Structural Studies on Co-ordinated Macrocyclic Ligands. Part III.[1] Preparations and Crystal Structure Analyses of Salts of the Nickel(II) Complex *C-rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane, $[Ni(tetb)]^{2+}$, in the α-, β-, and γ-Configurations

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The preparations and *X*-ray structural analyses of three configurational isomers of the $[Ni(tetb)]^{2+}$ complex cation are described: $[Ni(\alpha\text{-}tetb)](ClO_4)_2$, a = 19·298(9), b = 17·34(1), c = 14·078(6) Å, space group *Pbca*; $[Ni(\beta\text{-}tetb)]ZnCl_4,H_2O$, a = 19·442(8), b = 9·926(4), c = 12·657(7) Å, space group $Pna2_1$; $[Ni(\gamma\text{-}tetb)](ClO_4)_2$, a = 17·08(2), b = 9·01(1), c = 8·19(1) Å, β = 107·1(2)°, space group $P2_1/a$. The structures of the α- and β-isomer were solved from diffractometer data and of the γ-isomer from photographic data by the heavy-atom method. The structures were refined by least-squares techniques to R 0·071 (α, 1536 reflections), 0·039 (β, 1698 reflections), and 0·075 (γ, 1184 reflections). All are co-ordinatively planar and thus strained with respect to the preferred conformation attained by co-ordination of the ligand to adjacent octahedral sites. The strain induced in the macrocycle is particularly manifest in the α-isomer in the distortion of both six-membered chelate rings, in the β-isomer by the distortion of the five-membered rings, and in the γ-isomer by distortion of just one six-membered ring. Details of these deviations from preferred geometry are presented and discussed.

THE preparation of the nickel(II) complex of the cyclic tetra-secondary amine *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, known as tet*b*, has been reported.[2] (The complex cation is represented diagrammatically in Figure 1.) With anions which have a high tendency to co-ordinate to nickel(II), triplet ground-state, octahedrally co-ordinated compounds are formed, usually with the amine in folded (*abcd*) co-ordination and often with a chelating anion occupying the two additional sites.[1,3-5] The structure of one such compound, $[Ni(\alpha\text{-}tetb)(OAc)]ClO_4$, has been determined.[6]† With anions which show little tendency to co-ordinate, such as ClO_4^-, BF_4^-, *etc.*, singlet ground-state, square planar, salts are formed with nickel(II);[4] the structures of three such compounds are here described.

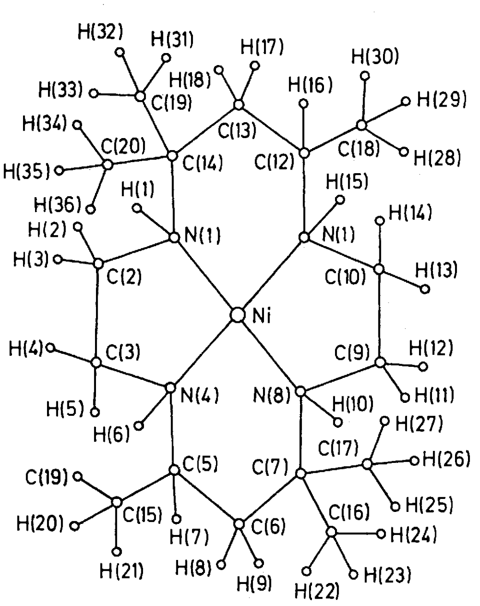

FIGURE 1 Crystallographic numbering scheme for the cation. The anions are numbered as Cl(1), O(1)—(4), and Cl(2), O(5)—(8) for the α- and γ-isomers; numbering for β is unambiguous

The four secondary amino-groups of the amine tet*b* become chiral centres when co-ordinated, giving rise to five possible nitrogen configurations. With the two chiral carbon centres also present, in *rac*-configuration, a total of ten non-enantiomorphic configurations are possible for co-ordinated tet*b*. These configurational isomers will, in general, differ in energy and the differences have been analysed in terms of the strain inherent in the unsubstituted macrocycle (cyclam) when the nitrogen atoms are constrained to occupy the specified co-ordinated sites,[7] combined with non-bonded interactions involving the methyl substituents present for tet*b*.[6,8] Interconversion of the nitrogen configurations requires inversion at one or more co-ordinated secondary amino-centres. In basic solution the inversion reaction is rapid and the thermodynamically favoured configuration(s) predominate. In the solid state, in aprotic solvents, and in strongly acid protic solvents, the inversion reaction is inhibited and non-optimum configurations become metastable.

The $[Ni^{II}(tetb)]$ moiety is extremely resistant to substitution, only cyanide ions displacing the amine, but the 'additional' chelate (or unidentate ligands) of octahedral compounds are labile. In polar solvents there is an equilibrium present between triplet ground-state 'octahedral' species and singlet ground-state square-planar species, the position of the equilibrium depending upon the particular 'additional' ligand present. The

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† The structure of $[Cu(\alpha\text{-}tetb)_2Cl](ClO_4)$, has recently been reported (R. A. Bauer, W. R. Robinson, and D. W. Margerum, *J.C.S. Chem. Comm.*, 1973, 289).

[1] Part II, N. F. Curtis, D. A. Swann and T. N. Waters, *J.C.S. Dalton*, **1973**, 1403.

[2] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644; *J. Chem. Soc.* (*C*), 1967, 1979.

[3] N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1579.

[4] N. F. Curtis, *J. Chem. Soc.*, 1965, 924.

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

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

[7] B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

[8] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962.

$[\mathrm{Ni^{II}}(\mathrm{tet}b)]$ moiety can readily rearrange from folded to planar co-ordination, with retention of configuration, and the square-planar species shows little tendency to interact with neutral ligands, such as water, to form octahedral species. [This latter effect apparently arises from steric interactions involving the 'axial' methyl substituents, a similar situation occurring for the bisnickel(II) complexes of *C*-methyldiaminoethanes]. Since the nitrogen configuration 'α' is only optimum for folded co-ordination the square planar $[\mathrm{Ni}(\alpha\text{-tet}b)]^{2+}$ cation will isomerise to a more stable form, the rate of the inversion reaction being very pH-sensitive. The position of the equilibrium will depend upon the particular 'additional' ligand present. When this is the anion of a weak acid the addition of a strong acid with poorly co-ordinating anion displaces the equilibrium by protonating the ligand. At the same time the high acidity inhibits the inversion reaction and thus preserves the metastable square planar Ni(tet*b*) species.

Isomerisation of $[\mathrm{Ni}(\alpha\text{-tet}b)]^{2+}$ occurs slowly in neutral, or rapidly in basic, solution. The nature of solids then isolated depends upon the anion(s) present and also on the maintenance, or otherwise, of configurational equilibrium. In the absence of anions with appreciable tendency to co-ordinate to nickel(II) the salts of square planar $[\mathrm{Ni}(\mathrm{tet}b)]^{2+}$ cations are obtained and the structures of two such compounds, $[\mathrm{Ni}(\beta\text{-tet}b)\mathrm{ZnCl_4,H_2O}$ and $[\mathrm{Ni}(\gamma\text{-tet}b)](\mathrm{ClO_4})_2$, crystallised under equilibrium conditions, are here reported. These compounds have the amine in different nitrogen configurations and it is concluded that the energy difference between the cations is small, as indicated by the analysis of the relative energies of their configurations, and that specific interactions with the anion in the solid state are sufficient to determine which configuration is optimum for particular salts.

Under conditions which inhibited inversion at the nitrogen centres it was possible to prepare the metastable compounds $[\mathrm{Ni}(\beta\text{-tet}b)](\mathrm{ClO_4})_2$ and $[\mathrm{Ni}(\gamma\text{-tet}b)]\mathrm{ZnCl_4,\frac{1}{2}H_2O}$ and, to complete the set, triplet ground-state $[\mathrm{Ni}(\alpha\text{-tet}b)\mathrm{ZnCl_4}]$.

EXPERIMENTAL

Preparations.—The preparations of $[\mathrm{Ni}(\alpha\text{-tet}b)](\mathrm{ClO_4})_2$ and $[\mathrm{Ni}(\beta\text{-tet}b)](\mathrm{ClO_4})_2$ have previously been reported.[2,9] The $[\mathrm{Ni}(\mathrm{tet}b)]^{2+}$ cation was prepared for the present study as follows.

Diaminoethane hydroperchlorate was treated with acetone[10] to give 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane-4,11-dienedihydroperchlorate $[\mathrm{H_2(Y)}](\mathrm{ClO_4})_2$. $[\mathrm{Ni(Y)}](\mathrm{ClO_4})_2$ was prepared from this by reaction with nickel(II) acetate. $[\mathrm{Ni(Y)}](\mathrm{ClO_4})_2$ was reduced with sodium borohydride to a mixture of the *C-racemic* and *C-meso* isomers of the (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) cation, $[\mathrm{Ni}(\mathrm{tet}b)]^{2+}$ and $[\mathrm{Ni}(\mathrm{tet}a)]^{2+}$, which were separated by the precipitation of insoluble $[\mathrm{Ni}(\alpha\text{-tet}b)(\mathrm{acac})]\mathrm{ClO_4}$ (acac = acetylacetonate).[1] $[\mathrm{Ni}(\alpha\text{-tet}b)(\mathrm{acac})]\mathrm{ClO_4}$ was treated with 2M-perchloric acid and yellow $[\mathrm{Ni}(\alpha\text{-tet}b)](\mathrm{ClO_4})_2$ subsequently crystallised.

Orange crystals of $[\mathrm{Ni}(\beta\text{-tet}b)](\mathrm{ClO_4})_2$ formed when the α-isomer was boiled in water containing a few drops of ammonia, followed by acidification with perchloric acid and cooling. This compound also crystallised when the β-tetrachlorozincate (see later) was dissolved in hot dilute perchloric acid.

$[\mathrm{Ni}(\gamma\text{-tet}b)](\mathrm{ClO_4})_2$. Orange crystals formed when a solution of the α- or β-perchlorate in dilute aqueous ammonia was allowed to crystallise by slow evaporation. Alternatively, when the β-perchlorate was dissolved in hot methanol and a few drops of triethylamine added, the γ-perchlorate crystallised (Found: C, 36·0; H, 6·5; Ni, 10·7. $\mathrm{C_{16}H_{36}Cl_2N_4NiO_8}$ requires C, 35·5; H, 6·7; Ni, 10·8%). The γ-fluoroborate was prepared analogously from the α-fluoroborate (in turn prepared from $[\mathrm{Ni}(\alpha\text{-tet}b)(\mathrm{acac})]\mathrm{Br}$).

$[\mathrm{Ni}(\alpha\text{-tet}b)\mathrm{ZnCl_4}]$. The α-perchlorate was dissolved in hot acetone containing 10% 1M-perchloric acid (the solubility in acetone being greatly enhanced by 10% of water). On addition of a solution of zinc chloride in ethanol, together with a few drops of concentrated hydrochloric acid, blue-green crystals of the product separated and were washed with ethanol.

$[\mathrm{Ni}(\beta\text{-tet}b)]\mathrm{ZnCl_4,H_2O}$. The α-tetrachlorozincate was boiled in water containing a few drops of ammonia solution. Zinc chloride was added, the solution faintly acidified with hydrochloric acid, and then allowed to evaporate. Yellow needles of the product were deposited.

