The Crystal Structure of *R,S,R,S*-(1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Bis(trifluoromethanesulphonate)–Acetone Hydrate, [Ni(tmtactd)][CF_3SO_3]$_2$·Me_2CO·H_2O, and a Strain-energy Minimization Analysis of Four-, Five-, and Six-co-ordinate Nickel(II)–tmtactd Solvento Complexes *

Trevor W. Hambley
Department of Inorganic Chemistry, University of Sydney, Sydney, Australia 2006

The crystal structure of [Ni(tmtactd)][CF_3SO_3]$_2$·Me_2CO·H_2O has been determined by *X*-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with a = 9.142(1), b = 13.674(2), c = 13.694(2) Å, α = 61.07(1), β = 83.14(1), γ = 84.54(1)°, and Z = 2. The complex cation is four-co-ordinate with a tetrahedral distortion from square-planar geometry. Strain-energy minimization analysis by the molecular mechanics method shows that for four-co-ordinate complexes the *R,S,R,S* isomer is preferred, while for six-co-ordinate complexes the *R,S,S,R* isomer is preferred.

When the macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (tmtactd) co-ordinates to four equatorial sites of a nickel(II) metal atom the subsequent disposition of each of the four methyl groups, either above or below the co-ordination plane, gives rise to 16 possible arrangements. These reduce to the five energetically distinct geometries proposed by Bosnich *et al.*[1] and shown in Figure 1. Two of these arrangements are well known; *N*-methylation of *R,S,S,R*-[Ni(tactd)]$^{2+}$ (tactd = 1,4,8,11-tetra-azacyclotetradecane) yields the *R,S,S,R* isomer [hereafter (**A**)] with two methyl groups disposed on each side of the ligand,[2] while reaction of tmtactd with [Ni(H_2O)$_6$]$^{2+}$ produces the *R,S,R,S* isomer (**B**) with all four methyl groups disposed on the same side of the ligand.[3] It has been suggested[4–6] that isomer (**A**) is the thermodynamically more stable and that (**B**) only occurs because it is the conformation adopted by the free ligand leading to a low-energy, kinetically favoured pathway and because subsequent interconversion of the two is not possible. However, Moore *et al.*[7] have recently shown that (**A**) and (**B**) interconvert easily in the presence of strongly co-ordinating solvents and evidently do so *via* the intermediate structure (**C**). Further, Lincoln *et al.*[8] have independently reported the observation of the intermediate isomer (**C**) and its ready isomerization to (**B**) in $MeNO_2$. These observations cast doubt on the suggestion that (**B**) is a metastable, kinetically preferred geometry.

I recently reported preliminary strain-energy minimization (molecular mechanics) calculations on four-, five-, and six-co-ordinate [Ni(tmtactd)]$^{2+}$ complexes with geometries (**A**), (**B**), and (**C**).[9] These results suggested[9] that when four-co-ordinate complexes occur, then (**B**) is the most stable isomer and when six-co-ordinate complexes occur, (**A**) should predominate. Here I report these calculations in full and have extended them to cover all five possible isomers.

The earlier calculations gave an energy-minimized geometry for the four-co-ordinate isomer (**B**) which revealed significant tetrahedral distortion about nickel.[9] This distortion relieved much of the strain present in the structure with the co-ordination geometry constrained to be planar. In order to check whether the unconstrained model adequately describes the nickel co-ordination geometry I have determined the structure of the four-co-ordinate complex [Ni(tmtactd)]$^{2+}$ as the $CF_3SO_3^-$ salt and report it herein.

