Structural Studies on Co-ordinated Macrocyclic Ligands. Part II.[1] Crystal and Molecular Structure of Acetylacetonato-C-*meso*-(5,5,7,12,12,-14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Perchlorate

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The title compound and the corresponding cobalt(III) compound have been prepared and the crystal and molecular structure of the former has been determined from *X*-ray diffractometer data. Crystals are monoclinic, a = 16·190(8), b = 12·678(7), and c = 13·197(6) Å, β = 100·52(8). Space group *Cc*. The structure was solved by the heavy-atom method and refined to R 0·0630 for 1580 independent reflections. The nickel(II) ion is in approximately octahedral co-ordination with the macrocycle folded at N(4) and N(11) to occupy four adjacent co-ordination sites, a symmetrical, planar acetylacetonato-chelate occupying the two remaining sites. In the structure the configuration of the amine is 1*RS*, 4*RS*, 7*RS*, 8*RS*, 11*RS*, 14*SR*. The five-membered chelate rings adopt unsymmetrical gauche conformations and the six-membered chelate ring including N(1) and N(11) adopts a chair conformation. That containing N(4) and N(8) adopts a twist-boat conformation which minimises non-bonded interactions of the methyl substituents. The strain inherent in this non-optimum geometry is considered to be responsible for the observed low stability of compounds in which the amine has this configuration.

THE preparations of nickel(II) complexes of the C-*meso* and C-*rac* isomers of the cyclic tetramine 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (represented as tet*a* and tet*b* respectively) have been reported.[2-4] With poorly co-ordinating anions such as ClO_4^-, BF_4^-, $ZnCl_4^{2-}$, *etc.*, singlet ground-state, square planar salts are generally formed, but with anions of greater co-ordinating power triplet ground-state, octahedrally bound compounds result. For the C-*meso* amine, (tet*a*), reported octahedral compounds all have *trans*-configurations with the amine in planar (*bcde*) co-ordination whereas with the C-*rac* amine, (tet*b*), most octahedral derivatives have the amine in folded (*abcd*) co-ordination, often with a chelate occupying the two additional co-ordination sites.[3] The structure of one such compound, [Ni(tet*b*)(OAc)]ClO_4, has been determined.[5] The difference in preferred stereochemistry of these isomeric amines has been attributed to non-bonded interactions involving the methyl substituents.[5,6] For this amine, in addition to the two chiral carbon centres which produce the non-interconvertible isomers tet*a* and tet*b*, the four secondary amine groups become chiral centres upon co-ordination. These give rise to five possible nitrogen configurations and hence, with the carbon centres, a total of 20 non-enantiomorphic configurations of the co-ordinated macrocycle. Interconversions of the nitrogen configurations can occur in solution, the inversion reaction being pH-dependent, rapid in base, and effectively inhibited in strongly acid solution.

For folded co-ordination of 1,4,8,11-tetra-azacyclotetradecane (cyclam, the macrocycle of tet*a* and tet*b* without the methyl substituents) the nitrogen configuration found [7] for *cis*-[Co(cyclam)Cl_2]Cl permits adoption of a relatively strain-free overall conformation, with each of the chelate rings in optimum (chair or gauche) conformation. The same nitrogen configuration and conformation of the macrocycle is present for [Ni(tet*b*)(OAc)]ClO_4, with the single methyl groups in equatorial sites.[5] Adoption of this configuration and conformation by the tet*a* analogue would place one of the single methyl groups in an axial site, with a very strained 1,3-di-axially substituted six-membered chelate ring. This strain could be relieved by some distortion from the chair

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[1] D. A. Swann, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 1115.

[2] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

[3] N. F. Curtis, *J. Chem. Soc.*, 1965, 924; *J. Chem. Soc.* (*A*), 1968, 1579; N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804; *Austral. J. Chem.*, 1966, **19**, pp. 609, 1423.

[4] N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1584.

[5] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

[6] L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **91**, 4092.

[7] P. O. Whimp and N. F. Curtis, *J. Chem. Soc.* (*A*), 1966, 867, 1827.

conformation, or alternatively, another nitrogen configuration which causes less non-bonded interactions of the methyl groups could be adopted, at the expense of a more strained cyclam framework. Here we report the preparation of some complexes with tet*a* in folded co-ordination, and an *X*-ray structural study of one [Ni(tet*a*)(acac)]ClO$_4$ (acac = acetylacetonate), to establish the configuration and conformation present.

The cation [Ni(tet*a*)]$^{2+}$ has previously resisted attempts to force adoption of the folded co-ordination by reaction with chelates, but *cis*-[Ni(α-tet*a*)(acac)]ClO$_4$ * has been synthesized by reaction of [Ni(β-tet*a*)](ClO$_4$)$_2$ with acetylacetone in aprotic solvents (*e.g.* methyl cyanide, acetone, or dichloromethane) in the presence of base, conveniently potassium carbonate.

The blue-violet, triplet ground-state compound is stable in the solid state, or in solution in aprotic solvents, but in solvents such as methanol it is rapidly converted into an isomeric singlet ground-state compound, [Ni(β-tet*a*)](acac)ClO$_4$, with reversion to the stable β-configuration. The same change occurs in water, but is very slow because of the very low solubility of [Ni(α-tet*a*)(acac)]ClO$_4$.