$[\mathrm{Ni}(\gamma\text{-tet}b)]\mathrm{ZnCl_4,\frac{1}{2}H_2O}$. Orange-pink crystals of this compound were prepared from the γ-perchlorate by a procedure analogous to that used for the α-isomer (Found: α-isomer, C, 35·0; H, 6·8; Ni, 10·5; β-isomer, C, 33·7; H, 6·6; Ni, 10·3; γ-isomer, C, 34·6; H, 6·6; Ni, 10·7. $\mathrm{C_{16}H_{36}Cl_4N_4NiZn}$ requires C, 34·9; H, 6·6; Ni, 10·7; ½-hydrate requires C, 34·3; H, 6·7; Ni, 10·5; monohydrate requires C, 33·8; H, 6·7; Ni, 10·3%).

X-Ray Crystallography

Unit-cell and space group information were collected for five of the compounds and three were subjected to three-dimensional structural analysis.

Crystal Data.—(i) $[\mathrm{Ni}(\alpha\text{-tet}b)](\mathrm{ClO_4})_2$. $\mathrm{C_{16}H_{36}Cl_2N_4NiO_8}$, $M = 542$, Orthorhombic, $a = 19{\cdot}298(9)$, $b = 17{\cdot}34(1)$, $c = 14{\cdot}078(6)$ Å (from least-squares fit to diffractometer co-ordinates of 12 reflexions), $U = 4712$ Å^3, $D_m = 1{\cdot}52$ (by flotation), $Z = 8$, $D_c = 1{\cdot}53$. Space group *Pbca*.

(ii) $[\mathrm{Ni}(\beta\text{-tet}b)]\mathrm{ZnCl_4,H_2O}$. $\mathrm{C_{16}H_{38}Cl_4N_4NiOZn}$, $M = 570$, Orthorhombic, $a = 19{\cdot}442(8)$, $b = 9{\cdot}926(4)$, $c = 12{\cdot}657(7)$ Å (from least-squares fit to diffractometer co-ordinates of 12 reflexions), $U = 2442$ Å^3, $D_m = 1{\cdot}55$ (by flotation), $Z = 4$, $D_c = 1{\cdot}54$. Space group $Pna2_1$ or *Pnam*.

(iii) $[\mathrm{Ni}(\beta\text{-tet}b)](\mathrm{ClO_4})_2$. $\mathrm{C_{16}H_{36}Cl_2N_4NiO_8}$, $M = 542$, Tetragonal, $a = 8{\cdot}46(4)$, $c = 16{\cdot}56(6)$ Å (by repeated measurements on Weissenberg and rotation photographs), $U = 1185$ Å^3, $Z = 2$ (based on volume). Space group $P4_2$ ($P4_2/m$ is excluded because the cation cannot be centrosymmetric).

(iv) $[\mathrm{Ni}(\gamma\text{-tet}b)](\mathrm{ClO_4})_2$. $\mathrm{C_{16}H_{36}Cl_2N_4NiO_8}$, $M = 542$, Monoclinic, $a = 17{\cdot}08(2)$, $b = 9{\cdot}01(1)$, $c = 8{\cdot}19(1)$ Å, $\beta = 107{\cdot}1(2)°$ (by repeated measurements on Weissenberg photographs), $U = 1205$ Å^3, $D_m = 1{\cdot}50$ (by flotation), $Z = 2$, $D_c = 1{\cdot}49$. Space group $P2_1/a$.

(v) $[\mathrm{Ni}(\gamma\text{-tet}b)]\mathrm{ZnCl_4,H_2O}$. $\mathrm{C_{16}H_{38}Cl_4N_4NiOZn}$, $M = 570$, Monoclinic, $a = 9{\cdot}93(5)$, $b = 31{\cdot}7(2)$, $c = 8{\cdot}96(5)$ Å,

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

[10] N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524.

β = 119·4(3)° (from repeated measurements on Weissenberg and rotation films), U = 2457 Å^3, Z = 4 (based on volume). Space group $P2_1/a$.

Structural Determinations.—These were undertaken for an α-, β-, and γ-isomer. (i) [Ni(α-tet*b*)](ClO$_4$)$_2$. Data were collected on a Hilger and Watts automatic four-circle diffractometer by use of Mo-K_α radiation (λ = 0·7107 Å) with a 60 step θ/ω scan. Of 2650 reflexions examined 1536 with intensities $> 2\sigma(F^2)$ were classed as observed. Absorption corrections [11] were applied (μ = 10·95 cm^{-1}).

Structure solution was by the heavy-atom method with an initial calculation of the sharpened Patterson function. Once all non-hydrogen atoms had been placed block-diagonal least-squares refinement was undertaken with the statistical weighting scheme $w = 4F^2/\sigma^2(F^2)$. At this early stage it became clear that only one oxygen of each perchlorate [O(1) and O(5)] would refine easily, the others having large thermal parameter and positional shifts. Electron-density syntheses were therefore computed at appropriate points in the refinement to check for disordered positioning of these particular atoms but no evidence for fractional occupancy was found. The molecular model was increasingly relaxed to include all hydrogen atoms (their positions being found from difference-Fourier syntheses) and to account for anisotropic thermal motion in the remaining atoms. The resulting fall in R was, in all instances, acceptable at the 0·5% confidence level.[12] Refinement converged at R 0·071.

Atom co-ordinates, temperature parameters, bond lengths and bond angles are listed for all three compounds in Tables 1—4, the numbering scheme being that of Figure 1.* Structure factor data for all compounds are listed in Supplementary Publication No. SUP 20695 (8 pp., 1 microfiche).†

(ii) [Ni(β-tet*b*)]ZnCl$_4$,H$_2$O. Data were collected as before with a 70 step θ/ω scan. 1698 Reflexions were classed as observed and corrected for absorption (μ = 22·9 cm^{-1}).

The Patterson map was analysed on the assumption of the non-centrosymmetric space group, positions for both metal atoms being obtained, although they could not be distinguished, at 0·14, 0·25, z and 0·11, 0·23, z + 0·34. Because of the particular y co-ordinates, some difficulty was experienced in breaking the extra symmetry initially imposed, but eventually all major peaks were assigned in electron-density maps, except one which was later found to be the water molecule. Refinement was undertaken as for the previous compound, the structural model being progressively relaxed until all hydrogen atoms were included (after location by difference-Fourier synthesis) and all non-hydrogen atoms were assumed to have anisotropic thermal motion. The water molecule was brought into the model during this process. Convergence was reached with R at 0·039.

(iii) [Ni(γ-tet*b*)](ClO$_4$)$_2$. Data were collected by Weissenberg photography using nickel-filtered Cu-K_α radiation

TABLE 1

Atom co-ordinates with estimated standard deviations in parentheses

(*a*) [Ni(α-tet*b*)](ClO$_4$)$_2$

Atom	x/a	y/b	z/c
Ni	0·37057(7)	0·40481(8)	0·2961(1)
Cl(1)	0·5348(2)	0·3163(2)	0·4208(3)
Cl(2)	0·3131(2)	0·1067(2)	0·4252(3)
O(1)	0·5535(5)	0·3920(5)	0·3862(7)
O(2)	0·5883(8)	0·2827(9)	0·4589(14)
O(3)	0·4836(8)	0·3200(8)	0·4785(15)
O(4)	0·5169(14)	0·2726(9)	0·3498(11)
O(5)	0·3561(7)	0·0554(7)	0·4720(8)
O(6)	0·3381(7)	0·1757(6)	0·4172(13)
O(7)	0·2873(13)	0·0790(10)	0·3457(11)
O(8)	0·2540(10)	0·1084(13)	0·4690(20)
N(1)	0·3107(5)	0·3172(6)	0·2843(7)
N(4)	0·4137(6)	0·3741(5)	0·1809(8)
N(8)	0·4352(5)	0·4859(6)	0·3169(7)
N(11)	0·3273(5)	0·4360(5)	0·4108(7)
C(2)	0·3250(8)	0·2804(8)	0·1915(11)
C(3)	0·3996(8)	0·2903(8)	0·1706(9)
C(5)	0·4826(7)	0·4007(8)	0·1571(10)
C(6)	0·4913(8)	0·4861(9)	0·1590(11)
C(7)	0·4548(7)	0·5345(7)	0·2330(9)
C(9)	0·4153(8)	0·5311(8)	0·4023(10)
C(10)	0·3818(7)	0·4752(8)	0·4676(10)
C(12)	0·2918(7)	0·3734(8)	0·4645(10)
C(13)	0·2285(7)	0·3474(8)	0·4101(11)
C(14)	0·2359(6)	0·3314(7)	0·3045(11)
C(15)	0·5150(8)	0·3656(9)	0·0704(12)
C(16)	0·5044(9)	0·5989(10)	0·2631(14)
C(17)	0·3884(9)	0·5685(10)	0·1928(12)
C(18)	0·2669(9)	0·4019(9)	0·5609(11)
C(19)	0·2123(7)	0·3996(9)	0·2429(12)
C(20)	0·1911(7)	0·2616(9)	0·2791(14)
H(1)	0·325(5)	0·290(6)	0·334(7)
H(2)	0·301(5)	0·302(6)	0·147(8)
H(3)	0·311(5)	0·237(6)	0·207(7)
H(4)	0·407(5)	0·274(6)	0·105(7)
H(5)	0·429(5)	0·271(6)	0·220(7)
H(6)	0·379(5)	0·404(6)	0·165(7)
H(7)	0·513(5)	0·380(6)	0·206(7)
H(8)	0·475(5)	0·497(6)	0·097(7)
H(9)	0·543(5)	0·496(6)	0·161(8)
H(10)	0·469(5)	0·457(6)	0·331(8)
H(11)	0·389(5)	0·569(6)	0·382(7)
H(12)	0·455(5)	0·553(6)	0·440(8)
H(13)	0·357(5)	0·496(6)	0·517(8)
H(14)	0·410(5)	0·431(6)	0·498(8)
H(15)	0·297(5)	0·468(6)	0·393(7)
H(16)	0·327(5)	0·331(6)	0·473(8)
H(17)	0·192(5)	0·386(6)	0·417(7)
H(18)	0·208(5)	0·305(6)	0·453(7)
H(19)	0·567(5)	0·390(6)	0·060(7)
H(20)	0·484(5)	0·368(6)	0·013(8)
H(21)	0·524(5)	0·313(6)	0·072(7)
H(22)	0·543(5)	0·571(6)	0·298(7)
H(23)	0·528(5)	0·616(6)	0·205(7)
H(24)	0·477(5)	0·637(6)	0·284(7)
H(25)	0·401(5)	0·601(6)	0·145(8)
H(26)	0·359(5)	0·530(6)	0·159(8)
H(27)	0·367(5)	0·592(6)	0·241(7)
H(28)	0·301(5)	0·416(6)	0·605(7)
H(29)	0·237(5)	0·446(6)	0·555(7)
H(30)	0·245(5)	0·350(6)	0·594(7)
H(31)	0·249(6)	0·438(6)	0·252(8)
H(32)	0·214(5)	0·381(6)	0·176(7)
H(33)	0·169(5)	0·411(6)	0·252(8)
H(34)	0·205(5)	0·225(6)	0·315(7)
H(35)	0·196(5)	0·261(6)	0·210(7)
H(36)	0·140(5)	0·269(6)	0·309(7)