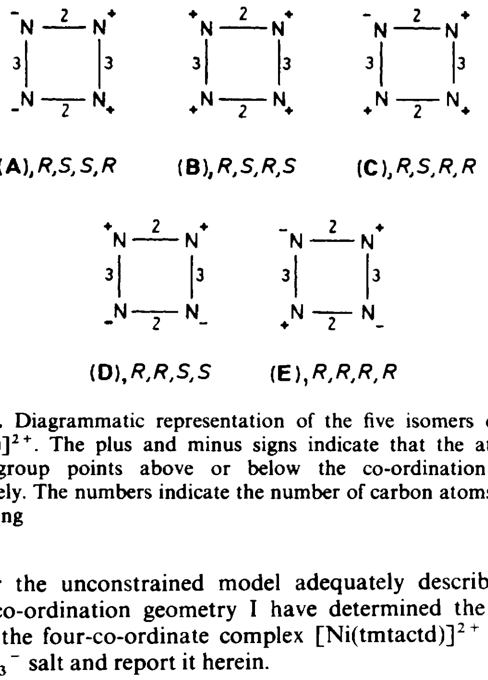

Figure 1. Diagrammatic representation of the five isomers of [Ni(tmtactd)]$^{2+}$. The plus and minus signs indicate that the attached methyl group points above or below the co-ordination plane respectively. The numbers indicate the number of carbon atoms in the chelate ring

Experimental

Preparation.—The complex was prepared as described in ref. 8 and crystals were obtained by vapour diffusion of light petroleum (b.p. 40—60 °C) into an acetone solution of the triflate salt.

Crystal Data.—$C_{19}H_{39}F_6N_4NiO_{7.5}S_2$, M = 680.4, triclinic, a = 9.142(1), b = 13.674(2), c = 13.694(2) Å, α = 61.07(1), β = 83.14(1), γ = 84.54(1)°, U = 1 486.2 Å^3 (by least-squares refinement of diffractometer setting angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P\bar{1}$, Z = 2, D_c = 1.520 g cm^{-3}. Red moisture-sensitive needles; crystal dimensions, 0.20 × 0.22 × 0.20 mm, μ(Mo-K_α) = 8.26 cm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, $3\omega/4\theta$ mode with ω scan width (1.00 + 0.35tanθ)°, aperture width (2.40 + 0.50tanθ) mm, graphite-monochromated Mo-K_α radiation; 5 819 reflections measured ($1.0 \leqslant \theta \leqslant 25°$, $+h$, $\pm k$,

---

* *Supplementary data available* (No. SUP 56395, 5 pp.): H-atom co-ordinates, thermal parameters, least-squares planes, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates for $[Ni(tmtactd)][CF_3SO_3]_2{\cdot}Me_2CO{\cdot}H_2O$

Atom	x	y	z	Atom	x	y	z
Ni(1)	0.243 9(1)	0.179 2(1)	0.182 3(1)	O(1)	0.287 1(6)	0.075 2(5)	0.696 2(5)
N(1)	0.247 9(6)	0.059 4(4)	0.339 4(4)	O(2)	0.148 0(7)	0.144 3(6)	0.814 0(5)
N(2)	0.411 9(6)	0.256 7(5)	0.188 7(4)	O(3)	0.409 5(8)	0.119 9(7)	0.816 9(6)
N(3)	0.209 2(6)	0.314 1(5)	0.038 0(4)	C(15)	0.305 9(28)	0.276 4(10)	0.643 9(10)
N(4)	0.104 4(6)	0.086 4(5)	0.164 7(4)	F(1)	0.431 7(10)	0.283 4(6)	0.582 8(5)
C(1)	0.359 0(8)	−0.034 7(6)	0.356 2(6)	F(2)	0.200 9(13)	0.308 9(8)	0.580 0(7)
C(2)	0.262 6(8)	0.098 0(6)	0.421 0(5)	F(3)	0.313 1(13)	0.344 9(6)	0.685 2(7)
C(3)	0.400 7(9)	0.160 7(7)	0.400 8(6)	S(2)	0.142 1(2)	0.691 2(1)	0.692 7(1)
C(4)	0.404 6(9)	0.267 9(7)	0.293 4(6)	O(4)	0.206 8(7)	0.797 1(5)	0.629 6(5)
C(5)	0.555 1(8)	0.197 7(6)	0.178 8(6)	O(5)	0.220 1(7)	0.612 7(5)	−0.215 7(5)
C(6)	0.412 9(9)	0.371 2(6)	0.092 1(7)	O(6)	0.986 5(6)	0.699 7(5)	0.717 3(5)
C(7)	0.259 6(9)	0.404 3(5)	0.055 9(6)	C(16)	0.162 2(27)	0.637 7(11)	−0.403 0(11)
C(8)	0.295 0(9)	0.313 0(6)	−0.061 3(5)	F(4)	0.094 6(11)	−0.293 6(8)	0.505 8(6)
C(9)	0.051 3(8)	0.342 2(6)	0.014 9(6)	F(5)	0.098 7(12)	0.541 9(7)	−0.361 6(9)
C(10)	−0.026 9(9)	0.252 0(7)	0.012 5(6)	F(6)	0.296 9(11)	0.620 5(8)	−0.430 8(8)
C(11)	−0.040 0(8)	0.147 0(6)	0.123 1(6)	O(7)	0.671 6(8)	0.401 6(6)	0.853 8(6)
C(12)	0.174 6(10)	0.044 1(7)	0.088 7(6)	C(17)	0.699 7(13)	0.382 4(9)	0.778 9(9)
C(13)	0.070 2(8)	−0.013 8(6)	0.277 6(5)	C(18)	0.746 0(29)	0.275 2(12)	0.788 8(12)
C(14)	0.098 8(8)	0.014 5(6)	0.364 1(5)	C(19)	0.687 4(20)	0.460 8(14)	0.670 4(13)
S(1)	0.285 5(2)	0.137 1(2)	0.756 8(2)	O(8)	0.533 9(20)	0.091 0(14)	0.009 8(27)

