Structural Studies on Co-ordinated Macrocyclic Ligands. Part I. Crystal and Molecular Structure of [(1*RS*,3*SR*,8*RS*,10*SR*)-3,5,7,7,10,12,-14,14-Octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene]nickel(II) Perchlorate

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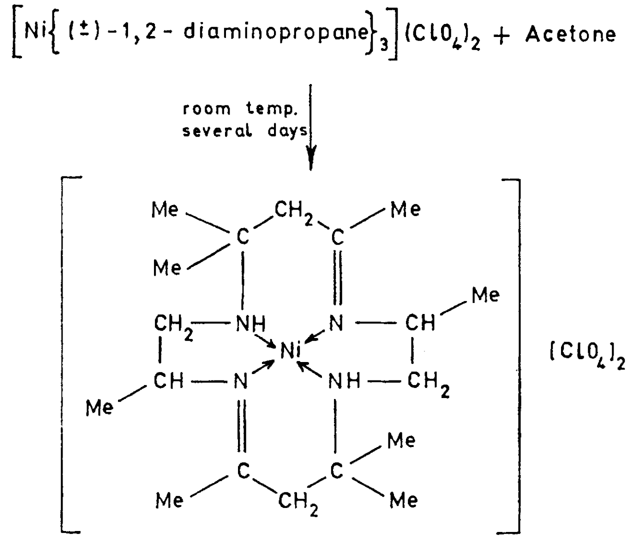
The *X*-ray structural analysis of the title compound has been determined from diffractometer data and refined by least-squares to R 0·08 for 2211 independent reflexions. Crystals are monoclinic, space-group $P2_1/c$, $a = 16{\cdot}401(4)$, $b = 10{\cdot}856(6)$, $c = 15{\cdot}072(4)$ Å, $\beta = 91{\cdot}07(3)°$, $Z = 4$. In the complex cation the two secondary amine and two imino-donor groups are in *trans* planar co-ordination. The two asymmetric carbon centres and the two asymmetric nitrogen centres occur in racemic pairs, the configuration of the racemate being (1*RS*, 3*SR*, 8*RS*, 10*SR*).

TRIS[(±)-1,2-DIAMINOPROPANE]NICKEL(II) perchlorate reacts with acetone at room temperature yielding, over a period of days, approximately equal amounts of two non-interconvertible isomeric cations [(octamethyl-1,4,8,11-tetra-azacyclotetradecadiene)nickel(II)] isolated as yellow (I) and orange (II) singlet ground-state perchlorate salts.[1] The colour difference persists for salts of other anions, *e.g.* nitrates prepared from tris-[(±)-1,2-diaminopropane]nickel(II) nitrate, or thiocyanates and tetrachlorozincates prepared by metathesis.



(I) *C-rac*-isomer (yellow crystals)
(II) *C-meso*-isomer (orange crystals)

Consideration of the overall planar structure expected for the complex cation, and of the nature of the condensation reaction producing the ligand,[2] suggest a number of sites for isomerism. Geometrical isomers result from a *cis*- or *trans*-arrangement of imino-groups, as observed for the isomeric pair of complexes arising from the reaction of tris(diaminoethane)nickel(II) perchlorate with acetone,[3] or from a *cis*- or *trans*-disposition of the methyl groups on the diaminopropane residue, or from their positioning with respect to the imine and amine nitrogen atoms. Optical isomerism is also possible through the presence of two asymmetric carbon centres. Similar isomers deriving from the two asymmetric nitrogen centres of the co-ordinated macrocycle should be interconvertible, as observed in complexes with the analogous hexamethyl macrocycle.[3] Of the possible configurations, some will clearly be preferred, although the determining factors may well lie in the reaction pathway leading to the complex cation, rather than in the relative energies of configurations. For a given configuration, details of conformation will be largely determined by non-bonded interactions. *X*-Ray crystallographic studies have therefore been undertaken to characterise the isomers and to assess the steric forces.

The orange isomer has been shown from space-group arguments to possess a centrosymmetric cation[4] which thus has the amino- and imino-groups mutually *trans*, the methyl groups of the diaminopropane residues similarly disposed, and the asymmetric carbon and nitrogen centres both *meso*. The yellow isomer has no imposed symmetry and has therefore been chosen for a full structural analysis.

EXPERIMENTAL

Crystal Data.—$C_{18}H_{36}Cl_2N_4NiO_8$,† $M = 566$, Monoclinic, $a = 16{\cdot}401(4)$, $b = 10{\cdot}856(6)$, $c = 15{\cdot}072(4)$ Å, $\beta = 91{\cdot}07(3)°$, $U = 2682$ Å^3, $D_m = 1{\cdot}45$, $Z = 4$, $D_c = 1{\cdot}40$. Space-group $= P2_1/c$. Mo-K_α radiation, $\lambda = 0{\cdot}7093$ Å; $\mu(\text{Mo-}K_\alpha) = 10{\cdot}06$ cm^{-1}.

