Variable Geometry of Nickel(II) Complexes with N^1-Isopropyl-2-methyl-1,2-propanediamine(L). Crystal Structures of $[NiL_2]Br_2{\cdot}3H_2O$, $[NiL_2Br]Br$ and $[NiL_2(NCS)_2]$ and Solid-state Thermochromism in $[NiL_2]Br_2{\cdot}3H_2O$†

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The complexes $NiL_2X_2{\cdot}nH_2O$ (L = N^1-isopropyl-2-methylpropane-1,2-diamine; $n = 0$, X = Cl, NCS or Br; $n = 3$, X = Br) have been prepared and the crystal structures of $[NiL_2]Br_2{\cdot}3H_2O$ **2**, $[NiL_2Br]Br$ **3** and $[NiL_2(NCS)_2]$ **4** determined. The metal co-ordination in complex **2** is square planar (N_4 chromophore), whereas in **3** it is a distorted trigonal bipyramid with one of the bromine atoms and the two primary nitrogen atoms defining the basal plane, the secondary nitrogen atoms being in axial positions. Complex **4** is *trans* octahedral with a N_6 chromophore. The geometry of NiL_2Cl_2 **1** is proposed to be five-co-ordinate as in **3**. Complex **2**, on heating, undergoes an irreversible exothermic isomerisation after dehydration transforming into **3**, a unique example of a change from square-planar to trigonal-bipyramidal nickel(II), accompanied by a yellow to green thermochromism in the solid state.

One of the most prominent features of nickel(II) complexes is the large variability in their molecular geometry, *i.e.* four-co-ordinate (tetrahedral, square planar), five-co-ordinate (square pyramidal, trigonal bipyramidal) or six-co-ordinate (octahedral, trigonal prismatic).[1] With N- and/or C-substituted diamines square-planar or octahedral nickel(II) moieties are well documented but no five-co-ordinate nickel(II) complex has yet been reported. The square-planar complexes are preferred when bulky substituents are attached to the nitrogen atom of the diamine preventing any higher co-ordination of the metal centre.[2] On the other hand several C-substituted diamine complexes of nickel(II) exhibit solid-state yellow to green–blue thermochromism which has so far been ascribed to the square-planar to octahedral isomeric transformation mainly on the basis of spectral and magnetic data and are not supplemented by crystal structure analyses.[3-7] To study the effect of the substituents at the N and C atoms in the diamine on the structures of the resulting nickel(II) complexes the ligand N^1-isopropyl-2-methylpropane-1,2-diamine(L) was chosen and this paper reports the synthesis and structural characterisation of NiL_2X_2 (X = Cl, Br or NCS) together with the solid-state thermal square-planar to trigonal-bipyramidal transformation in the bromide complex. To our knowledge, the five-co-ordinate nickel(II) complex with a substituted diamine as a ligand and the square-planar to trigonal-bipyramidal transformation reported here are the first ever examples of this kind.

Experimental

All the chemicals used were of A.R. grade and high-purity N^1-isopropyl-2-methylpropane-1,2-diamine was purchased from Aldrich. The instruments used for recording the IR and electronic spectra (visible and near-IR regions) and for the thermal investigations [thermal gravimetric analysis (TGA) and differential thermal analysis (DTA)], elemental analyses and magnetic susceptibility measurements were as reported earlier.[8]

Synthesis of the Complexes.—$[NiL_2Cl]Cl$ **1**.—N^1-Isopropyl-2-methylpropane-1,2-diamine (10 mmol) was added dropwise to nickel(II) chloride (5 mmol) dissolved in ethanol–water (9 : 1, 10 cm^3) on stirring. The resulting yellow solution on slow evaporation in a desiccator yielded the desired green crystalline complex. The crystals were separated and washed with ethanol and dried in a desiccator (Found: C, 43.2; H, 9.2; N, 14.5; Ni, 14.9. Calc. for $C_{14}H_{36}Cl_2N_4Ni$: C, 43.1; H, 9.3; N, 14.4; Ni, 15.0%), μ_{eff} 3.3 μ_B, λ_{max} (Nujol) 1186, 637 and 392 nm.