Although the Ni^{II}(tet*a*) moiety is inert to substitution reactions, 'additional' ligands such as the acetylacetonato-group are labile. Because acetylacetone is also a very weak acid, reaction of [Ni(α-tet*a*)(acac)]ClO$_4$ with stronger acids leads to its displacement with the α-configuration being retained in acid medium. With co-ordinating anions, triplet ground-state 'octahedral' compounds are formed (*e.g.* [Ni(α-tet*a*)(OAc)]ClO$_4$ [{Ni(α-tet*a*)}$_2$(C$_2$O$_4$)](ClO$_4$)$_2$, [Ni(α-tet*a*)(NO$_3$)]ClO$_4$, [{Ni(α-tet*a*)}$_2$Cl$_2$](ClO$_4$)$_2$, [{Ni(α-tet*a*)}$_2$(NCS)$_2$](ClO$_4$)$_2$, *etc.*) whereas with acids with poorly co-ordinating anions, singlet ground state, square planar, salts are formed {*e.g.* [Ni(α-tet*a*)](ClO$_4$)$_2$, [Ni(α-tet*a*)](BF$_4$)$_2$, *etc.*}. These compounds usually have properties similar to their tet*b* analogues except that they are stable only under conditions which inhibit inversion at the nitrogen centres (*i.e.* in solids, aprotic solvents, or acidic protic solvents).

The stereochemistry of the cobalt(III) complexes of tet*a* and tet*b* is similar to that with triplet ground-state nickel(II), *i.e. cis*-folded macrocycle derivatives have been reported only with tet*b*.[7] However, reaction of acetylacetone with *trans*-[Co(tet*a*)Cl$_2$]$^+$ under basic conditions gave *cis*-[Co(α-tet*a*)(acac)]$^{2+}$, analogous to the previously reported tet*b* cation. The cation is resistant to acid hydrolysis and hence could not be used to prepare other derivatives with retention of the α-configuration.

The amines C-*meso*- and C-*rac*-5,5,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet*c* and tet*d* respectively) which are geometrical isomers of tet*a* and tet*b* have stereochemical properties similar to theirs. Derivatives of tet*d* with the amine in folded co-ordination are readily prepared, but none have been reported for tet*c*.[8] Procedures analogous to those described for tet*a* enable preparation of [Ni(α-tet*c*)(acac)]ClO$_4$, from which a range of compounds with the amine in the α-configuration have been prepared, and of [Co(α-tet*c*)(acac)](ClO$_4$)$_2$.

EXPERIMENTAL

Acetylacetonato-C-rac-(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*nickel*(II) *Perchlorate*, [Ni(α-tet*b*)(acac)]ClO$_4$.—Acetylacetone was added to a hot aqueous solution of [Ni(tet*b*)](ClO$_4$)$_2$, followed by dilute ammonia. The blue violet solid was filtered from the cold solution and recrystallised from methyl cyanide by the addition of water (Found: C, 46·7; H, 8·0; Ni, 10·7. $C_{21}H_{43}ClN_4NiO_6$ requires C, 46·5; H, 8·2; Ni, 10·8%).

The precipitation of this compound as a means of separating [Ni(tet*a*)]$^{2+}$ and [Ni(tet*b*)]$^{2+}$ formed by the reduction of (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradeca-7,14-diene)nickel(II) has advantages over the previously reported[2] procedure involving the precipitation of [{Ni(tet*b*)}$_2$(C$_2$O)$_4$](ClO$_4$)$_2$, since acetylacetone is a very much weaker acid than is oxalic. Thus other derivatives of [Ni(tet*b*)]$^{2+}$ have to be prepared from the oxalate *via* [Ni(α-tet*b*)](ClO$_4$)$_2$, which is formed from the oxalato-compound only in concentrated perchloric acid. However, treatment of [Ni(α-tet*b*)(acac)]ClO$_4$ with dilute perchloric acid yields [Ni(α-tet*b*)](ClO$_4$)$_2$, and a wide range of compounds, *e.g.* [Ni(α-tet*b*)(OAc)]ClO$_4$, [Ni(α-tet*b*)(NO$_3$)]ClO$_4$, [{Ni(α-tet*b*)}$_2$Cl$_2$](ClO$_4$)$_2$, *etc.* can be prepared by treatment with the appropriate acid. Salts of [Ni(α-tet*b*)(acac)]$^+$ with other large anions are also insoluble in water and can be used for separation of the tet*a* and tet*b* isomers formed, for example, by reduction of the bromide salt of the diene complex.

Acetylacetonato-C-*meso*-(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *Perchlorate*, [Co(α-tet*a*)(acac)](ClO$_4$)$_2$.—Ammonia solution was added to a suspension of *trans*-[Co(β-tet*a*)Cl$_2$]ClO$_4$ (5 g) in hot methanol (30 ml) until the solid dissolved. Acetylacetone (1 g) was added, and the solution heated for 30 m. The red product was filtered from the cold solution, and recrystallized from hot methyl cyanide–propan-2-ol (Found: C, 39·2; H, 6·8; Co, 9·3. $C_{21}H_{43}Cl_2CoN_4O_{10}$ requires C, 39·3; H, 6·7; Co, 9·2%).

