

Table 5. Selected angles (°) with e.s.d.'s in 2,2, Cd-2,2-I₂ and Hg-2,2-I₂

The superscript refers to the following transformation of the coordinates x, y, z : (i) $-x, -y, -z$.

	2,2	Cd-2,2-I ₂	Hg-2,2-I ₂
I-M-N		86.3 (4)	86.2 (2)
I-M-O(1)		94.1 (4)	93.9 (2)
I-M-O(2)		85.9 (4)	83.7 (2)
N-C(1)-C(2)	109.7 (3)	111.4 (2.7)	110.4 (1.1)
C(1)-C(2)-O(1)	108.5 (3)	103.5 (2.5)	107.7 (1.1)
C(2)-O(1)-C(3)	111.5 (4)	107.8 (2.4)	112.0 (1.1)
O(1)-C(3)-C(4)	110.5 (4)	104.7 (2.6)	107.0 (1.1)
C(3)-C(4)-O(2)	110.1 (4)	102.9 (2.5)	107.7 (1.2)
C(4)-O(2)-C(5)	111.9 (6)	108.9 (2.4)	112.7 (1.1)
O(2)-C(5)-C(6)	108.1 (3)	102.9 (2.5)	107.9 (1.2)
C(5)-C(6)-N ⁱ	110.4 (3)	104.3 (2.5)	111.4 (1.2)
C(6)-N ⁱ -C(1 ⁱ)	114.2 (4)	102.0 (2.4)	110.2 (1.1)
I-N-I ⁱ		97.5 (5)	89.1 (2)
N-I-N ⁱ		82.5 (5)	90.9 (2)

two axial I⁻ ions. Tables 4 and 5 give selected interatomic distances and angles. Uncomplexed 2,2 is included for comparison (Herceg & Weiss, 1972).

The formation constants in aqueous solution for the first complex between the weak (*b*)-acceptor (Ahrlund, Chatt & Davies, 1958) Cd²⁺ and NH₃ and I⁻ respectively are of about the same order of magnitude. With the marked (*b*)-acceptor Hg²⁺ the difference is about four log units in favour of I⁻ (*Stability Constants of Metal-Ion Complexes*, 1964), indicating a very strong Hg²⁺-I⁻ interaction.

When the central ion is changed from Cd²⁺ to the larger Hg²⁺ a ring expansion should follow. The change in O-Oⁱ distance reflects this fact. However, the ionic radius change cannot be responsible for the large (~0.50 Å) N-Nⁱ expansion. The reason must be related to the very strong linear I⁻-Hg²⁺-I⁻ coordination which thus weakens the Hg²⁺-N interaction.

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N-rac-C-rac-(5,6,12,13-Tetramethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene)-nickel(II) Diperchlorate

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Abstract. C₁₄H₂₈N₄Ni²⁺·2ClO₄⁻, [Ni(C₁₄H₂₈N₄)(ClO₄)₂ (isomer *c*), *M_r* = 510.0, monoclinic, *P*2₁/*c*, *a* = 10.99 (3), *b* = 13.46 (5), *c* = 16.28 (3) Å, β = 117.72 (2)° (from diffractometer measurements, Mo Kα radiation), *V* = 2131.8 Å³, *Z* = 4, *F*(000) = 1064,

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The Hg-I length is about the same as in other Hg²⁺-I⁻ complexes (Sandström, 1978). The similar affinities of Cd²⁺ for N and I⁻ result in a longer Cd-I distance than that found, for example, in CdI₂ (2.60 Å).

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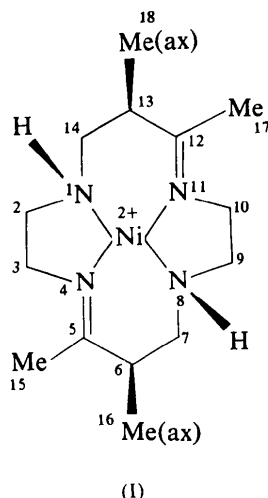
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μ = 0.80 mm⁻¹. The crystals contain *N-rac-C-rac*-[NiL]²⁺ cations, in which the N-H bonds at N(1) and N(8) are *cis* to the adjacent axial methyl groups at C(6) and C(13) respectively. The perchlorate anions are disordered.

