}09$, monoclinic, $P2_1/c$, $a = 9{\cdot}950\,(3)$, $b = 13{\cdot}592\,(5)$, $c = 17{\cdot}261\,(4)$ Å, $\beta = 92{\cdot}83\,(2)°$, $V = 2331{\cdot}54$ Å^3, $Z = 4$, $D_x = 1{\cdot}576$, $D_m = 1{\cdot}57$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}70926$ Å, $\mu = 1{\cdot}116$ mm^{-1}, $F(000) = 1160$, $T = 298$ K. Final $R = 0{\cdot}036$ for 2218 observed reflections. The Ni$^{\text{II}}$ ion lies in a slightly distorted square-planar environment surrounded by the four N atoms of the tetradentate macrocyclic ring [Ni—N distances vary from 1·889 (3)–1·955 (3) Å]. The conformations of the chelate rings and chiralities of the asymmetric N atoms are discussed.

Introduction. The title compound $[\text{Ni}(L)](\text{ClO}_4)_2$ was supplied and prepared by Professor Neil Curtis (Curtis, 1982) *via* the Schiff-base-type condensation reaction shown.



The reaction gave rise to both yellow and orange crystalline products. It is the yellow compound which is the subject of the present study. Of special interest from a structural viewpoint was the potentially flexible seven-membered chelate ring. Complete crystallographic analysis was performed to determine the precise conformation.

Experimental. Pale-yellow plates, 0·4 × 0·4 × 0·2 mm; Picker FACS-I four-circle diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from 40 reflections ($2\theta = 28$–$35°$); symmetrical θ–2θ scans (2° min^{-1}) of $(1{\cdot}4 + 0{\cdot}694 \tan \theta)°$, peak-profile analysis (Grant & Gabe, 1977); scale correction (variation ± 2%); 3068 independent reflections with $2\theta \leq 45°$, 2218 with $I \geq 2{\cdot}3\sigma(I)$; intensities corrected for Lp, absorption ignored; Fourier methods; Gauss–Seidel block-diagonal, non-H atoms anisotropic, H (from ΔF synthesis) isotropic; final $R = 0{\cdot}036$, $R_w = 0{\cdot}046$, 421 variables, $w = [\sigma^2(F_o) + (0{\cdot}02F_o)^2]^{-1}$; max. LS shift/e.s.d. (for non-H atoms) = 0·17; atomic scattering factors with f' and f'' (Cromer & Waber, 1974); final ΔF map featureless apart from peak of 0·35 (6) e Å^{-3} in vicinity of a perchlorate ion; PDP-8e computer of crystallography laboratory, Chemistry Department, Simon Fraser University, BC, Canada, computer programs: *NRC* (Gabe, Larsen, Lee & Wang, 1979).

Discussion. Final positional parameters and isotropic temperature factors for all atoms are given in Table 1.† The structure of the $[\text{Ni}(L)]^{2+}$ cation is shown in Fig. 1. Bond distances and angles are to be found in Table 2.

The Ni$^{\text{II}}$ ion lies in an approximate square-planar coordination environment. The four N atoms of the tetradentate macrocycle surrounding the Ni$^{\text{II}}$ ion are slightly but significantly tetrahedrally distorted from the true square-planar configuration [N(1) and N(9) lie 0·074 (3) and 0·088 (3) Å, respectively below, whilst N(6) and N(12) lie 0·079 (3) and 0·083 (3) Å, respectively above the NiN$_4$ plane]. Similar but more extreme distortions (0·26–0·30 Å) have been observed for $[\text{Ni}(C_{18}H_{34}N_6)](\text{ClO}_4)_2$ (Davis, Einstein & Willis, 1982*b*) and the four-coordinate Cu$^{\text{II}}$ complex of Me$_4$C$_6$H$_{10}$[15]diene N$_4$(N$_2$) (Curtis, de Courcey & Waters, 1979).

