Conformational Changes of Nickel(II) Diamine Complexes in the Solid State †

Goutam De, Prasanta K. Biswas, and Nirmalendu Ray Chaudhuri *
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadvapur, Calcutta 700 032, India

Conformational changes in some nickel(II) diamine complexes have been studied by differential scanning calorimetry. Two tris(ethylenediamine)nickel(II) thiocyanates, (1) and (3), have been synthesised. Complex (1) undergoes a phase transition on heating, transforming into species (2) (at 416 K, ΔH = 1.7 kJ mol^{-1}) which reverts to (1) upon cooling. Complex (3) does not undergo a phase transition. Conformational forms with a particular configuration about the metal ion, δδλ, δλλ, and δδδ, have been suggested for complexes (1)—(3) respectively on the basis of the enthalpy change for (1) ⟶ (2) and the interconversion (1) ⟶ (3) in solution. The complex [$Ni_2(en)_4(NCS)_4$] (4), having both bridging and chelating ethylenediamine, has also been synthesised. On heating it undergoes a solid-state reaction (406—434 K, ΔH = 9.8 kJ mol^{-1}) yielding *trans*-chelated monomeric [$Ni(en)_2(NCS)_2$] (5). The complex [$Ni(pd)_2(NCS)_2$] (6) (pd = 1,3-propanediamine) has been found to transform into an isomer (7) after two overlapping phase transitions (446—467.5 K, ΔH = 20.1 kJ mol^{-1}). Isomer (7), on keeping overnight in a humid atmosphere (relative humidity 60—70%), is transformed into another isomer (8) which on heating undergoes phase transitions in two steps (445—462 K, ΔH = 9.7 kJ mol^{-1}; 465—477 K, ΔH = 3.9 kJ mol^{-1}). The intermediate species (9) has been isolated. Conformational changes such as *trans*-chair-chair (6) ⟶ skew boat-skew boat (7) ⟶ *cis*-chair-chair (8) ⟶ skew boat-skew boat (9) ⟶ species (10) [≡(7)] have been proposed on the basis of enthalpy changes for the interconversions. The complex [$Ni(pd)_3]Br_2 \cdot H_2O$ (11) after dehydration shows a phase change yielding an isomer (13) (408—428 K, ΔH = 7.1 kJ mol^{-1}). Isomer (13) reverts to (11) on addition of one molecule of water. This phenomenon is probably due to a chair ⇌ skew boat transformation of the chelated ligand.

In the solid-state reactions and purely physical phase changes of tris- and bis-(diamine) metal complexes the following are of interest: (*i*) isomerisations [1,2] such as geometrical, optical, and linkage; (*ii*) racemisation [3-6] of optically active species; (*iii*) conformational changes [7] of individual chelate rings; (*iv*) configurational changes [8] around the metal ion. In 1938, Pfeiffer and Glaser [9] observed phase changes in structurally related complexes of substituted ethylenediamines with Cu^{II}. These were due to a change in the crystal state [10] from triclinic to monoclinic due to conformational changes as proposed by Hatfield *et al.*[10] Exhaustive work [11-14] on Lifschitz [15] complexes of nickel(II) has been carried out, and configurational changes around the metal ion in Lifschitz salts have been suggested by Higginson and co-workers.[11] A molecular structure determination by Nyburg and Wood [14] confirmed the proposed [13] stereochemistry of the nickel ion in such salts. Conformational analysis of five- and six-membered chelate rings has had important implications in studies of the stereochemistry of complex inorganic compounds.[16-34] Various experimental procedures have focused attention on conformational analysis [35-37] but little has been accomplished as regards the phase changes of compounds in the solid state. Accordingly, we attempted a logical approach to the phase changes of some nickel(II) diamine complexes on the basis of an analysis of the general stereochemistry of chelate compounds and the stereospecific effects of the individual chelate rings in complex ions.

Experimental

All the chemicals used were A.R. grade and the diamines were distilled before use. Bromine, chlorine, nickel, and sulphur were estimated gravimetrically in our laboratory using standard procedures.[38] Carbon, H, and N were determined by the Microanalytical section of the Australian Mineral Development Laboratories, as well as by the microanalytical laboratory of this Institute. Phase transitions and solid-state reactions were investigated with a Perkin-Elmer DSC-2 differential scanning calorimeter and a Shimadzu DT-30 thermal analyser. Indium metal was used as calibrant for the evaluation of enthalpy changes. Infrared spectra of KBr discs and electronic spectra of mulls (Nujol) were recorded with Beckman IR 20A and Pye-Unicam SP 8-150 spectrophotometers respectively. The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG and G PAR 155 vibrating-sample magnetometer at room temperature. The mean susceptibility per g mol of the powdered sample (1) was measured at *ca.* 416 K in a Curie-type electrodynamic balance of comparable sensitivity. *X*-Ray powder diffraction patterns were taken by a Philips powder diagram camera using Cu-K_α and Co-K_α radiation; the exposure time for all samples was *ca.* 15 h. Just after the phase transition, samples were cooled in a fused $CaCl_2$ desiccator and sealed immediately in a very fine glass capillary as far as was practicable at room temperature.

Preparation of the Complexes.—Tris(*ethylenediamine*)*nickel*(II) *thiocyanate* (1). Ethylenediamine (*ca.* 4 mmol) was added dropwise to the nickel thiocyanate (1 mmol) dissolved in ethanol–water (9 : 1). The resulting mixture was stirred vigorously for about 10 h and kept overnight at *ca.* 15 °C. The shiny pink crystals were separated out, washed with ethanol, and dried in air (Found: C, 27.0; H, 6.7; N, 31.6; Ni, 16.6; S, 18.2. Calc. for $C_8H_{24}N_8NiS_2$: C, 27.1; H, 6.8; N, 31.6; Ni, 16.5; S, 18.0%).

Tris(*ethylenediamine*)*nickel*(II) *thiocyanate* (3). Ethylenediamine (3 mmol) was added dropwise to nickel thiocyanate (1 mmol) dissolved in ethanol, in the cold. A pinkish powder immediately separated out. It was filtered off, washed with

---

† *Non-S.I. units employed:* cal = 4.184 J; B.M. ~ 9.27 × 10^{-24} A m^2.