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Introduction. The title compound (I) was recrystallized from water/methanol.



Systematic absences (from precession photographs)
0k0, k odd, and h0l, l odd, indicated space group $P2_1/c$.

Table 1. Fractional atomic coordinates ($\times 10^3$; for Cl, Ni $\times 10^4$) with e.s.d.'s in parentheses

	x	y	z	Occupancy ($\times 10^2$)
C(2)	91 (2)	124 (1)	163 (1)	
C(3)	-27 (2)	58 (1)	150 (1)	
C(5)	-192 (2)	67 (1)	206 (1)	
C(6)	-254 (2)	96 (1)	269 (1)	
C(7)	-186 (2)	192 (1)	322 (1)	
C(9)	23 (2)	265 (2)	443 (1)	
C(10)	178 (2)	239 (2)	503 (1)	
C(12)	353 (2)	215 (1)	454 (1)	
C(13)	408 (2)	190 (2)	387 (1)	
C(14)	299 (2)	198 (2)	284 (1)	
C(15)	-289 (2)	1 (2)	123 (1)	
C(16)	-253 (2)	5 (2)	329 (1)	
C(17)	465 (2)	248 (2)	552 (1)	
C(18)	482 (2)	90 (2)	412 (1)	
N(1)	188 (1)	124 (1)	264 (1)	
N(4)	-72 (1)	89 (1)	219 (1)	
N(8)	-368 (1)	176 (1)	383 (1)	
N(11)	222 (1)	209 (1)	430 (1)	
O(11)	31 (5)	850 (4)	297 (3)	46 (2)
O(12)	205 (3)	790 (3)	412 (2)	46 (2)
O(13)	209 (3)	927 (3)	356 (2)	46 (2)
O(14)	26 (3)	872 (3)	433 (2)	46 (2)
O(21)	390 (2)	39 (1)	146 (1)	
O(22)	341 (3)	-58 (2)	240 (2)	58 (1)
O(23)	211 (3)	-73 (2)	85 (2)	58 (1)
O(24)	436 (3)	-126 (2)	147 (2)	58 (1)
O(111)	182 (3)	967 (3)	398 (2)	54 (2)
O(121)	87 (3)	944 (3)	442 (2)	54 (2)
O(131)	-20 (5)	864 (4)	292 (3)	54 (2)
O(141)	182 (3)	799 (3)	442 (2)	54 (2)
O(211)	471 (4)	-121 (3)	220 (3)	42 (1)
O(221)	307 (4)	-122 (3)	74 (3)	42 (1)
O(231)	257 (4)	-71 (3)	197 (3)	42 (1)
Cl(1)	1155 (4)	8752 (3)	3840 (3)	
Cl(2)	3497 (4)	-600 (4)	1521 (3)	
Ni	753 (2)	1510 (1)	3239 (1)	

Data were collected for $h0-12l$ with $\theta_{\max} = 25^\circ$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation). This gave 2581 data of which 1696 unique reflexions with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections were applied (but no corrections were made for extinction or absorption), and the data scaled by a Wilson plot. The structure was solved by Patterson and Fourier methods with *SHELX-76* (Sheldrick, 1976) which was used for all calculations. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). After refinement with isotropic temperature factors to $R = 0.140$ a difference map showed that the perchlorate O atoms were disordered. When a disordered model was introduced for the anions, R fell to 0.124. Full-matrix least-squares refinement with anisotropic temperature factors for Ni, Cl, N, C and one O atom (see Table 1) converged at $R = 0.0872$ for 1696 observed reflexions ($R = \sum |F_o| - |F_c| / \sum |F_o|$). Unit weights were used for all reflexions, and because of the disorder H atoms were omitted. In the final cycle all

