Table 4. *Structural results for the* CuN_2X *plane in* $[Cu(bpy)_2X]^+$ *cations* (X = Cl, Br, I)

X	Balancing anion, etc.	Cu–X bond length (Å)	Cu–N(2); N(4) bond lengths (Å)	N(2)–Cu–N(4) angle (°)	Reference
Cl	$S_2O_6^{2-}$; $6H_2O$	2·292 (4)	2·092 (6); 2·106 (5)	107·3 (2)	(a)
Cl	Cl$^-$; $6H_2O$	2·361 (4)	2·077 (10); 2·087 (11)	122·8 (4)	(b)
Br	BF_4^-	2·419 (3)	2·068 (8); 2·114 (9)	99·4 (3)	(c)
Br	Br$^-$	2·429 (2)	2·085 (7); 2·075 (8)	106·7 (3)	(d)
I	ClO_4^-	2·675 (4)	2·090 (8); 2·100 (7)	114·3 (3)	(c)
I	I$^-$	2·697	1·961; 2·106	113·8	(e)

References: (a) Harrison, Hathaway & Kennedy (1979); (b) Stephens & Tucker (1973); (c) Hathaway & Murphy (1980); (d) present work; (e) Barclay, Hoskins & Kennard (1963).

$[Cu(bpy)_2OAc]^+$ is significantly dependent upon the nature of the anion (BF_4^- or $ClO_4^-.H_2O$). Until the differences between (say) $[Cu(bpy)_2Br]Br$ and $[Cu(bpy)_2Br]BF_4$ can be rationalized, there seems little point in trying to discuss different $[Cu(bpy)_2L]^{+,2+}$ structures in any systematic manner.

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Structure of (1R,2R,4S,7S,8R,9R,11S,14S)-1,2,4,7,8,9,11,14-Octamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Perchlorate

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Abstract. $[Ni(C_{18}H_{40}N_4)](ClO_4)_2$, tetragonal, $P4_32_12$, $a = 8·872$ (1), $c = 33·368$ (2) Å, $U = 2626·5$ (2) Å^3, $Z = 4$, $D_m = 1·44$, $D_x = 1·44$ Mg m^{-3}, μ(Cu $K\alpha$) = 3·30 mm^{-1}, $R = 0·034$ and $R_w = 0·044$ for 2343 independent reflexions. The Ni^{II} ion is surrounded by a square-planar array of N atoms. The 14-membered ring takes a basket configuration with all four NH groups on the same side of the coordination plane. The absolute configurations of the eight chiral centers have been determined.

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Introduction. Metal-chelate complexes that contain several chiral centers exhibit intricate stereochemistries and large numbers of possible isomers. The structure of the title compound, [NiL](ClO$_4$)$_2$, which has eight chiral centers, has been discussed on the basis of detailed analyses of the NMR spectra including a novel observation of the intramolecular nuclear Overhauser effect combined with stereospecific deuteration and strain-energy calculations (Ito & Busch, 1973). In this paper, the structure determined by single-crystal X-ray diffraction is described.

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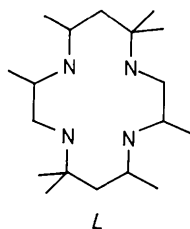
The compound was prepared as described previously (Ito & Busch, 1973). Orange plate crystals were obtained from an aqueous solution. A crystal with dimensions 0·26 × 0·26 × 0·28 mm was used for the study. X-ray diffraction data were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Within the range $2\theta < 155°$, 2343 independent reflexions with $|F_o| > 3\sigma(|F_o|)$ were obtained. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.

The structure was solved by the heavy-atom method and refined by block-diagonal least squares. The weighting scheme $w = [\sigma^2_{count} + (0·015 |F_o|)^2]^{-1}$ was employed and anisotropic temperature factors were used for non-H atoms. All H atoms were located by difference Fourier syntheses and included in the final refinement with isotropic temperature factors. At the final stage, refinements were carried out on two enantiomeric structures. The R and R_w values were reduced to 0·0338 and 0·0444, respectively, for the