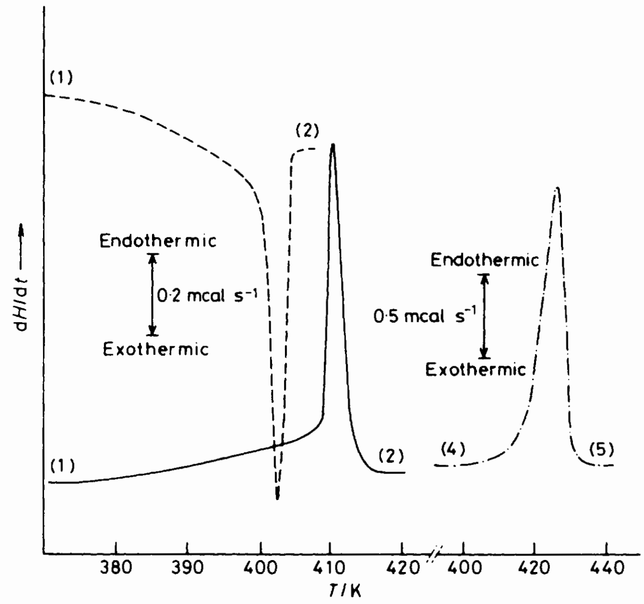
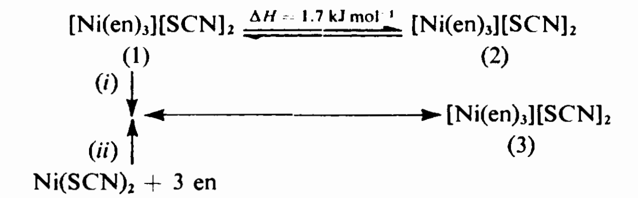


Figure 1. D.s.c. curves showing the transformations of: complex (1) (19.10 mg) into (2), heating curve (———); (2) into (1), cooling curve (– – – –); and (4) (13.70 mg) into (5), heating curve (– · – · – · –)



Scheme 1. (*i*) water–ethanol (1 : 1), 24-h reflux; (*ii*) dry ethanol

ethanol, and dried in air (Found: C, 27.1; H, 6.8; N, 31.7; Ni, 16.5; S, 18.1%).

Bis(ethylenediamine)di-isothiocyanatonickel(II) (4). Nickel thiocyanate (1 mmol) and complex (3) (2 mmol) were gently refluxed for 10 min with a mixture of methanol (47.5 cm^3) and water (2.5 cm^3). The hot mixture was filtered quickly. Bluish pink crystals of complex (4) separated slowly upon cooling the filtrate. These were filtered off, washed with ethanol, and dried in air (Found: C, 24.2; H, 5.3; N, 28.4; Ni, 20.0; S, 21.1. Calc. for $C_6H_{16}N_6NiS_2$: C, 24.4; H, 5.4; N, 28.5; Ni, 19.9; S, 21.7%).

Bis(ethylenediamine)di-isothiocyanatonickel(II) (5). This complex was prepared by mixing stoicheiometric amounts of K[SCN] and [Ni(en)$_2$Cl$_2$] dissolved in ethanol–water (9 : 1). The bluish pink crystals obtained were filtered off, washed with ethanol–water (1 : 1), and dried in air (Found: C, 24.3; H, 5.4; N, 28.4; Ni, 19.8; S, 21.0%).

Di-isothiocyanatobis(1,3-*propanediamine*)*nickel*(II) (6). 1,3-Propanediamine (pd) (3 mmol) was added to nickel thiocyanate (1 mmol) dissolved in ethanol–water (9 : 1). Shiny bluish crystals immediately separated out. These were filtered off, washed with water, and dried in air. The same compound may be prepared by the method of Curtis and Curtis[39] (Found: C, 29.7; H, 6.1; N, 25.8; Ni, 18.0; S, 20.0. Calc. for $C_8H_{20}N_6NiS_2$: C, 29.8; H, 6.2; N, 26.0; Ni, 18.2; S, 19.8%).

Tris(1,3-*propanediamine*)*nickel*(II) *bromide monohydrate* (11). 1,3-Propanediamine (3 mmol) was added dropwise with stirring to an aqueous solution of nickel(II) bromide (1 mmol). The mixture was concentrated on a steam-bath. On cooling shiny bluish pink crystals separated out. These were filtered off, washed thoroughly with ethanol, and dried in air (Found: C, 23.4; H, 6.8; Br, 33.1; N, 18.3; Ni, 12.7. Calc. for $C_9H_{32}Br_2N_6NiO$: C, 23.5; H, 7.0; Br, 34.9; N, 18.3; Ni, 12.8%).

Table 1. Electronic spectral (mull) and magnetic data of nickel(II) diamine complexes

Compound	$\lambda_{max.}$/nm	$\mu_{eff.}$/B.M.
[Ni(en)$_3$][SCN]$_2$ (1), (3)	542, 338	2.90
[Ni$_2$(en)$_4$(NCS)$_4$] (4)	543, 352	3.28
[Ni(en)$_2$(NCS)$_2$] (5)	528, 324	3.34
[Ni(pd)$_2$(NCS)$_2$] (6), (8)	563, 362	3.24
[Ni(pd)$_2$(NCS)$_2$] (7), (9), (10)	548, 353	3.29
[Ni(pd)$_3$]Br$_2$·H$_2$O (11)		
[Ni(pd)$_3$]Br$_2$ (12), (13)	548, 345	3.06

Analytical, i.r., and thermogravimetric data for compounds (1) and (3)—(6) confirmed the absence of water of crystallisation.

Results and Discussion

Tris(ethylenediamine)nickel(II) *Thiocyanate*.—The reaction of Ni(SCN)$_2$ with ethylenediamine (en) in ethanol–water (9 : 1) yielded [Ni(en)$_3$][SCN]$_2$ (1), whilst complex (3) was obtained if dry ethanol was used as the reaction medium. It is interesting to note that complex (1) is transformed into a non-isolable species (2) upon heating. This transformation is reversible (Figure 1, Scheme 1), whilst complex (3) does not undergo any phase change.