$[NiL_2]Br_2{\cdot}3H_2O$ **2**. This complex was synthesised following the procedure adopted for complex **1** (Found: C, 31.5; H, 7.9; N, 10.6; Ni, 11.2. Calc. for $C_{14}H_{42}Br_2N_4NiO_3$: C, 31.6; H, 7.9; N, 10.5; Ni, 11.0%), diamagnetic, λ_{max} (Nujol) 457 nm. Recrystallisation from ethanol yielded yellow crystals suitable for X-ray analysis.

$[NiL_2Br]Br$ **3**. The same procedure as adopted for complex **1** resulted in the desired green crystalline complex using methanol instead of ethanol–water (Found: C, 35.0; H, 7.5; N, 11.8; Ni, 12.3. Calc. for $C_{14}H_{36}Br_2N_4Ni$: C, 35.2; H, 7.6; N, 11.7; Ni, 12.3%), μ_{eff} 3.3 μ_B, λ_{max} (Nujol) 1214, 648 and 397 nm. Recrystallisation from methanol yielded green crystals suitable for X-ray analysis.

$[NiL_2(NCS)_2]$ **4**. N'-Isopropyl-2-methylpropane-1,2-diamine (10 mmol) was added dropwise to nickel(II) isothiocyanate dissolved in ethanol (10 cm^3) on stirring. Fine blue crystals separated immediately from the resulting solution and were washed with ethanol and dried in a desiccator (Found: C, 44.2; H, 8.0; N, 19.2; Ni, 13.4. Calc. for $C_{16}H_{36}N_6NiS_2$: C, 44.1; H, 8.3; N, 19.3; Ni, 13.5%), μ_{eff} 3.1 μ_B, λ_{max}(Nujol) 990, 570

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.274\,02 \times 10^{-24}$ J T^{-1}.

Table 1 Crystallographic data for complexes **1**–**4**

	$[NiL_2Cl]Cl$ **1**	$[NiL_2]Br_2\cdot3H_2O$ **2**	$[NiL_2Br]Br$ **3**	$[NiL_2(NCS)_2]$ **4**
Molecular formula	$C_{14}H_{36}Cl_2N_4Ni$	$C_{14}H_{36}Br_2N_4Ni\cdot3H_2O$	$C_{14}H_{36}Br_2N_4Ni$	$C_{16}H_{36}N_6NiS_2$
M	390.09	533.03	478.98	435.33
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	*Pbna*	$P\bar{1}$	$P2_1/c$
a/Å	11.12(2)	11.376(6)	9.240(1)	8.6354(9)
b/Å	12.02(2)	16.997(9)	9.998(1)	12.1415(9)
c/Å	14.06(3)	24.392(15)	13.188(2)	11.0576(12)
α/°			110.61(1)	
β/°			108.77(1)	100.210(9)
γ/°			94.43(1)	
U/Å^3	1879(6)	4716(4)	1054.5(3)	1140.99(19)
Z	4	8	2	2
D_c/g cm^{-3}	1.38	1.501	1.509	1.267
$F(000)$		2208	492	468
Crystal size/mm		0.4 × 0.25 × 0.2	0.6 × 0.4 × 0.3	0.6 × 0.5 × 0.4
μ/mm^{-1}		4.2	5.8	2.98
Maximum, minimum transmission coefficients		1.00, 0.72	1.00, 0.78	1.00, 0.85
θ Range/°	2–30	1.5–25	2–60	1–64.8
No. of unique reflections		4141	2626	1860
No. of reflections used in refinement [$I > 3\sigma(I)$]		1664	2332	1633
$R1(F)$		0.0502	0.043	0.0594
$wR2(F^2)$		0.1032	0.111	0.1542
Weighting parameters A, B		0.059, 0.0	0.085, 1.74	0.073, 1.10
Goodness of fit		1.096	0.976	1.136
Highest peak in difference map/e Å^{-3}		0.65	0.95	0.75

