Thermal Investigations of 1,4-Butanediamine Complexes of Nickel(II) in the Solid Phase

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(Received December 8, 1983)

$[NiL_3]Cl_2 \cdot H_2O$, $[NiL_2(H_2O)_2]Br_2$, and $[NiL_2(NCS)_2]$ (L=1,4-butanediamine) have been synthesized and their thermal investigations have been carried out. $[Ni_2L_3Cl_4]$, $[NiLCl_2]$, $[Ni_4L_3Br_8]$, and $[NiL(NCS)_2]$ have been synthesized pyrolytically in solid phase by temperature arrest technique from their corresponding parent diamine complexes. All the parent tris and bis(diamine)complexes possess O_h geometry. $[NiLCl_2]$ possesses T_d geometry, whereas, $[NiL(NCS)_2]$ possesses O_h though 1,4-butanediamine is chelated in both of these mono-(diamine) complexes. Thiocyanate is found to be bridged in $[NiL(NCS)_2]$. The probable mechanistic paths of decomposition of these diamine complexes have been propsoed.

Chelating and bridging bidentate character of 1,4-butanediamine (L) in metal complexes are well documented in literature.[1-3] Metal complex having unidentate diamine is also known.[4] Synthesis of $[NiL_3]^{2+}$ is not yet reported. But tris chelate complexes like $[CoL_3]^{3+}$ are known, where L attains seven-membered chelate rings and possesses chair conformations.[5,6] Recently, some 1,4-butanediamine complexes are being used for the preparation of macrocyclic complexes.[7]

We have recently reported a series of thermal investigations of metal 1,2-ethanediamine and 1,3-propanediamine complexes in the solid phase.[8-12] In these investigations we synthesized a good number of novel metal diamine complexes. Besides these, thermally induced structural and conformational changes in nickel(II) diamine complexes were observed by us.[13]

The purpose of this paper is to report the thermochemical studies of nickel diamine complexes having seven-membered chelate rings and to compare their decomposition patterns with those of five and six-membered chelate complexes.

Experimental

The metal salts used were all of A.R. grade purity. 1,4-Butanediamine was supplied from Fluka AG, Switzerland.

Preparation: $[NiL_3]Cl_2 \cdot H_2O$ (**1**), $[NiL_2(H_2O)_2]Br_2$ (**2**), and $[NiL_2(NCS)_2]$ (**3**).

1,4-Butanediamine (L) (3—4 mmol) was added to the ethanolic solution of nickel salt (1 mmol) dropwise with stirring. On mixing immediate separation of complex took place. The resulting heterogeneous mixture was stirred for ≈10 h and the desired complexes were collected by filtration, washed thoroughly with ethanol and dried over fused $CaCl_2$ desiccator.

$[Ni_2L_3Cl_4]$ (**1A**): This was synthesized by keeping the complex (**1**) at ≈185 °C in a nitrogen atmosphere. The thermolysis was stopped when no more diamine was lost as evident by getting a constant weight.

$[NiLCl_2]$ (**1B**): This was synthesized following the method adopted for the synthesis of complex (**1A**) from complex (**1**) at ≈245 °C.

$[NiL_2Br_2]$ (**2A**): This was synthesized by heating the complex (**2**) upto ≈135 °C.

$[Ni_4L_3Br_8]$ (**2B**): This was synthesized from complex (**2**) at ≈260 °C by the similar procedure to that adopted for the synthesis of complex (**1A**).

$[NiL(NCS)_2]$ (**3A**): This was also synthesized from complex (**3**) at ≈235 °C by the similar procedure to that adopted for the synthesis of complex (**1A**).

Molar conductance data of these complexes could not be taken since these complexes decompose in water and are insoluble in all the available solvents.

Analytical, spectral band maxima and magnetic data are shown in Table 1.

The apparatus employed for carrying out thermal analysis is the same as reported earlier.[8,9] Table 2 lists the thermal

Table 1. Analytical, magnetic and electronic spectral data of Ni^{II} 1,4-butanediamine(L) complexes

Compound		Color	Elemental analyses/%[a]			μ_{eff} (B.M.)	λ_{max} (nm)
			Nickel	Nitrogen	Halogen/Sulfur		
$[NiL_3]Cl_2 \cdot H_2O$	(**1**)	Blue	14.3(14.2)	20.5(20.4)	17.0(17.2)	3.32	600, 370
$[Ni_2L_3Cl_4]$[b]	(**1A**)	Green	22.3(22.4)	16.1(16.0)	26.9(27.1)	3.29	670, ≈470(sh), 400
$[NiLCl_2]$[b]	(**1B**)	Greenish yellow	26.9(26.9)	12.9(12.8)	32.2(32.6)	3.50	680, ≈530(sh), ≈440(sh), 400
$[NiL_2(H_2O)_2]Br_2$	(**2**)	Light blue	13.6(13.6)	12.9(13.0)	36.7(37.1)	3.20	580, 365
$[NiL_2Br_2]$[b]	(**2A**)	Light blue	14.8(14.8)	14.2(14.1)	40.2(40.5)	3.22	580, 364
$[Ni_4L_3Br_8]$[b]	(**2B**)	Greenish yellow	20.5(20.6)	7.3(7.3)	56.0(56.1)	3.56	≈740(sh), 685, ≈520(sh), ≈460(sh), 405
$[NiL_2(NCS)_2]$	(**3**)	Light blue	16.7(16.7)	23.9(23.9)	18.0(18.2)	3.23	580, 370
$[NiL(NCS)_2]$[b]	(**3A**)	Blue black	22.3(22.3)	21.1(21.3)	24.2(24.3)	3.16	≈710(sh), 580 ≈470(sh), 350

a) Figures in parentheses are the calculated values. b) Compounds synthesized in the solid state.