Regarding the structures of the isomers (1)—(3), it is reasonable to consider either (*i*) the orientation of the donor atoms around the central metal ion and/or (*ii*) the spatial arrangements of the individual chelate rings. However, the similar electronic spectral and magnetic data (Table 1) of complexes (1) and (3) do not permit orientations of the donor atoms to be distinguished. Also, the *X*-ray powder pattern and electronic spectrum of (2) at 416 K could not be taken due to limitations of our facilities. However, the similar magnetic moment of complex (2) (at 416 K) to that of (1) and the pink colour of the latter even on heating to *ca.* 420 K suggest tentatively that configurational changes around the metal ion as in Lifschitz salts are not present. As a consequence, the changes in spatial arrangements of the individual chelate rings may be considered to account for the formation of the different isomers as is evident from the non-identical skeletal[40] [ν(C–C) and ν(C–N)], $\rho_w(NH_2)$,[41-44] and NH$_2$ twisting[42] vibrations (Table 2) of complexes (1) and (3) in the i.r. spectra.[45-47,*] On the basis of the relative energies of the different conformers with a particular configuration about the metal in the tris(ethylenediamine) complexes, the order of stability is as follows: δδδ > δδλ > δλλ > λλλ, where δ and λ designate the two enantiomeric conformations of the metal ethylenediamine ring. Considering the energy (1.25 kJ mol^{-1}) and enthalpy (1.5 kJ mol^{-1}) change for the δ $\rightleftharpoons$ λ conversion

---

[*] Regarding the applicability of i.r. spectroscopy in distinguishing conformational changes in the solid state, molecular symmetry selection rules for polycrystalline substances are invalid as the crystal site symmetry could split degenerate modes resulting in certain forbidden i.r. vibrations becoming allowed.[45] However, it is reasonable to expect that conformational changes in chelate rings would require changes in crystal packing as is evident from non-identical *d* lines (Table 2) of the present compounds and also that the molecular symmetry may also change. Moreover, a *gauche* configuration of chelated ethylenediamine has been established in the solid state by i.r. spectroscopy[46] and *X*-ray studies.[47]

Table 2. I.r. spectral data (cm^{-1}) of nickel(II) diamine complexes

	Compound	$\nu(NH_2)$	$\nu(CH_2)$	$\nu(CN)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2) + \rho_w(NH_2) + \tau(CH_2)$	Stretching vibrations of skeleton $\nu(C-N) + \nu(C-C)$	$\rho_r(CH_2)$	$\nu(CS)$	$\rho_r(CH_2) + \nu(MN)$
(1)	$[Ni(en)_3][SCN]_2$	3 310 (sh), 3 280s, 3 228s, 3 140w	2 940m, 2 922 (sh), 2 865m, 2 783w	2 044vs	1 590 (sh), 1 580m, 1 567m, 1 560 (sh)	1 450m	1 385w, 1 360vw	1 322s, 1 315s, 1 270s, 1 135s	1 125 (sh), 1 092s, 1 072vw, 1 018vs, 970w	932w, 875 (sh), 860w	732m	644s, 550w, 508m
(3)	$[Ni(en)_3][SCN]_2$	3 280s, 3 225s, 3 124w	2 940m, 2 922 (sh), 2 866m, 2 783w	2 041vs	1 582 (sh), 1 572m, 1 560m, 1 556 (sh)	1 450m	1 385vw, 1 360w	1 315s, 1 268s, 1 135s	1 102m, 1 090w, 1 018vs, 965m	928w, 875vw, 860w	731m	642s, 551w, 510m
(4)	$[Ni_2(en)_4(NCS)_4]$	3 303s, 3 242s, 3 148w	2 960w, 2 930w, 2 876w, 2 820vw	2 040vs	1 597m	1 460w, 1 450w	1 388w, 1 366vw	1 324w, 1 280 (sh), 1 275m, 1 140m	1 086m, 1 066w, 1 012vs, 1 008 (sh), 970s	940vw, 865vw	770m	654s, 555vw, 510s
(5)	$[Ni(en)_2(NCS)_2]$	3 338m, 3 280s, 3 148vw	2 970m, 2 950m, 2 890w, 2 860vw	2 052vs	1 576s	1 450w	1 385vw, 1 360vw	1 312m, 1 270vw, 1 115w	1 075w, 1 046m, 998vs	950s, 865vw	772m	630s, 490s
(6)	$[Ni(pd)_2(NCS)_2]$ [a]	3 298 (sh), 3 278s, 3 250m, 3 160w	2 960m, 2 950m, 2 935m, 2 925 (sh), 2 880m, 2 850vw	2 060vs	1 600 (sh), 1 586m, 1 572ms	1 460 (sh), 1 450w, 1 431w	1 395w, 1 385w	1 315w, 1 271m, 1 241w, 1 147s, 1 129m	1 095vw, 1 078w, 1 064m, 1 052w, 1 005s	943vw, 881s	775m	615m, 548w
(7)	$[Ni(pd)_2(NCS)_2]$	3 329w, 3 292s, 3 250 (sh), 3 230s, 3 184 (sh), 3 150m	2 970w, 2 938m, 2 920 (sh), 2 882 (sh) 2 873m	2 060vs	1 590s, 1 578ms	1 460w, 1 451w, 1 435m	1 394w, 1 384w,	1 315vw, 1 305w, 1 295vw, 1 270 (sh), 1 264m, 1 245vw, 1 230vw, 1 148s, 1 127s	1 100vw, 1 078w, 1 072w, 1 059ms, 1 055 (sh), 990s	940w, 882s, 867m	770m	617m, 545m
(9)	$[Ni(pd)_2(NCS)_2]$	3 309vw, 3 308 (sh), 3 273s, 3 235m, 3 218m, 3 170vw, 3 150w, 3 135w	2 952m, 2 940 (sh), 2 925w, 2 870w	2 060vs	1 588ms, 1 570m	1 460vw, 1 448w, 1 430m	1 390w, 1 382w	1 314w, 1 303w, 1 295vw, 1 270m, 1 260m, 1 240vw, 1 230vw, 1 147s, 1 128s	1 096vw, 1 077w, 1 062 (sh), 1 058m, 1 055 (sh), 1 001 (sh), 995s	942w, 890 (sh), 884s, 869m	775m	620s, 543m
(11)	$[Ni(pd)_3]Br_2 \cdot H_2O$ [b]	3 298 (sh), 3 260s, 3 230 (sh), 3 140m	2 925m, 2 870m		1 580s	1 470w, 1 456w, 1 447 (sh), 1 425w	1 397w, 1 380w, 1 350vw	1 320m, 1 309w, 1 268m, 1 250w, 1 155s, 1 130m	1 085w, 1 055m, 1 000s	905m, 890 (sh), 882ms, 860w		655 (sh), 618ms
(12)	$[Ni(pd)_3]Br_2$	3 298 (sh), 3 255s, 3 235 (sh), 3 120m	2 925 (sh), 2 920 (sh), 2 910m, 2 860m		1 585s	1 470w, 1 453m, 1 450 (sh), 1 425w	1 400w, 1 381w	1 320, 1 307w, 1 270m, 1 250w, 1 185 (sh), 1 155s 1 130m	1 090w, 1 057m, 1 000s	905 (sh), 892ms, 880ms, 866m 852 (sh)		660 (sh), 618ms
(13)	$[Ni(pd)_3]Br_2$	3 298 (sh), 3 240s, 3 215 (sh), 3 140m	2 953 (sh), 2 930 (sh), 2 917m, 2 868m		1 585s	1 474 (sh), 1 457m, 1 452w	1 404w, 1 385w	1 322m, 1 310 (sh), 1 270m, 1 255w, 1 155s	1 091w, 1 061m, 1 000s	910 (sh), 895ms, 865w		650 (sh), 625ms