Unit-cell dimensions were obtained by a least-squares fit to 12 reflexions located by four-circle diffractometry. Intensity data were collected on a Hilger and Watts automatic diffractometer, 2211 independent reflexions having $F_o^2 > 3\sigma(F_o^2)$ being collected. Absorption corrections were made ($\mu = 10{\cdot}06$ cm^{-1}).

The structure analysis proceeded normally, the ' heavy-atom ' electron-density map revealing the positions of the two chlorine atoms of the asymmetric unit and fifteen of the thirty light atoms. After the remainder were located from subsequent maps, refinement by the block-diagonal least-squares method was begun. Six cycles of ' isotropic '

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† The crystals studied were of the originally reported[1] anhydrous salt. A hydrate has since been obtained.

[1] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 1204.

[2] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

[3] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.* (*A*), 1966, 1015.

[4] N. F. Curtis, D. A. Swann, T. N. Waters, and I. E. Maxwell, *J. Amer. Chem. Soc.*, 1969, **91**, 4588.

TABLE 1

Atom positions

	x/a	y/b	z/c
Ni	0·24842(7)	0·1733(1)	0·14776(8)
Cl(1)	0·3682(2)	0·4802(3)	0·3448(2)
Cl(2)	0·1360(2)	−0·1363(3)	0·3739(2)
O(1)	0·3900(8)	0·4883(14)	0·4311(7)
O(2)	0·4241(7)	0·4116(13)	0·2934(9)
O(3)	0·2931(6)	0·4186(13)	0·3299(7)
O(4)	0·3753(10)	0·5937(11)	0·3040(9)
O(5)	0·2080(8)	−0·0792(14)	0·3311(8)
O(6)	0·0742(9)	−0·0571(13)	0·3446(11)
O(7)	0·1161(9)	−0·2524(11)	0·3361(9)
O(8)	0·1531(11)	−0·1439(15)	0·4620(8)
N(1)	0·3410(5)	0·2793(8)	0·1343(6)
N(4)	0·3213(5)	0·0382(8)	0·1432(5)
N(8)	0·1547(5)	0·0664(8)	0·1591(5)
N(11)	0·1779(5)	0·3084(7)	0·1654(5)
C(2)	0·4145(6)	0·2026(10)	0·1166(8)
C(3)	0·4060(6)	0·0822(11)	0·1649(8)
C(5)	0·3064(7)	−0·0747(11)	0·1303(8)
C(6)	0·2225(7)	−0·1238(10)	0·1142(7)
C(7)	0·1546(7)	−0·0366(10)	0·0926(7)
C(9)	0·0801(6)	0·1442(10)	0·1623(7)
C(10)	0·1023(7)	0·2624(10)	0·2111(8)
C(12)	0·1885(7)	0·4229(10)	0·1536(7)
C(13)	0·2660(7)	0·4706(10)	0·1113(8)
C(14)	0·3244(7)	0·3825(11)	0·0677(7)
C(15)	0·4158(7)	0·1005(13)	0·2657(8)
C(16)	0·3744(9)	−0·1745(12)	0·1358(10)
C(17)	0·0721(8)	−0·1080(11)	0·0988(8)
C(18)	0·1615(7)	0·0167(12)	−0·0002(8)
C(19)	0·1197(7)	0·2480(12)	0·3090(7)
C(20)	0·1311(8)	0·5232(12)	0·1814(9)
C(21)	0·4034(8)	0·4523(13)	0·0484(9)
C(22)	0·2871(8)	0·3279(11)	−0·0172(7)
H(1)	0·461(7)	0·24(1)	0·135(8)
H(2)	0·413(7)	0·18(1)	0·051(8)
H(3)	0·445(7)	0·02(1)	0·140(8)
H(4)	0·201(7)	−0·18(1)	0·167(8)
H(5)	0·225(7)	−0·19(1)	0·071(8)
H(6)	0·157(7)	0·03(1)	0·209(8)
H(7)	0·033(7)	0·09(1)	0·187(7)
H(8)	0·065(7)	0·17(1)	0·104(7)
H(9)	0·052(7)	0·33(1)	0·205(8)
H(10)	0·290(7)	0·52(1)	0·152(8)
H(11)	0·248(7)	0·53(1)	0·067(8)
H(12)	0·351(7)	0·31(1)	0·187(8)
H(13)	0·139(7)	0·32(1)	0·329(8)
H(14)	0·154(7)	0·18(1)	0·320(8)
H(15)	0·070(7)	0·22(1)	0·340(8)
H(16)	0·077(7)	−0·19(1)	0·088(8)
H(17)	0·041(7)	−0·10(1)	0·051(8)
H(18)	0·036(7)	−0·09(1)	0·142(8)
H(19)	0·215(7)	0·06(1)	−0·003(8)
H(20)	0·156(7)	−0·06(1)	−0·039(8)
H(21)	0·121(7)	0·08(1)	−0·010(8)
H(22)	0·422(7)	−0·16(1)	0·182(7)
H(23)	0·403(7)	−0·18(1)	0·075(8)
H(24)	0·350(7)	−0·24(1)	0·147(8)
H(25)	0·479(7)	0·13(1)	0·280(8)
H(26)	0·376(7)	0·16(1)	0·280(8)
H(27)	0·298(7)	0·03(1)	0·294(8)
H(28)	0·161(7)	0·59(1)	0·195(8)
H(29)	0·095(7)	0·55(1)	0·132(8)
H(30)	0·096(7)	0·50(1)	0·230(8)
H(31)	0·426(7)	0·48(1)	0·103(8)
H(32)	0·438(7)	0·39(1)	0·012(8)
H(33)	0·385(7)	0·52(1)	0·010(8)
H(34)	0·319(7)	0·27(1)	−0·031(8)
H(35)	0·282(7)	0·39(1)	−0·064(8)
H(36)	0·228(7)	0·29(1)	−0·002(8)