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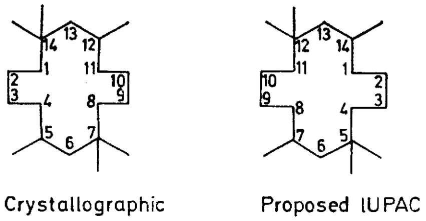
* Numbering schemes:



Crystallographic Proposed IUPAC

† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[11] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

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

TABLE 1 (*Continued*)

(*b*) [Ni(β-tet*b*)]ZnClO$_4$,H$_2$O

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Zn	0·15416(5)	0·25928(10)	0·34060(11)
Ni	0·11234(5)	0·21491(10)	0·67789(11)
Cl(1)	0·25301(13)	0·33008(28)	0·42014(24)
Cl(2)	0·06695(14)	0·38148(30)	0·41260(27)
Cl(3)	0·13452(13)	0·03687(25)	0·37299(23)
Cl(4)	0·16149(15)	0·27669(34)	0·16534(24)
N(1)	0·1105(4)	0·3930(7)	0·7358(6)
N(4)	0·0165(4)	0·2370(7)	0·6388(6)
N(8)	0·1196(4)	0·0322(7)	0·6295(8)
N(11)	0·2096(4)	0·2075(8)	0·7100(6)
O(1)	0·2294(4)	0·5161(9)	0·6282(7)
C(2)	0·0467(5)	0·4619(9)	0·6995(8)
C(3)	−0·0109(5)	0·3634(9)	0·6908(9)
C(5)	−0·0331(5)	0·1222(10)	0·6482(9)
C(6)	−0·0033(6)	−0·0090(12)	0·6028(9)
C(7)	0·0605(5)	−0·0636(8)	0·6519(8)
C(9)	0·1892(5)	−0·0227(9)	0·6587(9)
C(10)	0·2384(4)	0·0922(10)	0·6464(8)
C(12)	0·2211(5)	0·2066(9)	0·8265(8)
C(13)	0·1987(5)	0·3435(11)	0·8700(8)
C(14)	0·1246(5)	0·3941(9)	0·8544(8)
C(15)	−0·0993(5)	0·1549(13)	0·5916(11)
C(16)	0·0758(6)	−0·2003(11)	0·5975(13)
C(17)	0·0540(6)	−0·0842(11)	0·7705(9)
C(18)	0·2952(5)	0·1780(11)	0·8569(9)
C(19)	0·1217(6)	0·5379(12)	0·8975(10)
C(20)	0·0725(6)	0·3036(14)	0·9117(9)
H(1)	0·151(4)	0·429(9)	0·707(8)
H(2)	0·034(4)	0·542(9)	0·750(8)
H(3)	0·066(5)	0·502(9)	0·632(8)
H(4)	−0·055(4)	0·393(9)	0·646(8)
H(5)	−0·026(5)	0·335(9)	0·772(8)
H(6)	0·018(5)	0·258(9)	0·568(8)
H(7)	−0·046(5)	0·118(9)	0·722(8)
H(8)	0·006(5)	0·007(10)	0·523(8)
H(9)	−0·042(5)	−0·072(9)	0·594(8)
H(10)	0·118(5)	0·050(10)	0·552(8)
H(11)	0·201(5)	−0·094(9)	0·606(8)
H(12)	0·180(5)	−0·060(9)	0·741(8)
H(13)	0·247(5)	0·126(9)	0·572(8)
H(14)	0·277(4)	0·057(9)	0·679(8)
H(15)	0·230(5)	0·283(9)	0·693(8)
H(16)	0·191(5)	0·123(9)	0·858(8)
H(17)	0·230(4)	0·418(9)	0·837(8)
H(18)	0·207(5)	0·337(9)	0·945(8)
H(19)	−0·091(5)	0·218(10)	0·531(8)
H(20)	−0·116(5)	0·081(10)	0·558(8)
H(21)	−0·133(5)	0·180(9)	0·638(8)
H(22)	0·118(5)	−0·247(9)	0·644(8)
H(23)	0·082(5)	−0·189(10)	0·524(8)
H(24)	0·043(5)	−0·264(9)	0·609(8)
H(25)	0·051(5)	0·004(9)	0·804(8)
H(26)	0·094(5)	−0·138(10)	0·797(8)
H(27)	0·015(5)	−0·147(9)	0·781(8)
H(28)	0·327(5)	0·246(9)	0·823(8)
H(29)	0·315(5)	0·087(9)	0·821(8)
H(30)	0·300(5)	0·176(9)	0·928(8)
H(31)	0·138(4)	0·537(9)	0·968(8)
H(32)	0·162(4)	0·596(9)	0·857(8)
H(33)	0·082(4)	0·576(9)	0·870(8)
H(34)	0·088(5)	0·303(9)	0·982(8)
H(35)	0·075(5)	0·203(9)	0·874(8)
H(36)	0·033(5)	0·344(9)	0·911(8)

(*c*) [Ni(γ-tet*b*)](ClO$_4$)$_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni	0·0000	0·0000	0·5000
Cl(1)	0·0651(1)	0·2715(2)	0·1886(2)
O(1)	0·1188(7)	0·2105(14)	0·3423(12)
O(2)	0·0239(6)	0·1557(10)	0·0833(11)
O(3)	0·1080(5)	0·3587(10)	0·1047(9)
O(4)	0·0083(5)	0·3550(9)	0·2440(11)
N(1)	0·0456(3)	−0·1955(6)	0·4904(7)
N(4)	−0·0796(4)	−0·0519(8)	0·2867(8)
N(8)	−0·0456(3)	0·1955(6)	0·5096(7)
N(11)	0·0796(4)	0·0519(8)	0·7133(8)
C(2)	0·0012(5)	−0·2684(10)	0·3242(10)
C(3)	−0·0846(5)	−0·2135(9)	0·2801(10)
C(5)	−0·1476(10)	0·0536(22)	0·2101(20)
C(6)	−0·1852(13)	0·0921(27)	0·3468(29)
C(7)	−0·1399(10)	0·2115(18)	0·4691(21)
C(9)	−0·0012(5)	0·2684(10)	0·6758(10)
C(10)	0·0846(5)	0·2135(9)	0·7199(10)
C(12)	0·1703(9)	0·0040(17)	0·7501(20)
C(13)	0·1700(7)	−0·1704(15)	0·7354(16)
C(14)	0·1353(8)	−0·2333(17)	0·5505(21)
C(15)	−0·2071(10)	−0·0091(19)	0·0431(20)
C(16)	−0·1717(12)	0·1499(27)	0·6185(29)
C(17)	−0·1649(10)	0·3715(20)	0·4116(24)
C(18)	0·2254(10)	0·0642(22)	0·9136(21)
C(19)	0·1738(12)	−0·1762(25)	0·4148(28)
C(20)	0·1449(10)	−0·4034(20)	0·5535(28)
H(1)	0·040	−0·268	0·582
H(2)	0·004	−0·388	0·335
H(3)	0·029	−0·241	0·225
H(4)	−0·116	−0·255	0·368
H(5)	−0·120	−0·251	0·155
H(6)	−0·066	0·021	−0·822
H(7)	−0·125	0·152	0·162
H(8)	−0·248	0·127	0·288
H(9)	−0·189	−0·007	0·417
H(10)	−0·040	0·268	0·418
H(11)	−0·004	0·388	0·665
H(12)	−0·029	0·241	0·775
H(13)	0·116	0·255	0·632
H(14)	0·120	0·251	0·845
H(15)	0·066	0·021	0·822
H(16)	0·198	0·055	0·661
H(17)	0·232	−0·211	0·789
H(18)	0·135	−0·216	0·814

(λ = 1·5418 Å). Two crystals were used to record the reciprocal lattice layers *h*0—6*l* and *hk*0—4 and intensities were estimated visually. After correction for absorption (μ = 36·5 cm^{-1}) the two sets of axial data were brought to a common scale by a least-squares method,[13] the correlation factor of 0·056 obtained for this process being regarded as very satisfactory. A total of 1184 reflexions was available.

A difficulty arose at the outset, the space group being $P2_1/a$ with $Z = 2$. This presupposes nickel atoms on centres of symmetry, confirmed by the enhanced intensities of reflexions for which $h + k = 2n$, and this is untenable for tet*b* complexes which have a *C-racemic* configuration. Since only tet*a* complexes in some of their configurations can be centrosymmetric there was considerable effort to test the facts, but we were compelled to accept that single crystals with space-group absences characteristic of $P2_1/a$ (and not Pa) also gave the light blue product characteristic of [Ni(α-tet*b*)C$_2$O$_4$](ClO$_4$)$_2$ when treated with oxalate under basic conditions.[14] The analysis was begun, therefore, with the possibility of disorder in mind.

Structure solution by the heavy-atom method and subsequent refinement by block-diagonal least-squares methods reduced R to 0·150 before difficulties with the centrosymmetric model imposed on the complex cation became obvious. These were particularly associated with the central carbon atom of the six-membered chelate ring and a difference-Fourier synthesis indicated that this atom should be half-weighted. Models then showed that a *C-racemic* cation in which one six-membered ring had a chair conformation and the other a twist-boat geometry could be superimposed on itself to produce a centrosymmetric com-

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[13] A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

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

TABLE 2

Anisotropic thermal parameters * (× 10^4) with estimated standard deviations in parentheses