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2 X-Ray powder diffraction data for $[NiL_2Cl]Cl$ **1**

d_{obs}/Å	d_{calc}/Å	$h\ k\ l$	I/I_0(%)
8.385	8.165	1 1 0	100
5.946	5.941	1 0 2	56
5.556	5.564	2 0 0	72
4.518	4.567	0 2 2	11
4.374	4.365	0 1 3	94
3.926	3.921	2 2 1	56
3.867	3.853	0 3 1	55
3.708	3.695	0 2 3	28
3.663	3.641	1 3 1	12
3.507	3.501	1 2 3	43
3.284	3.281	3 0 2	70
3.209	3.227	1 1 4	43
3.008	3.005	0 4 0	28
2.876	2.879	3 2 2	7
2.780	2.782	4 0 0	19
2.618	2.618	3 2 3	17
2.553	2.551	3 0 4	37
2.488	2.485	4 2 1	33
2.436	2.456	2 1 5	15
2.332	2.335	3 0 4	40
2.241	2.240	3 0 5	20
2.178	2.181	4 0 4	11
2.156	2.152	3 3 4	15
2.099	2.099	3 2 5	19
2.036	2.032	2 2 6	11
1.985	1.985	0 5 4	16
1.884	1.881	3 2 6	30
1.833	1.833	6 1 0	13
1.759	1.761	4 5 2	11

and 355 nm. The recrystallisation was from hot acetonitrile yielding blue crystals suitable for X-ray analysis.

X-Ray Data Collection and Structure Refinement.—Since all attempts to synthesise suitable single crystals failed, complex **1** was examined by X-ray powder diffraction. Accurate d_{hkl} spacings (Å) were obtained from the powder pattern recorded on a Philips XRD diffractometer (PW 1730/1710) at 22 °C operating at 40 kV and 20 mA with 2° min^{-1} scan rate. The results are summarised in Tables 1 and 2.

A single crystal of complex **2** was mounted on a Nicolet R3m/V diffractometer, while crystals of complexes **3** and **4** were mounted on an Enraf–Nonius CAD-4 diffractometer. Lattice constants were determined by least-squares refinement of angular settings of 20 reflections for **2** and 25 for **3** and **4**; crystal data are summarised in Table 1.

Intensity data were collected using Mo-Kα radiation (λ = 0.710 73 Å) for complex **2** and Cu-Kα radiation (λ = 1.5418 Å) for complexes **3** and **4**, with the ω–2θ scan technique. All data were corrected for Lorentz and polarisation effects. An absorption correction[9] was applied, based on the empirical ψ-scan method, in all cases. The structures were solved by Patterson techniques followed by Fourier syntheses and refined through full-matrix least-squares calculations. Anisotropic refinements were carried out for the non-hydrogen atoms. The hydrogen atoms in complex **2** were introduced in the final structure-factor calculation in calculated positions (H atoms belonging to the solvent molecules from the difference map), in complexes **3** and **4** the hydrogen atoms were located in electron-density maps and treated as fixed contributors. Complex neutral-atom scattering factors[10] were used throughout. All calculations were carried out on a VAX 3400 computer of the Computer Center, Indian Association for the Cultivation of Science, using SHELX 76,[11] SHELXS 86,[12] SHELXL 93,[13] PARST[14] and ORTEP II[15] programs. The final fractional coordinates, selected bond distances and angles of complexes **2**–**4** are listed in Tables 3–7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Thermochromism of $[NiL_2]Br_2\cdot3H_2O$ **2**.—On heating, $[NiL_2]Br_2\cdot3H_2O$ loses its water molecules and changes colour from yellow to green at *ca.* 130 °C. This change in colour can also be achieved by keeping complex **2** in a desiccator (P_4O_{10})

Table 3 Fractional atomic coordinates for $[NiL_2]Br_2\cdot3H_2O$ **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Br(1)	0.119 90(13)	0.678 35(8)	0.221 62(5)
Br(2)	0.786 79(11)	0.430 21(8)	0.451 69(5)
Ni	0.268 89(11)	0.544 62(7)	0.378 89(5)
N(1)	0.230 9(7)	0.458 5(5)	0.425 5(3)
N(2)	0.379 3(7)	0.473 8(4)	0.343 3(3)
N(3)	0.318 1(7)	0.635 2(5)	0.337 8(3)
N(4)	0.160 5(7)	0.615 0(5)	0.416 0(3)
O(1)	0.032 4(7)	0.369 7(5)	0.386 5(4)
O(2)	0.398 1(7)	0.039 3(6)	0.373 9(4)
O(3)	0.401 5(8)	0.759 6(5)	0.195 2(4)
C(1)	0.329 4(10)	0.399 3(6)	0.425 5(5)
C(2)	0.289 1(10)	0.319 7(6)	0.445 8(5)
C(3)	0.427 9(11)	0.431 7(7)	0.460 2(5)
C(4)	0.361 5(9)	0.392 4(6)	0.365 4(4)
C(5)	0.377 2(11)	0.475 4(6)	0.281 0(4)
C(6)	0.257 2(11)	0.466 9(7)	0.258 6(5)
C(7)	0.463 3(10)	0.413 8(6)	0.259 0(4)
C(8)	0.297 9(10)	0.705 8(6)	0.372 5(4)
C(9)	0.308 9(11)	0.781 2(6)	0.338 7(5)
C(10)	0.389 2(11)	0.705 3(6)	0.418 5(5)
C(11)	0.174 8(10)	0.696 8(6)	0.394 5(4)
C(12)	0.035 0(10)	0.587 3(6)	0.417 1(5)
C(13)	−0.044 8(11)	0.644 4(7)	0.447 6(5)
C(14)	−0.010 8(10)	0.569 8(6)	0.359 8(5)