TABLE 2

Temperature parameters * (× 10^4)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	37·2(4)	72·0(10)	40·9(5)	−4·0(2)	1·8(8)	2·0(20)
Cl(1)	61(2)	154(4)	59(2)	−39(4)	−2(3)	−3(4)
Cl(2)	93(2)	132(4)	69(2)	−16(5)	−32(3)	11(5)
O(1)	153(8)	399(21)	68(6)	−242(20)	−74(11)	72(19)
O(2)	77(6)	336(20)	164(9)	−24(20)	13(12)	−199(22)
O(3)	67(5)	370(19)	84(6)	−148(16)	−12(9)	30(19)
O(4)	187(10)	175(14)	136(9)	−92(21)	−55(16)	84(19)
O(5)	105(7)	350(21)	117(8)	−107(21)	12(12)	102(22)
O(6)	137(9)	204(16)	211(13)	30(22)	−61(18)	90(24)
O(7)	165(9)	168(13)	156(10)	−103(19)	−35(16)	−94(19)
O(8)	238(12)	364(22)	78(7)	−262(27)	−56(16)	50(22)
N(1)	36(4)	94(9)	53(4)	−8(10)	7(7)	8(11)
N(4)	40(4)	73(8)	55(5)	4(9)	8(7)	2(10)
N(8)	34(3)	91(8)	48(4)	−18(10)	−2(6)	−14(10)
N(11)	42(4)	75(8)	51(4)	10(10)	3(7)	14(10)
C(2)	35(4)	109(13)	69(6)	−19(13)	5(9)	−17(15)
C(3)	32(4)	121(13)	64(6)	18(13)	−6(9)	7(16)
C(5)	64(6)	93(11)	57(6)	10(15)	14(10)	−2(15)
C(6)	51(5)	85(11)	60(6)	−19(13)	−12(10)	−30(14)
C(7)	48(5)	100(11)	47(5)	−35(13)	7(9)	−6(14)
C(9)	27(4)	97(11)	63(6)	0(11)	−10(8)	−1(14)
C(10)	44(5)	94(11)	61(6)	4(13)	9(9)	8(15)
C(12)	54(5)	81(10)	54(6)	4(14)	−16(9)	−11(14)
C(13)	66(6)	77(11)	55(6)	−6(14)	7(10)	16(14)
C(14)	52(5)	105(12)	55(6)	−13(14)	7(9)	38(14)
C(15)	59(6)	150(15)	56(6)	10(17)	−27(10)	−16(17)
C(16)	79(7)	89(12)	104(9)	40(18)	0(14)	−19(20)
C(17)	71(6)	115(13)	60(6)	−71(16)	7(11)	−10(16)
C(18)	57(6)	123(13)	54(6)	−21(16)	1(10)	−16(16)
C(19)	51(5)	140(14)	49(6)	2(15)	16(9)	−36(16)
C(20)	66(6)	108(13)	86(8)	24(16)	1(12)	−21(18)
C(21)	68(7)	135(15)	86(8)	−52(17)	24(12)	33(19)
C(22)	75(6)	106(12)	48(5)	−6(17)	2(10)	17(15)

* In the form $f = f_0 \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

TABLE 3

Bond lengths (Å)