Acetylacetonato-C-meso-(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*nickel*(II) *Perchlorate*, [Ni(α-tet*a*)(acac)]ClO$_4$.—A suspension of [Ni(β-tet*a*)](ClO$_4$)$_2$ (5 g), anhydrous potassium carbonate (5 g), acetylacetone (1·5 g), and methyl cyanide (50 ml) in a stoppered flask was gently stirred magnetically (or occasionally agitated) until all the orange perchlorate salt dissolved (1—3 days). The blue solution was filtered from the potassium carbonate and evaporated to half volume. Diethyl ether was added dropwise until the solution became turbid, and the solution set aside for a period of days while the blue-violet product crystallised. This was filtered off and recrystallised from methyl cyanide–diethyl ether by a repetition of the foregoing procedure. Further product was obtained by evaporation of the filtrates (Found: C, 46·8; H, 8·2; Ni, 10·7. $C_{21}H_{43}ClN_4NiO_6$ requires C, 46·5; H, 8·2; Ni, 10·8%).

Crystal Data for [Ni(α-teta)(acac)]ClO$_4$.—$C_{21}H_{43}ClN_4NiO_6$, *M* = 541, Monoclinic, *a* = 16·190(8), *b* = 12·678(8), *c* = 13·197(6) Å, β = 100·52(8)° (standard deviations from a

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* The configuration of these amines stable in planar co-ordination has been represented as 'β' and the configuration stable in folded co-ordination as 'α,' and this symbolism will be retained.[2,5]

[8] N. F. Curtis, *J. Chem. Soc.* (*C*), 1967, 1979; P. O. Whimp and N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 188.

least squares fit to diffractometer co-ordinates of 12 reflexions), $D_m = 1{\cdot}33$, $Z = 4$, $D_c = 1{\cdot}35$, $U = 8{\cdot}6$ cm^{-1}. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 8·6 cm^{-1}. Space group *Cc*.

Intensity data were collected by four-circle diffractometry, a total of 1591 reflexions being observed at the $2\sigma(F^2)$ level. Absorption corrections were applied.[9a]

Structure solution was by the conventional heavy-atom method, all non-hydrogen atoms being located when *R* was 0·214. Atomic scattering factors were taken from ref. 9(*b*) and the weighting scheme for subsequent block-diagonal least squares refinement was of the form $w = 4F_o^2/\sigma^2(F^2)$. The initial molecular model was relaxed in stages to allow increasingly for anisotropic thermal vibrations and for the inclusion of hydrogen atoms. Difference syntheses were computed during this process to check the course of the refinement, particularly with regard to the perchlorate ion, to verify hydrogen atom positions and to locate those belonging to methyl groups. As parameters were added to the refinement significance tests[10] were applied to check the validity of their inclusion. The final refinement cycles assumed anisotropic vibrations for all non-hydrogen atoms and allowed adjustments to the positions of the hydrogens (but not to their temperature factors which were fixed at 5·0 Å^2 throughout). The *R* index converged to 0·062.

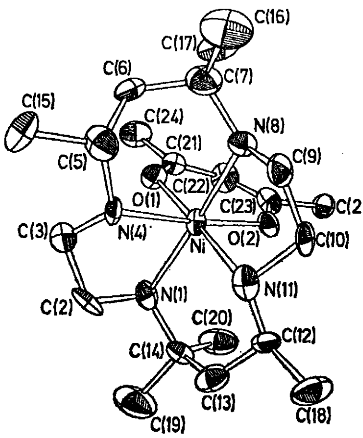

FIGURE 1 Crystallographic numbering scheme and ORTEP diagram of the complex cation [the perchlorate anion contains O(3)—(6)]

Final atom co-ordinates and anisotropic thermal parameters are listed in Tables 1 and 2.* Bond lengths and angles computed from the data of Table 1 are in Tables 3 and 4.* The crystallographic numbering system is shown in Figure 1. In the subsequent discussion of the analysis this system is used exclusively. Structure factor data are listed in Supplementary Publication No. SUP 20678 (5 pp., 1 microfiche).†

