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102. The Crystal Structure of (2*R*, 7*S*, 10*R*)-2,10-diamino-5,5,7-trimethyl-4,8-diazaundecanenickel (II) perchlorate

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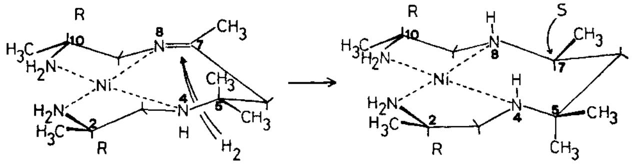
(12. I. 76)

Summary. The structure of the title compound, a tricyclic Ni(II) tetra-amine complex has been determined from analysis of photographic X-ray data. The crystal system is orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 9.802$, $b = 8.998$, $c = 24.378$ Å. The Ni atom is square planar coordinated. The six-membered chelate ring has a chair conformation. One of the five-membered chelate rings has a distorted *gauche* (λ) conformation with the methyl substituent in an equatorial position, the other has an unsymmetrical *gauche* (δ) conformation with the methyl substituent axial.

1. Introduction. – In the presence of ethylene diamine the unsaturated complex (2*R*,10*R*)-diamino-5,5,7-trimethyl-4,8-diaza-7-undecenenickel(II) is violet and the Ni atom octahedrally coordinated. On catalytic hydrogenation, in the presence of ethylene diamine, two diastereoisomeric products are obtained [1].

In the absence of ethylene diamine, the same complex is yellow, and the Ni atom is believed to be square planar coordinated (structure I, Fig. 1). The absolute configuration is known, being defined by the structure of the propylene diamine used in its synthesis [1]. On catalytic hydrogenation in the absence of ethylene diamine, a single product is obtained. The reaction is believed to be stereospecific [1], with the hydrogen molecule attacking on the side of the macrocycle opposite to the axial methyl group (see Fig. 1). Hence, the product obtained should have the ligand with the *R*,*S*,*R* configuration, structure II.



Absolute configuration of I Absolute configuration of II

Figure 1. *Stereochemistry of hydrogenation of the planar complex I*

2. Experimental. – The crystals were yellow rectangular plates. Examination of preliminary X-ray photographs showed that the crystals were orthorhombic with space group $P2_12_12_1$, containing four formula units. Accurate unit cell dimensions were obtained by use of a Syntex $P2_1$ automated diffractometer. Crystal data:

$C_{12}H_{30}N_4Ni(ClO_4)_2$, Mol.Wt. = 487.6, $a = 9.802$, $b = 8.998$, $c = 24.378$ Å, $V = 2150$ Å^3, $D_m = 1.51$, $Z = 4$, $D_x = 1.50$, space group $P2_12_12_1$, $\mu_{\mathrm{CuK}_\alpha} = 26.2$ cm^{-1}. The layers h0*l* to h8*l* were recorded by the equi-inclination *Weissenberg* method, using Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å) on multiple film packs. Intensities were estimated visually by comparison with a standard calibration strip. A total of 1329 reflections were measured and corrected for *Lorentz*-polarization effects. No absorption correction was applied to the intensities. 985 reflections were considered 'observed' and used in all subsequent calculations.