Table 1. *Observed and calculated intensity relations between some Bijvoet pairs*

h k l	$F_o(hkl)/F_c(hkl)$	$F_o(khl)/F_c(khl)$	$\dfrac{F_o(khl)}{F_o(hkl)}$	$\left[\dfrac{F_c(khl)}{F_c(hkl)}\right]$
3 1 11	18·5 (17·9)	21·0 (20·2)	1·13 (1·13)	
3 1 14	17·3 (17·7)	14·7 (14·9)	0·85 (0·84)	
3 1 15	17·7 (17·1)	15·6 (15·0)	0·88 (0·88)	
3 1 18	21·2 (20·3)	18·4 (17·7)	0·87 (0·87)	
4 1 24	8·0 (8·0)	9·1 (8·8)	1·14 (1·10)	
5 1 8	12·4 (12·3)	14·3 (14·4)	1·16 (1·17)	
7 1 9	8·6 (9·0)	7·6 (8·0)	0·88 (0·89)	
4 2 14	9·2 (8·4)	11·7 (10·8)	1·27 (1·28)	
4 2 25	11·4 (11·1)	10·0 (9·9)	0·88 (0·89)	
8 2 13	6·9 (6·6)	8·5 (8·1)	1·22 (1·22)	
4 3 17	12·2 (11·8)	14·1 (13·8)	1·16 (1·16)	
7 3 20	13·1 (13·5)	15·1 (14·7)	1·15 (1·09)	

Table 2. *Fractional positional parameters ($\times 10^5$) and equivalent isotropic temperature factors for non-H atoms with e.s.d.'s in parentheses*

The equivalent isotropic temperature factor is calculated using the expression $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$, where the $\mathbf{a}_i$'s are the unit-cell edges in direct space.

	x	y	z	B_{eq} (Å^2)
Ni	2783 (8)	2783	0	2·58 (1)
N(1)	1816 (20)	1481 (20)	−5755 (5)	2·95 (4)
N(2)	−10368 (21)	20117 (20)	61 (6)	3·09 (5)
C(1)	25673 (27)	−10671 (34)	−4336 (7)	3·79 (6)
C(2)	12007 (28)	−11155 (30)	−6973 (7)	3·67 (6)
C(3)	−13994 (27)	367 (30)	−7483 (7)	3·74 (6)
C(4)	−22409 (29)	14836 (31)	−6445 (8)	3·85 (6)
C(5)	−25378 (28)	18634 (31)	−1991 (8)	3·73 (6)
C(6)	−12843 (37)	−635 (41)	−12046 (8)	5·49 (9)
C(7)	−22105 (34)	−13317 (34)	−5790 (10)	5·02 (8)
C(8)	−34570 (38)	33140 (40)	−1810 (10)	5·46 (9)
C(9)	35548 (30)	2920 (44)	−5014 (8)	5·17 (9)
Cl	11271 (9)	−55249 (7)	−7998 (2)	4·64 (2)
O(1)	23924 (32)	−46341 (32)	−8738 (8)	7·57 (8)
O(2a)	11241 (49)	−68737 (36)	−10203 (11)	6·65 (11)
O(3a)	8810 (90)	−57142 (84)	−4075 (11)	16·19 (30)
O(4a)	−673 (70)	−46310 (70)	−9572 (22)	14·28 (31)
O(2b)	15832 (134)	−66850 (100)	−5344 (30)	8·82 (36)
O(3b)	4035 (131)	−61604 (139)	−11310 (24)	9·78 (40)
O(4b)	−448 (82)	−48873 (91)	−5833 (27)	6·02 (22)

space group $P4_32_12$, whereas the values were 0·0441 and 0·0587 for $P4_12_12$, indicating $P4_32_12$ to be the true space group of the crystal. This result was also confirmed by comparison of the observed relation between hkl and khl reflexions with the calculated intensity relations (Table 1). Atomic parameters are listed in Table 2.*

Discussion. A perspective drawing of the complex ion is shown in Fig. 1. Bond lengths and angles within the complex ion are listed in Table 3. The Ni^{II} ion sits on a crystallographic C_2 axis and is surrounded by an approximately square-planar array of four N atoms of the ligand. The 14-membered ring has a basket configuration (Curtis, Swann & Waters, 1973) with all four NH groups on the same side of the coordination plane. The six-membered chelate rings take the chair form with the C(5)—CH$_3$ bonds in equatorial positions. The five-membered chelate rings adopt a very distorted δ *gauche* conformation (see below) rather than the eclipsed geometry presupposed from the N configurations of tetraaza 14-membered macrocycles (Waner & Busch, 1969; Curtis, Swann & Waters, 1973). The methyl groups on the five-membered rings, C(9)H$_3$, have an axial orientation. Crystal structures of many

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35978 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
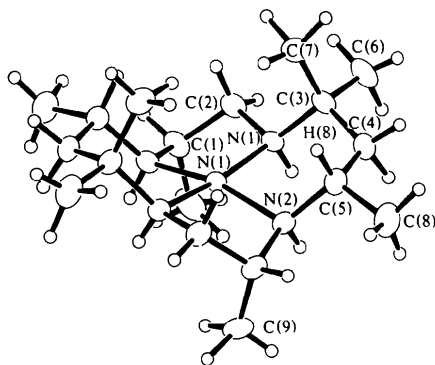
Fig. 1. A perspective drawing of the complex ion, showing the atom-numbering scheme.