Ni–N(1)	1·919(8)	C(2)–H(1)	0·9(1)
Ni–N(4)	1·893(8)	C(2)–H(2)	1·0(1)
Ni–N(8)	1·936(8)	C(3)–H(3)	1·0(1)
Ni–N(11)	1·890(8)	C(6)–H(4)	1·1(1)
N(1)–C(2)	1·49(1)	C(6)–H(5)	0·9(1)
C(2)–C(3)	1·50(2)	N(8)–H(6)	0·8(1)
C(3)–N(4)	1·50(1)	C(9)–H(7)	1·1(1)
N(4)–C(5)	1·26(1)	C(9)–H(8)	0·9(1)
C(5)–C(6)	1·49(2)	C(10)–H(9)	1·1(1)
C(6)–C(7)	1·49(2)	C(13)–H(10)	0·9(1)
C(7)–N(8)	1·50(1)	C(13)–H(11)	1·0(1)
N(8)–C(9)	1·49(1)	C(15)–H(25)	1·1(1)
C(9)–C(10)	1·52(2)	C(15)–H(26)	0·9(1)
C(10)–N(11)	1·51(1)	C(15)–H(27)	0·9(1)
N(11)–C(12)	1·27(1)	C(16)–H(22)	1·1(1)
C(12)–C(13)	1·52(2)	C(16)–H(23)	1·0(1)
C(13)–C(14)	1·51(2)	C(16)–H(24)	0·9(1)
C(14)–N(1)	1·53(1)	C(17)–H(16)	0·9(1)
C(3)–C(15)	1·54(2)	C(17)–H(17)	0·9(1)
C(5)–C(16)	1·56(2)	C(17)–H(18)	0·9(1)
C(7)–C(17)	1·56(2)	C(18)–H(19)	1·0(1)
C(7)–C(18)	1·52(2)	C(18)–H(20)	1·0(1)
C(10)–C(19)	1·51(2)	C(18)–H(21)	1·0(1)
C(12)–C(20)	1·50(2)	C(19)–H(13)	0·9(1)
C(14)–C(21)	1·53(2)	C(19)–H(14)	0·9(1)
C(14)–C(22)	1·53(2)	C(19)–H(15)	1·0(1)
Cl(1)–O(1)	1·35(1)	C(20)–H(28)	0·9(1)
Cl(1)–O(2)	1·42(1)	C(20)–H(29)	1·0(1)
Cl(1)–O(3)	1·42(1)	C(20)–H(30)	1·0(1)
Cl(1)–O(4)	1·38(1)	C(21)–H(31)	1·0(1)
Cl(2)–O(5)	1·49(1)	C(21)–H(32)	1·0(1)
Cl(2)–O(6)	1·39(1)	C(21)–H(33)	1·0(1)
Cl(2)–O(7)	1·42(1)	C(22)–H(34)	0·9(1)
Cl(2)–O(8)	1·35(1)	C(22)–H(35)	1·0(1)
N(1)–H(12)	1·0(1)	C(22)–H(36)	1·1(1)

refinement led to R 0·151. Refinement of anisotropic temperature parameters as well as positional parameters for all non-hydrogen atoms lowered R to 0·079. Two subsequent cycles in which hydrogen positional parameters were also refined produced final reliability factors of R

0·0767 and the weighted value R' 0·0894. The weighting scheme used was $\omega = 4\,F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o)^2$ being derived from the counting statistics.

TABLE 4

Bond angles (°)