sh = shoulder, v = very, s = strong, m = medium, and w = weak. [a] The i.r. spectrum of complex (8) is similar to that of (6) in all respects except the appearance of two very weak bands at 3 310 [$\nu(NH_2)$] and 1 310 cm^{-1} [$\rho_w(CH_2)$]. [b] Bands at 3 520ms and 3 460ms cm^{-1} due to $\nu(OH)$ and at 1 610w cm^{-1} due to $\delta(HOH)$.

Table 3. Prominent lines (d/Å) in the X-ray powder patterns of the nickel(II) diamine complexes

$[Ni(en)_3][SCN]_2$ (1)	$[Ni(en)_3][SCN]_2$ (3)	$[Ni(pd)_2(NCS)_2]$ (6)	$[Ni(pd)_2(NCS)_2]$ (7)	$[Ni(pd)_2(NCS)_2]$ (8)	$[Ni(pd)_2(NCS)_2]$ (9)	$[Ni(pd)_3]Br_2 \cdot H_2O$ (11)	$[Ni(pd)_3]Br_2$ (12)	$[Ni(pd)_3]Br_2$ (13)
9.98 (mbr)	9.87 (mbr)	9.93 (w)	10.16 (m)	8.79 (s)	8.64 (vw)	8.65 (s)	7.39 (vw)	7.67 (vw)
6.49 (s)	6.41 (s)	8.82 (s)	8.22 (s)	6.95 (s)	6.65 (vs)	7.19 (m)	6.22 (vw)	5.67 (vw)
5.79 (s)	5.77 (s)	7.81 (vw)	5.78 (w)	5.53 (w)	6.09 (vs)	6.58 (w)	4.99 (w)	4.91 (s)
4.27 (sbr)	4.21 (sbr)	6.94 (s)	5.12 (vs)	5.12 (vw)	4.85 (vw)	5.98 (w)	4.52 (s)	4.43 (m)
4.07 (m)	3.85 (m)	5.49 (vw)	4.72 (w)	4.64 (m)	4.46 (m)	5.55 (w)	4.18 (s)	3.89 (s)
3.74 (m)	3.73 (m)	5.13 (vw)	4.05 (m)	4.33 (vs)	4.22 (w)	4.41 (s)	3.83 (s)	3.38 (vw)
3.65 (s)	3.65 (s)	4.80 (m)	3.69 (s)	3.97 (vw)	3.96 (vs)	4.20 (m)	3.54 (vw)	3.09 (m)
3.46 (m)	3.44 (mbr)	4.61 (m)	3.40 (vw)	3.79 (vw)	3.72 (m)	3.69 (w)	3.27 (vw)	2.71 (w)
3.23 (w)	3.25 (w)	4.35 (vs)	3.01 (s)	3.55 (w)	3.40 (m)	3.62 (w)	3.06 (vw)	2.55 (w)
3.13 (sbr)	3.16 (w)	3.66 (vw)	2.82 (w)	3.44 (w)	3.18 (m)	3.39 (s)	2.80 (w)	2.33 (vw)
2.81 (mbr)	3.10 (s)	3.47 (w)	2.56 (m)	3.19 (w)	3.00 (w)	3.24 (vw)	2.62 (w)	2.20 (w)
2.64 (m)	2.79 (mbr)	3.40 (w)	2.37 (vw)	3.10 (s)	2.88 (s)	3.03 (w)	2.34 (w)	
2.56 (w)	2.61 (m)	3.33 (w)	2.23 (w)	2.94 (vw)	2.81 (w)	2.92 (w)		
2.45 (mbr)	2.55 (w)	3.19 (m)	2.09 (m)	2.84 (vw)	2.72 (m)	2.78 (s)		
2.33 (m)	2.43 (mbr)	3.11 (m)	1.92 (w)	2.75 (vw)	2.62 (w)	2.65 (vw)		
2.27 (m)	2.30 (m)	3.05 (vw)	1.90 (w)	2.64 (w)	2.49 (w)	2.50 (m)		
2.22 (m)	2.23 (m)	2.95 (vw)		2.52 (m)	2.41 (w)	2.36 (m)		
2.19 (m)	2.19 (w)	2.77 (vw)		2.38 (m)	2.37 (w)	2.27 (w)		
2.15 (w)	2.17 (m)	2.65 (vw)		2.32 (w)	2.32 (w)	2.17 (vw)		
2.03 (w)	2.14 (w)	2.55 (m)		2.18 (w)	2.24 (w)	2.09 (w)		
1.98 (m)	2.02 (w)	2.35 (w)		2.14 (vw)	2.11 (w)	1.91 (w)		
1.96 (w)	1.96 (m)	2.32 (w)		2.10 (vw)	2.03 (w)	1.74 (w)		
1.86 (w)	1.92 (w)	2.19 (w)		2.05 (vw)	1.99 (vw)			
1.82 (w)	1.84 (m)	2.15 (w)		1.90 (w)	1.90 (w)			
1.78 (m)	1.80 (w)	2.11 (w)		1.85 (vw)	1.85 (vw)			
1.73 (vw)	1.77 (m)	2.06 (vw)		1.81 (vw)				
1.71 (vw)	1.66 (mbr)	1.89 (vw)		1.77 (m)				
1.67 (mbr)	1.61 (w)	1.79 (m)						
1.62 (mbr)	1.59 (w)							
1.58 (vw)	1.56 (vw)							
1.55 (vw)	1.53 (vw)							
1.52 (m)	1.51 (m)							
1.47 (w)	1.43 (w)							
1.43 (w)	1.42 (w)							
1.39 (w)	1.37 (w)							
1.37 (w)	1.35 (w)							

Intensities were estimated visually: v = very, s = strong, br = broad, m = medium, and w = weak.

in D-$[Ni(en)_3]^{2+}$, it may be presumed that the conversion (1) ⟶ (2) may be due to δδδ ⟶ δδλ, δδλ ⟶ δλλ, or δλλ ⟶ λλλ as the enthalpy change * (1.7 kJ mol^{-1}) required for (1) ⟶ (2) corresponds almost exactly to that for δ ⇌ λ. Moreover, as this the enthalpy change is of the same order for racemisation of an optically active compound, a question arises as to the optical activity of complex (1). However, due to the particular crystal habit no optic axis could be located. Consequently we could not record the circular dichroism (c.d.) spectrum of (1).