TABLE 1

Atom co-ordinates

Atom	*x/a*	*y/b*	*z/c*
Ni	0·50000	0·26671(9)	0·50000
Cl	0·00000(36)	0·36701(24)	0·50000(24)
O(3)	0·0427(17)	0·4390(12)	0·4422(12)
O(4)	−0·0565(11)	0·4376)14)	0·5417(18)
O(5)	−0·0351(27)	0·3082(18)	0·4255(14)
O(6)	0·0558(12)	0·3160(25)	0·5711(16)
N(1)	0·4074(8)	0·2571(9)	0·5924(7)
N(4)	0·5614(7)	0·1474(9)	0·6006(7)
N(8)	0·5978(7)	0·2552(9)	0·4134(8)
N(11)	0·4393(9)	0·1534(9)	0·3972(8)
C(2)	0·4354(11)	0·1752(13)	0·6690(13)
C(3)	0·5321(11)	0·1664(15)	0·6957(12)
C(5)	0·6533(11)	0·1255(13)	0·6016(14)
C(6)	0·6973(9)	0·2266(14)	0·5826(12)
C(7)	0·6875(11)	0·2544(16)	0·4699(16)
C(9)	0·5747(11)	0·1641(14)	0·4301(10)
C(10)	0·4820(10)	0·1687(10)	0·3054(8)
C(12)	0·3482(9)	0·1672(14)	0·3713(11)
C(13)	0·3076(10)	0·1591(13)	0·4618(13)
C(14)	0·3152(9)	0·2534(11)	0·5395(11)
C(15)	0·6925(12)	0·0796(18)	0·7068(14)
C(16)	0·7509(15)	0·1916(19)	0·4169(21)
C(17)	0·7121(12)	0·3735(19)	0·4704(18)
C(18)	0·3060(12)	0·0837(16)	0·2887(15)
C(19)	0·2594(14)	0·2188(23)	0·6175(24)
C(20)	0·2862(12)	0·3591(16)	0·4953(18)
O(1)	0·5481(6)	0·3833(7)	0·6012(7)
O(2)	0·4513(6)	0·3837(7)	0·3995(6)
C(21)	0·5421(9)	0·4814(10)	0·5907(10)
C(22)	0·4967(9)	0·5311(10)	0·5060(9)
C(23)	0·4609(10)	0·4832(10)	0·4142(11)
C(24)	0·5860(12)	0·5473(14)	0·6799(15)
C(25)	0·4222(9)	0·5500(12)	0·3233(11)
H(1)	0·40(1)	0·32(1)	0·61(1)
H(2)	0·41(1)	0·18(1)	0·73(1)
H(3)	0·42(1)	0·11(1)	0·64(1)
H(4)	0·56(1)	0·24(1)	0·72(1)
H(5)	0·55(1)	0·10(1)	0·74(1)
H(6)	0·54(1)	0·08(1)	0·59(1)
H(7)	0·67(1)	0·08(1)	0·54(1)
H(8)	0·67(1)	0·29(1)	0·63(1)
H(9)	0·76(1)	0·21(1)	0·61(1)
H(10)	0·60(1)	0·32(1)	0·38(1)
H(11)	0·61(1)	0·16(1)	0·29(1)
H(12)	0·59(1)	0·10(1)	0·38(1)
H(13)	0·46(1)	0·24(1)	0·27(1)
H(14)	0·47(1)	0·11(1)	0·25(1)
H(15)	0·44(1)	0·09(1)	0·42(1)
H(16)	0·34(1)	0·25(1)	0·34(1)
H(17)	0·25(1)	0·15(1)	0·43(1)
H(18)	0·33(1)	0·09(1)	0·49(1)
H(19)	0·75(1)	0·10(1)	0·71(1)
H(20)	0·67(1)	0·01(1)	0·70(1)
H(21)	0·66(1)	0·11(1)	0·76(1)
H(22)	0·81(1)	0·20(1)	0·43(1)
H(23)	0·73(1)	0·24(1)	0·36(1)
H(24)	0·73(1)	0·12(1)	0·40(1)
H(25)	0·76(1)	0·41(1)	0·50(1)
H(26)	0·72(1)	0·36(1)	0·40(1)
H(27)	0·66(1)	0·41(1)	0·47(1)
H(28)	0·33(1)	0·02(1)	0·30(1)
H(29)	0·31(1)	0·11(1)	0·22(1)
H(30)	0·25(1)	0·06(1)	0·29(1)
H(31)	0·29(1)	0·17(1)	0·67(1)
H(32)	0·27(1)	0·29(1)	0·63(1)
H(33)	0·20(1)	0·21(1)	0·63(1)
H(34)	0·28(1)	0·37(1)	0·56(1)
H(35)	0·33(1)	0·40(1)	0·47(1)
H(36)	0·23(1)	0·37(1)	0·45(1)
H(37)	0·60(1)	0·51(1)	0·74(1)
H(38)	0·64(1)	0·56(1)	0·66(1)
H(39)	0·55(1)	0·60(1)	0·70(1)
H(40)	0·50(1)	0·61(1)	0·50(1)
H(41)	0·45(1)	0·55(1)	0·27(1)
H(42)	0·37(1)	0·54(1)	0·30(1)
H(43)	0·42(1)	0·63(1)	0·34(1)

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* The standard deviation quoted in Tables 1—4 are those obtained from the block-diagonal least-squares approximation and it is expected that they will be under-estimated. A check of internal consistency between bonds of known equality is not possible but experience suggests that the standard deviations in length and angles are *ca.* 1·3 times those computed.

† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are supplied as full-sized copies.