Table 4 Fractional atomic coordinates for $[NiL_2Br]Br$ **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Br(1)	0.700 65(6)	0.450 64(6)	0.401 36(4)
Br(2)	−0.005 19(7)	0.244 81(6)	−0.010 48(4)
Ni	0.103 52(9)	0.353 57(8)	0.207 07(6)
N(1)	0.298 0(4)	0.332 7(4)	0.326 4(3)
N(2)	−0.002 0(4)	0.154 1(4)	0.205 7(3)
N(3)	0.028 5(4)	0.493 8(4)	0.326 0(3)
N(4)	0.208 5(5)	0.551 9(4)	0.206 4(3)
C(1)	0.281 5(6)	0.176 8(5)	0.311 7(4)
C(2)	0.395 5(8)	0.163 1(6)	0.418 8(5)
C(3)	0.315 9(7)	0.092 8(6)	0.204 3(5)
C(4)	0.114 3(6)	0.125 2(5)	0.298 4(4)
C(5)	−0.160 2(6)	0.141 7(6)	0.214 0(5)
C(6)	−0.221 7(8)	−0.004 5(7)	0.211 5(7)
C(7)	−0.275 3(6)	0.172 7(7)	0.117 9(5)
C(8)	0.029 6(6)	0.634 6(5)	0.312 2(4)
C(9)	0.024 2(8)	0.755 7(6)	0.419 4(5)
C(10)	−0.111 3(7)	0.610 8(6)	0.203 8(5)
C(11)	0.183 7(6)	0.672 2(5)	0.297 7(4)
C(12)	0.374 0(6)	0.571 9(5)	0.213 8(5)
C(13)	0.392 7(6)	0.445 0(7)	0.118 1(5)
C(14)	0.433 3(7)	0.717 4(7)	0.212 6(7)

for several weeks. The complexes **1**, **3** and **4** do not show any colour changes until they decompose.

Thermal Analysis.—The results of simultaneous TGA–DTA for complex **2** are shown in Fig. 1. The weight loss observed in the TGA curve and the corresponding endothermic peak are due to the liberation of three water molecules. A sharp exothermic peak overlapped with the preceding endotherm in the DTA curve, appearing just after the cessation of weight loss in the TGA curve, is attributable to the yellow to green colour change. Synthesis of the anhydrous yellow complex by heating is extremely difficult as a part of it usually transforms to the green complex **3**.* However, this partial transformation can be avoided if deaquation is carried out at ambient temperature under high vacuum (0.01 mmHg ≈ 1.33 Pa) for 10 min. The anhydrous species thus obtained is yellow and is metastable. It transforms to the green complex **3** on keeping in a desiccator for several hours, and in open atmosphere it reverts to **2** absorbing three molecules of water. Thermal analysis of the anhydrous species shows the exothermic peak at *ca.* 144 °C in the DTA curves without any mass loss in the corresponding TGA curve. The DTA and TGA curves of chloro **1** and isothiocyanato **4** complexes remain flat until their decomposition at 218 and 210 °C respectively.