Table 2. Force-field parameters for nickel(II) amine complexes*

(*i*) Bond length deformation, $U_b = \frac{1}{2}k_r(r - r_0)^2$

	r_0/Å	k_r/kJ mol^{-1} Å^{-2}
Ni–N^4	1.83	410
Ni–N^5	1.92	410
Ni–N^6	2.01	410
C–C	1.50	3 012
C–N	1.49	3 615
C–H	0.97	3 012

(*ii*) Valence angle deformation, $U_\theta = \frac{1}{2}k_\theta(\theta - \theta_0)^2$

	θ_0/°	k_θ/kJ mol^{-1} rad^{-2}
Ni–N–C	110.0	120
C–C–N	109.5	271
C–C–C	109.5	271
C–N–C	109.5	271
N–C–H	109.4	217
C–C–H	109.4	217
H–C–H	109.0	193

(*iii*) Torsion angle deformation, $U_\varphi = \frac{1}{2}k_\varphi(1 + \cos 3\varphi)$

	k_φ/kJ mol^{-1}
–C–N–	0.72
–C–C–	1.15

(*iv*) Non-bonded interactions, $U_{nb} = ae^{-br} - cr^{-6}$

	a/10^3 kJ mol^{-1}	b/Å^{-1}	c/kJ mol^{-1} Å^6
N···N	63.1	3.472	1 065
N···C	57.0	3.378	1 134
C···C	53.4	3.289	1 247
N···H	59.4	3.846	543
C···H	55.8	3.742	601
H···H	63.1	4.167	322

* For N^4,N^5,N^6, superscripts indicate the co-ordination number to which the parameter applies.

$\pm l$), 4 168 unique non-zero (merging $R = 0.008$). Lorentz, polarization and crystal decay (*ca.* 15%), but not absorption, effects corrected for.

Structure Analysis and Refinement.—The structure was solved by heavy-atom (Patterson) methods and successive Fourier synthesis. Hydrogen atoms were included at sites calculated assuming tetrahedral geometry about carbon (C–H 0.97 Å) with group isotropic thermal parameters, while non-hydrogen atoms were assigned anisotropic thermal parameters. Blocked-matrix least-squares refinement converged with R = 0.051, R' = 0.052, and $w = 1.40/[\sigma^2(F_o) + 0.000\,56F_o^2]$ for 2 451 reflections with $I > 2.5\sigma(I)$.* The largest peak in a final difference map was less than 0.5 e Å^{-3} in height. Scattering factors (neutral Ni for Ni^{II}) and anomalous dispersion terms were taken from International Tables.[10] All calculations were carried out using SHELX 76,[11] ORTEP,[12] and local data reduction programs implemented on a CYBER 825 computer. Final atomic co-ordinates are listed in Table 1.