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
(*a*) [Ni(α-tet*b*)]$(ClO_4)_2$						
Ni	26·8(4)	22·9(5)	58·5(8)	−1·2(9)	−2·7(13)	−10·1(13)
Cl(1)	44(1)	30(1)	72(2)	3(2)	−8(3)	−6(3)
Cl(2)	37(1)	38(1)	85(2)	−9(2)	−8(3)	0(3)
O(1)	48(3)	44(4)	80(6)	−24(6)	−7(9)	28(9)
O(2)	87(7)	147(7)	388(17)	61(12)	−21(19)	367(15)
O(3)	139(6)	38(5)	535(19)	11(10)	444(13)	49(19)
O(4)	315(16)	99(7)	125(11)	−197(15)	−100(23)	−68(14)
O(5)	79(5)	65(5)	233(10)	24(9)	−73(12)	106(11)
O(6)	99(6)	55(5)	345(18)	−88(9)	−173(17)	161(15)
O(7)	303(15)	89(8)	176(11)	50(19)	−323(19)	−66(16)
O(8)	95(7)	188(14)	495(29)	58(19)	224(25)	261(34)
N(1)	30(3)	34(4)	66(7)	−5(6)	−15(9)	−11(9)
N(4)	44(4)	18(4)	101(9)	13(6)	8(11)	−24(9)
N(8)	31(3)	30(4)	62(7)	−5(6)	−5(8)	−4(9)
N(11)	36(3)	21(4)	67(7)	−5(6)	5(9)	−2(8)
C(2)	48(5)	40(6)	79(10)	−20(9)	−22(13)	−14(13)
C(3)	52(5)	48(6)	51(9)	15(10)	−10(12)	−29(12)
C(5)	40(4)	33(5)	86(10)	15(9)	33(12)	−17(13)
C(6)	39(5)	55(7)	87(11)	−10(10)	22(13)	29(15)
C(7)	35(4)	35(5)	60(9)	−7(8)	5(11)	−24(11)
C(9)	45(5)	36(5)	70(10)	−24(9)	14(12)	−42(11)
C(10)	33(4)	43(6)	69(9)	−9(9)	−2(12)	−16(12)
C(12)	34(4)	44(6)	73(10)	1(9)	18(12)	7(13)
C(13)	30(4)	42(6)	112(12)	−5(9)	30(12)	45(14)
C(14)	31(4)	28(5)	109(11)	−8(8)	−27(13)	25(13)
C(15)	48(6)	53(7)	96(11)	29(10)	−4(15)	5(16)
C(16)	56(6)	64(8)	123(13)	−45(12)	37(16)	−43(18)
C(17)	59(6)	65(8)	92(12)	30(12)	19(17)	20(16)
C(18)	64(7)	41(6)	86(11)	15(11)	20(15)	18(15)
C(19)	34(4)	58(7)	117(12)	0(11)	−46(13)	14(17)
C(20)	32(4)	55(7)	154(16)	−25(10)	−5(16)	37(18)
(*b*) [Ni(β-tet*b*)]$ZnCl_4$,H_2O						
Zn	23·3(2)	114·9(9)	56·1(5)	−2·6(10)	−1·4(9)	8·5(17)
Ni	18·9(2)	83·7(8)	53·9(6)	−3·3(9)	−1·4(9)	8·6(17)
Cl(1)	26(1)	131(3)	90(2)	−5(3)	−27(2)	1(4)
Cl(2)	30(1)	156(3)	104(2)	32(3)	27(2)	31(5)
Cl(3)	36(1)	108(2)	76(2)	−6(3)	0(2)	3(4)
Cl(4)	44(1)	218(4)	61(2)	−63(3)	−8(3)	33(5)
N(1)	21(2)	73(7)	71(5)	−12(7)	−4(6)	−18(11)
N(4)	23(2)	98(8)	65(5)	1(7)	−10(6)	41(11)
N(8)	21(2)	83(8)	74(6)	7(7)	−8(6)	19(11)
N(11)	22(2)	115(9)	73(6)	4(8)	−2(6)	19(13)
O(1)	40(3)	195(11)	88(6)	−31(9)	21(7)	11(15)
C(2)	38(3)	85(9)	73(8)	12(10)	11(9)	−10(15)
C(3)	25(3)	106(10)	82(8)	33(9)	−5(9)	4(17)
C(5)	20(3)	133(12)	86(8)	−19(10)	−5(8)	32(16)
C(6)	22(2)	122(10)	88(8)	−31(9)	−27(8)	15(17)
C(7)	24(3)	75(8)	75(8)	−1(8)	4(7)	11(13)
C(9)	25(2)	84(9)	83(8)	5(9)	−5(8)	1(15)
C(10)	16(2)	118(11)	76(7)	19(9)	9(7)	10(15)
C(12)	21(2)	120(11)	75(7)	−11(9)	−7(8)	24(17)
C(13)	24(3)	138(12)	68(7)	−18(10)	−20(8)	3(16)
C(14)	29(3)	117(10)	56(6)	−23(9)	−10(8)	−38(16)
C(15)	22(3)	160(15)	129(11)	−18(11)	−42(10)	2(23)
C(16)	32(3)	93(11)	159(13)	−29(11)	−23(12)	−23(22)
C(17)	32(3)	126(12)	88(9)	−14(11)	−1(9)	58(18)
C(18)	32(3)	154(13)	89(9)	−4(11)	−39(9)	1(21)
C(19)	38(3)	172(9)	92(8)	0(9)	−55(9)	−74(17)
C(20)	34(3)	237(15)	61(9)	−36(10)	3(9)	23(15)
(*c*) [Ni(γ-tet*b*)]$(ClO_4)_2$						
Ni	29·5(4)	79·9(19)	112·9(20)	15·1(18)	32·7(16)	−4·4(41)
Cl(1)	49(1)	152(3)	168(3)	−21(3)	86(2)	−13(6)
O(1)	101(5)	523(26)	306(17)	88(21)	−7(16)	245(38)
O(2)	149(5)	304(13)	352(17)	−257(15)	158(15)	−260(29)
O(3)	102(3)	332(14)	327(12)	−167(12)	210(9)	−11(26)
O(4)	105(3)	214(12)	602(17)	77(12)	340(10)	142(28)
N(1)	22(2)	73(7)	130(9)	23(7)	18(7)	−14(16)
N(4)	37(3)	113(9)	134(10)	47(9)	2(8)	−51(19)
N(8)	22(2)	73(7)	130(9)	23(7)	18(7)	−14(16)
N(1)	37(3)	113(9)	134(10)	47(9)	2(8)	−51(19)
C(2)	55(4)	131(11)	182(13)	60(11)	0(12)	−145(22)
C(3)	39(3)	134(11)	174(13)	4(11)	−2(11)	−90(23)

* The scattering factor for an atom is expressed by: $f = f_0 \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

TABLE 2 (*Continued*)

(*c*) [Ni(γ-tet*b*)]$(ClO_4)_2$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(5)	36(6)	211(25)	165(26)	41(23)	−6(20)	2(51)
C(6)	53(8)	282(38)	441(39)	57(35)	115(29)	−217(69)
C(7)	32(5)	108(21)	222(28)	32(20)	25(20)	−14(48)
C(9)	55(4)	131(11)	182(13)	60(11)	0(12)	−145(22)
C(10)	39(3)	134(11)	174(13)	4(11)	−2(11)	−90(23)
C(12)	28(5)	108(20)	235(25)	29(18)	21(18)	−55(45)
C(13)	24(4)	61(16)	164(19)	22(15)	9(15)	42(35)
C(14)	31(5)	115(20)	240(27)	−11(19)	69(19)	−46(46)
C(15)	39(6)	155(24)	155(26)	4(22)	−20(21)	13(50)
C(16)	80(8)	253(37)	481(43)	−12(33)	265(27)	206(76)
C(17)	47(6)	102(22)	296(36)	44(23)	65(24)	30(53)
C(18)	45(6)	198(26)	181(27)	−5(24)	5(22)	−40(52)
C(19)	57(7)	213(33)	419(39)	18(28)	207(25)	272(67)
C(20)	32(6)	126(25)	444(44)	58(23)	23(28)	36(61)

posite in which all non-hydrogen atoms, except the carbons referred to, came close to occupying the same spatial positions. The model was therefore revised until all the carbon atoms of the six-membered ring were half-weighted but no evidence suggesting the relaxation of the centrosymmetric relation between the remaining atoms could be found. Refinement continued on this basis, all atoms being eventually ascribed anisotropic temperature parameters. With a weighting scheme of the form $w = \{1 + (F_o - b)^2/a^2\}^{-1}$ being adjusted periodically to ensure constant $\langle w\Delta F^2\rangle$ over $|F_o|$ ranges and with all hydrogen atoms, except those on the methyl groups, placed in theoretical positions, the R was reduced to a final value of 0·075.

Spectra.—The ^{1}H n.m.r. spectra of [Ni(β-tet*b*)]$^{2+}$ * and [Ni(β-tet*a*)]$^{2+}$ have been published.[15] The spectrum of [Ni(γ-tet*b*)$^{2+}$ has been recorded and is reproduced in Figure 2 for comparison. Resonances are sharp suggesting that the configuration present in solution is well defined.

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

(*a*) [Ni(α-tet*b*)]$(ClO_4)_2$

Ni–N(1)	1·916(10)	C(2)–H(3)	0·9(1)
Ni–N(4)	1·899(11)	C(3)–H(4)	1·0(1)
Ni–N(8)	1·903(10)	C(3)–H(5)	1·0(1)
Ni–N(11)	1·897(10)	N(4)–H(6)	0·90(1)
N(1)–C(2)	1·48(2)	C(5)–H(7)	1·0(1)
C(2)–C(3)	1·48(2)	C(6)–H(8)	0·9(1)
C(3)–N(4)	1·48(2)	C(6)–H(9)	1·0(1)
N(4)–C(5)	1·45(2)	N(8)–H(10)	0·8(1)
C(5)–C(6)	1·49(2)	C(9)–H(11)	0·9(1)
C(6)–C(7)	1·51(2)	C(9)–H(12)	1·0(1)
C(7)–N(8)	1·50(2)	C(10)–H(13)	0·9(1)
N(8)–C(9)	1·49(2)	C(10)–H(14)	1·0(1)
C(9)–C(10)	1·48(2)	N(11)–H(15)	0·8(1)
C(10)–N(11)	1·49(2)	C(12)–H(16)	1·0(1)
N(11)–C(12)	1·49(2)	C(13)–H(17)	1·0(1)
C(12)–C(13)	1·51(2)	C(13)–H(18)	1·0(1)
C(13)–C(14)	1·52(2)	C(15)–H(19)	1·1(1)
C(14)–N(1)	1·49(2)	C(15)–H(20)	1·0(1)
C(5)–C(15)	1·50(2)	C(15)–H(21)	0·9(1)
C(7)–C(16)	1·53(2)	C(16)–H(22)	0·9(1)
C(7)–C(17)	1·52(2)	C(16)–H(23)	1·0(1)
C(12)–C(18)	1·52(2)	C(16)–H(24)	1·0(1)
C(14)–C(19)	1·54(2)	C(17)–H(25)	0·9(1)
C(14)–C(20)	1·53(2)	C(17)–H(26)	1·0(1)
Cl(1)–O(1)	1·30(2)	C(18)–H(28)	0·9(1)
Cl(1)–O(3)	1·28(2)	C(18)–H(29)	1·0(1)
Cl(1)–O(4)	1·30(2)	C(18)–H(30)	1·1(1)
Cl(2)–O(5)	1·38(1)	C(19)–H(31)	1·0(1)
Cl(2)–O(6)	1·29(1)	C(19)–H(32)	1·0(1)
Cl(2)–O(7)	1·32(2)	C(19)–H(33)	0·9(1)
Cl(2)–O(8)	1·30(2)	C(20)–H(34)	0·9(1)
N(1)–H(1)	0·9(1)	C(20)–H(35)	1·0(1)
C(2)–H(2)	0·9(1)	C(20)–H(36)	1·1(1)

TABLE 3 (*Continued*)