Table 5 Fractional atomic coordinates for $[NiL_2(NCS)_2]$ **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ni	1	0	1
S	1.2534(2)	0.1111(1)	0.6609(1)
N(1)	1.1289(4)	0.0521(3)	0.8664(3)
N(2)	0.8700(4)	−0.0992(3)	0.8603(3)
N(3)	0.8088(4)	0.1109(3)	0.9385(4)
C(1)	1.1806(4)	0.0771(3)	0.7809(3)
C(2)	0.7199(5)	−0.0464(4)	0.8003(4)
C(3)	0.5895(5)	−0.0866(4)	0.8665(5)
C(4)	0.6821(6)	−0.0768(5)	0.6651(4)
C(5)	0.7462(5)	0.0781(4)	0.8128(5)
C(6)	0.8245(6)	0.2321(4)	0.9637(6)
C(7)	0.6778(9)	0.2869(6)	0.9689(9)
C(8)	0.9190(7)	0.2882(4)	0.8786(6)

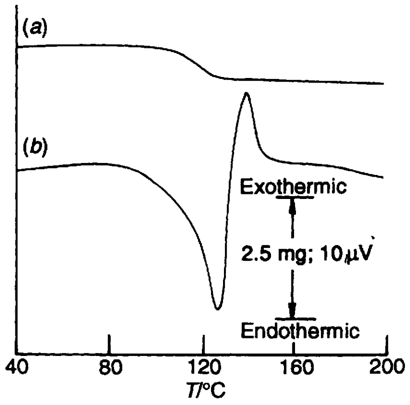

Fig. 1 TGA (*a*) and DTA (*b*) curves for complex **2** (weight taken = 11.50 mg)

Electronic Spectra and Magnetic Moments.—The yellow complex **2** is diamagnetic and its electronic spectrum (Nujol) shows a relatively strong band at *ca.* 457 nm (Fig. 2) indicating the square-planar geometry of the nickel(II).[5] The electronic spectrum and magnetic moment of the anhydrous yellow species were measured as quickly as possible after deaquation under vacuum and the results suggest a square-planar geometry similar to the parent complex **2**. Complex **4** is paramagnetic and its electronic spectrum (Nujol) is characteristic of octahedral nickel(II) (Fig. 2). The ratio ν_2/ν_1 (where ν_1 is assigned to $^3A_{2g} \longrightarrow {}^3T_{2g}$ and the second main peak, ν_2, $^3A_{2g} \longrightarrow {}^3T_{1g}$) is 1.74 for complex **4**, which corroborates the octahedral geometry. From the electronic spectra (Nujol) of complexes **1** and **3** (Fig. 2) it is not clear whether the complexes are *trans* octahedral or five-co-ordinate. The ν_2/ν_1 ratio of 1.86 and 1.87 respectively for complexes **1** and **3** suggests the possibility of five-co-ordinate geometry.[16–20] However, several chloride and bromide complexes of other diamines obtained *via* similar thermochromic transformation have been reported to possess *trans*-octahedral geometry,[21,22] although the ν_2/ν_1 ratio is calculated to be *ca.* 2.0.

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* Comparison of the X-ray powder diffraction patterns, magnetic moments, IR and electronic spectra revealed that the green species obtained after the exothermic phase transition of complex **2** was identical to $[NiL_2Br]Br$ **3**.

Table 6 Selected bond distances (Å) and angles (°) for $[NiL_2]Br_2{\cdot}3H_2O$ **2** and $[NiL_2Br]Br$ **3**

	2	3		2	3
Ni–Br(2)	—	2.491(1)	N(1)–C(1)	1.506(13)	1.491(7)
Ni–N(1)	1.904(8)	2.054(4)	N(2)–C(4)	1.498(13)	1.478(7)
Ni–N(2)	1.945(8)	2.143(4)	N(2)–C(5)	1.519(13)	1.500(8)
Ni–N(3)	1.921(8)	2.051(4)	N(3)–C(8)	1.486(12)	1.482(7)
Ni–N(4)	1.942(8)	2.143(5)	N(4)–C(11)	1.495(13)	1.466(6)
N(4)–C(12)	1.503(14)	1.494(7)			
Br(2)–Ni–N(1)	—	131.6(1)	Br(2)–Ni–N(2)	—	89.6(1)
Br(2)–Ni–N(3)	—	131.7(1)	Br(2)–Ni–N(4)	—	89.8(1)
N(1)–Ni–N(2)	86.4(3)	83.4(2)	N(1)–Ni–N(3)	174.0(4)	96.7(2)
N(1)–Ni–N(4)	92.9(4)	96.9(2)	N(2)–Ni–N(3)	94.3(3)	97.2(2)
N(2)–Ni–N(4)	178.7(4)	179.3(1)	N(3)–Ni–N(4)	86.3(4)	83.3(2)
Ni–N(1)–C(1)	110.2(6)	109.1(3)	Ni–N(2)–C(4)	108.9(6)	106.5(3)
Ni–N(3)–C(8)	107.8(6)	109.7(3)	Ni–N(4)–C(11)	109.8(6)	106.3(3)
N(1)–C(1)–C(4)	103.4(8)	106.5(4)	N(2)–C(4)–C(1)	108.0(8)	112.0(4)
N(3)–C(8)–C(11)	105.3(8)	106.0(4)	N(4)–C(11)–C(8)	108.8(8)	112.9(4)