[9] (*a*) W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180; (*b*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[10] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	37·9(4)	40·9(5)	36·2(5)	32·6(9)	12·4(7)	2·7(10)
Cl	85(2)	61(2)	77(2)	36(4)	5(3)	−33(4)
O(3)	290(24)	100(13)	120(13)	−12(29)	269(30)	47(22)
O(4)	69(9)	152(18)	329(30)	57(22)	95(27)	49(38)
O(5)	610(60)	178(23)	108(15)	−434(64)	299(50)	−166(32)
O(6)	75(10)	430(41)	174(19)	138(34)	−105(22)	76(47)
N(1)	57(6)	58(8)	39(6)	3(11)	39(9)	−18(11)
N(4)	37(5)	70(8)	33(6)	17(10)	−6(8)	39(11)
N(8)	36(5)	69(9)	69(8)	−3(11)	33(10)	−10(14)
N(11)	72(7)	39(7)	58(8)	11(12)	27(12)	5(12)
C(2)	64(10)	83(13)	88(12)	−39(18)	95(18)	48(21)
C(3)	56(9)	108(15)	66(11)	−28(19)	9(15)	34(21)
C(5)	60(9)	73(12)	100(14)	30(17)	47(18)	43(20)
C(6)	26(6)	106(14)	88(11)	−16(16)	−11(12)	28(22)
C(7)	41(8)	128(19)	130(17)	41(21)	45(18)	81(30)
C(9)	67(9)	100(14)	41(8)	−54(19)	26(13)	−36(18)
C(10)	66(8)	54(10)	24(6)	−9(14)	15(11)	−27(13)
C(12)	35(7)	116(15)	64(9)	−62(17)	22(13)	−41(20)
C(13)	36(7)	79(12)	104(14)	9(16)	−10(15)	9(21)
C(14)	42(6)	62(11)	71(9)	−13(13)	49(13)	1(16)
C(15)	58(10)	135(20)	96(14)	41(23)	−47(18)	35(28)
C(16)	73(13)	126(20)	199(27)	80(27)	105(31)	−34(39)
C(17)	44(9)	138(22)	156(22)	−9(22)	12(23)	−77(34)
C(18)	56(10)	113(17)	123(16)	−67(22)	13(20)	−91(28)
C(19)	49(10)	195(29)	229(31)	26(29)	100(24)	174(51)
C(20)	46(9)	93(16)	180(24)	11(19)	52(23)	26(30)
O(1)	47(5)	48(6)	71(7)	−17(9)	6(9)	−5(10)
O(2)	50(5)	46(6)	50(6)	−8(8)	27(8)	23(9)
C(21)	39(7)	48(8)	61(9)	4(12)	29(12)	−21(14)
C(22)	62(8)	63(9)	97(11)	44(16)	30(14)	21(16)
C(23)	53(8)	42(8)	72(10)	27(13)	46(14)	28(15)
C(24)	60(10)	77(14)	121(17)	−23(18)	34(20)	−36(23)
C(25)	41(7)	76(12)	66(10)	15(14)	0(13)	44(17)

* The scattering factor for an atom is expressed by: $f = f_o \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

DISCUSSION

The principal interest in the structure lies in the stereochemistry of the complex cation (Figure 1). As discussed later, hydrogen bonding interactions are thought to be relatively weak so that the geometry of this ion is due to intramolecular forces. This cation contains nickel(II) octahedrally co-ordinated to the four secondary amino-groups of the cyclic tetra-amine in folded (*abcd*) co-ordination, and to the two oxygen atoms of the acetylacetonato-ligand present as a planar symmetrical chelate. The configuration of the amine is 1*RS*, 4*RS*, 5*RS*, 8*RS*, 11*RS*, 12*SR*,[†] *i.e.* configuration 20*f* of ref. 5, with mirror-related pairs of chiral cations in the unit cell, the same nitrogen configurations as found for *cis*-[Co(cyclam)Cl_2]Cl[11] and [Ni(tet*b*)(OAc)]ClO_4.[5] The fold-line of the macrocycle is N(1)–N(8), *i.e.* adjacent to the *gem*-dimethyl groups, with the axial components of the *gem*-dimethyl groups folded away from the acetylacetonato chelate. The Ni, O(1), O(2) plane is slightly twisted relative to the plane of Ni, N(1), N(8), the distortion having the effect of moving the acetylacetonato-methyl groups closer to the five-membered chelate rings of the macrocycle and away from the methyl substituents on the six-membered chelate rings. Details of these distortions, and of the configurations

TABLE 3

Bond lengths (Å) *

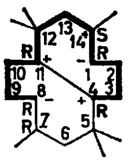
Ni–N(1)	2·10(1)	C(12)–C(18)	1·58(3)
Ni–N(4)	2·13(1)	C(12)–C(13)	1·47(2)
Ni–N(8)	2·12(1)	C(13)–C(14)	1·56(2)
Ni–N(11)	2·09(1)	C(14)–C(19)	1·55(3)
N(1)–C(2)	1·46(2)	C(14)–C(20)	1·50(2)
C(2)–C(3)	1·54(3)	C(14)–N(1)	1·53(2)
C(3)–N(4)	1·44(2)	Ni–O(1)	2·05(1)
N(4)–C(5)	1·51(2)	O(1)–C(21)	1·25(2)
C(5)–C(15)	1·53(3)	C(21)–C(24)	1·51(2)
C(5)–C(6)	1·51(2)	C(21)–C(22)	1·37(2)
C(6)–C(7)	1·51(3)	C(22)–C(23)	1·38(2)
C(7)–C(16)	1·56(3)	C(23)–C(25)	1·51(2)
C(7)–C(17)	1·56(3)	C(23)–O(2)	1·28(2)
C(7)–N(8)	1·51(2)	O(2)–Ni	2·05(1)
N(8)–C(9)	1·51(2)	Cl–O(3)	1·44(2)
C(9)–C(10)	1·49(2)	Cl–O(4)	1·46(2)
C(10)–N(11)	1·51(2)	Cl–O(5)	1·28(3)
N(11)–C(12)	1·46(2)	Cl–O(6)	1·34(3)

* C–H and N–H bond lengths are 0·9(1)—1·0(1) Å.