Energy Minimization.—The total strain energy was described as the sum of bonded (U_b), valence angle (U_θ), and torsion angle (U_φ) deformations and non-bonded (U_{nb}) interaction energies: equation (1). Most of the functions describing these interactions

$$E_{tot} = \Sigma U_b + \Sigma U_\theta + \Sigma U_\varphi + \Sigma U_{nb} \qquad (1)$$

and the parameters which define them have been described previously,[13,14] and only those developed in this work are now discussed. The non-bonded interactions were modelled using Buckingham functions and the parameters refined by Allinger[15,16] to reproduce best the properties of organic compounds. A force constant for Ni–N bond length deformation has been reported previously in an energy minimization study of $[Ni(dien)_2]^{2+}$ (dien = diethylenetriamine) and $[Ni(en)_3]^{2+}$ (en = ethylenediamine),[17] and this value was adopted here. It was necessary to determine an unstrained Ni–N bond length for each co-ordination number and this was done by adjusting the length until a best fit to the relevant crystallographically determined bond length was obtained. The Ni–N–C parameters were taken from those used previously for Co–N–C deformation.[14] To model five- and six-co-ordinate complexes axial ligands were included as lone nitrogen atoms with the same Ni–N bond deformation parameters as the other metal–ligand bonds. The use of lone nitrogen atoms produces 'artificial' complexes but was adopted to provide results of more general applicability than would use of any particular ligand. Force field parameters are listed in Table 2.

The total energy, E_{tot}, was minimized by co-operative minimization of all cartesian co-ordinates. A program based on

---

* $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R' = \Sigma(||F_o| - |F_c||)w^{\frac{1}{2}}/\Sigma(|F_o|w^{\frac{1}{2}})$.

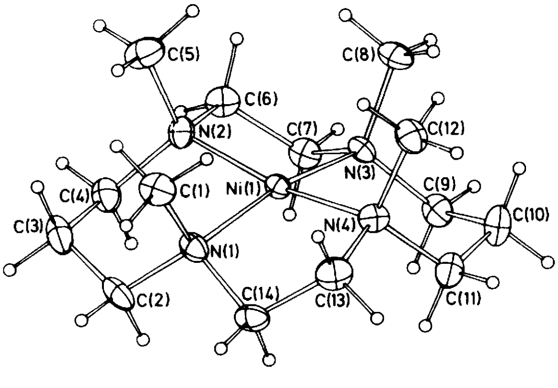

Figure 2. Thermal ellipsoid plot (50% probability) of the $[Ni(tmtactd)]^{2+}$ cation and atom numbering scheme

the Newton–Raphson method described by Boyd[18] was employed.[19] All derivatives were calculated analytically. Starting co-ordinates for the refinement were taken from crystal structure co-ordinates for isomer (**B**) and those for the other isomers were derived from these by application of appropriate symmetry operations. No symmetry constraints were applied in the final stages of refinement.

Results and Discussion

Crystal Structure.—The structure consists of the complex cation, triflate ($CF_3SO_3^-$) anions, and water and acetone molecules. There are two weak hydrogen bonds between the water molecule and an oxygen atom of one triflate anion. The triflate and acetone geometries are unremarkable and accordingly bond lengths and angles are in SUP 56395.