Table 2. Thermal parameters of Ni^{II} 1,4-butanediamine(L) complexes

Decomposition reaction	Temperature range/°C	DTA peak temperature/°C	
		Endo	Exo
$[NiL_3]Cl_2 \cdot H_2O \rightarrow [NiL_3]Cl_2$	50— 85	80	—
$[NiL_3]Cl_2 \rightarrow [NiL_2Cl_2]$	135—185	180	—
$[NiL_2Cl_2] \rightarrow [Ni_2L_3Cl_4]$	185—205	200	—
$[Ni_2L_3Cl_4] \rightarrow [NiLCl_2]$	215—245	240	—
$[NiLCl_2] \rightarrow [Ni_2LCl_4]$	285—315	—	314
$[Ni_2LCl_4] \rightarrow NiCl_2$	315—375	—	335, 360
$[NiL_2(H_2O)_2]Br_2 \rightarrow [NiL_2Br_2]$	75—130	105, 120	—
$[NiL_2Br_2] \rightarrow [Ni_4L_3Br_8]$	155—260	178, 202, 250	—
$[Ni_4L_3Br_8] \rightarrow NiBr_2$	275—345	—	284, 312 332, 340
$[NiL_2(NCS)_2] \rightarrow [NiL(NCS)_2]$	175—230	224	—
$[NiL(NCS)_2] \rightarrow Ni(SCN)_2$	280—340	—	270, 280

data.

Infrared spectra in KBr (4000—400 cm^{-1}) and in polythene discs (400—250 cm^{-1}, in some cases) were recorded using a Beckman IR-20A and Perkin-Elmer 597 IR spectrophotometers respectively and the corresponding data were given in Table 3.

Results

$[NiL_3]Cl_2 \cdot H_2O$ (**1**) becomes anhydrous at 85 °C (Fig. 1, Table 2) showing an endothermic peak at 80 °C. The blue-colored anhydrous species starts decomposition at 135 °C and transforms to $[Ni_2L_3Cl_4]$ at 205 °C through the formation of nonisolable intermediate, $[NiL_2Cl_2]$. The derived $[Ni_2L_3Cl_4]$ on further heating results $[NiLCl_2]$ at 245 °C. The unis(diamine) species is stable upto 285 °C and then decomposes to $NiCl_2$ through the formation of nonisolable intermediate, $[Ni_2LCl_4]$ at 315 °C. DTA curve shows three endotherms for the elimination of first two moles of diamine and three exotherms for the elimination of residual diamine.

$[NiL_2(H_2O)_2]Br_2$ (**2**) starts deaquation (Fig. 2, Table 2) at 75 °C and becomes deaquated completely at 130 °C showing two overlapping endotherms in the DTA profile. The deaquated species starts deamination at 155 °C and transforms to $[Ni_4L_3Br_8]$ at 260 °C, through the formation of nonisolable intermediates. The derived $[Ni_4L_3Br_8]$ starts decomposition at 275 °C and transforms to $NiBr_2$ at 345 °C. The corresponding DTA curve shows three endotherms for elimination of 1.25 mole of diamine and four exotherms overlapping to each other for the elimination of residual diamine.

$[NiL_2(NCS)_2]$ starts deamination (Fig. 2, Table 2) at 175 °C and generates thermally stable $[NiL(NCS)_2]$ at 230 °C. Unis(diamine) species starts decomposition at 280 °C and transforms to $Ni(SCN)_2$ at 340 °C. The DTA curve shows initially an endotherm followed by an exotherm for the elimination of first molecule of diamine. It shows two overlapping exotherms for the elimination of last molecule of diamine.

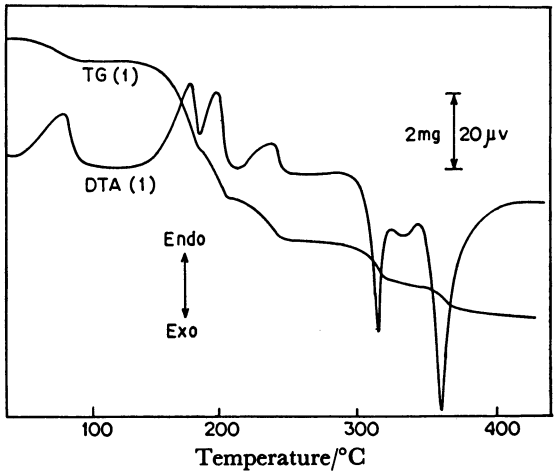


Fig. 1. Thermal curves of $[NiL_3]Cl_2 \cdot H_2O$ (**1**) sample mass, 11.60 mg.