N(1)–Ni–N(8)	179·0(6)	C(7)–C(6)–H(4)	105(3)
N(4)–Ni–N(11)	173·9(6)	C(7)–C(6)–H(5)	110(3)
N(1)–Ni–N(4)	87·7(6)	H(4)–C(6)–H(5)	98(3)
N(4)–Ni–N(8)	92·4(6)	C(7)–N(8)–H(6)	105(3)
N(8)–Ni–N(11)	87·9(6)	N(8)–C(9)–H(7)	107(3)
N(11)–Ni–N(1)	92·1(6)	N(8)–C(9)–H(8)	108(3)
Ni–N(1)–C(2)	109·1(8)	C(10)–C(9)–H(8)	108(3)
Ni–N(1)–C(14)	112·2(8)	H(7)–C(9)–H(8)	107(3)
Ni–N(4)–C(3)	109·2(8)	C(9)–C(10)–H(9)	108(3)
Ni–N(4)–C(5)	129·5(9)	N(11)–C(10)–H(9)	113(3)
Ni–N(8)–C(7)	112·2(8)	C(19)–C(10)–H(9)	107(3)
Ni–N(8)–C(9)	108·5(8)	C(12)–C(13)–H(10)	106(3)
Ni–N(11)–C(10)	108·5(8)	C(12)–C(13)–H(11)	106(3)
Ni–N(11)–C(12)	130·9(9)	C(14)–C(13)–H(10)	112(3)
N(1)–C(2)–C(3)	108·4(9)	C(14)–C(13)–H(11)	107(3)
C(2)–C(3)–N(4)	105·3(9)	H(10)–C(13)–H(11)	104(3)
C(3)–N(4)–C(5)	121·2(9)	C(14)–N(1)–H(12)	108(3)
N(4)–C(5)–C(6)	123·2(10)	C(2)–N(1)–H(12)	105(3)
C(5)–C(6)–C(7)	119·4(10)	C(10)–C(19)–H(13)	107(3)
C(6)–C(7)–N(8)	109·5(9)	C(10)–C(19)–H(14)	111(3)
C(7)–N(8)–C(9)	117·0(8)	C(10)–C(19)–H(15)	110(3)
N(8)–C(9)–C(10)	107·8(9)	H(13)–C(19)–H(14)	114(3)
C(9)–C(10)–N(11)	104·4(9)	H(14)–C(19)–H(15)	98(3)
C(10)–N(11)–C(12)	120·2(9)	H(15)–C(19)–H(13)	116(3)
N(11)–C(12)–C(13)	120·6(10)	C(7)–C(17)–H(16)	114(3)
C(12)–C(13)–C(14)	120·5(10)	C(7)–C(17)–H(17)	113(3)
C(13)–C(14)–N(1)	106·5(9)	C(7)–C(17)–H(18)	121(3)
C(2)–N(1)–C(14)	115·2(9)	H(16)–C(17)–H(17)	90(4)
C(2)–C(3)–C(15)	110·9(10)	H(17)–C(17)–H(18)	101(4)
N(4)–C(3)–C(15)	109·6(9)	H(18)–C(17)–H(16)	113(4)
N(4)–C(5)–C(16)	122·0(10)	C(7)–C(18)–H(19)	107(3)
C(6)–C(5)–C(16)	114·7(10)	C(7)–C(18)–H(20)	103(3)
C(6)–C(7)–C(17)	108·4(9)	C(7)–C(18)–H(21)	110(3)
N(8)–C(7)–C(17)	108·6(9)	H(19)–C(18)–H(20)	113(3)
C(6)–C(7)–C(18)	112·9(10)	H(20)–C(18)–H(21)	116(3)
N(8)–C(7)–C(18)	109·4(10)	H(21)–C(18)–H(19)	108(3)
C(17)–C(7)–C(18)	108·9(9)	C(5)–C(16)–H(22)	115(3)
C(9)–C(10)–C(19)	115·2(9)	C(5)–C(16)–H(23)	108(3)
N(11)–C(10)–C(19)	109·8(9)	C(5)–C(16)–H(24)	106(3)
N(11)–C(12)–C(20)	125·6(10)	H(22)–C(16)–H(23)	105(3)
C(13)–C(12)–C(20)	113·7(10)	H(23)–C(16)–H(24)	112(3)
C(13)–C(14)–C(21)	108·3(10)	C(10)–C(9)–H(7)	119(3)
C(21)–C(14)–C(22)	111·1(10)	H(24)–C(16)–H(22)	111(3)
N(1)–C(14)–C(21)	110·3(10)	C(3)–C(15)–H(25)	108(3)
C(13)–C(14)–C(22)	111·2(10)	C(3)–C(15)–H(26)	105(3)
N(1)–C(14)–C(22)	109·3(9)	C(3)–C(15)–H(27)	109(3)
O(1)–Cl(1)–O(2)	113·5(9)	H(25)–C(15)–H(26)	114(3)
O(2)–Cl(1)–O(3)	103·5(9)	H(26)–C(15)–H(27)	119(3)
O(3)–Cl(1)–O(4)	115·5(9)	H(27)–C(15)–H(25)	102(3)
O(4)–Cl(1)–O(1)	110·4(9)	C(12)–C(20)–H(28)	110(3)
O(1)–Cl(1)–O(3)	113·5(9)	C(12)–C(20)–H(29)	112(3)
O(2)–Cl(1)–O(4)	99·4(9)	C(12)–C(20)–H(30)	116(3)
O(5)–Cl(2)–O(6)	100·6(9)	H(28)–C(20)–H(29)	103(3)
O(6)–Cl(2)–O(7)	105·0(9)	H(29–C(20)–H(30)	106(3)
O(7)–Cl(2)–O(8)	112·4(9)	H(30)–C(20)–H(28)	108(3)
O(8)–Cl(2)–O(5)	107·4(9)	C(14)–C(21)–H(31)	108(3)
O(5)–Cl(2)–O(7)	111·9(9)	C(14)–C(21)–H(32)	106(3)
O(6)–Cl(2)–O(8)	119·0(10)	C(14)–C(21)–H(33)	102(3)
N(1)–C(2)–H(1)	110(3)	H(31)–C(21)–H(32)	117(3)
N(1)–C(2)–H(2)	107(3)	H(32)–C(21)–H(33)	109(3)
C(3)–C(2)–H(1)	110(3)	H(33)–C(21)–H(31)	113(3)
C(3)–C(2)–H(2)	107(3)	C(14)–C(22)–H(34)	105(3)
H(1)–C(2)–H(2)	102(3)	C(14)–C(22)–H(35)	112(3)
C(2)–C(3)–H(3)	111(3)	C(14)–C(22)–H(36)	108(3)
C(15)–C(3)–H(3)	114(3)	H(34)–C(22)–H(35)	113(3)
N(4)–C(3)–H(3)	106(3)	H(35)–C(22)–H(36)	111(3)
C(5)–C(6)–H(4)	113(3)	H(36)–C(22)–H(34)	108(3)
C(5)–C(6)–H(5)	109(3)		

Atom positions, temperature factors, bond lengths, and bond angles, together with appropriate standard deviations, are listed in Tables 1—4. Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20337 (4 pp., 1 microfiche). The numbering scheme is seen in Figure 1.