Table 2. Interatomic distances (Å) and angles ($^\circ$) with e.s.d.'s in parentheses

C(2)-C(3)	1.51 (2)	O(11)-O(131)	0.56 (7)
C(2)-N(1)	1.49 (2)	O(11)-Cl(1)	1.33 (4)
C(3)-N(4)	1.48 (1)	O(12)-O(141)	0.66 (4)
C(5)-C(6)	1.52 (2)	O(12)-Cl(1)	1.44 (3)
C(5)-C(15)	1.55 (2)	O(13)-O(111)	1.02 (3)
C(5)-N(4)	1.27 (2)	O(13)-Cl(1)	1.47 (3)
C(6)-C(7)	1.54 (2)	O(14)-O(121)	1.14 (4)
C(6)-C(16)	1.57 (2)	O(14)-Cl(1)	1.53 (3)
C(7)-N(8)	1.49 (2)	O(21)-Cl(2)	1.42 (2)
C(9)-C(10)	1.56 (2)	O(22)-O(231)	0.88 (3)
C(9)-N(8)	1.49 (2)	O(22)-Cl(2)	1.47 (2)
C(10)-N(11)	1.53 (2)	O(23)-O(221)	1.33 (4)
C(12)-C(13)	1.52 (2)	O(23)-Cl(2)	1.41 (2)
C(12)-C(17)	1.56 (2)	O(24)-O(211)	1.07 (3)
C(12)-N(11)	1.31 (2)	O(24)-O(221)	1.37 (4)
C(13)-C(14)	1.54 (2)	O(24)-Cl(2)	1.33 (3)
C(13)-C(18)	1.53 (3)	O(111)-Cl(1)	1.40 (3)
C(14)-N(1)	1.50 (2)	O(121)-Cl(1)	1.46 (3)
N(1)-Ni	1.93 (1)	O(131)-Cl(1)	1.56 (4)
N(4)-Ni	1.91 (1)	O(141)-Cl(1)	1.36 (3)
N(8)-Ni	1.90 (1)	O(211)-Cl(2)	1.51 (4)
N(11)-Ni	1.90 (1)	O(221)-Cl(2)	1.41 (4)
		O(231)-Cl(2)	1.51 (3)
N(1)-C(2)-C(3)	106.1 (10)	C(14)-N(1)-C(2)	109.2 (10)
N(4)-C(3)-C(2)	107.4 (11)	Ni-N(1)-C(2)	105.3 (7)
C(15)-C(5)-C(6)	113.3 (12)	Ni-N(1)-C(14)	114.4 (8)
N(4)-C(5)-C(6)	125.3 (13)	C(5)-N(4)-C(3)	119.4 (11)
N(4)-C(5)-C(15)	121.4 (12)	Ni-N(4)-C(3)	111.1 (8)
C(7)-C(6)-C(5)	110.5 (12)	Ni-N(4)-C(5)	129.3 (9)
C(16)-C(6)-C(5)	109.9 (13)	C(9)-N(8)-C(7)	109.5 (11)
C(16)-C(6)-C(7)	116.0 (12)	Ni-N(8)-C(7)	117.3 (7)
N(8)-C(7)-C(6)	110.9 (11)	Ni-N(8)-C(9)	106.9 (9)
N(8)-C(9)-C(10)	103.9 (13)	C(12)-N(11)-C(10)	117.1 (12)
N(11)-C(10)-C(9)	103.0 (11)	Ni-N(11)-C(10)	111.7 (9)
C(17)-C(12)-C(13)	114.4 (14)	Ni-N(11)-C(12)	130.5 (10)
N(11)-C(12)-C(13)	121.5 (13)	N(4)-Ni-N(1)	86.6 (4)
N(11)-C(12)-C(17)	124.0 (14)	N(8)-Ni-N(1)	179.4 (5)
C(14)-C(13)-C(12)	113.5 (12)	N(8)-Ni-N(4)	93.2 (4)
C(18)-C(13)-C(12)	109.3 (15)	N(11)-Ni-N(1)	93.7 (4)
C(18)-C(13)-C(14)	114.0 (15)	N(11)-Ni-N(4)	178.3 (5)
N(1)-C(14)-C(13)	109.6 (12)	N(11)-Ni-N(8)	86.6 (5)

shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1, bond distances and angles in Table 2.*