The complex cation, Figure 2, is four-co-ordinate, the closest axial contact [3.148(7) Å] being to an oxygen atom of a triflate anion. It adopts the arrangement with all methyl groups disposed on the same side of the molecule, isomer (**B**). The geometry about nickel approximates to square planar, though there is a significant tetrahedral distortion; N(1) and N(3) lie 0.201(4) and 0.192(4) Å below the least-squares plane through the co-ordinating atoms while N(2) and N(4) lie 0.197(4) and 0.196(4) Å above the plane. The *trans* N–Ni–N bond angles, 168.2(3) and 169.0(3) (Table 3), also reveal this distortion. A similar tetrahedral distortion was observed in β-[Ni(hmtactd)]-$[ClO_4]_2$ (hmtactd = 5,5,7,12,12,14-hexamethyl-1,4,18,11-tetra-azacyclotetradecane) but the deviations there were only ±0.06 Å and the *trans* angles 175°.[20] In contrast, the nickel atom in $[Ni(tmtacdd)][ClO_4]_2 \cdot 2H_2O$ (tmtacdd = 1,4,7,10-tetra-methyl-1,4,7,10-tetra-azacyclododecane) lies 0.3 Å from the plane of the four nitrogens to the same side as the methyl groups.[21] This is a consequence of the smaller hole size of the 12-membered macrocycle. The Ni–N bond lengths range from 1.978(4) to 1.992(7) Å which are longer than those present in α-, β-, and γ-$[Ni(hmtactd)]^{2+}$ [1.90(1)—1.94(1) Å][20] and $[Ni(tmtacdd)]^{2+}$ [1.89(2)—1.99(2) Å].[21] The longer bond lengths here probably reflect the increased strain arising from methyl–methyl repulsions. The closest methyl–methyl contacts, between hydrogen atoms of C(1) and C(5) (1.87 Å) and C(8) and C(12) (1.92 Å), are in the highly repulsive range of H···H contacts. These distances are between calculated hydrogen atom positions and are probably underestimated since some relaxation from ideal stereochemistry could be expected. The Ni–N bond lengths are shorter than those observed in high-spin five- and six-co-ordinate complexes of the same ligand; *viz.* $[Ni(tmtactd)(dmf)][CF_3SO_3]_2$ (dmf = *NN*-dimethyl-formamide), 2.09(1)—2.12(1) Å,[22] $[Ni_2(tmtactd)_2(N_3)_3]I$, 2.15(1)—2.16(1) Å.[4]

Table 3. Comparison of solid-state and strain-energy minimized bond lengths (Å) and angles (°) for the cation of $[Ni(tmtactd)][CF_3SO_3]_2 \cdot Me_2CO \cdot H_2O$

Atoms	Crystal structure	Energy minimized
N(1)–Ni(1)	1.978(4)	1.977
N(2)–Ni(1)	1.981(7)	2.022
N(3)–Ni(1)	1.980(4)	1.977
N(4)–Ni(1)	1.992(7)	2.022
N(2)–Ni(1)–N(1)	94.3(2)	93.7
N(3)–Ni(1)–N(1)	168.2(3)	163.8
N(3)–Ni(1)–N(2)	86.6(2)	88.1
N(4)–Ni(1)–N(1)	86.4(2)	88.1
N(4)–Ni(1)–N(2)	169.0(3)	166.7
N(4)–Ni(1)–N(3)	95.0(2)	93.7
C(1)–N(1)–Ni(1)	114.2(4)	111.3
C(2)–N(1)–Ni(1)	115.0(4)	114.1
C(2)–N(1)–C(1)	109.8(6)	111.9
C(14)–N(1)–Ni(1)	102.6(4)	101.1
C(14)–N(1)–C(1)	107.8(5)	109.5
C(14)–N(1)–C(2)	106.8(5)	108.3
C(4)–N(2)–Ni(1)	113.9(4)	113.6
C(5)–N(2)–Ni(1)	110.6(5)	108.9
C(5)–N(2)–C(4)	108.7(6)	112.2
C(6)–N(2)–Ni(1)	108.5(5)	106.4
C(6)–N(2)–C(4)	107.3(7)	107.0
C(6)–N(2)–C(5)	107.6(5)	108.3
C(7)–N(3)–Ni(1)	101.9(4)	101.0
C(8)–N(3)–Ni(1)	114.3(4)	111.3
C(8)–N(3)–C(7)	110.1(6)	109.5
C(9)–N(3)–Ni(1)	114.7(4)	114.1
C(9)–N(3)–C(7)	106.3(6)	108.3
C(9)–N(3)–C(8)	108.9(6)	111.9
C(11)–N(4)–Ni(1)	113.7(5)	113.6
C(12)–N(4)–Ni(1)	110.0(5)	108.9
C(12)–N(4)–C(11)	109.6(7)	112.2
C(13)–N(4)–Ni(1)	108.6(5)	106.4
C(13)–N(4)–C(11)	107.4(5)	107.0
C(13)–N(4)–C(12)	107.4(6)	108.3
C(3)–C(2)–N(1)	115.0(6)	115.3
C(4)–C(3)–C(2)	112.3(7)	112.2
C(3)–C(4)–N(2)	115.5(8)	117.1
C(7)–C(6)–N(2)	108.3(6)	107.5
C(6)–C(7)–N(3)	107.4(6)	108.5
C(10)–C(9)–N(3)	114.6(7)	115.3
C(11)–C(10)–C(9)	113.8(8)	112.2
C(10)–C(11)–N(4)	114.9(6)	117.1
C(14)–C(13)–N(4)	107.8(6)	107.5
C(13)–C(14)–N(1)	109.6(6)	108.5