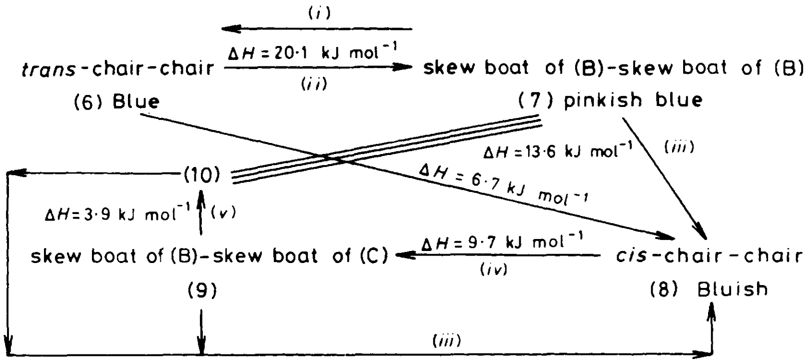
If complex (1) were to be optically active,[48] then the phase change (1) ⟶ (2) may occur due to two reasons: (*i*) racemisation of an optically active compound; (*ii*) transformation of one particular conformation into another. However, the conversion (1) ⟶ (2) is proposed to be of a stable optically active conformer (1) into another unstable optically active conformer (2),† since a racemate would be stable because of its lower energy and higher crystal symmetry [4] and would result in an exotherm. In practice, the conversion (1) ⟶ (2) requires energy and results in the formation of complex (2) in a higher energy state which is neither stable nor isolable. An ambiguity may arise about the conformational form of complex (1) which can be overcome by the following arguments. If complex (1) is refluxed in ethanol–water (1 : 1) for 24 h it is transformed into complex (3) ‡ which does not undergo a phase change during heating. However, complexes (1) and (3) are proposed to possess the δδλ and δδδ configurations as refluxing of (1) in ethanol–water (1 : 1) for 24 h converts it into the most stable form,[49,50] δδδ, of (3). It is, therefore, reasonable to infer that the conversion (1) ⟶ (2) follows δδλ ⟶ δλλ. The λλλ form is not considered at all because of severe hydrogen–carbon interaction [17] which would make it very unstable. The small difference in d lines (Table 3) between complexes (1) and (3) is possibly due to conversion of the λ form of (1) into the δ of (3).

---

* The difference in enthalpy changes (0.2 kJ mol^{-1}) is possibly due to the different techniques employed for evaluating this parameter.

† As the formation of complex (2) is reversible and the enthalpy change [30] (ΔH) for the transformation of the phases remains the same on repeating the cycle, it is logical to infer that the optical activity of (2) is not lost during heating and cooling if (1) is at all optically active.

‡ There may be an ambiguity about complex (3) which may be a racemic modification of the δδλ or δδδ form. If (3) is a racemised form of (1), *i.e.* ± δδλ, then prolonged refluxing would not be necessary for the (1) ⟶ (3) transformation, rather racemisation of (1) should occur just by dissolving it at ambient temperature in ethanol–water (1 : 1). In practice, the product obtained from the mixed solvent which is only (1) does undergo a phase transition. Also, dissolution of (3) in ethanol–water (1 : 1) and subsequent crystallisation yields (1), which precludes the possibility of it being a racemate of (3).



Scheme 2. Skew-boat forms of compounds (B) and (C) in Table 4 are proposed to exist in the respective chelate rings of compounds (7) and (8). Complexes (7), (9), and (10) were isolated and collected in a vacuum desiccator. (*i*) Water; (*ii*) 446—467.5 K; (*iii*) 20 h in humid atmosphere (relative humidity 60—70%) at ambient temperature; (*iv*) 445—462 K; (*v*) 465—477 K

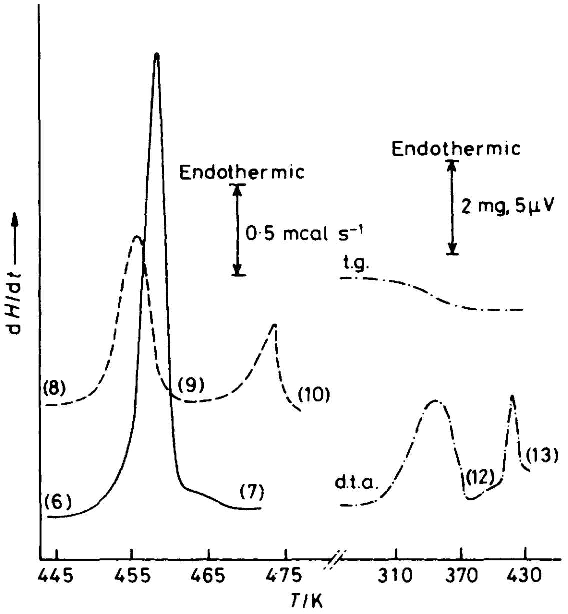


Figure 2. D.s.c. curves showing the transformations of: complex (6) (9.63 mg) into (7), heating curve (———); (8), derived from (7) in humid air, into (9) and (10), heating curve (- - - -). (– · – · – · –), T.g.–d.t.a. curves showing the transformation of complex (11) (20.15 mg) into (12) and (13), heating curve

Bis(ethylenediamine)di-isothiocyanatonickel(II).—Treatment of $[Ni(en)_3][SCN]_2$ (3) with $Ni(SCN)_2$ in methanol afforded bluish pink, octahedral $[Ni_2(en)_4(NCS)_4]$ (4) in which two en are bridging [51–53] and two are chelated,[43,51a,54] as is evident from the appearance of extra bands at 1 324, 1 140, and 1 008 (sh) cm^{-1} in addition to the bands responsible for chelated en in the i.r. spectrum (Table 2). The thiocyanate groups in (4) are N-bonded and in *trans* position,[55,56] as indicated by ν(CN) and ν(CS) bands at 2 040 and 770 cm^{-1} respectively. Upon heating, complex (4) is converted into $[Ni(en)_2(NCS)_2]$ (5) following a solid-state reaction (Figure 1) and the bridged en in (4) becomes chelated as can be inferred from a comparison of the i.r. spectra of the two species. Moreover, the i.r. and electronic spectral data of complex (5) closely resemble those of the *trans*-chelated ethylenediamine complex synthesised by the addition of K[SCN] to *cis*-$[Ni(en)_2Cl_2]$ in ethanol–water (9 : 1). The shift (Table 1) of the absorption band at 543 nm of (4) towards lower energy in the case of (5) is possibly due to the loss of the bridging en in (5). Regarding the structure of complex (5), the δλ form is proposed as this is statistically preferred [57] on the basis of the requirements for close packing of rigid molecules.