Table 1. *Final positional and vibrational parameters* (× *10*^{4}) (standard deviations in parentheses)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	2274(3)	– 684(3)	989(1)	121	178	28	– 9	– 3	– 2
N(1)	2123(16)	– 765(22)	206(6)	148	337	25	21	– 4	– 29
N(2)	3775(13)	691(18)	870(5)	129	204	25	– 23	7	5
N(3)	2352(15)	– 513(16)	1784(6)	154	195	25	– 50	16	10
N(4)	733(14)	–2048(20)	1095(7)	101	287	35	27	12	– 15
C(1)	2771(20)	487(24)	– 59(7)	171	265	25	– 82	– 3	19
C(2)	4176(19)	675(29)	322(8)	136	296	35	35	– 11	22
C(3)	5021(21)	454(29)	1234(9)	144	288	37	26	18	– 10
C(4)	4611(20)	571(23)	1830(8)	181	202	31	44	23	7
C(5)	2728(19)	– 733(31)	2026(9)	130	320	37	7	22	4
C(6)	1290(24)	–1544(22)	1999(9)	222	161	37	11	– 9	2
C(7)	69(20)	–1808(24)	1617(7)	154	240	20	– 15	6	– 1
C(8)	3146(23)	278(25)	654(9)	248	253	30	– 21	– 4	2
C(9)	5977(21)	1871(26)	1108(11)	165	221	55	97	12	– 2
C(10)	4343(23)	–2260(26)	1877(10)	163	245	52	– 59	13	17
C(11)	3579(28)	– 525(35)	2674(9)	288	401	33	17	38	20
C(12)	– 780(12)	– 275(30)	1597(9)	150	331	41	– 97	3	– 19
Cl(1)	1606(7)	3618(6)	1779(3)	245	190	41	– 52	– 21	4
O(1)	527(22)	4641(21)	1749(8)	443	375	52	–319	– 17	2
O(2)	2705(29)	4431(28)	1927(16)	373	363	151	112	32	46
O(3)	1734(22)	2899(22)	1269(7)	385	380	49	–153	– 74	20
O(4)	1372(20)	2592(20)	2173(7)	311	329	40	– 63	– 23	45
Cl(2)	–1577(6)	– 472(7)	– 172(2)	190	229	42	19	15	6
O(5)	–2912(20)	– 624(37)	– 342(10)	254	699	85	112	68	16
O(6)	– 948(25)	–1669(23)	26(12)	414	290	137	120	181	81
O(7)	– 779(31)	100(40)	– 459(20)	411	735	193	–192	– 92	246
O(8)	–1411(57)	– 694(31)	135(13)	1310	341	88	190	6	– 76
H(1.1)	1129	– 777	103						
H(1.2)	2551	–1710	72						
H(2)	3430	1730	936						
H(3)	2021	504	1888						
H(4.1)	1078	–3096	1081						
H(4.2)	59	–1897	794						

Anisotropic thermal parameters are expressed in the form
$\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot hk + 2\beta_{13} \cdot hl + 2\beta_{23} \cdot kl)]$

3. Structure Analysis and Refinement. – The positions of all the non-hydrogen atoms were obtained by analysis of *Patterson* and *Fourier* syntheses. Refinement was initially by cycles of isotropic full-matrix least-squares, followed by cycles of anisotropic block-diagonal least-squares (BDLS). Interlayer scale factors were refined before every second cycle of BDLS. Atomic scattering factors were taken from [2]. Those of Ni and Cl were corrected for anomalous dispersion [2]. The amino and aza hydrogen atoms were included at calculated positions, but not refined ($B = 5$ Å^2). Their coordinates were obtained assuming tetrahedral geometry about the nitrogen atom and an N–H bond length of 1 Å.

Refinement was terminated at $R = 8.5\%$ and $R_w = 11.1\%$ (average parameter shift $\leqslant 0.3$ e.s.d.). The weighting scheme used in the final stages of refinement was $\sqrt{w} = 1$ if $F_0 \leqslant 24$, else $\sqrt{w} = 24/F_0$. Final positional and vibrational parameters are given in Table 1. Because the intensities showed a rapid fall-off as $\sin\theta/\lambda$ increased, the vibrational parameters and correspondingly the standard deviations in the coordinates are rather large. Structure factor tables are available from the author.

4. Results and Discussion. – The final interatomic distances and angles are given in Tables 2 and 3. Fig. 2, a projection of the cation on the least-squares plane defined by the four nitrogen atoms, shows the atom-labelling scheme used for the cation.