Discussion. The analysis confirms that the yellow isomer (*c*) of $[NiL](ClO_4)_2$ (Hay, Piplani & Jeragh, 1977) contains the cation (I) (Fig. 1), in which there is

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34361 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

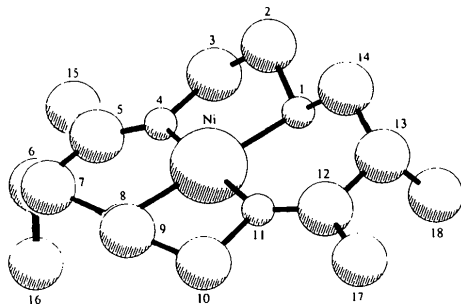


Fig. 1. General view of the cation.

an approximate twofold axis through Ni perpendicular to the NiN_4 plane. Ni has one close $O[ClO_4]$ contact of 2.79 Å with O(11) which lies on the opposite side of the NiN_4 plane from the axial methyl groups. The five-membered rings have close to envelope conformations $[C(3)-N(4)-Ni-N(1)$ and $N(8)-Ni-N(11)-C(10) \simeq 0^\circ$], and the six-membered rings are in approximate sofa conformations.

The crystal structure of isomer (*b*) of this compound contains centrosymmetric *N-meso-C-meso* cations (Ferguson, Restivo & Hay, 1979), in which the geometries of the five- and six-membered rings are similar to those found in the present study.

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Dicadmium Dimethylammonium Pentachloride Dihydrate

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Abstract. $(CH_3)_2NH_2Cd_2Cl_5 \cdot 2H_2O$, $C_2H_8N^+ \cdot 2Cd^{2+} \cdot 5Cl^- \cdot 2H_2O$, monoclinic, *Ic*, $Z = 4$, $a = 9.047(2)$, $b = 21.694(6)$, $c = 6.529(1)$ Å, $\beta = 90.57(2)^\circ$, $V = 1281.4(5)$ Å³ at 294 K, $D_c = 2.51$, $D_m = 2.49(1)$ Mg m⁻³, $\mu = 4.49$ mm⁻¹, 1885 diffractometer data up to $\sin \theta/\lambda = 0.70$ Å⁻¹, final $R(F) = 0.018$. The structure consists of corner-sharing $CdCl_6$ and $CdCl_5(H_2O)$ octahedra, forming infinite zigzag chains along *c*. The dimethylammonium ions are located in the free space between the chains. They and the hydrate molecules are involved in hydrogen bonding.

Introduction. Colourless plates of the title compound were obtained from an aqueous solution of equimolar

quantities of $(CH_3)_2NH_2Cl$ and $CdCl_2$. Chemical analyses (wt%): theoretical: C 4.96, H 2.50, N 2.89, Cl 36.61, Cd 46.43, H₂O 7.44; experimental: C 4.95, H 2.31, N 2.94, Cl 36.74, Cd 46.27, H₂O 7.29.

A crystal 0.60 × 0.26 × 0.11 mm was selected for the experiments. Precession photographs showed the space group to be either *Cc* or *C2/c*; the former was found to be correct during the structure determination. In order to avoid an unfavourable β angle of 126°, a transformation was made according to $a_{new} = a_{old} + c_{old}$. The space group then is *Ic*.

Data were collected on a Syntex P2₁ diffractometer with Nb-filtered Mo *K*α radiation. Reflections were measured in two quadrants of reciprocal space (*h, k, ±l*;