Di-isothiocyanatobis(1,3-*propanediamine*)*nickel*(II).—Treatment of 1,3-propanediamine with $Ni(SCN)_2$ in ethanol–water (9 : 1) afforded an interesting compound $[Ni(pd)_2(NCS)_2]$ (6) which undergoes several phase changes under different conditions such as heat treatment, humid atmosphere, *etc.* (Figure 2 and Scheme 2).

Four factors may cause the above phenomena: (*i*) geometrical isomerisation, *i.e. cis* $\rightleftharpoons$ *trans*; (*ii*) orientation of donor atoms around the metal ion; (*iii*) linkage isomerisation [2,55] of the NCS groups; and (*iv*) conformational changes of the individual six-membered chelate rings as in tris(ethylenediamine) complexes (see below). However, the strong *trans* effect [58] of NCS and the appearance of similar ν(CS) and ν(CN) bands [55,59] in the i.r. spectra (Table 2) of all the isomeric forms tend to rule out geometrical as well as linkage isomerism. The configuration (O_h) of the donor atoms around the metal ion is expected to be the same in all the cases, as is evident from their absorption bands (Table 1). The small deviations in peak positions probably result in those cases where the normal angles between metal–ligand bonds conflict [17] with the geometrical requirements of the chelate rings. As a consequence, the phase changes of (6) are presumably responsible for the relatively stable spatial arrangements of individual chelate rings. Moreover, the *X*-ray powder patterns (Table 3) of complexes (6)—(9) are not similar, indicating changes in the spatial arrangements. On the other hand, the *X*-ray powder patterns of (7) and (10) are the same, which supports their identical conformations (≡ in Scheme 2) which is also evident from their similar i.r. data.

It is of great interest that the enthalpy changes * for the transformation are consistent (Scheme 2, Table 4) with the conformational energies [45] of six-membered diamine chelate rings, and accordingly the conformational changes in $[Ni(pd)_2(NCS)_2]$ are illustrated in Scheme 2 on the basis that the interactions of the chelate rings with the NCS groups of complexes (6)—(10) match those of the respective compounds in Table 4. Complexes (7), (9), and (10) exist in higher energy forms than do (6) and (8). Woldbye [60] states that the skew-boat form would minimise the very serious hydrogen–hydrogen interatomic repulsions between rings of tris(1,3-propanediamine) complexes. However, the differing stability of the bis complexes is possibly due to the stereospecific

---

* $\Delta H = \Delta E$ is assumed, as $\Delta V = 0$ for solid-state transformations.

Table 4. Correlation of conformational energies of proposed forms of $[Ni(pd)_2(NCS)_2]$ with those of typical[45] six-membered diamine chelate rings

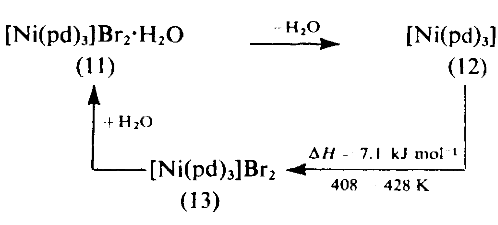
Ref. 45			Proposed		
Compound	Conformation	ε^a ($\pm$0.1)	ε^b ($\pm$0.1)	Conformation	Compound
(A) *trans*-$M(pd)_2L_2$					
($L = Cl^-$ or NH_3)	Chair	10.9	21.8	*trans*-Chair-chair	(6)
(B) *trans*-$M(pd)_2L_2$					
($L = OH_2$)	Skew boat	20.9	41.8	Skew boat of (B)-skew boat of (B)	(7)
(C) $M(pd)L_2L'_2$					
($L = OH_2$)	Skew boat	18.0	38.9	Skew boat of (B)-skew boat of (C)	(9)
($L' = NH_3$, Cl^-, or NO_2^-)					

^{a} Conformational energy in kJ mol^{-1} per ring. ^{b} Conformational energy in kJ mol^{-1}.

spatial preference in the system. It is also of interest that the energy difference between the proposed forms of complexes (6) and (8) (Scheme 2) is in accord with that (6.7 kJ mol^{-1}) between Λpp and Λpa * forms, as is evident from calculations of the energy of the corresponding conformations by Geue and Snow,[61] who inferred that the Λap conformer is less stable than the Λpa and the Λpp forms by 24.3 and 17.6 kJ mol^{-1} respectively. As a consequence, complexes (6) and (8) are expected to possess the conformational forms pa and pp respectively for a particular absolute configuration. As greater interactions are expected between two NCS groups with two chair rings in *cis* positions,[45] it is wise to consider complex (8), which exists in a higher energy state (6.7 kJ mol^{-1}) than (6), to possess the pp conformation. Consequently complex (6) would exist in pa form suggesting that the two chair rings are *trans*.

The appearance of non-identical $\nu(NH_2)$ and $\rho_w(CH_2)$ vibrations (Table 2) in the regions 3 400—3 300 and 1 350—1 280 cm^{-1} of the i.r. spectra of complexes (6) and (8) is possibly due to the existence of two different conformational forms. On the other hand, splitting of $\delta(CH_2)$, $\rho_w(CH_2)$, and $\rho_r(CH_2)$ bands [41,62,63] (Table 2) in the i.r. spectra of complexes (7) and (9) is possibly due to the *gauche* or *cis* form of chelated pd. As to the skew-boat forms of (7) and (9), it may be stated that the NH_2 hydrogens of complex (9) are more skewed than those of (7) as is evident from splitting of the $\nu(NH_2)$ and $\rho_w(NH_2)$ bands of the latter. In addition, $\nu(CH)$ of (7) at 2 970 cm^{-1} disappears in the case of (9), indicating the existence of a $>CH_2$ group in (9) analogous to that in (6) and (8). On the other hand, another $\nu(CH)$ band of complex (9) at 2 952 cm^{-1} is split in the cases of (6) and (8), indicating that CH_2 hydrogens of the former are more staggered rather than those in the latter.