TABLE 4

Bond angles (deg.)

N(1)–Ni–N(4)	84·2(7)	C(6)–C(7)–C(17)	104·0(12)
N(1)–Ni–N(8)	172·2(7)	C(6)–C(7)–N(8)	114·1(12)
N(1)–Ni–N(11)	92·0(7)	C(16)–C(7)–C(17)	107·9(13)
N(1)–Ni–O(1)	83·7(7)	C(7)–N(8)–C(9)	114·5(11)
N(1)–Ni–O(2)	100·7(6)	N(8)–C(7)–C(16)	115·7(13)
N(4)–Ni–N(8)	88·8(7)	N(8)–C(7)–C(17)	102·5(12)
N(4)–Ni–N(11)	91·5(7)	N(8)–C(9)–C(10)	106·6(11)
N(4)–Ni–O(1)	91·6(6)	C(9)–C(10)–N(11)	109·4(11)
N(4)–Ni–O(2)	174·8(7)	C(10)–N(11)–C(12)	112·7(11)
N(8)–Ni–N(11)	85·0(7)	N(11)–C(12)–C(18)	111·8(11)
N(8)–Ni–O(1)	99·7(7)	N(11)–C(12)–C(13)	112·5(11)
N(8)–Ni–O(2)	86·4(6)	C(13)–C(12)–C(18)	108·3(12)
N(11)–Ni–O(1)	174·4(7)	C(12)–C(13)–C(14)	119·1(12)
N(11)–Ni–O(2)	90·0(7)	C(13)–C(14)–C(19)	103·5(12)
O(1)–Ni–O(2)	87·4(6)	C(13)–C(14)–C(20)	116·4(12)
Ni–N(1)–C(2)	106·2(9)	C(19)–C(14)–C(20)	109·4(13)
Ni–N(1)–C(14)	118·5(9)	C(13)–C(14)–N(1)	105·6(11)
Ni–N(4)–C(3)	103·5(9)	C(14)–N(1)–C(2)	116·6(11)
Ni–N(4)–C(5)	118·8(10)	N(1)–C(14)–C(19)	110·1(12)
Ni–N(8)–C(7)	118·7(10)	N(1)–C(14)–C(20)	111·0(11)
Ni–N(8)–C(9)	106·0(9)	O(1)–C(21)–C(24)	116·5(11)
Ni–N(11)–C(10)	101·6(9)	O(1)–C(21)–C(22)	124·4(12)
Ni–N(11)–C(12)	113·8(10)	C(22)–C(21)–C(24)	119·1(12)
Ni–O(1)–C(21)	129·2(9)	C(21)–C(22)–C(23)	125·9(12)
Ni–O(2)–C(23)	126·3(9)	C(22)–C(23)–C(25)	119·7(12)
N(1)–C(2)–C(3)	112·5(12)	C(22)–C(23)–O(2)	125·8(12)
C(2)–C(3)–N(4)	107·1(12)	O(2)–C(23)–C(25)	114·2(11)
C(3)–N(4)–C(5)	120·2(11)	O(3)–Cl–O(4)	101·9(11)
N(4)–C(5)–C(15)	108·8(12)	O(3)–Cl–O(5)	98·7(13)
N(4)–C(5)–C(6)	109·6(12)	O(3)–Cl–O(6)	110·3(12)
C(5)–C(6)–C(7)	113·3(12)	O(4)–Cl–O(5)	115·2(13)
C(6)–C(5)–C(15)	110·1(12)	O(4)–Cl–O(6)	114·8(12)
C(6)–C(7)–C(16)	111·3(13)	O(5)–Cl–O(6)	113·8(14)

[†] 

The configuration at asymmetric centres is shown by indicating whether or not the hydrogen atom of the centre is above (+) or below (−) the plane of the (flattened) macrocycle. The numbering scheme here is that of the IUPAC convention so that the configuration can be designated as 1*RS*, 4*RS*, 7*RS*, 8*RS*, 11*RS*, 14*SR*.

[11] G. B. Robertson and P. O. Whimp, personal communication.

adopted by sections of the complex, can be deduced from Table 5 which lists planes of best fit through selected regions of the cation and deviations therefrom.

TABLE 5

Equations of planes of best fit in the form $AX + BY + CZ + D = 0$, where X, Y, and Z are orthogonal co-ordinates in Å, related to the crystallographic axes by: $X = x + z \cos \beta$, $Y = y$, $Z = z \sin \beta$

Plane (1):
Ni, O(1), O(2), C(21)—(25) $0{\cdot}9307X - 0{\cdot}0043Y - 0{\cdot}3657Z - 4{\cdot}0169 = 0$
[Ni 0·009, N(1) −2·03, N(4) 0·24, N(8) 2·09, N(11) −0·18, O(1) 0·02, C(21) 0·00, C(22) −0·10, C(23) 0·01, C(24) 0·03, C(25) 0·06, O(2) −0·03]