The absolute configuration at two centers being known, Fig. 2 gives the absolute configuration of the title compound as *2R,7S,10R*, as previously proposed [1]. The Ni(II) ion has a square planar coordination with slight tetrahedral distortions. As observed for tetracyclic Ni(II) complexes [3–5] the bond angles at the metal are less than 90° for the 5-membered chelate rings, and greater than 90° for the 6-membered chelate ring. The mean Ni–N bond length of 1.94 Å is typical for tetrahedral nitrogen [3–5].

The conformation of the cation may be deduced from the planes of best fit given in Table 4. For the 6-membered chelate ring a chair conformation was proposed [1] and this is confirmed by the structure analysis (Plane (3), Table 4). However, the angle at the methylene carbon C(4) is smaller (113°) than observed (*ca.* 118°) [3] [5] in other saturated 6-membered chelate rings having chair conformations.

Table 2. *Bond lengths* (Å) (standard deviations in parentheses)

Ni–N(1)	1.916(14)	C(5)–N(3)	1.50(2)
Ni–N(2)	1.943(15)	N(3)–C(6)	1.49(3)
Ni–N(3)	1.945(14)	C(6)–C(7)	1.53(3)
Ni–N(4)	1.963(16)	C(7)–N(4)	1.45(2)
N(1)–C(1)	1.45(3)	C(7)–C(12)	1.61(3)
C(1)–C(2)	1.67(3)	Cl(1)–O(1)	1.40(2)
C(1)–C(8)	1.51(3)	Cl(1)–O(2)	1.35(3)
C(2)–N(2)	1.39(2)	Cl(1)–O(3)	1.41(2)
N(2)–C(3)	1.52(2)	Cl(1)–O(4)	1.35(2)
C(3)–C(4)	1.51(3)	Cl(2)–O(5)	1.38(2)
C(3)–C(9)	1.61(3)	Cl(2)–O(6)	1.33(2)
C(4)–C(5)	1.53(3)	Cl(2)–O(7)	1.17(4)
C(5)–C(10)	1.54(4)	Cl(2)–O(8)	1.30(3)
C(5)–C(11)	1.60(3)		

Table 3. *Bond angles* (degrees) (standard deviations in parentheses)

N(1)–Ni–N(4)	92.7(1)	N(3)–C(5)–C(11)	106.6(7)
N(1)–Ni–N(2)	86.3(2)	C(10)–C(5)–C(11)	112.1(3)
N(2)–Ni–C(3)	93.9(1)	Ni–N(3)–C(5)	114.7(4)
N(3)–Ni–N(4)	87.0(1)	Ni–N(3)–C(6)	105.9(4)
N(1)–Ni–N(3)	176.8(2)	C(5)–N(3)–C(6)	114.5(1)
N(2)–Ni–N(4)	178.6(3)	N(3)–C(6)–C(7)	115.4(5)
Ni–N(1)–C(1)	112.4(3)	C(6)–C(7)–N(4)	101.9(1)
N(1)–C(1)–C(2)	101.1(2)	C(6)–C(7)–C(12)	106.8(5)
N(1)–C(1)–C(8)	116.1(2)	N(4)–C(7)–C(12)	109.4(2)
C(8)–C(1)–C(2)	110.3(8)	Ni–N(4)–C(7)	111.6(5)
C(1)–C(2)–N(2)	107.6(8)	O(1)–Cl(1)–O(2)	105.0(6)
Ni–N(2)–C(2)	110.5(4)	O(1)–Cl(1)–O(3)	108.8(3)
Ni–N(2)–C(3)	115.5(2)	O(1)–Cl(1)–O(4)	110.9(3)
C(2)–N(2)–C(3)	109.3(7)	O(2)–Cl(1)–O(3)	114.4(5)
N(2)–C(3)–C(4)	109.6(9)	O(2)–Cl(1)–O(4)	108.4(7)
N(2)–C(3)–C(9)	104.2(2)	O(3)–Cl(1)–O(4)	109.2(6)
C(9)–C(3)–C(4)	106.4(3)	O(5)–Cl(2)–O(6)	117.9(3)
C(3)–C(4)–C(5)	113.3(4)	O(5)–Cl(2)–O(7)	120.0(1)
C(4)–C(5)–N(3)	106.5(4)	O(5)–Cl(2)–O(8)	111.8(9)
C(4)–C(5)–C(11)	105.9(3)	O(6)–Cl(2)–O(7)	105.3(4)
C(4)–C(5)–C(10)	113.3(7)	O(6)–Cl(2)–O(8)	112.7(5)
N(3)–C(5)–C(10)	112.0(5)	O(7)–Cl(2)–O(8)	84.5(6)