Table 3. *Bond distances* (Å) *and angles* (°) *within the complex ion*

Ni–N(1)	1·926 (2)	C(3)–C(4)	1·525 (4)
Ni–N(2)	1·931 (2)	C(4)–C(5)	1·546 (4)
N(1)–C(2)	1·497 (3)	C(1)–C(9)	1·508 (5)
N(1)–C(3)	1·520 (3)	C(3)–C(6)	1·529 (4)
N(2)–C(1')	1·510 (3)	C(3)–C(7)	1·520 (4)
N(2)–C(5)	1·503 (3)	C(5)–C(8)	1·525 (4)
C(1)–C(2)	1·499 (3)		

N(1)–Ni–N(2)	91·80 (8)	C(2)–N(1)–C(3)	113·95 (17)
N(1)–Ni–N(2')	89·35 (8)	C(1')–N(2)–C(5)	116·32 (19)
N(1)–Ni–N(1')	171·52 (8)	C(3)–C(4)–C(5)	119·02 (22)
N(2)–Ni–N(2')	164·37 (8)	N(2')–C(1)–C(9)	108·50 (21)
Ni–N(1)–C(2)	106·78 (13)	C(2)–C(1)–C(9)	113·89 (23)
Ni–N(2)–C(1')	106·32 (14)	N(1)–C(3)–C(6)	108·66 (20)
Ni–N(1)–C(3)	115·04 (14)	C(4)–C(3)–C(6)	107·94 (22)
Ni–N(2)–C(5)	117·44 (15)	N(1)–C(3)–C(7)	110·36 (21)
N(1)–C(2)–C(1)	107·94 (20)	C(4)–C(3)–C(7)	110·86 (21)
N(2')–C(1)–C(2)	106·93 (19)	N(2)–C(5)–C(8)	112·44 (22)
N(1)–C(3)–C(4)	108·12 (19)	C(4)–C(5)–C(8)	108·26 (22)
N(2)–C(5)–C(4)	107·82 (19)	C(6)–C(3)–C(7)	110·81 (24)

tetraaza 14-membered macrocyclic metal complexes have been reported. Of these, similar basket-type structures have been found for the four-coordinate Ni^II complex of hexamethylcyclam (β form) (Curtis, Swann & Waters, 1973), the four-coordinate Ag^II complex of cyclam (*Pbnm* form) (Toriumi, Ito & Ito, unpublished), the five-coordinate Ni^II complex of *N*-tetramethyl-cyclam (D'Aniello, Mocella, Wagner, Barefield & Paul, 1975), and the five-coordinate Hg^II complex of cyclam (Alcock, Curson, Herron & Moore, 1979).

The absolute configurations of the eight chiral centers in the macrocyclic ligand were assigned as C(1)*R*, C(1')*R*, C(5)*S*, C(5')*S*, N(1)*S*, N(1')*S*, N(2)*R*, and N(2')*R*.* Because of the mode of synthesis, the complex ion contains C atoms C(1) and C(1') having *R* chirality. Assuming chelate-ring conforma-tions analogous to those predicted to be the most strain

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* Throughout this paper, a prime (') designates an atom trans-formed by the symmetry operation y,x,z.

free for a tetraaza 14-membered macrocyclic complex with no methyl substituent, [Co*X*₂(cyclam)]⁺ (Bosnich, Poon & Tobe, 1965), there are 36 diastereomers with C(1)*R* and C(1')*R* configurations for the present complex ion. The total stereochemistry described above was exactly the same as deduced from the previous NMR study (Ito & Busch, 1973).

The coordination bond lengths, 1·926 (2) Å [Ni–N(1)] and 1·931 (2) Å [Ni–N(2)], are normal for Ni^II complexes with four planar N donors. However, the square-planar array of N atoms is very distorted as compared with analogous tetraaza 14-membered macrocyclic Ni^II complexes (*e.g.* Ito & Toriumi, 1981). Deviations of Ni and the four coordinating atoms from the best plane defined by these five atoms are: Ni, −0·048 (2); N(1), −0·190 (3) and N(2), 0·214 (3) Å. The large distortion is most likely due to the presence of eight methyl groups in the ligand. Deviations of C atoms in the five-membered chelate ring from the plane defined by Ni, N(1), and N(2) are: C(1), 0·996 (3) and C(2), 0·071 (3) Å. From a novel observation of the intramolecular nuclear Overhauser effect in the NMR study, a C(7)H₃–H(8) (Fig. 1) separation in solution has been reported to be ~2·6 Å (Ito & Busch, 1973). This may be compared to the distance of 2·82 (2) Å found in the crystal.