The six-membered chelate rings adopt chair conformations. Least-squares planes through the four central atoms of these chairs [N(1),C(2),C(4),N(2) and N(3),N(4),C(9),C(11)] reveal no significant deviations from planarity. The five-membered chelate rings have opposed skew conformations giving the molecule approximate C_2 symmetry.

Energy Minimization.—All five isomers of four-, five-, and six-co-ordinate geometries were subjected to energy minimization. Additional isomerism arises in the case of the five-co-ordinate complexes of isomers (**B**) and (**C**) from the disposition of the additional ligand, toward the same side of the co-ordination plane as the majority of the methyl groups, ($\mathbf{B}^u$) and ($\mathbf{C}^u$), or toward the other side, ($\mathbf{B}^d$) and ($\mathbf{C}^d$).

A comparison of the energy-minimized geometry, obtained for the four-co-ordinate isomer (**B**), with that observed in the crystal structure is given in Table 3. Generally, good agreement between these geometries is observed. Of particular note is the agreement of the *trans* N–Ni–N angles. The energy-minimiz-

Table 4. Minimized strain energies (kJ mol^{-1}) for four-, five-, and six-co-ordinate $[Ni(tmtactd)]^{2+}$ complexes

Isomer	Symmetry *	U_b	U_{nb}	U_θ	U_φ	U_{tot}
(*i*) Four co-ordinate						
(A)	$C_{2/m}$	34.9	75.6	29.9	15.0	155.4
(B)	C_2	31.6	69.8	28.3	14.5	144.2
(C)	C_1	28.8	67.4	31.9	19.1	147.2
(D)	$C_{2/m}$	31.9	89.9	29.7	59.5	211.0
(E)	C_1	23.8	61.7	34.0	25.6	145.1
(*ii*) Five-co-ordinate						
(A)	C_m	30.4	72.1	28.6	12.3	143.4
(B^u)	C_2	34.0	79.4	25.7	7.3	146.4
(B^d)	C_2	26.0	73.2	29.5	16.8	145.5
(C^u)	C_1	27.9	74.7	32.1	23.2	158.1
(C^d)	C_1	31.1	73.6	27.6	15.9	148.2
(D)	C_1	29.8	88.7	34.1	46.5	199.1
(E)	C_2	29.6	70.1	29.0	21.5	150.2
(*iii*) Six-co-ordinate						
(A)	$C_{2/m}$	28.0	82.5	32.2	7.0	149.5
(B)	C_2	27.1	85.7	29.7	11.1	153.6
(C)	C_1	28.5	85.8	35.8	14.1	164.2
(D)	$C_{2/m}$	29.2	87.8	44.6	24.4	186.2
(E)	C_1	30.5	85.8	39.3	13.9	169.5

* The symmetries quoted are those of the energy minimized geometries.