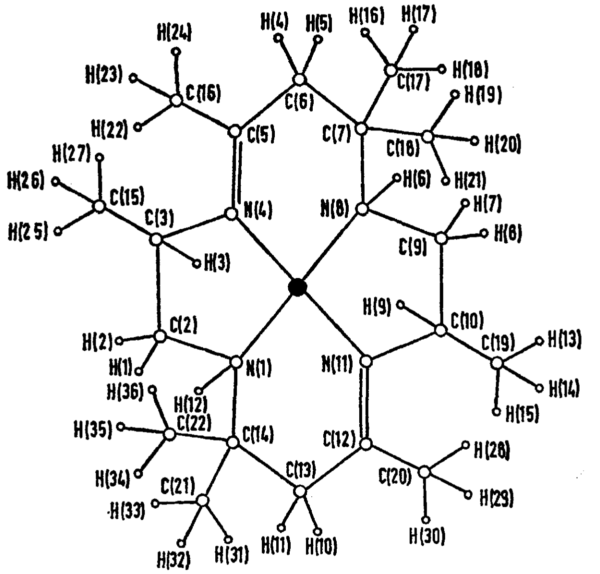

FIGURE 1 Atom numbering scheme

DISCUSSION

The yellow isomer (I) is found to be [(1*RS*,3*SR*,8*RS*,10*SR*)-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene]nickel(II) perchlorate (Figure 1). The co-ordination geometry in the complex cation is square planar, the pairs of amine and imine donor atoms each having a *trans*-disposition. The methyl groups on the diaminopropane residues are adjacent to the imino-nitrogen atoms. The asymmetric carbon and nitrogen centres are in racemic pairs such that the two C–H bonds C(3)–H(3) and C(10)–H(10) are on the opposite side of the macrocycle from the N–H bonds N(1)–H(12) and N(8)–H(6). The unit cell contains two pairs of enantiomeric cations.

The dimensions within the complex ion closely resemble those observed in the related compounds (*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)nickel(II) perchlorate[5] and its *cis*-analogue (*rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-diene)nickel(II) perchlorate.[6]

For each, the co-ordination geometry approximates to a square plane with slight tetrahedral distortions, the nickel–trigonal nitrogen distances being slightly shorter than those involving amino-nitrogens, and there are some distortions from standard lengths and angles in the six-membered chelate rings. For the present complex the mean Ni–N bonds are 1·89 for trigonal and 1·93 Å for tetrahedral nitrogen, with the distortions in the chelate rings evidenced by bond angles at the central carbon atoms of 119·4 [(C(6)] and 120·5° [C(13)] and a slight shortening of the C(6)–C(7) and C(13)–C(14) bonds to

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[5] M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, 1966, 908; *J.C.S. Dalton*, 1972, 938.

[6] B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc.* (*A*), 1969, 2407.

1·49 and 1·51 Å. There is no evidence that anisotropic effects account for these values, and in view of the consistent pattern among the compounds cited there can be little doubt that the effects are genuine. It can immediately be deduced that there is very little π interaction between the central-metal ion and the imino-donor atom, the marginal bond shortening being readily accounted for by reduced non-bonded contacts and differences in electronic configuration at this trigonal nitrogen.

Detailed geometrical relationships between portions of the cation may be deduced from the planes of best fit and deviations therefrom (Table 5). Thus the methyl groups, C(15) and C(19), of the diaminopropane residues occupy ' axial ' sites, *i.e.* the most out-of-plane positions *ca.* 2·1 Å above the plane specified by the metal and four nitrogen atoms. These positions are clearly preferred since they reduce interactions with the methyl substituents C(16) and C(20) which are restricted to in-plane sites because of the inflexibility of the imino-groups. All four carbon atoms of the *gem*-dimethyl groups are below the plane, two, C(17) and C(21), by *ca.* −1·2 Å and two, C(18) and C(22), by *ca.* −2·4 Å.

TABLE 5

Equations of best least-squares planes in the form $lX + mY + nZ = P$ where X, Y, and Z are orthogonal co-ordinates in Å, and $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (A): Co-ordination plane

Ni, N(1), N(4), N(8), N(11) $0·1282X - 0·0106Y + 0·9917Z = 2·7387$

[Ni −0·033, N(1) −0·05, C(2) −0·15, C(3) 0·56, N(4) 0·07, C(5) −0·14, C(6) −0·55, C(7) −1·03, N(8) −0·05, C(9) −0·17, C(10) 0·59, N(11) 0·07, C(12) −0·10, C(13) −0·57, C(14) −1·09, C(15) 2·09, C(16) 0·09, C(17) −1·10, C(18) −2·40, C(19) 2·09, C(20) 0·18, C(21) −1·20, C(22) −2·40]

Plane (B): Double-bond plane

Ni, C(3), N (4), C(5) $-0·1553X - 0·1518Y + 0·9761Z = 1·2550$

[Ni 0·006, C(2) −0·92, C(3) 0·01, N(4) −0·02, C(5) 0·01, C(6) 0·07, C(15) 1·44, C(16) 0·08]

Plane (C): Double-bond plane

Ni, C(10), N(11), C(12) $0·4059X + 0·1209Y + 0·9059Z = 3·8705$

[Ni 0·011, C(9) −0·95, C(10) 0·01, N(11) −0·04, C(12) 0·02, C(13) 0·02, C(19) 1·43, C(20) 0·15]