Table 7 Selected bond distances (Å) and angles (°) for $[NiL_2(NCS)_2]$ **4**

Ni–N(1)	2.098(4)	Ni–N(2)	2.117(3)
Ni–N(3)	2.146(4)	N(1)–C(1)	1.156(6)
S–C(1)	1.619(4)	N(2)–C(2)	1.492(5)
N(3)–C(5)	1.454(6)	N(3)–C(6)	1.499(6)
N(1)–Ni–N(2)	86.4(1)	N(1)–Ni–N(3)	93.6(1)
N(2)–Ni–N(3)	81.2(1)	Ni–N(1)–C(1)	170.2(3)
N(1)–C(1)–S	179.5(4)	Ni–N(2)–C(2)	112.8(3)
Ni–N(3)–C(5)	105.4(3)	N(2)–C(2)–C(5)	106.3(3)
N(3)–C(5)–C(2)	112.3(4)		

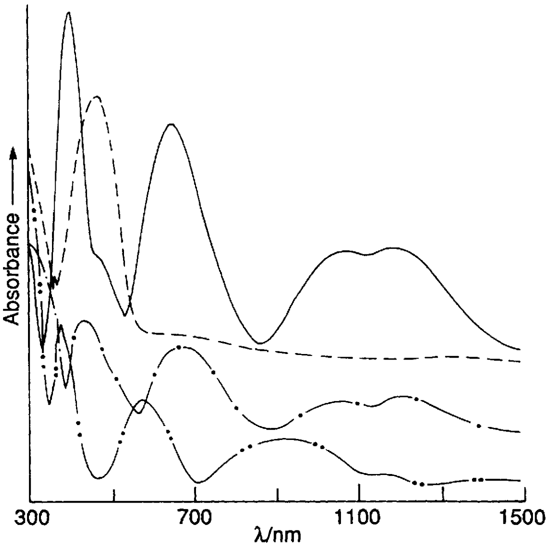

Fig. 2 Electronic spectra (Nujol) of $[NiL_2Cl]Cl$ **1** (——), $[NiL_2]Br_2{\cdot}3H_2O$ **2** (– – –), $[NiL_2Br]Br$ **3** (— · — · —) and $[NiL_2(NCS)_2]$ **4** (— ·· — ·· —)

Complexes **1**–**3** are soluble in water and methanol–ethanol. The solutions are yellow and the electronic spectra of the aqueous solutions show a single band at *ca.* 450 nm with absorption coefficients 66, 56 and 54 l mol^{-1} cm^{-1} for complexes **1**–**3** respectively, characteristic of square-planar nickel(II). Complex **4** is soluble in hot acetonitrile giving rise to a blue solution. The appearance of three bands at *ca.* 990, 580 and 350 nm having absorption coefficients 10, 11 and 160 l mol^{-1} cm^{-1} respectively in the electronic spectra indicates that the octahedral structure of **4** is retained in solution. The intensity (ε = 160 l mol^{-1} cm^{-1}) of the band appearing at 350 nm is affected by overlap by the charge-transfer transition of the acetonitrile.