Table 5. Calculated isomer proportions for the isomers of $[Ni(tmtactd)]^{2+}$

	(A)	**(B)**	**(C)**	**(D)**	**(E)**
(*i*) Four-co-ordinate					
Strain energy (kJ mol^{-1})	155.4	144.2	147.2	211.0	145.1
Relative strain energy (kJ mol^{-1})	11.2	0.0	3.0	66.8	0.9
Isomer proportions (%; T = 300 K)	0.5	49.8	15.0	0.0	34.7
(*ii*) Six-co-ordinate					
Strain energy (kJ mol^{-1})	149.5	153.6	164.2	196.2	169.5
Relative strain energy (kJ mol^{-1})	0.0	4.1	14.7	36.7	20.0
Isomer proportions (%; T = 372 K)	78.4	20.8	0.7	0.0	0.1

ation calculations in the four-co-ordinate case were performed with no imposition of coplanarity on the nickel and four nitrogens. The tetrahedral distortion about nickel, observed in the energy-minimized geometry, is also observed in the crystal structure indicating that the unconstrained model is reasonable, at least for the degree of distortion observed in the current complex.

Minimized strain energies for all geometries considered are listed in Table 4.

The results for the four-co-ordinate complexes indicate that isomer **(B)** is the most stable with isomers **(C)** and **(E)** of similar stability. It has long been assumed that isomer **(A)** would be the most stable since it has two methyl groups disposed toward each side of the co-ordination plane, reducing methyl–methyl interactions, and the six-membered chelate rings adopt preferred chair conformations.[4–6] However, it can be seen from Table 4 that non-bonded interactions are responsible for the relatively high strain energy of isomer **(A)**. The largest individual contributor to this strain is a H(methyl) ··· H(methyl) interaction (2.22 Å, 2.8 kJ mol^{-1}). Consideration of the energy-minimized geometry, isomer **(B)**, shows that H(methyl)··· H(methyl) contacts between groups adjacent across six-membered chelate rings (2.25 Å, 2.4 kJ mol^{-1}) are more important than those between groups adjacent across five-membered rings (2.57 Å, 0.15 kJ mol^{-1}). Thus, little is gained by the particular arrangement of methyl groups on opposite sides of the co-ordination plane in isomer **(A)**, and, in addition, the more regular geometry of this isomer results in closer methyl–methyl contacts. In contrast, the disposition of methyl groups, adjacent across the six-membered chelate rings, toward opposite sides of the co-ordination plane, as in isomer **(E)**, leads to a lower non-bonded interaction energy. However, this arrangement also requires that the six-membered rings adopt skew-boat conformations with a consequent increase in torsional and non-bonded interaction energies[14] and a destabilization of isomer **(E)**. Isomer **(C)** can be considered as being intermediate between isomers **(A)** and **(E)**. Isomer **(D)** is particularly unstable because the six-membered rings are forced to adopt skew-boat conformations and the five-membered rings, envelope conformations with N–C–C–N torsion angles near 0°.

On the addition of one axial ligand, to give a five-co-ordinate complex, the relative stabilities alter markedly. Now **(A)** is the most stable geometry, **(B)** slightly less stable, and **(C)** and **(E)** are of similar but lower stability. The non-bonded interaction contribution to the strain energy is relatively increased for isomers **(B)**, **(C)**, and **(E)** compared with **(A)** on going to the five-co-ordinate complex. This is apparently due to the fifth ligand restricting the amount the tmtactd ligand can relax and reduce methyl–methyl interactions. For example, a H(methyl)··· H(methyl) contact of 2.20 Å (3.1 kJ mol^{-1}) is observed in isomer **(B)**, considerably closer than the contact observed in the four-co-ordinate case.

The minimized strain energies for the six-co-ordinate complexes show a continuation of the change observed on going from four-co-ordination to five-co-ordination. Isomer **(A)** is significantly more stable than **(B)** and all other isomers have strain energies too high to be present at significant levels. Isomer **(A)** had the lowest contribution from non-bonded interaction energies but it also has a much lower torsional strain contribution.

On going from four-co-ordination to six-co-ordination the Ni–N bond lengths increase from 1.98 to 2.15 Å. The variation of the relative stabilities of the isomers with co-ordination number may, in part, be due to a differing ability of each isomer to adapt to a given Ni–N bond length. Energy minimization with a force constant of zero for the Ni–N bond, to give the ideal hole sizes,[23] shows little difference for each isomer: **(A)** 2.20, **(B)** 2.19, **(E)** 2.18 Å. However, this calculation does not indicate the compressibility of the geometry. It is notable that for the four-co-ordinate case, isomer **(A)** refines with a Ni–N bond length of 2.012 Å, isomer **(B)**, 1.999 Å, and isomer **(E)**, 1.973 Å, suggesting that **(E)** is more compressible than **(A)**. Consistent with this is the reduction, both in real and relative terms, on going from four-co-ordination to six-co-ordination, of the bond-deformation energy contribution to the strain energy of isomer **(A)**.