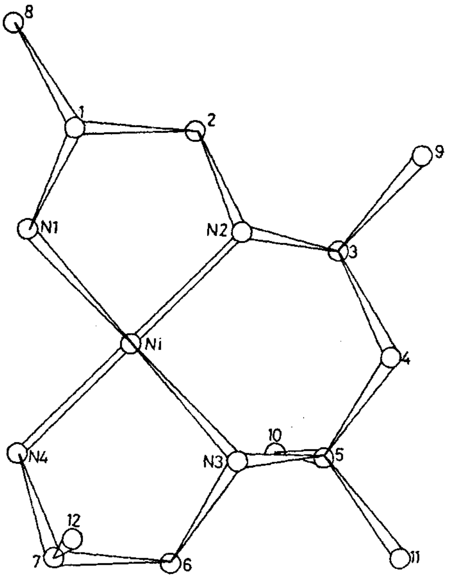


Figure 2. *Projection of the cation on the least-squares plane defined by atoms N(1)–N(4)*

For the 5-membered chelate rings, two possibilities were discussed [1]:

(a) both rings adopt *gauche* conformations with one methyl substituent in an axial position and the other in an equatorial position;

(b) both methyl substituents take equatorial positions with one chelate ring having an *envelope* conformation, the other a *gauche* conformation.

Possibility (b) was favoured for this complex but the present structure analysis shows that in the crystalline state the conformation of the two 5-membered chelate rings corresponds to (a). Chelate ring Ni, N(1), C(1), C(2), N(2) adopts a distorted *gauche* (λ) conformation (see Plane (1), Table 4). The C(1)-methyl substituent is equatorial. Chelate ring Ni, N(3), C(6), C(7), N(4) adopts an unsymmetrical *gauche* (δ) conformation (see Plane (2), Table 4). The C(7)-methyl substituent occupies an axial position. Similar conformations have been observed for the α- and β-isomers of the Ni(II) complex *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane [3].

Table 4. *Various least-squares planes in the molecule*

Coordination plane Ni, N(1), N(2), N(3), N(4)

Equation: $-0.638x-0.770y+0.008z+1.887=0$
Deviations in Å: Ni, −0.03; N(1), 0.03; N(2), −0.01; N(3), 0.03; N(4), −0.01; C(1), 0.49; C(2), −0.26; C(3), −0.96; C(4), −0.64; C(5), −1.00; C(6), −0.03; C(7), 0.56; C(8), 0.13; C(9), −0.58; C(10), −2.43; C(11), −0.77; C(12), 2.15:

Plane (1): N(2), Ni, N(1)

Equation: $-0.641x-0.767y-0.021z+1.852=0$
Deviations in Å: C(1), 0.44; C(2), −0.29; C(8), 0.03:

Plane (2): N(4), Ni, N(3)

Equation: $-0.634x-0.773y+0.036z+1.976=0$
Deviations in Å: C(6), −0.08; C(7), 0.53; C(12), 2.13:

Plane (3): N(2), C(3), C(5), N(3)

Equation: $-0.090x-0.908y-0.410z-1.127=0$
Deviations in Å: N(2), −0.03; C(3), 0.03; C(5), −0.03; N(3), 0.03; Ni, −0.90; C(4), 0.76; C(9), 0.98; C(10), −1.48; C(11), 0.80:

Fig. 3 illustrates the molecular packing in the complex viewed along the *a*-axis, and shows the non-bonded N–O distances less than 3.4 Å. The complex cation and the two perchlorate anions are hydrogen-bonded into units, the geometry of which is included in Table 5. Perchlorate anion (1) [Cl(1), O(1) – O(4)], appears less disordered than anion (2) [Cl(2), O(5) – O(8)], with an average apparent Cl–O bond length of 1.38 Å, compared with 1.30 Å in the latter. Anion (1) is hydrogen-bonded *via* oxygen atoms O(3) and O(4), and anion (2) through oxygen atom O(6).

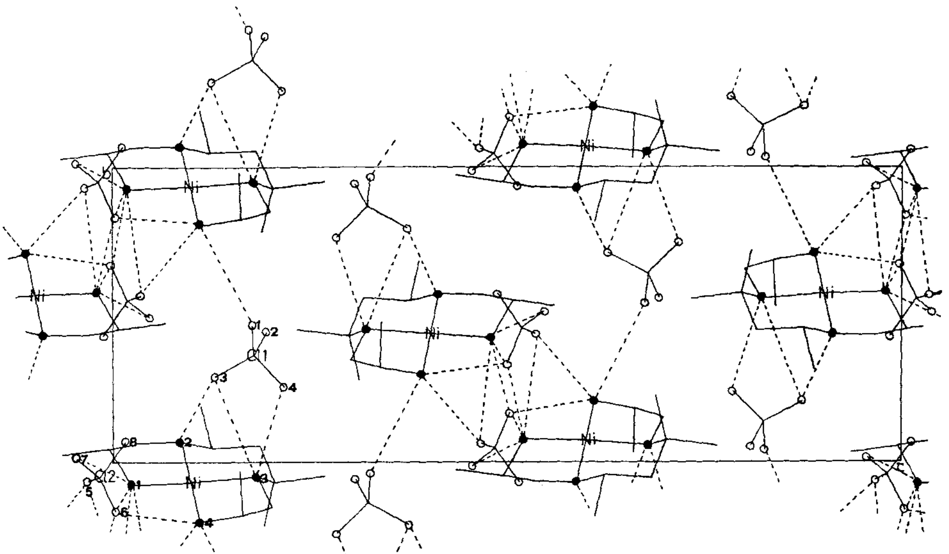


Figure 3. *The structure viewed along the a-axis, showing non-bonded N–O distances < 3.4* Å

Table 5. *Non-bonded N–O distances < 3.4* Å *and hydrogen-bond geometries*

N(1) ..... O(5)$^{b)}$	3.27	N(3) ..... O(3)	3.37
N(1) ..... O(6)	3.15	N(3) ..... O(4)	3.10
H(1.1) ..... O(6)	2.2	H(3.1) ..... O(4)	2.1
N(1)–H(1.1) ... O(6)	157.4°	N(3)–H(3.1) ... O(4)	175.3°
N(1) ..... O(6)$^{b)}$	3.04	N(4) ..... O(1)$^{a)}$	3.39
H(1.2) ..... O(6)$^{b)}$	2.1	N(4) ..... O(5)$^{b)}$	3.09
N(1)–H(1.2) ... O(6)$^{b)}$	157.7°		
N(1) ..... O(7)	3.36	N(4) ..... O(6)	3.10
		H(4.2) ..... O(6)	2.1
N(2) ..... O(3)	2.98	N(4)–H(4.2) ... O(6)	165.7°
H(2.1) ..... O(3)	2.1		
N(2)–H(2.1) ... O(3)	141.4°		

Symmetry operations to be applied to the perchlorate anions (see Fig. 3) $^{a)}$ x, y – 1, z and $^{b)}$ x + $^1/_2$, $^1/_2$ – y, – z

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