Plane (2):
Ni, N(4), N(11), O(1), O(2) $-0{\cdot}8975X + 0{\cdot}0075Y + 0{\cdot}4409Z + 3{\cdot}3519 = 0$
[Ni 0·023, N(1) 2·78, N(4) −0·08, N(8) −2·10, N(11) 0·09, O(1) 0·09, O(2) −0·09]

Plane (3):
Ni, N(1), N(8), N(11), O(1) $-0{\cdot}3858X + 0{\cdot}7060Y - 0{\cdot}5939Z + 4{\cdot}1518 = 0$
[Ni 0·030, N(1) −0·11, N(4) −2·10, N(8) −0·10, N(11) 0·09, O(1) 0·09, O(2) 2·06]

Plane (4):
Ni, N(1), N(4), N(8), O(2) $0{\cdot}3997X + 0{\cdot}6938Y + 0{\cdot}5991Z - 8{\cdot}9761 = 0$
[Ni 0·01, N(1) −0·05, N(4) 0·04, N(8) −0·05, N(11) −2·08, O(1) 2·04, O(2) 0·04]

Plane (5):
Ni, N(1), N(4) $0{\cdot}3703X + 0{\cdot}7055Y + 0{\cdot}6043Z - 8{\cdot}8574 = 0$
[C(2) −0·03, C(3) 0·65]

Plane (6):
Ni, N(4), N(8) $0{\cdot}4177X + 0{\cdot}7036Y + 0{\cdot}5749Z - 8{\cdot}9867 = 0$
[C(6) 1·51, C(16) 0·49, C(7) 0·96, C(15) 0·97, C(17) 2·20, C(5) 0·43]

Plane (7):
Ni, N(8), N(11) $-0{\cdot}3214X + 0{\cdot}7273Y - 0{\cdot}6064Z + 3{\cdot}6898 = 0$
[C(9) −0·20, C(10) 0·57]

Plane (8):
Ni, N(11), N(1) $-0{\cdot}4286X + 0{\cdot}7226Y - 0{\cdot}5423Z + 4{\cdot}0277 = 0$
[C(12) 0·91, C(13) 0·58, C(14) 0·92, C(18) 0·94 C(19) 0·52, C(20) 2·36]

Plane (9):
N(11), C(12), C(14), N(1) $0{\cdot}1837X + 0{\cdot}9035Y - 0{\cdot}3871Z - 0{\cdot}9060 = 0$
[Ni 0·904, N(11) −0·01, C(12) 0·02, C(13) −0·69, C(14) −0·01, N(1) 0·01]

The conformation of the co-ordinated macrocycle is similar to that found for [Ni(α-tet*b*)(OAc)]ClO_4 with one notable exception. (Compare Figure 1 with the [Ni-(α-tet*b*)(OAc)]$^+$ cation shown in Figure 1 of ref. 5.) The five-membered chelate rings are in asymmetrical gauche conformations (δδ or λλ configuration), see Table 5 and Figure 2. The six-membered chelate ring including N(1) and N(11) is in a chair conformation, similar to the conformation found in [Ni(tet*b*)(OAc)]ClO_4, but more puckered, an effect presumably arising from interaction with the bulkier acetylacetonato-chelate. However the second six-membered chelate ring, including N(4) and N(8), has quite different conformations in the two structures, adopting a chair conformation similar to the first in the tet*b* acetate compound and a 'twist-boat' conformation in the tet*a* acetylacetonato-compound (Table 5 and Figure 3). For tet*a* in the α-configuration with folded co-ordination a chair conformation for this chelate ring would have 1,3-diaxial methyl substituents (as well as a 3-equatorial methyl and 4-equatorial and 6-axial methylene groups). The strain inherent in this situation

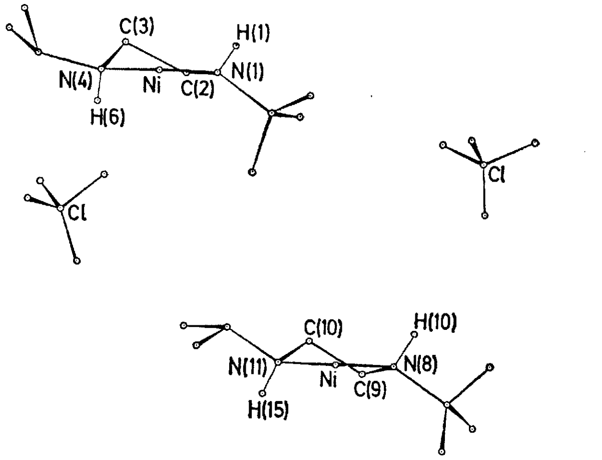


FIGURE 2 The conformation of the five-membered chelate rings: the ring atoms are projected on a plane perpendicular to that through the nickel and two nitrogen atoms and are shown on separate ions in correct relative positions.