It is interesting (Scheme 2) that a humid atmosphere would catalyse the conversion of complex (7) into (8). It is expected that a water molecule first becomes attached to complex (7) due to van der Waals attraction. Since (7) exists in a high-energy state, attachment of the water molecule transforms it into the stable, low-energy form (8) or (6). Contact of liquid water with complex (7) (Scheme 2) minimises the hydrogen–hydrogen and carbon–hydrogen interactions, which are at a minimum in (6), as the number of water molecules attached is comparatively more than those in the presence of a humid atmosphere. As a consequence, the water may be regarded as acting as a heterogeneous catalyst.



Scheme 3.

The occurrence of phase changes in $[Ni(pd)_2(NCS)_2]$, but not in $[Ni(pd)_2X_2]$ (X = Cl or Br), is probably due to the intramolecular interaction of the NCS group (the ionic radius of which is larger than that of Cl or Br) with hydrogen atoms of the six-membered chelate ring owing to its unfavourable internal-entropy effect [17] due to a highly folded conformation, resulting in lower stability.

Tris(1,3-*propanediamine*)*nickel*(II) *Bromide Monohydrate*.—Treatment of $NiBr_2$ with 1,3-propanediamine (pd) affords bluish pink $[Ni(pd)_3]Br_2{\cdot}H_2O$ (11). Heating of this product (Figure 2) results in a characteristic transformation as depicted in Scheme 3, but no visible change. The similar absorption spectra of complexes (11)—(13) suggest that the transformation does not account for distortion of O_h symmetry. The crystal structures of these complexes are different as evidenced by the *X*-ray powder patterns (Table 3). This observation suggests that water is a major factor in stabilising the crystal lattice. It is not unlikely that the transformation (12) ⟶ (13) involves the stereospecific spatial arrangements of the individual chelate rings which also results in different crystal symmetries.† Six-membered chelate rings may exist in chair, skew-boat, or boat form. Complexes containing three such chelate rings would either possess identical or mixed conformations according to their relative stabilities. It is difficult to predict which conformation is prevalent. However, Dettayes and Busch[25] found that entropy effects favour the mixed conformations and significantly lower their calculated relative free energies. Niketic

---

* Using Jurnak and Raymond's[22,31] nomenclature, p and a are the chair ring conformers which fold such that the central carbon atom defines a rotation direction parallel or antiparallel to the direction defined by the metal ion.

† The transformation (12) ⟶ (13) may also be a racemisation of complex (12), if the latter is optically active. The optical activity of (12) could not be determined because attempts to crystallise it yielded (11). However, racemisation would not, in general, change the crystal symmetry of the parent optically active compound. In this case, the *X*-ray diffraction data (*d* lines) (Table 3) of complexes (12) and (13) are distinctly different, suggesting that (12) ⟶ (13) does not involve racemisation. The optical activity of (11) could not be determined because of the lack of a suitably sized crystal.

and Woldbye[26] also found a mixed conformer to be the most stable conformation in calculations. When all the rings possess similar specific orientations Woldbye,[60] Snow and co-workers,[61,64] and Gollogly and Hawkins[24] predicted theoretically that the skew-boat conformation, *i.e.* $\delta\delta\delta$ for a particular absolute configuration of the tris(1,3-propanediamine) complex, should be lowest in energy. Hydrogen bonds[22] to amine protons also result in the existence of conformers (mixed or pure) in lower-energy states. It is evident[65,66] that intramolecular hydrogen bonds are responsible for powerful attractive forces capable of modifying or reversing normal conformational preferences. However, comparing the value of the enthalpy change (7.1 kJ mol^{-1}) for the transformation (12) → (13) with the total conformational energy of the skew boat (89.1 kJ mol^{-1}) and chair (82.8 kJ mol^{-1}) for $[M(pd)_3]$,[45] it may be inferred that the transformation (12) → (13) corresponds to the conversion of a chair conformation into a skew-boat form.

The i.r. spectrum (Table 2) of complex (13) after absorption of one molecule of water is similar to that of (11). The changes in the characteristic bands,[41–44] *i.e.* $\rho_r(CH_2)$ of (11)—(13) in the region 800—950 cm^{-1} (Table 2), suggest those of the methylene hydrogens reflect the increasing trend towards a staggered conformation, (13) > (11) > (12), also evident from the disappearance of the medium-intensity band of (11) and (12) at 1 130 cm^{-1}, in the case of (13). The higher degree of stagger of the CH_2 hydrogens in complex (13) is probably due to the symmetric skew-boat conformation formed after water absorption. It is reasonable that the presence of a water molecule in the crystal lattice would decrease the van der Waals interactions in a symmetric skew-boat, facilitating other interactions. As donor NH_2 groups of different rings interact more seriously[17] in the case of six- than five-membered rings, the presence of lattice water is probably the reason for the stability of the form (11). A comparison of the *d* lines at higher Bragg angles of complexes (11)—(13) indicates that a mixture of chair and skew-boat conformations may exist in (11). As a consequence, the extent of staggering of the CH_2 hydrogens lies between that in complexes (13) and (12). It seems, therefore, that dehydration and conformational change from skew-boat to chair run parallel in (11). The presence of a shoulder at 371 K in the d.t.a. curve (Figure 2) together with the absence of any inflection in the t.g. curve supports this.

References

1 R. Tsuchiya, K. Murari, A. Uehara, and E. Kyuno, *Bull. Chem., Soc. Jpn.*, **43**, 1383; S. Mitra, A. Uehara, and R. Tsuchiya, *Thermochim. Acta*, 1979, **34**, 189; R. Tsuchiya, A. Uehara, and Y. Muramatsu, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3770; R. Tsuchiya, A. Uehara, and T. Yoshikuni, *Inorg. Chem.*, 1982, **21**, 590.

2 J. Gazo, R. Boca, E. Jona, M. Kabesova, L. Macaskova, and J. Sima, *Coord. Chem. Rev.*, 1982, **43**, 87.

3 H. E. LeMay, jun., and J. C. Bailar, jun., *J. Am. Chem. Soc.*, 1968, **90**, 1729.

4 C. Kutul and J. C. Bailar, jun., *J. Phys. Chem.*, 1972, **76**, 119.

5 N. Serpone and D. G. Bickley, in 'Progress in Inorganic Chemistry,' ed. J. O. Edwards, Wiley, New York, 1972, vol. 17, p. 545.