(*b*) [Ni(β-tet*b*)]$ZnCl_4,H_2O$

Ni–N(1)	1·914(7)	C(3)–H(5)	1·0(1)
Ni–N(4)	1·940(8)	N(4)–H(6)	0·9(1)
Ni–N(8)	1·920(7)	C(5)–H(7)	1·0(1)
Ni–N(11)	1·935(7)	C(6)–H(8)	1·0(1)
N(1)–C(2)	1·49(1)	C(6)–H(9)	1·0(1)
C(2)–C(3)	1·49(1)	N(8)–H(10)	1·0(1)
C(3)–N(4)	1·51(1)	C(9)–H(11)	1·0(1)
N(4)–C(5)	1·50(1)	C(9)–H(12)	1·1(1)
C(5)–C(6)	1·54(2)	C(10)–H(13)	0·9(1)
C(6)–C(7)	1·49(1)	C(10)–H(14)	1·0(1)
C(7)–N(8)	1·52(1)	N(11)–H(15)	0·9(1)
N(8)–C(9)	1·50(1)	C(12)–H(16)	1·1(1)
C(9)–C(10)	1·49(1)	C(13)–H(17)	1·1(1)
C(10)–N(11)	1·51(1)	C(13)–H(18)	1·0(1)
N(11)–C(12)	1·49(1)	C(15)–H(19)	1·0(1)
C(12)–C(13)	1·53(1)	C(15)–H(20)	0·9(1)
C(13)–C(14)	1·54(1)	C(15)–H(21)	0·9(1)
C(14)–N(1)	1·53(1)	C(16)–H(22)	1·1(1)
C(5)–C(15)	1·51(1)	C(16)–H(23)	0·9(1)
C(7)–C(16)	1·55(1)	C(16)–H(24)	0·9(1)
C(7)–C(17)	1·52(2)	C(17)–H(25)	1·0(1)
C(12)–C(18)	1·52(1)	C(17)–H(26)	1·0(1)
C(14)–C(19)	1·53(2)	C(17)–H(27)	1·0(1)
C(14)–C(20)	1·54(2)	C(18)–H(28)	1·0(1)
Zn–Cl(1)	2·281(3)	C(18)–H(29)	1·1(1)
Zn–Cl(2)	2·275(3)	C(18)–H(30)	0·9(1)
Zn–Cl(3)	2·278(3)	C(19)–H(31)	0·9(1)
Zn–Cl(4)	2·230(3)	C(19)–H(32)	1·1(1)
N(1)–H(1)	0·9(1)	C(19)–H(33)	0·9(1)
C(2)–H(2)	1·0(1)	C(20)–H(34)	0·9(1)
C(2)–H(3)	1·1(1)	C(20)–H(35)	1·1(1)
C(3)–H(4)	1·1(1)	C(20)–H(36)	0·9(1)

(*c*) [Ni(α-tet*b*)]$(ClO_4)_2$

Ni–N(1)	1·937(6)	C(6)–C(7)	1·51(3)
Ni–N(4)	1·929(6)	C(7)–C(16)	1·58(3)
Ni–N(8)	1·937(6)	C(7)–C(17)	1·54(2)
Ni–N(11)	1·929(6)	C(7)–N(8)	1·55(2)
Cl(1)–O(1)	1·43(1)	N(8)–C(9)	1·50(1)
Cl(1)–O(2)	1·40(1)	C(9)–C(10)	1·49(1)
Cl(1)–O(3)	1·39(1)	C(10)–N(11)	1·46(1)
Cl(1)–O(4)	1·40(1)	N(11)–C(12)	1·55(2)
N(1)–C(2)	1·50(1)	C(12)–C(18)	1·49(2)
C(2)–C(3)	1·49(1)	C(12)–C(13)	1·58(2)
C(3)–N(4)	1·46(1)	C(13)–C(14)	1·56(2)
N(4)–C(5)	1·49(2)	C(14)–N(1)	1·50(2)
C(5)–C(15)	1·55(2)	C(14)–C(19)	1·54(2)
C(5)–C(6)	1·49(3)	C(14)–C(20)	1·54(2)

The i.r. spectra of the perchlorate and tetrachlorozincate salts of the three configurational isomers of [Ni(tet*b*)]$^{2+}$ are dissimilar. For perchlorates: ν(NH); α, 3210sh, 3190s,sp,

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* The spectra reported by Barefield and Busch for the supposedly stable configuration of [Ni(tet*b*)]$(ClO_4)_2$, which they designated β, are in agreement with those of our metastable β isomer.

[15] D. H. Busch and E. K. Barefield, *Inorg. Chem.*, 1971, **10**, 1216.

3180sh; β, 3205s; γ, 3190s,sp, 3205s,sp. For tetrachlorozincates: ν(OH); β, 3480s,br; γ, 3450w,vbr; δ(HOH); β, 1610m,sp, (H_2O libration mode, 475m,br); γ, 1610w,vbr: ν(NH); α, 3200sh, 3210s, 3250s,sp; β, 3230m, 3180m, 3115w, 3080s; γ, 3110s,br, all in cm^{-1}. The i.r. spectra of the tetrachloro-cobaltate(II) and -nickelate(II) compounds are very similar to that of the tetrachlorozincate.

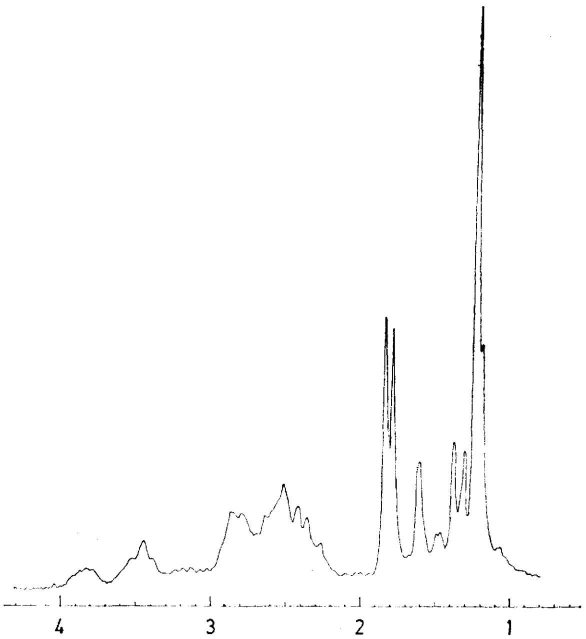

FIGURE 2 The p.m.r. spectrum of $[Ni(\gamma\text{-tet}b)](ClO_4)_2$ measured at 100 MHz, chemical shifts (p.p.m.) from tetramethylsilane as internal reference, in CF_3CO_2D

The *d–d* spectra of the isomers all show a single fairly symmetrical absorption band with small differences in band maxima. Data (cm^{-1}) for $[Ni(\gamma\text{-tet}b)](ClO_4)_2$ in 1M-H_2SO_4 are (ε in parentheses m^2 mol^{-1}): 21 750 (11·0), *cf.* $[Ni(\alpha\text{-tet}b)]^{2+}$ 22 570 (7·0),[2] 22 400 (6·8),[9] $[Ni(\beta\text{-tet}b)]^{2+}$ 2 220 (10·4),[2] 22 100 (10·5).[9]

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

(*a*) $[Ni(\alpha\text{-tet}b)](ClO_4)_2$

N(1)–Ni–N(11)	92·0(7)	N(8)–C(7)–C(17)	107·4(11)
N(1)–Ni–N(8)	174·2(7)	N(8)–C(9)–C(10)	105·6(10)
N(1)–Ni–N(4)	88·2(7)	C(9)–C(10)–N(11)	105·9(10)
N(11)–Ni–N(9)	86·9(7)	C(10)–N(11)–C(12)	112·7(10)
N(11)–Ni–N(4)	179·7(7)	N(11)–C(12)–C(13)	109·4(10)
N(8)–Ni–N(4)	93·0(7)	N(11)–C(12)–C(18)	111·1(11)
Ni–N(1)–C(2)	107·8(9)	C(12)–C(13)–C(14)	118·3(11)
Ni–N(1)–C(14)	115·9(9)	C(13)–C(12)–C(18)	107·1(11)
Ni–N(4)–C(3)	106·1(9)	C(13)–C(14)–N(1)	107·9(10)
Ni–N(4)–C(5)	120·7(9)	C(13)–C(14)–C(19)	112·5(11)
Ni–N(8)–C(7)	117·3(9)	C(13)–C(14)–C(20)	108·7(11)
Ni–N(8)–C(9)	110·2(9)	C(14)–N(1)–C(2)	114·8(10)
Ni–N(11)–C(10)	106·1(9)	N(1)–C(14)–C(19)	107·9(11)
Ni–N(11)–C(12)	115·2(9)	N(1)–C(14)–C(20)	111·9(11)
N(1)–C(2)–C(3)	107·8(10)	C(19)–C(14)–C(20)	108·0(11)
C(2)–C(3)–N(4)	105·8(10)	O(1)–Cl(1)–O(2)	110·3(9)
C(3)–N(4)–C(5)	117·2(10)	O(1)–Cl(1)–O(3)	111·1(9)
N(4)–C(5)–C(6)	114·6(11)	O(1)–Cl(1)–O(4)	109·7(10)
N(4)–C(5)–C(15)	116·2(11)	O(2)–Cl(1)–O(3)	111·9(10)
C(5)–C(6)–C(7)	120·8(11)	O(2)–Cl(1)–O(4)	105·5(11)
C(6)–C(5)–C(15)	111·8(11)	O(3)–Cl(1)–O(4)	108·2(11)
C(6)–C(7)–C(16)	107·6(11)	O(5)–Cl(2)–O(6)	114·3(10)
C(6)–C(7)–C(17)	110·6(11)	O(5)–Cl(2)–O(7)	113·4(10)
C(6)–C(7)–N(8)	110·4(10)	O(5)–Cl(2)–O(8)	108·4(11)
C(7)–N(8)–C(9)	114·0(10)	O(6)–Cl(2)–O(7)	113·8(11)
N(8)–C(7)–C(16)	110·4(11)	O(6)–Cl(2)–O(8)	110·4(11)
C(16)–C(7)–C(17)	110·4(11)	O(7)–Cl(2)–O(8)	95·0(12)

TABLE 4 (*Continued*)

(*b*) $[Ni(\beta\text{-tet}b)]ZnCl_4,H_2O$

N(1)–Ni–N(11)	88·4(6)	C(16)–C(7)–C(17)	109·7(9)
N(1)–Ni–N(8)	175·0(6)	C(7)–N(8)–C(9)	114·1(8)
N(1)–Ni–N(4)	88·6(6)	N(8)–C(7)–C(16)	108·7(9)
N(11)–Ni–N(8)	87·7(6)	N(8)–C(7)–C(17)	*109·4(9)*
N(11)–Ni–N(4)	174·9(6)	N(8)–C(9)–C(10)	105·8(9)
N(8)–Ni–N(4)	95·5(6)	C(9)–C(10)–N(11)	106·7(9)
Ni–N(1)–C(2)	108·8(8)	C(10)–N(11)–C(12)	117·9(8)
Ni–N(1)–C(14)	112·3(7)	N(11)–C(12)–C(13)	107·9(9)
Ni–N(4)–C(3)	108·7(7)	N(11)–C(12)–C(18)	113·3(9)
Ni–N(4)–C(5)	120·8(8)	C(12)–C(13)–C(14)	120·7(9)
Ni–N(8)–C(7)	118·5(8)	C(13)–C(12)–C(18)	110·2(9)
Ni–N(8)–C(9)	109·3(8)	C(13)–C(14)–N(1)	107·0(9)
Ni–N(11)–C(10)	106·2(7)	C(13)–C(14)–C(19)	107·1(9)
Ni–N(11)–C(12)	110·8(8)	C(13)–C(14)–C(20)	111·4(9)
N(1)–C(2)–C(3)	110·3(9)	C(19)–C(14)–C(20)	110·7(9)
C(2)–C(3)–N(4)	108·1(9)	C(14)–N(1)–C(2)	116·7(8)
C(3)–N(4)–C(5)	111·6(8)	N(1)–C(14)–C(19)	110·6(9)
N(4)–C(5)–C(6)	111·8(9)	N(1)–C(14)–C(20)	110·0(9)
N(4)–C(5)–C(15)	110·4(9)	Cl(1)–Zn–Cl(2)	106·7(3)
C(5)–C(6)–C(7)	117·8(10)	Cl(1)–Zn–Cl(3)	111·1(3)
C(6)–C(5)–C(15)	109·0(9)	Cl(1)–Zn–Cl(4)	111·2(3)
C(6)–C(7)–C(16)	107·0(9)	Cl(2)–Zn–Cl(3)	108·6(3)
C(6)–C(7)–C(17)	113·0(9)	Cl(2)–Zn–Cl(4)	113·9(4)
C(6)–C(7)–N(8)	109·0(9)	Cl(3)–Zn–Cl(4)	105·4(3)