The Ni—N distances, which range from 1·889 (3)–1·955 (3) Å, are typical of Ni$^{\text{II}}$ macrocyclic compounds (Curtis, 1979). Two major factors which affect Ni—N distances in this type of compound appear to be the nature of the nitrogen donor atom, *i.e.* amine or imine,

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† Lists of structure factors, anisotropic thermal parameters, bonds and angles for perchlorate anions, and mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38468 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional* (×10^5 *for* Ni *and* Cl *atoms*; ×10^4 *for* O, N *and* C *atoms*; ×10^3 *for* H *atoms*) *parameters and isotropic temperature factors* (Å^2) *for* [Ni(*L*)](ClO$_4$)$_2$

	x	*y*	*z*	B_{eq}*/B_{iso}
Ni	23700 (4)	7055 (4)	29122 (3)	2·55
Cl(1)	60364 (10)	24370 (8)	44070 (6)	3·90
Cl(2)	−14235 (12)	−5132 (8)	34184 (6)	4·64
O(11)	6596 (4)	2966 (3)	3789 (2)	6·7
O(12)	6919 (3)	2473 (3)	5070 (2)	6·7
O(13)	5814 (4)	1442 (3)	4179 (2)	7·3
O(14)	4799 (4)	2890 (3)	4578 (2)	8·3
O(21)	−1166 (3)	158 (3)	4042 (2)	5·7
O(22)	−183 (5)	−921 (4)	3245 (3)	10·5
O(23)	−1918 (3)	−11 (3)	2744 (2)	6·1
O(24)	−2360 (5)	−1219 (3)	3621 (2)	10·8
N(1)	1069 (3)	1064 (2)	2111 (2)	2·7
N(2)	1059 (3)	526 (2)	1396 (2)	3·2
N(6)	3670 (3)	129 (2)	2230 (2)	2·8
N(9)	3500 (3)	192 (2)	3726 (2)	3·1
N(12)	1306 (3)	1241 (2)	3701 (2)	2·9
C(3)	2051 (4)	685 (3)	974 (2)	3·0
C(4)	3188 (4)	1360 (3)	1199 (2)	3·4
C(5)	4331 (4)	848 (3)	1692 (2)	3·0
C(7)	4661 (4)	−494 (3)	2697 (3)	3·9
C(8)	4047 (4)	−742 (3)	3448 (2)	4·0
C(10)	2730 (4)	145 (3)	4445 (2)	4·0
C(11)	2023 (4)	1104 (3)	4478 (2)	4·0
C(13)	803 (4)	2268 (3)	3547 (2)	3·1
C(14)	−253 (4)	2186 (3)	2878 (2)	3·4
C(15)	37 (4)	1624 (3)	2164 (2)	2·9
C(31)	2065 (4)	123 (4)	228 (2)	4·4
C(51)	5095 (4)	1616 (3)	2166 (3)	4·3
C(52)	5281 (4)	301 (3)	1179 (3)	4·0
C(131)	111 (5)	2679 (3)	4249 (2)	4·4
C(132)	1965 (4)	2925 (3)	3344 (2)	3·7
C(151)	−1007 (4)	1736 (4)	1508 (2)	4·3
H(4*A*)	356 (3)	156 (3)	76 (2)	3·6 (8)
H(4*B*)	292 (3)	185 (2)	149 (2)	2·5 (7)
H(6*A*)	324 (3)	−26 (3)	195 (2)	2·9 (7)
H(7*A*)	536 (3)	−12 (2)	283 (2)	2·9 (7)
H(7*B*)	482 (4)	−103 (3)	242 (2)	3·9 (9)
H(8*A*)	467 (5)	−99 (3)	386 (2)	6·4 (11)
H(8*B*)	323 (4)	−116 (3)	338 (2)	4·7 (9)
H(9*A*)	423 (3)	61 (2)	383 (2)	2·5 (7)
H(10*A*)	210 (3)	−36 (2)	439 (2)	2·8 (7)
H(10*B*)	328 (3)	6 (3)	491 (2)	3·5 (8)
H(11*A*)	263 (3)	167 (2)	454 (2)	2·8 (7)
H(11*B*)	138 (3)	115 (3)	486 (2)	3·6 (8)
H(12*A*)	66 (3)	86 (3)	371 (2)	3·0 (8)
H(14*A*)	−48 (3)	283 (3)	273 (2)	3·5 (8)
H(14*B*)	−106 (4)	−35 (3)	25 (2)	4·4 (9)
H(31*A*)	229 (5)	55 (4)	−20 (3)	7·9 (13)
H(31*B*)	122 (4)	−14 (3)	8 (2)	5·9 (10)
H(31*C*)	267 (4)	−35 (3)	25 (2)	4·3 (9)
H(51*A*)	541 (4)	206 (3)	182 (2)	4·6 (9)
H(51*B*)	583 (4)	139 (3)	244 (2)	4·6 (9)
H(51*C*)	455 (3)	195 (3)	250 (2)	3·7 (8)
H(52*A*)	562 (4)	75 (3)	75 (2)	5·7 (10)
H(52*B*)	610 (4)	11 (3)	149 (2)	4·2 (9)
H(52*C*)	481 (4)	−30 (3)	90 (2)	4·4 (9)
H(131*A*)	−46 (3)	226 (3)	441 (2)	3·7 (8)
H(131*B*)	83 (4)	274 (3)	472 (2)	4·7 (9)
H(131*C*)	−23 (4)	332 (3)	410 (2)	4·1 (9)
H(132*A*)	237 (3)	272 (2)	288 (2)	2·5 (7)
H(132*B*)	270 (3)	288 (3)	376 (2)	3·6 (8)
H(132*C*)	167 (3)	358 (3)	333 (2)	3·6 (8)
H(151*A*)	−62 (4)	210 (3)	113 (2)	6·8 (11)
H(151*B*)	−121 (4)	114 (3)	133 (2)	6·4 (11)
H(151*C*)	−170 (4)	207 (3)	164 (2)	6·4 (11)