Three of the perchlorate O atoms, O(2), O(3), and O(4), are disordered and located at two positions with populations $P_{O(2a)} = P_{O(3a)} = P_{O(4a)} = 0\cdot7$ and $P_{O(2b)} = P_{O(3b)} = P_{O(4b)} = 0\cdot3$ respectively. The positions of the disordered atoms, O(2a), O(3a) and O(4a), and O(2b), O(3b) and O(4b), are respectively related by a pseudo C_3 axis passing through Cl and the ordered O(1) atom. Fig. 2 shows a stereoscopic drawing of the crystal structure, in which the disordered O(2b), O(3b), and O(4b) are not depicted. Intermolecular contacts appear to be normal.
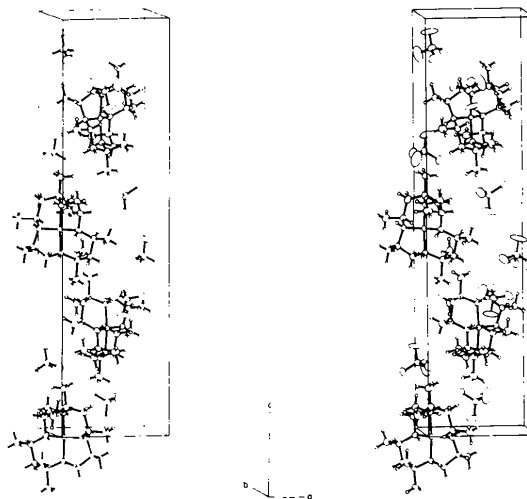

Fig. 2. Stereoscopic drawing of the crystal structure.

Calculations were carried out on the HITAC-M200H computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System, UNICS* III (Sakurai & Kobayashi, 1979).

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Dimethylammonium Hexachlorostannate(IV)

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Abstract. [NH$_2$(CH$_3$)$_2$]$_2$[SnCl$_6$], orthorhombic, *Pmnn*, $Z = 2$, $a = 7 \cdot 220$ (1), $b = 7 \cdot 340$ (2), $c = 14 \cdot 446$ (3) Å, $V = 765 \cdot 6$ (3) Å^3, $D_c = 1 \cdot 837$, $D_m = 1 \cdot 83$ (5) Mg m^{-3}; 1207 non-equivalent diffractometer data up to $\sin \theta/\lambda = 0 \cdot 7$ Å^{-1}; final $R(F) = 0 \cdot 046$, $R_w(F) = 0 \cdot 048$. The structure consists of [SnCl$_6$]$^-$ octahedra and [NH$_2$(CH$_3$)$_2$]$^+$ groups, connected by a weak bifurcated hydrogen bond. The Sn—Cl distances corrected for libration are 2·437 (1) and 2·450 (1) Å.

Introduction. Single crystals of [NH$_2$(CH$_3$)$_2$]$_2$[SnCl$_6$] were obtained by slow evaporation of an acid solution containing stoichiometric amounts of [NH$_2$(CH$_3$)$_2$]Cl and SnCl$_4$. A prismatic crystal with dimensions 0·2 × 0·3 × 0·35 mm was selected for the experiments. Precession photographs showed the space group to be either *P2nn* or *Pmnn*; the latter was confirmed during the structure refinement. Data were collected in a quadrant of reciprocal space up to $\sin \theta/\lambda = 0 \cdot 7$ Å^{-1} with Mo $K\alpha$ radiation on a Syntex $R3$ diffractometer equipped with a graphite monochromator. 2661 reflections were obtained, of which 1207 were unique. Three standard reflections observed after every 100 reflections showed a gradual intensity increase of 5% during the measurement. The data were rescaled with respect to the standards. No absorption correction was performed. A weight was assigned to each reflection

according to $w(I) = [\sigma^2(I)_{\text{counting}} + (0 \cdot 03I)^2]^{-1}$. The equivalent reflections were averaged $[R(I) = \sum |I - \langle I \rangle|/\sum I = 0 \cdot 032]$.

The structure was determined by heavy-atom and Fourier techniques. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974), except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion factors were applied to Sn and Cl (Cromer & Liberman, 1970). A difference synthesis showed the positions of the H atoms. They were included in the refinement, but their isotropic thermal parameters were not varied. A correction was made for secondary extinction (Larson, 1969). The structure was refined to $R(F) = 0 \cdot 046$, $R_w(F) = 0 \cdot 048$ and $S = [\sum w(F_o - F_c)^2/(\text{NO} - \text{NV})]^{\frac{1}{2}} = 2 \cdot 65$.*

The calculations were carried out with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on the Univac 1108 computer of the University of Frankfurt. The positional parameters of the atoms are reported in Table 1, bond lengths and angles in Table 2.