In Table 5 are listed the predicted isomer proportions, calculated from the strain energies. When four-co-ordinate complexes predominate, isomer **(B)** is expected with smaller amounts of isomers **(E)** and **(C)**. Direct preparation of $[Ni(tmtactd)]^{2+}$ produces isomer **(B)**,[3] though recently isomer **(C)** has been detected,[8] both observations being consistent with the calculated proportions. No evidence for the presence of isomer **(E)** has been reported, however, this isomer was considered previously to be most unlikely[1] and its ^{13}C n.m.r. spectrum may coincide considerably with that of isomer **(C)**. When six-co-ordinate complexes predominate isomer **(A)** is expected and about one third as much of isomer **(B)**. This is in agreement with the observations of Moore *et al.*[7] who found an isomer **(A)**:**(B)** ratio of 2:1 at 372 K. The situation for five-co-ordinate complexes is intermediate between that for the four- and six-co-ordinate cases.

As mentioned above, it has long been thought[3–6] that isomer (**A**) was the preferred geometry. To some extent, this belief arose from the observation of that geometry in the preparation of [Ni(tactd)Cl_2].[24] The present calculations reveal that the presence of the chloro ligands, and the subsequent formation of a six-co-ordinate complex, probably stabilized isomer (**A**) in that preparation.

References

1 B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

2 F. Wagner, M. T. Mocella, M. J. D'Aniello, jun., A. H-J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, 1974, **96**, 2625.

3 E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.

4 M. J. D'Aniello, jun., M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Am. Chem. Soc.*, 1975, **97**, 192.

5 F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1976, **15**, 408.

6 M. Micheloni, P. Paoletti, S. Burki, and T. A. Kaden, *Helv. Chim. Acta*, 1982, **65**, 587.

7 P. Moore, J. Sachinidis, and G. R. Willey, *J. Chem. Soc., Chem. Commun.*, 1983, 522.

8 S. F. Lincoln, D. L. Pisaniello, J. H. Coates, and D. A. Hadi, *Inorg. Chim. Acta*, 1984, **81**, L9.

9 T. W. Hambley, *J. Chem. Soc., Chem. Commun.*, 1984, 1228.

10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

11 G. M. Sheldrick, SHELX 76, Program for *X*-Ray Crystal Structure Determination, University of Cambridge, 1976.

12 C. K. Johnson, ORTEP, Thermal Ellipsoid Plotting, Oak Ridge National Laboratories, Tennessee, 1965.

13 M. R. Snow, *J. Am. Chem. Soc.*, 1970, **92**, 3610.

14 T. W. Hambley, C. J. Hawkins, J. A. Palmer, and M. R. Snow, *Aust. J. Chem.*, 1981, **34**, 45.

15 N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.

16 N. L. Allinger, *Adv. Phys. Org. Chem.*, 1976, **13**, 1.

17 G. J. McDougall, R. D. Hancock, and J. C. A. Boeyens, *J. Chem. Soc., Dalton Trans.*, 1978, 1438.

18 R. H. Boyd, *J. Chem. Phys.*, 1968, **49**, 2574.

19 T. W. Hambley, MOMEC 84, Program for Energy Minimization, University of Sydney, 1984.

20 N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1963.

21 J. H. Coates, D. M. M. A. Hadi, T. W. Hambley, S. F. Lincoln, and J. R. Rodgers, *Cryst. Struct. Commun.*, 1982, **11**, 815.

22 S. F. Lincoln, T. W. Hambley, D. L. Pisaniello, and J. H. Coates, *Aust. J. Chem.*, 1984, **37**, 713.

23 L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 4046.

24 B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 1965, **4**, 1109.

Received 11th March 1985; Paper 5/400