6 P. O'Brien, *Polyhedron*, 1983, **2**, 233.

7 I. Grenthe, P. Paoletti, M. Sandstron, and S. Glikberg, *Inorg. Chem.*, 1979, **18**, 2687.

8 W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 463; R. Tsuchiya, S. Joba, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1454; Y. Ihara, E. Izumi, A. Uehara, R. Tsuchiya, N. Nakagawa, and E. Kyuno, *ibid.*, 1982, **55**, 1028.

9 P. Pfeiffer and H. Glaser, *J. Prakt. Chem.*, 1938, **151**, 134.

10 W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, 1963, **2**, 629 and refs. therein.

11 S. C. Nyburg, J. S. Wood, and W. C. E. Higginson, *Proc. Chem. Soc., London*, 1961, 297.

12 C. K. Ballhausen and A. D. Lehr, *J. Am. Chem. Soc.*, 1959, **81**, 538.

13 L. Katzin, *Nature (London)*, 1958, **182**, 1013.

14 S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 468.

15 I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. Anorg. Allg. Chem.*, 1939, **242**, 97; I. Lifschitz and J. G. Boz, *Recl. Trav. Chim. Pays-Bas*, 1940, **59**, 407.

16 A. M. Sargeson, 'Transition Metal Chemistry,' vol. 3, ed. R. L. Carlin, Marcel Dekker, New York, 1966, p. 303.

17 E. J. Corey and J. C. Bailar, jun., *J. Am. Chem. Soc.*, 1959, **81**, 2620.

18 J. R. Gollogly and C. J. Hawkins, *Aust. J. Chem.*, 1967, **20**, 2395.

19 J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168.

20 J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1970, **9**, 576.

21 Y. Saito, *Pure Appl. Chem.*, 1968, **17**, 21.

22 F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 2387.

23 P. G. Beddoe, M. J. Harding, S. F. Mason, and B. J. Peart, *Chem. Commun.*, 1971, 1283.

24 J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.

25 L. J. Dettayes and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1505.

26 S. R. Niketic and F. Woldbye, *Acta Chem. Scand.*, 1973, **27**, 621.

27 S. R. Niketic, K. Rasmussen, F. Woldbye, and S. Lifson, *Acta Chem. Scand., Ser. A*, 1976, **30**, 485.

28 J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, 1974, **13**, 977.

29 F. F-L. Ho and C. N. Reilley, *Anal. Chem.*, 1969, **41**, 1835.

30 F. F-L. Ho and C. N. Reilley, *Anal. Chem.*, 1970, **42**, 600.

31 F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, 1972, **11**, 3149.

32 J. K. Beattie, *Acc. Chem. Res.*, 1971, **4**, 253.

33 F. F-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, 1970, **9**, 1139.

34 R. F. Evilis, D. C. Young, and C. N. Reilley, *Inorg. Chem.*, 1971, **10**, 433.

35 C. J. Hawkins and J. A. Palmer, *Coord. Chem. Rev.*, 1982, **44**, 1.

36 A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 1965, 49; *J. Chem. Soc.*, 1965, 5094; A. J. McCaffery, S. F. Mason, B. J. Norman, and A. M. Sargeson, *J. Chem. Soc. A*, 1968, 1304.

37 M. Iwata, K. Nakatsu, and Y. Saito, *Acta Crystallogr., Sect. B*, 1969, **25**, 2562.

38 A. I. Vogel, 'A Text-Book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, Green, and Co., 1961, pp. 461, 467, 480, and 568.

39 N. F. Curtis and Y. M. Curtis, *Aust. J. Chem.*, 1966, **19**, 1423.

40 J. Bellanato, *An. R. Soc. Esp. Fis. Quim, Ser. B*, 1956, **52**, 363; S. Mizushima, I. Ichishima, I. Nakagawa, and J. V. Quagliano, *J. Phys. Chem.*, 1955, **59**, 293.

41 D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1959, 791.

42 M. E. Baldwin, *J. Chem. Soc.*, 1960, 4369.

43 M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 1521.

44 D. M. Sweeney, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, 1955, **77**, 6521.

45 C. J. Hawkins, 'Absolute Configuration of Metal Complexes,' Wiley-Interscience, New York, 1971, pp. 75, 89, 92, and 304.

46 J. V. Quagliano and S. Mizushima, *J. Am. Chem. Soc.*, 1953, **75**, 6084.

47 K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1957, **30**, 158.

48 Yu. I. Smolin, *Sov. Phys.-Crystallogr. (Engl. Transl.)*, 1970, **15**, 23.

49 J. C. Bailer, jun., and J. P. McReynolds, *J. Am. Chem. Soc.*, 1939, **62**, 3190.

50 Sister Mary Martinelte and J. C. Bailar, jun., *J. Am. Chem. Soc.*, 1952, **74**, 1054.

51 (*a*) R. D. Gillard and H. M. Irving, *Chem. Rev.*, 1965, **65**, 603; (*b*) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1959, 3083.

52 G. Newman and D. B. Powell, *J. Chem. Soc.*, 1961, 477; *Can. J. Chem.*, 1963, **51**, 1567.

53 P. K. Biswas and N. Ray Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 1981, 2376.

54 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 1640.

55 M. E. Fargo and J. M. James, *Inorg. Chem.*, 1965, **4**, 1706.

56 B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, 1963, **16**, 753.
57 M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, 1968, **13**, 644.
58 J. E. House, jun., and J. C. Bailar, jun., *J. Am. Chem. Soc.*, 1969, **91**, 67.
59 C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 1242.
60 F. Woldbye, 'Studies on Optical Activity,' Polyteknish Forlag, Copenhagen, 1969, p. 210.
61 R. J. Geue and M. R. Snow, *J. Chem. Soc. A*, 1971, 2981.
62 A. Sabatini and S. Califano, *Spectrochim. Acta*, 1960, **16**, 677.
63 D. B. Powell and N. Sheppard, *Spectrochim. Acta*, 1961, **17**, 70.
64 K. R. Butler and M. R. Snow, *Inorg. Chem.*, 1971, **10**, 1838.
65 L. P. Kuhn, *J. Am. Chem. Soc.*, 1952, **74**, 2492.
66 L. P. Kuhn, *J. Am. Chem. Soc.*, 1954, **76**, 4323.

Received 16*th February* 1983; *Paper* 3/242