The asymmetric centres can be described by noting that the C–H bonds point above the plane and the N–H bonds below. For the *R* configuration of the carbon centre C(3) the asymmetric centre at N(1), within the same five-membered chelate ring, could adopt either the *R* or *S* arrangement. The observed *RS* combination places the methyl group C(15) and the *gem*-dimethyl groups C(21) and C(22) on opposite sides of the molecular plane as found, the alternative *RR* combination placing them in close and unfavourable proximity on the same side of the molecule. The *S* configuration at N(1) then determines the chirality of the associated six-membered chelate ring as λ. Because of the near planarity of the imino-group this in turn dictates the configuration of the adjacent five-membered ring as δ [Figure 2(a)]. If displacements from the mean plane defined by the metal ion and four donor atoms are considered, *RC*(3) places C(15) at +2·08 Å and requires the *S* configuration at N(1). The central carbon atom of the six-membered ring [C(13)] is at −0·57 Å and hence the planar imino-group places C(10) at +0·59 Å and, because of the gauche conformation of this chelate ring, C(9) at −0·17 Å. In similar fashion the configuration at C(10), *R'*, determines the configuration of N(8) as *S'*, that of the six-membered chelate ring including N(8), as λ', and that of the five-membered chelate ring including N(4) as δ' [Figure 2(b)].

These arguments can be applied to the orange *C-meso*-isomer (II) with *RS* carbon centres. The fact that isomeric compounds (I) and (II) are formed in approximately equal amounts when (±)-1,2-diaminopropane is used in preparations whereas only an enantiomer of the yellow racemate is produced from the active amine, considered together with ^{1}H n.m.r. data and the space-group requirements,[4] make it almost certain that (II) and (I) are the *C-meso-* and *C-rac*-isomers of the same complex cation. Thus in (II) an *R* carbon centre will again be associated with an *S* configuration at the adjacent nitrogen centre and consequent λ and δ conformations of chelate rings as already described. Here, however, the second carbon centre must now be of *S* configuration with consequent inversion elsewhere [Figure 2(c)].

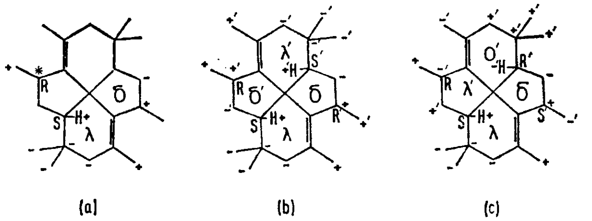

FIGURE 2 Configurations of the macrocycles as determined by the configurations at the carbon centres: (a) The *R* configuration at the centre marked with an asterisk determines the *S* configuration at the nitrogen centre and the λ and δ configurations of the six- and five-membered rings (a plus sign represents displacement above the plane defined by the metal and four donor atoms, a minus sign indicates displacement below); (b) when combined with a second *R* carbon centre, marked *R'*, the configuration of the C-*rac* (yellow) isomer is determined; and (c) when combined with a second centre of *S* chirality, marked *S'*, the C-*meso* (orange) isomer is determined

The importance of the methyl substituents in determining the overall structure of the cation is evident. Thus in the analogous hexamethyl compound [5] the cation exists as interconvertible *rac-* and *meso*-isomers based on the two asymmetric nitrogen centres, whereas (I) and (II) exist in one form only since the configuration at the carbon centres dictates that at the nitrogens. Only two of the six possible isomers have in fact been observed. In addition the (I) octamethyl cation adopts a more buckled conformation than does its *rac-*

TABLE 6

Deviations (Å) from the mean co-ordination plane shown by the *rac*-hexamethyl derivative (from ref. 5) and the present *rac*-octamethyl compound. The mean planes are respectively plane (1), Table 5, ref. 5 and plane (A) from the preceding Table. The numbering system is that of the octamethyl cation, atoms C(15) and C(19) being missing in the hexamethyl analogue

	Hexamethyl cation	Octamethyl cation
Ni	−0·05	−0·03
N(1)	−0·03	−0·05
C(2)	−0·24	−0·15
C(3)	0·45	0·56
N(4)	0·06	0·07
C(5)	0	−0·14
C(6)	−0·36	−0·55
C(7)	−0·95	−1·03
N(8)	−0·03	−0·05
C(9)	−0·30	−0·17
C(10)	0·43	0·59
N(11)	0·06	0·07
C(12)	0	−0·10
C(13)	−0·32	−0·57
C(14)	−0·90	−1·09
C(15)	—	2·09
C(16)	0·29	0·09
C(17)	−0·99	−1·10
C(18)	−2·38	−2·40
C(19)	—	2·09
C(20)	0·33	0·18
C(21)	−0·91	−1·20
C(22)	−2·36	−2·40

hexamethyl analogue, as indicated by a comparison of the deviations from the mean plane Ni, N(1), N(4), N(8), N(11) (Table 6), presumably to minimize the extra steric interactions of the additional methyl groups. At first sight is it surprising to find that the carbon atoms C(3) and C(10) of the ethylene bridges, those directly attached to the trigonally bonded nitrogen atoms, are most removed from the co-ordination plane (by *ca.* 0·60 Å) whereas the atoms adjacent to the tetrahedral nitrogen centres lie much closer (at *ca.* 0·15 Å). A model of the unsubstituted macrocycle suggests that a more 'obvious' geometry would be one in which the atoms bonded to the two trigonal nitrogen centres are approximately in the molecular plane with the ethylene carbons C(2) and C(9) being those furthest removed. The hexamethyl cations conform a little more closely to this prediction but by no means exactly, their overall conformations being similar to that of the octamethyl derivative where the skeletal geometry minimizes repulsions between methyl substituents and maintains planarity at the double bonds (Tables 5 and 6). The changes can be visualized as rotation of the planar imine group about the C–N axis, coupled with rotation about the Ni–N axis. Non-bonded interactions of the methyl substituents are