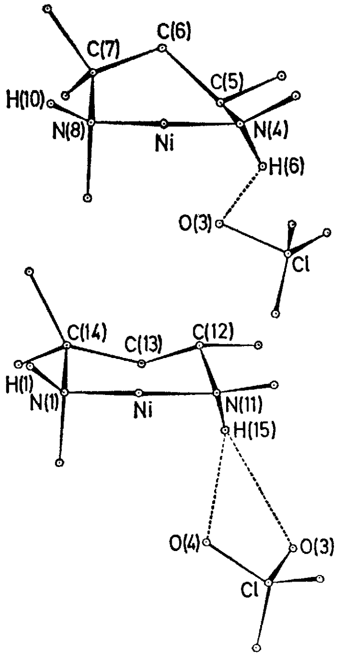


FIGURE 3 The conformation of the six-membered chelate rings: the ring atoms are projected on a plane perpendicular to that through the nickel and two nitrogen atoms (see caption to Figure 2).

is partially relieved by the adoption of the twist-boat conformation, which can be considered to arise by a counter rotation of C(5) and C(6) about an axis N(4)–C(7), which pivots the methyl substituent on C(5) into a site very similar to that found for the methyl substituent on C(12).

The primary co-ordination sphere of the nickel(II) ion of [Ni(α-tet*a*)(acad)]ClO$_4$ is closer to a regular octahedron than found for [Ni(α-tet*b*)(OAc)]ClO$_4$. This arises from the opening of the O–Ni–O chelate angle from 62·4 for the acetate to 87·4° for the acetylacetonate, with a compensating reduction in the ' opposite ' bond angle N(4)–Ni–N(11) from 103·3 to 91·5°.

The nickel-donor atom bond lengths are normal for secondary amine and acetylacetonate compounds of triplet ground-state nickel(II). Dimensions within the five-membered chelate rings and the chair conformation six-membered chelate ring are similar to those for [Ni(α-tet*b*)(OAc)]ClO$_4$. The N–Ni–N bond angle in the ' twist-boat ' six-membered chelate ring is 88·7°, less than the 92·0° observed for the ' chair ' ring. A related effect occurs with two compounds of dipropylenetriamine which have one six-membered chelate ring in a chair and the other in a distorted boat conformation, the N–M–N chelate bond angle being greatest for the ring with the chair conformation.[12] The large internal angle at the central methylene group of the ' chair ' six-membered chelate ring, 119·1° similar to the values found for [Ni(α-tet*b*)(OAc)]ClO$_4$, is reduced to 113·8° for the ' twist-boat ' ring. The large value of this angle seems to be a feature of chelate rings in the chair conformation which also have these three methyl substituents. It does not occur in the cyclam compounds,[11,13] or in a related macrocyclic complex with different substituents.[14] The mean internal ring angle at the ' tetrahedral ' atoms is 113·8 for the chair and 115·5° for the twist boat rings, suggesting that the latter has greater bond-angle strain. It also suffers greater torsional strain arising from the partial eclipsing of the C–H and substituent C–C bonds. The observed lower stability of the compounds with the folded tet*a* configuration, compared with the equivalent folded tet*b* configuration, is considered to arise predominantly from the greater strain energy of this chelate ring. The Ni^{II}(acac) moiety is planar (Table 5) and with dimensions similar to those reported for *trans*-Ni(acac)$_2$(H$_2$O)$_2$,[15] the principle difference being a closing of the O–Ni–O bond angle from 92·4° for the simple acetylacetonate to 87·4° for the tet*a* compound, with a compensating opening of the Ni–O–C angles by *ca.* 5°, an effect presumably arising from the more crowded co-ordination sphere of the tet*a* compound.

Several short interactions involving methyl groups must be important in determining details of the cation conformation [C(2) · · · C(19) 2·87, C(5) · · · C(16) 3·25, C(9) · · · C(16) 2·87, and C(12) · · · C(20) 3·19 Å].

Two of the bond lengths of the perchlorate ion indicate that its atom positions do not attain the level of accuracy found elsewhere [Cl · · · O(5) 1·28 and Cl · · · O(6) 1·34 Å]. Evidence from the difference syntheses suggested large thermal oscillations, or equivalent static disorder, for the oxygen atoms, but there was no indication that a fractional weighting over more than one site would have been a better model for the refinement of the ion.

There are three possible hydrogen bonds in the structure, involving the ' fold-line ' nitrogen atoms N(4) and (equivocably) N(8), and the oxygen atoms O(3) and O(4) of a perchlorate ion (Table 6). These oxygen atoms seem reasonably placed, as judged by their bond lengths of 1·44 and 1·46 Å,† so the geometry of the hydrogen bonds listed in Table 6 can be assumed basically correct. There is no hydrogen bonded network, and the crystal structure is the result of the packing of weakly hydrogen-bonded anion–cation pairs.

TABLE 6

Hydrogen bond geometries

(*a*) N(4)–H(6) · · · O(3′)			
N(4) · · · O(3′)	3·28 Å	H(6) · · · O(3′)	2·32
N(4)–H(6)	1·0	N(4)–H(6) · · · O(3′)	163°
(*b*) N(11)–H(15) · · · O(3′)			
N(11) · · · O(3′)	3·19 Å	H(15) · · · O(3′)	2·51 Å
N(11)–H(15)	0·9	N(11)–H(15) · · · O(3′)	137°
(*c*) N(11)–H(15) · · · O(4′)			
N(11) · · · O(4′)	3·33 Å	H(15) · · · O(4′)	2·51 Å
N(11)–H(15)	0·9	N(11)–H(15)–O(4′)	160°

[2/2037 *Received*, 30*th August*, 1972]

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† Although ' riding ' corrections [16] which satisfactorily adjust the short lengths make these too long.

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