* $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ and refers to all non-hydrogen atoms.

and also the number of atoms in the chelate rings encompassing the Ni—N bond (Curtis, 1979). Ni—N(amine) distances are generally longer than Ni—N(imine) distances for a given chelate ring size, whereas larger chelate rings are conducive to longer Ni—N distances. The range of Ni—N distances observed here is consistent with these arguments.

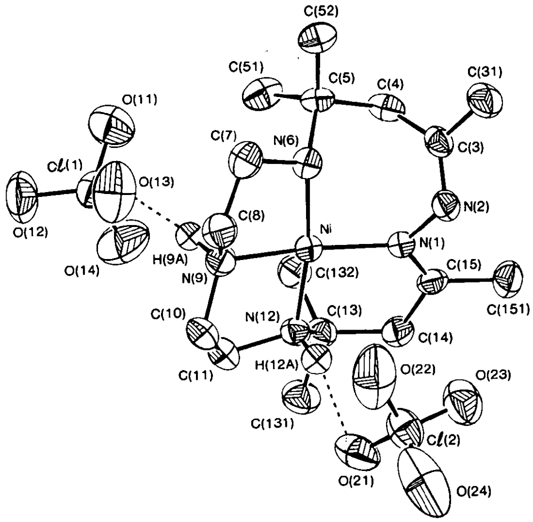

Fig. 1. A perspective view of [Ni(*L*)](ClO$_4$)$_2$ showing hydrogen bonding [*ORTEP* diagram (Johnson, 1965), 50% probability contours for all atoms].