Structures of $[NiL_2]Br_2{\cdot}3H_2O$ **2** *and* $[NiL_2Br]Br$ **3**.—The structure of complex **2** consists of monomeric units of $[NiL_2]^{2+}$ cations, bromide anions and lattic water molecules (Fig. 3), while that of complex **3** contains $[NiL_2Br]^+$ cations and bromide anions (Fig. 4). The Ni–N distances range between 1.904(8) and 1.945(8) Å in **2** [2.051(4)–2.143(5) Å in **3**] and the observed shortening of the metal–nitrogen (primary) bonds compared to the metal–nitrogen (secondary) bonds [*ca.* 0.03 in **2** and 0.08 Å in **3**] is in agreement with the corresponding values for other complexes of this diamine.[23,24] The nickel atom in complex **2** shows a square-planar *trans* co-ordination arising from the N_4 donor set of the two bidentate N^1-isopropyl-2-methylpropane-1,2-diamine ligands. The metal atom deviates by 0.058(2) Å from the least-squares plane through the four ligand nitrogen atoms and the N–Ni–N angles are within ±4.3° of the expected value (90°) for ideal square-planar symmetry. Contrary to reports on similar systems where six co-ordination (4 + 2) of the metal is attained *via* lattice solvent molecules, the water molecules in complex **2** prevent the co-ordination of bromide ions to the nickel(II) atom. The closest Ni···Br distance in complex **2** is Ni···Br(2) 4.203(3) Å. The co-ordination polyhedron of the metal atom in complex **3** is best described as a distorted trigonal bipyramid (Fig. 4) with Br(2) and two primary nitrogen atoms [N(1), N(3)] defining the basal plane [Ni atom 0.001(1) Å away] and secondary nitrogen atoms [N(2) and N(4)] in axial positions. The in-plane distortion in **3** is due to the asymmetric nature of the ligand atoms (Br, N) and is reflected by significant deviations in the angles formed by the basal plane atoms at the metal centre [96.7(2)–131.7(1)°] from 120°. The five-membered chelate rings in both the complexes are in the form of open envelopes with C(1) and C(8) atoms on the flaps. The dihedral angles between the planes through Ni, N(1), N(2), C(4) and Ni, N(3), N(4), C(11) for complexes **2** and **3** are 4.8 and 83.5° respectively. A three-dimensional network of hydrogen bonds involving water molecules, amine nitrogen atoms and bromide ions stabilises the crystal packing in **2** {shortest H bond N(2)–H[N(2)]···O(2) 2.87(1) Å}. In **3** the primary nitrogen atoms N(1) and N(3) are hydrogen bonded to the unco-ordinated bromide ion {N(1)–H[N(1B)]···Br(1) 3.475(4) and N(3)–H[N(3B)]···Br(1) 3.476(4) Å}. The transformation of the metal co-ordination sphere from square planar to trigonal bipyramidal (**2**→**3**) can be visualised as follows. The dehydration of complex **2** releases the amine N atoms from the hydrogen-bonding network, and that subsequent addition of the bromide ion which pushes the primary N atoms closer together completes the geometrical transformation. In this process the relative disposition of the two chelate rings from a near coplanarity (in complex **2**) to an approximate ortho-