(*c*) $[Ni(\gamma\text{-tet}b)](ClO_4)_2$

N(1)–Ni–N(4)	85·8(3)	C(16)–C(7)–C(17)	116·0(13)
N(1)–Ni–N(8)	180·0(0)	C(7)–N(8)–C(9)	111·6(7)
N(1)–Ni–N(11)	94·2(3)	N(8)–C(7)–C(16)	112·0(11)
N(11)–Ni–N(4)	180·0(0)	N(8)–C(7)–C(17)	109·2(10)
N(11)–Ni–N(8)	85·8(3)	N(8)–C(9)–C(10)	105·8(6)
N(4)–Ni–N(8)	94·2(3)	C(9)–C(10)–N(11)	106·3(6)
Ni–N(1)–C(2)	109·5(4)	C(10)–N(11)–C(12)	103·1(7)
Ni–N(1)–C(14)	125·2(6)	N(11)–C(12)–C(13)	106·5(9)
Ni–N(4)–C(3)	107·1(5)	N(11)–C(12)–C(18)	113·8(11)
Ni–N(4)–C(5)	118·8(8)	C(12)–C(13)–C(14)	115·3(10)
Ni–N(8)–C(7)	118·7(8)	C(13)–C(12)–C(18)	114·7(12)
Ni–N(8)–C(9)	109·5(4)	C(13)–C(14)–N(1)	107·2(9)
Ni–N(11)–C(10)	107·1(5)	C(13)–C(14)–C(19)	117·3(12)
Ni–N(11)–C(12)	120·4(7)	C(13)–C(14)–C(20)	109·7(11)
N(1)–C(2)–C(3)	105·8(6)	C(19)–C(14)–C(20)	106·2(12)
C(2)–C(3)–N(4)	106·3(6)	C(14)–N(1)–C(2)	113·1(7)
C(3)–N(4)–C(5)	126·3(8)	N(1)–C(14)–C(19)	107·4(11)
N(4)–C(5)–C(6)	107·1(13)	N(1)–C(14)–C(20)	108·9(11)
N(4)–C(5)–C(15)	111·5(12)	O(1)–Cl(1)–O(2)	109·3(6)
C(5)–C(6)–C(7)	114·4(14)	O(1)–Cl(1)–O(3)	111·0(6)
C(6)–C(5)–C(15)	115·8(14)	O(1)–Cl(1)–O(4)	104·3(6)
C(6)–C(7)–C(16)	92·4(13)	O(2)–Cl(1)–O(3)	111·0(6)
C(6)–C(7)–C(17)	114·6(13)	O(2)–Cl(1)–O(4)	109·1(6)
C(6)–C(7)–N(8)	111·9(12)	O(3)–Cl(1)–O(4)	111·9(6)

DISCUSSION

The three compounds $[Ni(\alpha\text{-tet}b)](ClO_4)_2$, $[Ni(\beta\text{-tet}b)]ZnCl_4,H_2O$, and $[Ni(\gamma\text{-tet}b)](ClO_4)_2$ have the nickel(II) ion in square planar co-ordination with slight tetrahedral distortions apparent in the first two [Figure 3, plane (1) of Table 5]. The nickel–nitrogen bond lengths are normal for co-ordination of a secondary amino-group to a diamagnetic nickel(II) ion (Table 3) and similarly, bond angles at the metal are generally less than 90° in five-membered chelate rings and a little greater than 90° in six-membered rings (Table 4). The configurations of the amines referred to the crystallographic numbering schemes are: α, 1*RS*, 4*RS*, 5*SR*, 8*RS*, 11*RS*, 12*SR*; β, 1*SR*, 4*RS*, 5*SR*, 11*RS*, 12*SR*;

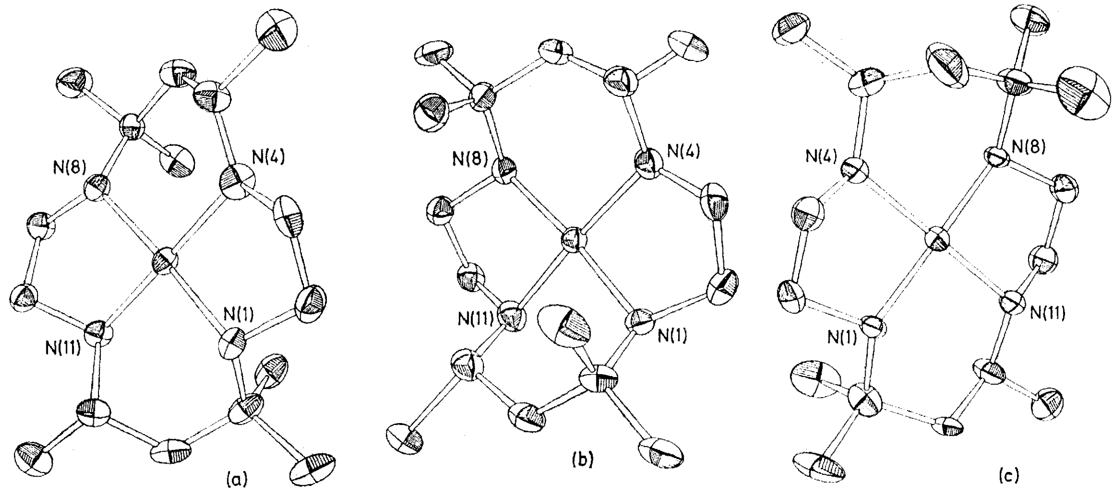

FIGURE 3 ORTEP diagrams of the structures of the complex cations: (a) [Ni(α-tet*b*)](ClO$_4$)$_2$; (b) [Ni(β-tet*b*]ZnCl$_4$,H$_2$O, and (c) Ni(γ-tet*b*)(ClO$_4$)$_2$

and γ, 1*SR*, 4*SR*, 5*SR*, 8*RS*, 11*RS*, 12*SR*. These represent, respectively, arrangements 9, 1, and 7 of Figure 5, ref. 6. The (±)-representation of the configuration at asymmetric centres, which is based on the position of substituted hydrogen atoms with respect to the molecular plane, may also be seen in this Figure. The configuration of the α-isomer is the same as that already seen in [Ni(α-tet*b*)(OAc)]ClO$_4$ [6] and the γ-configuration has the same nitrogen stereochemistry as in *trans*-[Ni(cyclam)Cl$_2$].[7] The β-isomer has a 'basket' configuration with all four NH groups on the same side

TABLE 5

Planes of best fit and deviations therefrom. The equations of the planes, referred to crystallographic axes, are in the cosine form $AX + BY + CZ + D = 0$, where $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$. Displacements (Å) of atoms are listed in square brackets

(*a*) [Ni(α-tet*b*)](ClO$_4$)$_2$

Plane (1): Co-ordination plane, Ni, N(1), N(4), N(8), N(11)
$-0{\cdot}6208X + 0{\cdot}5906Y - 0{\cdot}5155Z + 2{\cdot}4773 = 0$
[Ni 0·036, N(1) −0·06, C(2) 0·07, C(3) −0·57, N(4) 0·04, C(5) −0·34, C(6) 0·42, C(7) 0·81, N(8) −0·06, C(9) 0·02, C(10) −0·62, N(11) 0·04, C(12) −0·56, C(13) 0·32, C(14) 0·84, C(15) −0·46, C(16) 0·66, C(17) 2·25, C(18) −0·67, C(19) 2·26, C(20) 0·84, H(1) −0·9, H(6) 0·9, H(7) −1·3, H(10) −0·9, H(15) 0·9, H(16) −1·5]

Plane (2): Ni, N(1), N(4)
$-0{\cdot}6531X + 0{\cdot}5531Y - 0{\cdot}5170Z + 2{\cdot}9403 = 0$
[C(2) 0·14, C(3) −0·55]

Plane (3): Ni, N(8), N(11)
$-0{\cdot}5862X + 0{\cdot}6268Y - 0{\cdot}5133Z + 1{\cdot}9310 = 0$
[C(9) 0·10, C(10) −0·60]

Plane (4): Ni, N(4), N(8)
$-0{\cdot}5888X + 0{\cdot}6281Y - 0{\cdot}5086Z + 1{\cdot}9208 = 0$
C(5) −0·32, C(6) 0·50, C(7) 0·91, C(15) −0·45, C(16) 0·83, C(17) 2·32]

Plane (5): Ni, N(1), N(11)
$-0{\cdot}6506X + 0{\cdot}5520Y - 0{\cdot}5215Z + 2{\cdot}9512 = 0$
[C(12) −0·55, C(13) 0·40, C(14) 0·92, C(18) −0·67, C(19) 2·33, C(20) 1·07]

TABLE 5 (*Continued*)

(*b*) [Ni(β-tet*b*)]ZnCl$_4$,H$_2$O

Plane (1): Co-ordination plane, Ni, N(1), N(4), N(8), N(11)
$0{\cdot}2456X + 0{\cdot}3504Y - 0{\cdot}9038Z + 6{\cdot}4634 = 0$
[Ni 0, N(1) −0·6, C(2) 0·29, C(3) −0·23, N(4) 0·06, C(5) −0·69, C(6) −0·48, C(7) −0·93, N(8) −0·06, C(9) −0·25, C(10) 0·53, N(11) 0·06, C(12) −1·22, C(13) −1·35, C(14) −1·34, C(15) −0·24, C(16) −0·71, C(17) −2·39, C(18) −1·31, C(19) −1·35, C(20) −2·56, H(1) 0·6, H(6) 0·9, H(7) −1·6, H(10) 0·9, H(15) 0·6, H(16) −2·0]

Plane (2): Ni, N(1), N(4)
$0{\cdot}2791X + 0{\cdot}3722Y - 0{\cdot}8852Z + 6{\cdot}1914 = 0$
[C(2) 0·31, C(3) −0·27]

Plane (3): Ni, N(8), N(11)
$0{\cdot}2109X + 0{\cdot}3272Y - 0{\cdot}9211Z + 6{\cdot}7448 = 0$
[C(9) −0·23, C(10) 0·48]

Plane (4): Ni, N(4), N(8)
$0{\cdot}2785X + 0{\cdot}3264Y - 0{\cdot}9033Z + 6{\cdot}4455 = 0$
[C(5) −0·75, C(6) −0·49, C(7) −0·89, C(15) −0·35, C(16) −0·62, C(17) −2·34]

Plane (5): Ni, N(1), N(11)
$0{\cdot}2088X + 0{\cdot}3778Y - 0{\cdot}9021Z + 6{\cdot}4780 = 0$
[C(12) −1·29, C(13) −1·36, C(14) −1·29, C(18) −1·44, C(19) −1·26, C(20) −2·50]