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* [Ni(*L*)](ClO$_4$)$_2$

Ni—N(1)*	1·910 (3)	Ni—N(9)	1·889 (3)
Ni—N(6)	1·955 (3)	Ni—N(12)	1·911 (3)
N(1)—N(2)	1·434 (4)	N(9)—C(10)	1·491 (5)
N(2)—C(3)†	1·274 (5)	C(10)—C(11)	1·484 (6)
C(3)—C(4)	1·494 (6)	C(11)—N(12)	1·499 (5)
C(4)—C(5)	1·551 (5)	N(12)—C(13)	1·501 (5)
C(5)—N(6)	1·520 (5)	C(13)—C(14)	1·527 (5)
N(6)—C(7)	1·504 (5)	C(14)—C(15)	1·490 (5)
C(7)—C(8)	1·499 (6)	C(15)—N(1)†	1·286 (5)
C(8)—N(9)	1·472 (5)		
C(3)—C(31)	1·496 (6)	C(13)—C(131)	1·530 (5)
C(5)—C(51)	1·508 (6)	C(13)—C(132)	1·515 (6)
C(5)—C(52)	1·521 (5)	C(15)—C(151)	1·505 (5)
N(1)—Ni—N(6)	96·4 (1)	N(6)—Ni—N(9)	85·0 (1)
N(1)—Ni—N(9)	171·8 (1)	N(6)—Ni—N(12)	171·3 (1)
N(1)—Ni—N(12)	92·3 (1)	N(9)—Ni—N(12)	86·6 (1)
Ni—N(6)—C(5)	115·5 (2)	Ni—N(9)—C(10)	108·9 (2)
Ni—N(6)—C(7)	109·8 (2)	Ni—N(12)—C(11)	109·5 (2)
Ni—N(9)—C(8)	107·0 (2)	Ni—N(12)—C(13)	114·8 (2)
N(1)—N(2)—C(3)	115·7 (3)	C(31)—C(3)—C(4)	119·9 (3)
N(2)—C(3)—C(4)	123·6 (3)	N(2)—C(3)—C(31)	116·5 (4)
C(3)—C(4)—C(5)	113·1 (3)	C(4)—C(5)—C(51)	108·8 (3)
C(4)—C(5)—N(6)	107·2 (3)	N(12)—C(13)—C(131)	111·0 (3)
C(5)—N(6)—C(7)	113·4 (3)	N(12)—C(13)—C(132)	109·8 (3)
N(6)—C(7)—C(8)	107·8 (3)	C(14)—C(13)—C(131)	107·8 (3)
C(7)—C(8)—N(9)	105·2 (3)	C(4)—C(5)—C(52)	111·1 (3)
C(8)—N(9)—C(10)	116·6 (3)	N(6)—C(5)—C(51)	109·6 (3)
N(9)—C(10)—C(11)	105·0 (3)	N(6)—C(5)—C(52)	110·0 (3)
C(10)—C(11)—N(12)	106·3 (3)	C(51)—C(5)—C(52)	110·1 (3)
C(11)—N(12)—C(13)	114·5 (3)	C(14)—C(13)—C(132)	111·9 (3)
N(12)—C(13)—C(14)	106·1 (3)	C(131)—C(13)—C(132)	110·3 (3)
C(13)—C(14)—C(15)	120·6 (3)	N(1)—C(15)—C(151)	122·0 (3)
C(14)—C(15)—N(1)	123·4 (3)	C(14)—C(15)—C(151)	114·6 (3)
C(15)—N(1)—N(2)	113·1 (3)		

* Ni—N(imine) bond; all others are Ni—N(amine).
† Denotes C=N.

The conformations of each of the chelate rings do not appear unusual and have been previously observed (Fig. 2). The seven-membered ring adopts a similar conformation to that found for [{Ni($C_{18}H_{34}N_6$)}$_2$-(C_2O_4)](ClO$_4$)$_2$.2H$_2$O (Davis, Einstein & Willis, 1982*b*), the six-membered ring displays a type *A* conformation, as classified by Curtis (1979) and the five-membered rings exhibit both half-chair (Davis, Einstein & Willis, 1982*b*) and approximate envelope (Davis, Einstein & Willis, 1982*a*) conformations.