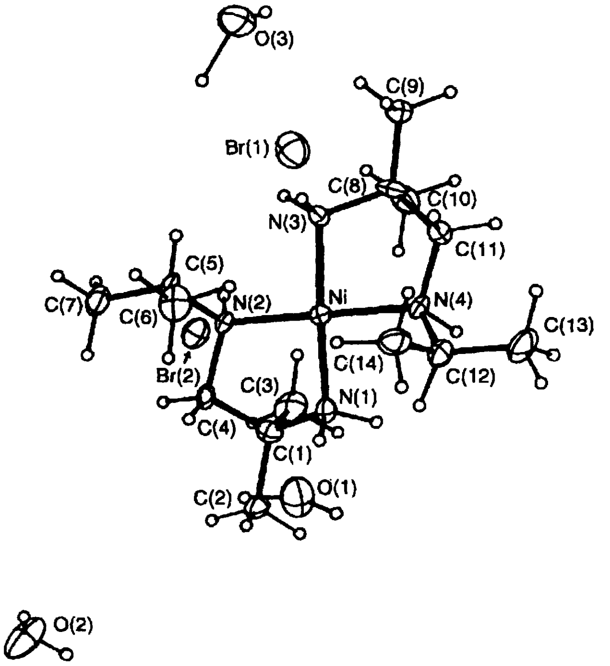

Fig. 3 ORTEP[15] view of $[NiL_2]Br_2 \cdot 3H_2O$ **2**

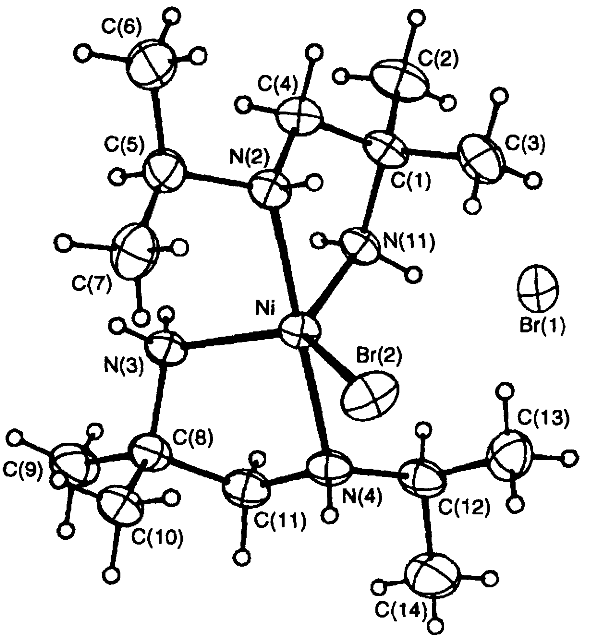

Fig. 4 ORTEP[15] view of $[NiL_2Br]Br$ **3**

gonality (in complex **3**) has changed in such a way that the N(1)–Ni–N(3) angle in **3** assumes a value of 96.7(2)° compared to 174.0(4)° in **2**. The N(2)–Ni–N(4) angle remains practically unaltered [179.3(1) in **3** and 178.7(4)° in **2**]. The configurations at the N(2), N(4) chiral centres in both the complexes are *S*,*S* respectively; the enantiomers are also present since the space groups are centrosymmetric. The conformations of the diamine chelate rings are δδ (λλ).

Structure of $[NiL_2(NCS)_2]$ **4**.—The nickel atom is octahedrally co-ordinated in which the four N atoms of two bidentate N^1-isopropyl-2-methylpropane-1,2-diamine molecules define an equatorial plane and the two isothiocyanato groups co-ordinate in *trans* axial positions (Fig. 5). In-plane distortion is introduced by a ligand bite angle N(2)–Ni–N(3) 81.2(1)°. The five-membered chelate ring displays an open-envelope geometry with the C(5) atom, on the flap, 0.604(5) Å away from the least-squares plane through the remaining endocyclic atoms. The bond distances and angles are consistent with similar systems.[25] The conformation of the diamine chelate rings is δλ as the molecule has a centre of inversion. The crystal packing is determined by van der Waals forces.

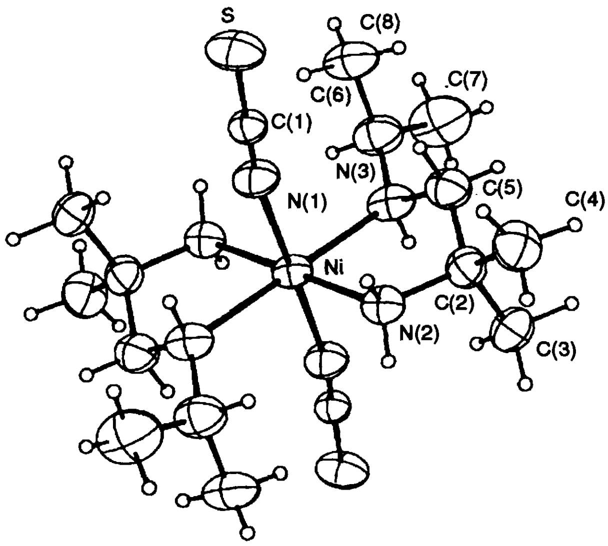

Fig. 5 ORTEP[15] view of $[NiL_2(NCS)_2]$ **4**

Conclusion

N^1-Isopropyl-2-methylpropane-1,2-diamine forms square-planar four-co-ordinate and trigonal-bipyramidal five-co-ordinate complexes with nickel(II) bromide. The square-planar complex is stabilised in the solid state by lattice water molecules or in solution, whereas the five-co-ordinate complex exists only as an anhydrous compound. On deaquation the square-planar complex became metastable and transformed to the five-co-ordinate complex giving rise to the yellow to green thermochromism in the solid phase. The isothiocyanato complex, however, exists only as a six-co-ordinate, octahedral complex in the solid state as well as in solution. The smaller size of the co-ordinating atom (N) and the higher ligand field of the isothiocyanate ion (NCS^-) compared to the chloride or bromide ion are sufficient to overcome the steric hindrance caused by the bulky diamines in accommodating both the NCS^- anions in the *trans* positions.

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