Plane (6): N(1), N(11), C(12), C(14)
$-0{\cdot}6825X - 0{\cdot}7218Y + 0{\cdot}1150Z + 0{\cdot}3226 = 0$
[Ni 1·18, N(1) 0·01, N(11) −0·01, C(12) 0·01, C(13) −0·69, C(14) −0·01]

Plane (7): N(4), C(5), C(7), N(8)
$0{\cdot}1058X + 0{\cdot}0843Y + 0{\cdot}9908Z - 8{\cdot}2049 = 0$
[Ni 0·71, N(4) 0·04, C(5) −0·04, C(6) −0·66, C(7) 0·04, N(8) −0·04]

(*c*) [Ni(γ-tet*b*)](ClO$_4$)$_2$

Plane (1): Co-ordination plane, Ni, N(1), N(4), N(8) N(11)
$-0{\cdot}7799X - 0{\cdot}3765Y + 0{\cdot}5000Z - 2{\cdot}8981 = 0$
[Ni 0, N(1) 0, C(2) −0·13, C(3) 0·58, N(4) 0, C(5) 0·10, C(6) 1·27, C(7) 0·97, N(8) 0, C(9) 0·13, C(10) −0·58, N(11) 0, C(12) −0·83, C(13) −0·32, C(14) −0·72, C(15) 0·14, C(16) 2·47, C(17) 0·42, C(18) −0·82, C(19) −2·21, C(20) −0·25, H(1) 0·9, H(6) −0·9, H(7) −0·8, H(10) −0·9, H(15) 0·9, H(16) −1·9]

Plane (2): N(1), N(11), C(12), C(14)
$0{\cdot}3512X + 0{\cdot}5576Y - 0{\cdot}7521Z + 4{\cdot}0394 = 0$
[Ni 0·67, N(11) −0·03, C(12) 0·03, C(14) −0·03, C(13) −0·75, N(1) 0·03]

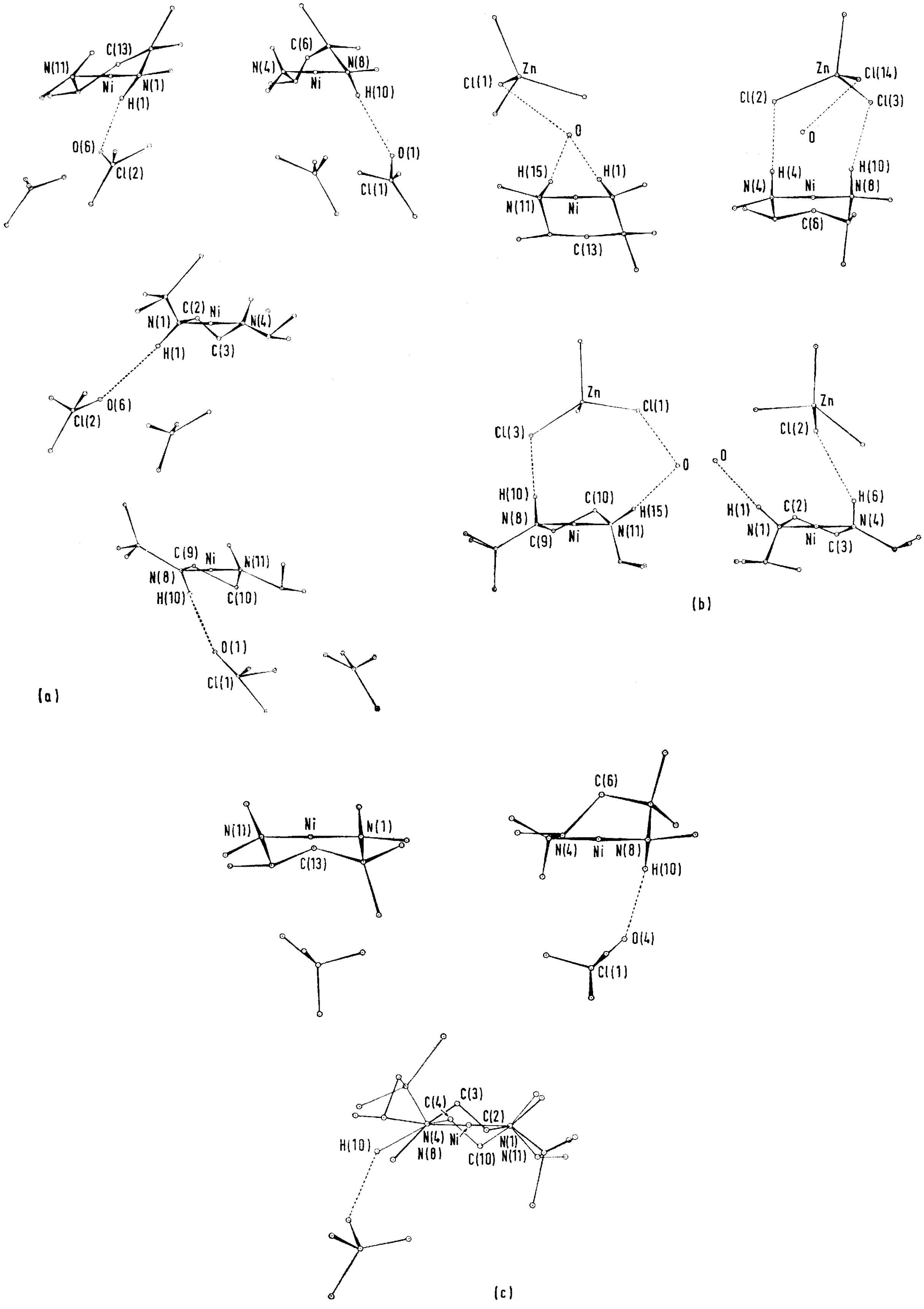

FIGURE 4 Conformations of chelate rings; carbon atoms are projected on a plane, normal to the N–Ni–N plane of each ring, which passes through the two N atoms of that ring. (a) α-isomer, (b) β-isomers, and (c) γ-isomer

of the molecular plane. More detailed discussion follows.

Conformations of the Co-ordinated Amines.—The conformations of all three cations can be deduced from the planes of best fit and deviations therefrom listed in Table 5. Projections normal to planes through specified nitrogen atoms are presented in Figure 4, which illustrates the geometry of the chelate rings.

(i) $[Ni(\alpha\text{-tet}b)]^{2+}$. The complex cation has approximate two-fold symmetry as an inherent property of the cyclic amine with the configuration shown. The deviations from such symmetry presumably result from forces operative in the crystal as discussed later. The five-membered chelate rings are in unsymmetrical *gauche* conformations ($\delta\delta$ or $\lambda\lambda$) with the six-membered rings in twist conformations [Figure 3(a) and Table 5(*a*)]. The asymmetry of the five-membered rings apparently reflects the presence of the axial methyl substituents C(19) and C(16) adjacent to C(2) and C(9). The twist conformations of the larger rings are a direct result of the nitrogen configurations which place the amino-hydrogen atoms on the opposite sides of the molecular plane contrary to the requirement for a chair (or boat) geometry. The methyl substituents occupy sites of equatorial [C(15), C(16), C(18), C(20)] or axial [C(17), C(19)] character similar to those found for the chelate ring in the chair conformation except that the two equatorial substituents on each chelate ring are displaced slightly to opposite sides of the molecular plane. The strain imposed on the cyclic amine is apparent in the bond angles subtended at atoms in the six-membered rings [Table 3(*a*)]. Those at the methylene carbons C(6) and C(13) have the large values (121 and 118°) commonly seen in these chelate rings [6,16,17] but those at the nitrogen atoms are also significantly different from 'tetrahedral' values.

Overall, the cation can be described in terms of structure 9 of ref. 6, with only the two five-membered rings in 'classical' conformations. That these are not entirely strain-free reflects the distribution, over the entire cation, of the imposed distortions from ideality.

(ii) $[Ni(\beta\text{-tet}b)]^{2+}$. The situation here is in some senses the reverse of that seen in the α-isomer since the six-membered rings now adopt 'classical' chair conformations, the five-membered rings having the unfavourable nitrogen configurations. Again, however, the strain is spread over the cation so that the five-membered rings still adopt a distorted *gauche* ($\delta\lambda$) conformation rather than the eclipsed geometry presupposed by the nitrogens. Consequently one of the six-membered rings [based on N(1), N(11)] is more puckered than usual and has the small N(1)–Ni–N(11) angle of 88·4°. The other six-membered ring has a more normal conformation similar to that found in $[Ni(\alpha\text{-tet}b)(OAc)]ClO_4$,[6] $[Ni(\alpha\text{-tet}a)(acac)]ClO_4$[1] and $[Ni(\gamma\text{-tet}b)](ClO_4)_2$ (see later). The *gem*-dimethyl substituents occupy axial and equatorial sites, as expected, with some deviation from ideality in the puckered ring [Table 5(*b*) and Figure 4(b)]. Overall, the conformation approximates to that idealised by structure 1 of ref. 6.

(iii) $[Ni(\gamma\text{-tet}b)]^{2+}$. The complex $[Ni(\beta\text{-tet}b)](ClO_4)_2$ crystallises in a centrosymmetric space group with the cation occupying special positions implying a centre of inversion. As already explained the cyclic amine contains *C-racemic* centres and cannot conform to this symmetry. The nitrogen configuration is the same as that of *trans*-$[Ni(cyclam)Cl_2]$ [7] and permits each of the chelate rings to adopt optimum chair or *gauche* conformations as seen in the cyclam complex. A difficulty arises in the present instance, however, because adoption of this conformation by the tet*b* amine requires the placement of one of the methyl substituents [C(18)] in an axial site, *i.e.* in a 1,3-diaxial relationship with C(20) of the neighbouring *gem*-dimethyl group. The strain inherent in this situation is relieved by distortion of the chelate ring to an approximate 'twist-boat' geometry. This can be visualised as a counter-movement of C(12) and C(13) so as to bring the methyl substituent C(18) into an equatorial position. As a result of this shift the complex cation approaches centro-symmetry and is able to crystallise with the chair or twist-boat moieties randomly occupying the 'six-membered ring' positions. A very similar chelate ring distortion, but not the accompanying crystal disorder, occurs in $[Ni(\alpha\text{-tet}a)(acac)]ClO_4$ for essentially the same reason.[1]

The five-membered chelate rings adopt unsymmetrical *gauche* ($\delta\lambda$) conformations. Their exact centrosymmetric relationship is a consequence of the refinement procedure which was adopted, but as indicated earlier there is no evidence that they do in fact depart significantly from this symmetry.

Geometry of the Anions.—This is as expected in all instances, the only point of comment being the large thermal motion apparent in some ions and the necessity to consider perchlorate oxygen positions in relation to postulated hydrogen bonds.

(i) $[Ni(\alpha\text{-tet}b)](ClO_4)_2$. One long bond (*ca.* 1·41 Å) and three short bonds (*ca.* 1·30 Å) were found for each anion, the long bonds being to the oxygens, O(1) and O(5), less affected by thermal vibration, or equivalent static disorder [Table 2(*a*)]. Adjustments made to the bond lengths on the basis of a riding model [18] produced values in the range 1·47—1·54 Å, a little long but regarded as satisfactory in view of the vibrational amplitudes. There was no evidence for the fractional occupancy of anion positions over a number of sites.