The structure of the cation (Fig. 1) indicates that the chiralities of N(6), N(9) and N(12) are *R*, *R* and *S*, respectively. Since the space group is centrosymmetric, the crystal must contain a racemic mixture of both *RRS* and *SSR* enantiomers.

The bond parameters of the perchlorate anions are in keeping with those found in other structures (Davis, Einstein & Willis, 1982*a*,*b*). Both perchlorate anions are hydrogen-bonded to the cation, *viz.* N(9)–H(9*A*)···O(13) = 2·01 (3) Å with N–H···O = 173 (3)° and N(12)–H(12*A*)···O(21) = 2·16 (3) Å with N–H···O = 162 (3)°.

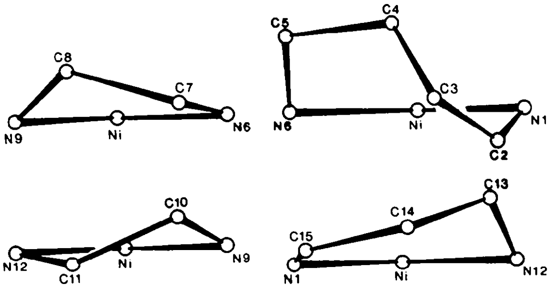

Fig. 2. The conformations of the chelate rings in $[Ni(L)](ClO_4)_2$ described, in each case, by the deviations of remaining ring atoms from the 'NiN$_2$' plane. Mean-plane equations have been deposited.

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Structure of Sodium Diisopropyldithiocarbamate Pentahydrate, $Na[C_7H_{14}NS_2].5H_2O$

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Abstract. $M_r = 289{\cdot}4$, triclinic, $P\bar{1}$, $a = 5{\cdot}983\ (1)$, $b = 7{\cdot}741\ (2)$, $c = 17{\cdot}545\ (1)$ Å, $\alpha = 92{\cdot}02\ (1)$, $\beta = 94{\cdot}73\ (1)$, $\gamma = 106{\cdot}97\ (3)°$, $V = 773\ (6)$ Å^3, $Z = 2$, $D_m = 1{\cdot}234\ (6)$, $D_x = 1{\cdot}243\ (9)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}37$ mm^{-1}, $F(000) = 312$, $T = 295$ K, $R = 0{\cdot}053$ for 1187 reflections. The structure is based on single-crystal diffractometer X-ray data. Pairs of distorted octahedra $[Na(H_2O)_6^+]$ are formed by edge sharing and these polyhedra are connected to form layers parallel to the *ab* plane by O–H···O and O–H···S hydrogen bonds. Along **c** the structure is kept together by van der Waals forces. The S(1)–C(1)–S(2) angle, 118·3 (3)°, in the organic ligand is the smallest so far observed in a Na dithiocarbamate.

Introduction. For Fe^{III} dithiocarbamates there is a strong correlation between the effective magnetic moment and the size of the ligand bite angle (Ståhl & Ymén, 1983). This angle is affected by the substituents R_2 in $^-S_2CNR_2$ as well as by the nature of the coordinating metal ion (Ymén, 1983*a*). In order to elucidate the influence of the R_2 groups a systematic study of compounds with weak metal–ligand interactions has been commenced. In $NaS_2CN(CH_3)_2.2H_2O$ (Oskarsson & Ymén, 1983) the ligand bite angle is smaller than in $NaS_2CN(CH_2)_4.2H_2O$ (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980; Ymén, 1982) as a result of a larger intramolecular steric interference, C–H···S, in the former compound. This paper reports the crystal structure of $NaS_2CN[CH(CH_3)_2]_2.5H_2O$ where an even larger steric interference is expected.

Experimental. Stoichiometric amounts of CS_2, $HN[CH(CH_3)_2]_2$ and NaOH in H_2O, efflorescent plate-like single crystals on evaporation under reduced

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