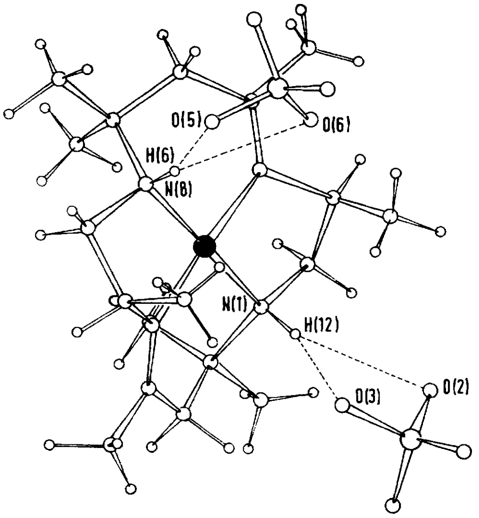

FIGURE 3 Hydrogen-bonding interactions

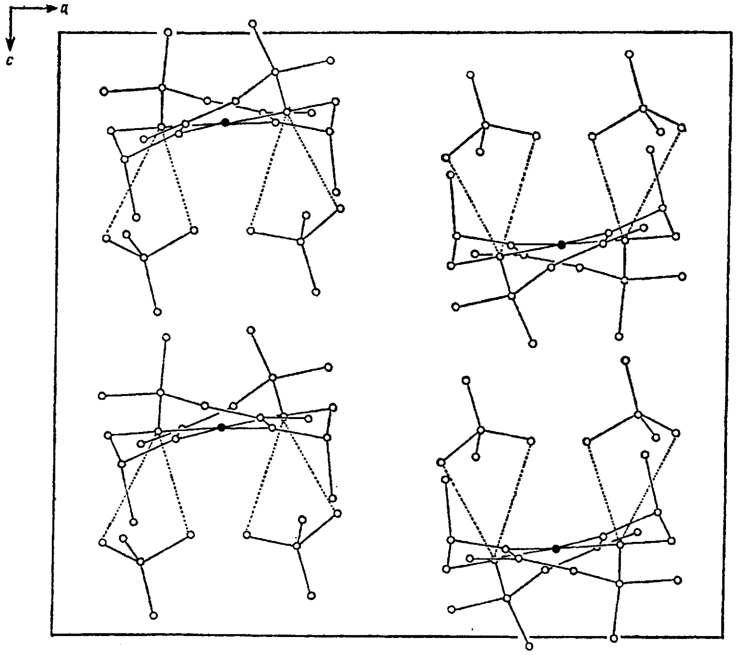

FIGURE 4 Projection on (010)

minimized at the expense of bond-angle deformation, particularly at C(5), where the chelate-ring angle opens to *ca.* 119°. These are features common to systems of this type,[5-7] the 120° angle at the carbons also persisting in complexes in which the double bonds have been reduced.[8]

The three constituents of the crystal, complex cation and two anions, are hydrogen bonded into units (Figure 3). Their arrangement in the crystal structure is shown in Figure 3. Geometrical details of the hydrogen bonding (Table 7) show that the interaction occurs between two oxygen atoms of each perchlorate ion and the two secondary nitrogen atoms of each macrocycle. Since the latter both project their associated hydrogen atoms on the same side of the co-ordination plane the perchlorate groups are similarly placed. One nitrogen–oxygen distance in each pair is slightly shorter than the other but it can be seen (Figure 3 and Table 7) that both hydrogen bonds are in fact bifurcated.

The bond lengths and angles in the perchlorate groups themselves are somewhat erratic but this is to be expected in view of the large thermal motion, or equivalent steric disorder, suggested by the anisotropic temperature parameters for the oxygen atoms. No attempt to adjust the 'raw' values to compensate for thermal effects has been made since the exact geometry of these ions is not crucial to the foregoing discussion.

TABLE 7

Geometry of hydrogen bonds

(*a*) Distances (Å)

O(2) · · · H(12)	2·25	O(5) · · · H(6)	2·33
O(3) · · · H(12)	2·62	O(6) · · · H(6)	2·65

(*b*) Angles (°)

N(1)–H(12)–O(2)	157	N(8)–H(6)–O(5)	160
N(1)–H(12)–O(3)	148	N(8)–H(6)–O(6)	147

[1/909 *Received, 4th June,* 1971]

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