(ii) $[Ni(\beta\text{-tet}b)]ZnCl_4,H_2O$. This anion also occupies a well defined position. Uncorrected Zn–Cl bond lengths reveal one at 2·230 Å and three in the range 2·275—2·281 Å. Correction for riding motion brings values into the more acceptable range 2·26—2·29 Å. The oxygen atom of the water molecule was readily located but its hydrogen atoms were not found.

(iii) $[Ni(\gamma\text{-tet}b)](ClO_4)_2$. The one perchlorate ion per

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asymmetric unit has a clearly defined site with no indication of disorder. Bond lengths, which ranged from 1·39 to 1·43 Å, were corrected by the riding model to 1·44—1·49 Å.

Interactions between Ions.—The conformational diagrams (Figure 4) show some hydrogen bonding interactions between the macrocycle and the anions, which may play some part in determining the detailed conformation of the three isomers. As explained later, these interactions are not, however, extensive, nor are there intra-ionic steric forces of significance as evidenced by the distances between atoms. On the other hand internal repulsion between groups is manifest in the intercation distances already discussed.

(i) [Ni(α-tet*a*)]$(ClO_4)_2$. The only inter-ionic interactions are a result of hydrogen bonding between the two nitrogen atoms [N(1) and N(8)] near the *gem*-dimethyl groups and the perchlorate groups. Details of the geometry of the bonding are given in Table 6(*a*). The perchlorates are on the same side of the cation, as required by the nitrogen configuration if they are to bond to N(1) and N(8). The crystal structure [Figure 5(a)] is thus derived from the packing of [Ni(α-tet*b*)]$(ClO_4)_2$ entities.

(ii) [Ni(β-tet*b*)]$ZnCl_4,H_2O$. In this isomer the hydrogens of the four secondary amines project to the same side of the macrocyclic plane and all are found to be hydrogen bonded. Two, N(4) and N(8), which span a six-membered ring, are bonded to separate chlorine atoms [Cl(2) and Cl(3)] of the anion, whereas N(1) and N(11) interact with the water molecule [Table 6(*b*), Figure 5(b)]. Further interactions involve Cl(1) and Cl(4′) which both hydrogen bond to the water molecule.

TABLE 6

Hydrogen bond geometries

(*a*) [Ni(α-tet*b*)]$(ClO_4)_2$			
N(1) $\cdots$ O(6)	3·13 Å	N(8) $\cdots$ O(1)	2·97 Å
N(1)–H(1)	0·9	N(8)–H(10)	0·9
H(1) $\cdots$ O(6)	2·3	H(10) $\cdots$ O(1)	2·1
N(1)–H(1) $\cdots$ O(6)	152°	N(8)–H(10) $\cdots$ 0(1)	172°
(*b*) [Ni(β-tet*b*)]$ZnCl_4,H_2O$			
N(1) $\cdots$ O(1)	2·94 Å	N(11) $\cdots$ O(1)	3·26 Å
N(1)–H(1)	0·9	N(11)–H(15)	0·9
H(1) $\cdots$ O(1)	2·0	H(15) $\cdots$ O(1)	2·5
N(1)–H(1) $\cdots$ O(1)	172°	N(1)–H(15) $\cdots$ O(1)	153°
Cl(1) $\cdots$ O(1)	3·25 Å	Cl(4) $\cdots$ O(1′)	3·38 Å
N(4) $\cdots$ Cl(2)	3·35 Å	N(8) $\cdots$ Cl(3)	3·26 Å
N(4)–H(6)	0·9	N(8)–H(10)	1·0
H(6) $\cdots$ Cl(2)	2·5	H(10) $\cdots$ Cl(3)	2·3
N(4)–H(6) $\cdots$ Cl(2)	153°	N(8)–H(10) $\cdots$ Cl(3)	164°
(*c*) [Ni(γ-tet*b*)]$(ClO_4)_2$			
N(4) $\cdots$ O(2)	3·34 Å	N(8) $\cdots$ O(4)	2·97 Å
N(4)–H(6)	1·0	N(8)–H(10)	1·0
H(6) $\cdots$ O(2)	2·5	H(10) $\cdots$ O(4)	2·0
N(4)–H(6) $\cdots$ O(2)	140°	N(8)–H(10) $\cdots$ O(4)	157°

There is thus the further interaction, *i.e.* Cl(4′)–H_2O, absent in the α- and γ-isomer, which binds the crystal together to some extent.

(iii) [Ni(γ-tet*b*)]$(ClO_4)_2$. Two hydrogen bonds to the cation are apparent, one to each of two centrosymmetrically related perchlorate groups. They involve the nitrogen atoms N(1) and N(8) which, as in the α-isomer, are adjacent to the *gem*-dimethyl groups. This time, however, the two interactions are on opposite sides of the cationic plane. The other possible interaction, N(4) $\cdots$ O(2) and N(11) $\cdots$ O(2′) is also listed in Table 6 but is

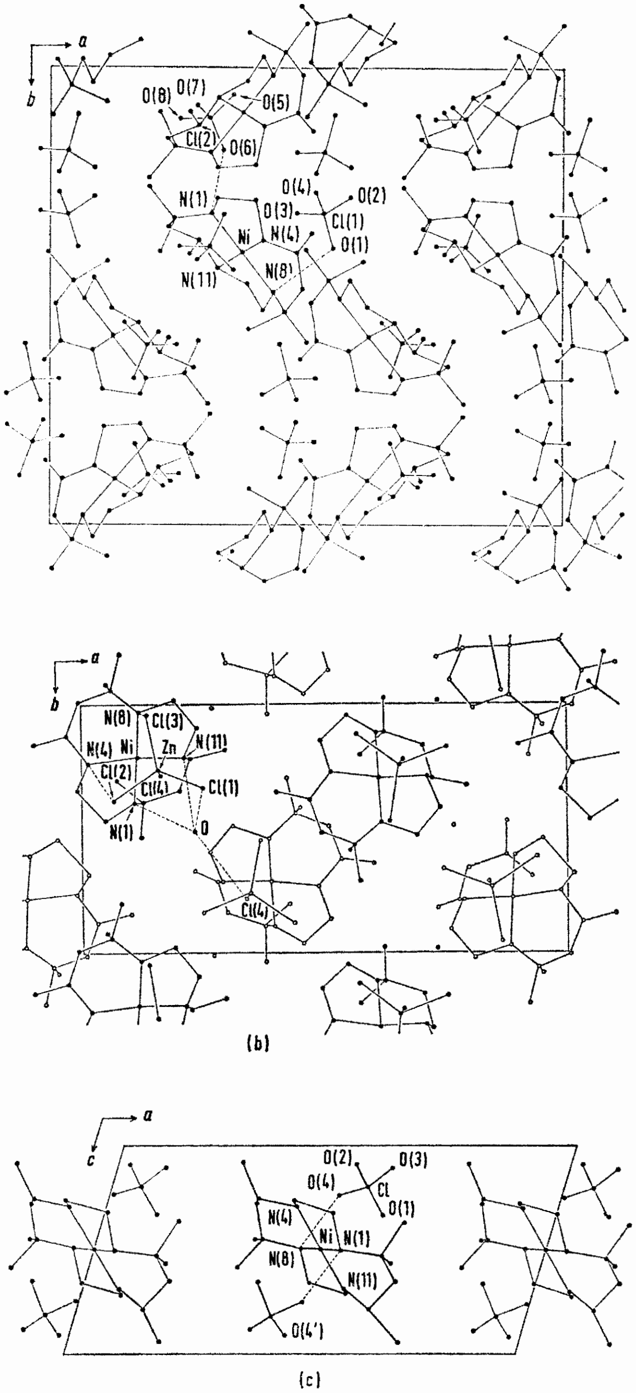

FIGURE 5 A projection of the crystal structure of (a) the α- and (b) the β-isomer viewed in the direction of the *c* axis; (c) a projection of the crystal structure of the γ-isomer viewed down the *b* axis

discounted on the basis of the long H(6) · · · O(2) distance of 2·49 Å. Again the situation of the α-isomer is present in this crystal with discrete $[Ni(\gamma\text{-tet}b)](ClO_4)_2$ entities being packed together without identifiable bonding between them [Figure 5(c)].

Conclusion.—These studies confirm in general terms the conclusions based on simple analyses of the strain present in individual chelate rings of the macrocyclic complexes.[6] Such considerations suggested that the α-configuration, which is optimum for folded co-ordination, would be metastable in planar co-ordination with the six-membered rings forced from a strain-free conformation. The least strained configurations for planar co-ordination were predicted to be those shown by the β- and γ-isomers (β less strained than γ but only just significantly so, considering the assumptions). It is found that, although the β-configuration does predominate in aqueous solution at equilibrium, either configuration can be stabilised in the solid state, apparently as a result of the choice of anion. The distinction is between perchlorate and tetrachlorozincate which are very similar in shape and hydrogen bonding properties and may turn on the necessity to accommodate two, or one, anion per complex as a result of their charge difference.

The structure of the β-isomer reveals a rather unsymmetrical arrangement with a more puckered chair-conformation for one six-membered chelate ring than with another. The ^1H n.m.r. spectrum of solutions of the β-isomer with perchlorate as anion suggests that the two six-membered rings are equivalent in solution. This could be achieved dynamically with retention of the asymmetry found in the crystal of the tetrachlorozincate, or statically if the five-membered rings were to adopt an eclipsed (or approximately eclipsed) conformation. In this connection we note that the large downfield shift observed for the ^1H n.m.r. absorption of the axial methyl groups of the β-perchlorate (2·3 as against 1·8 p.p.m. for the γ-isomer or the β-tet*a* isomer) indicates that these protons are subject to a larger non-bonded interaction which probably arises from their being sited closer than normal to the tetragonal axis of the nickel atom. The crystal structure of $[Ni(\beta\text{-tet}b)]ZnCl_4,H_2O$ places the ' averaged ' positions of the axial methyl groups closer to the tetragonal axis than that of the group on the six-membered ring with the ' normal ' chair conformation, evidence taken as supporting the view that the observed conformation is largely determined by intra-cationic interactions rather than by hydrogen bonding or other forces in the crystal. This conformation, which maintains *gauche*, albeit unsymmetrical, ethylene bridging therefore represents the least strained arrangement for the β-configuration there being a dynamic two-fold symmetry on the n.m.r. timescale in solution. This reluctance of the ethylene group to take the eclipsed conformation is in accord with other observations.[19]

The ^1H n.m.r. spectrum of the $[Ni(\gamma\text{-tet}b)]^{2+}$ cation shows a doublet methyl resonance (6H) with chemical shift typical of ' axial ' substituents and one singlet and one doublet (12H total) in the ' equatorial ' substituent region. Since the two six-membered chelate rings cannot be equivalent for the γ-nitrogen configuration the spectrum must be reflecting the pseudo centrosymmetry of the methyl group sites found in the solid, with the apparent ' axial ' doublet indicating the slightly differing sites of the ' axial ' substituents on the two chelate rings. This supports the view that the conformation of the cation is similar in the solid and solution so again the cationic structure as reported is probably close to the least strained arrangement for the particular configuration imposed by the nitrogen atoms. The absence of strong hydrogen-bonding networks in the three solids, as well as the lack of evidence for tight distorting packing, further confirms this suggestion.

[2/2675 *Received, 27th November,* 1972]

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