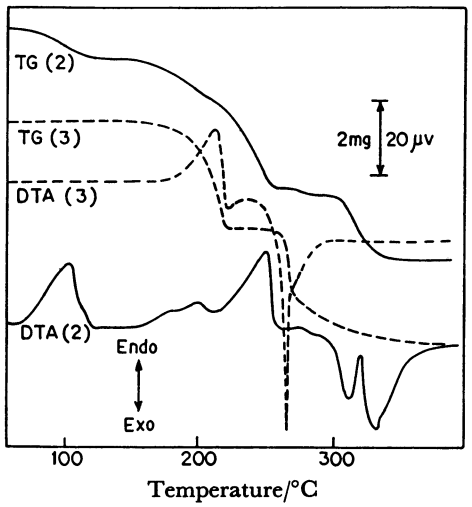


Fig. 2. Thermal curves of $[NiL_2(H_2O)_2]Br_2$ (**2**) (——), sample mass 12.86 mg and $[NiL_2(NCS)_2]$ (**3**) (- - -), sample mass 11.50 mg.

Discussion

Possession of bands at 3300, 3245, 3220, and 3140 cm^{-1} due to $\nu(NH_2)$ and at 2945, 2940, 2860, and 2850 cm^{-1} due to $\nu(CH_2)$ in IR spectrum (Table 3) of $[NiL_3]Cl_2 \cdot H_2O$ (**1**) is well consistent with chela-

Table 3. IR Spectral data (cm^{-1}) of Ni^{II} 1,4-butanediamine(L) complexes in KBr

Compound	Assignments										
	$\nu(NH_2)$	$\nu(CH_2)$	$\nu(CN)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2)+\rho_w(NH_2)+\tau(CH_2)$	Stretching Vibrations of skeleton $\nu(C-N)+\nu(C-C)$	$\rho_r(CH_2)$	$\nu(CS)/\rho_r(H_2O)$	$\rho_r(CH_2)+\nu(M-N)$
$[NiL_3]Cl_2\cdot H_2O$[a]	3300m, 3245sh, 3220 s, 3140ms	2945ms, 2940ms, 2860m, 2850m	—	1595 s, 1550 sh	1458m, 1440w, 1435sh	1370 sh, 1360 mbr	1260m, 1250 sh, 1220vw, 1176m, 1145 s	1118 s, 1090w, 1065 sh, 1030 s	950 s, 920w, 730w	—	590sbr
$[Ni_2L_3Cl_4]$	3315w, 3265 s, 3230 s, 3180sh, 3140m	2945m, 2920sh, 2910m, 2865m, 2845m	—	1590 s, 1575sh, 1550sh	1470sh, 1452m, 1445sh, 1435sh	1395w, 1385w, 1362w	1335vw, 1306vw, 1250vw, 1215m, 1182m, 1158ms	1125m, 1110sh, 1092 s, 1068m, 1045 s, 1030m, 1010 s, 990sh, 965sh	950m, 920vw, 825vw, 730w	—	630sh, 600sbr
$[NiLCl_2]$	3295m, 3250 s, 3200sh, 3160w	2975w, 2935w, 2930m, 2890w, 2862vw	—	1590 s, 1550sh	1460m, 1450sh	1360m, 1355w	1270sh, 1175 s, 1132vs	1112sh, 1050sh, 1040 s	958 s, 720w	—	645w, 580sh, 550 s
$[NiL_2(H_2O)_2]Br_2$[b]	3330sh, 3296 s, 3277sh, 3240 s, 3160m	2975m, 2950m, 2930m, 2890w, 2880sh, 2860m	—	1592 s, 1565m, 1545m, 1532sh, 1500mbr	1472sh, 1462m, 1450w, 1435m	1390sh, 1380m, 1347m	1320sh, 1290w, 1255m, 1235vw, 1220vw, 1200w, 1172m, 1135 s	1110m, 1105sh, 1090m, 1056w, 1045w, 1010 s, 995 s, 967m	952m, 940w, 905w, 895w, 855vw, 842vw, 815w, 800w, 755sh, 740sh	710w	650vw, 618ms, 560m
$[NiL_2Br_2]$	3340vw, 3280w, 3230 s, 3160m	2970sh, 2940m, 2920m, 2890sh, 2880m, 2855sh	—	1585 s, 1575m, 1562sh, 1540m, 1530w, 1500mbr	1480sh, 1460sh, 1450m, 1445sh, 1430w	1390sh, 1375m, 1860m, 1345sh	1335w, 1310sh, 1255wbr, 1215m, 1188 s, 1145sh, 1140m	1100sh, 1085 s, 1044m, 1030sh, 1012m, 1000m, 980vw	955w, 938w, 918vw, 875w, 815sh, 795wbr, 750sh, 735vw	—	670wbr, 605ms, 560m
$[Ni_4L_3Br_8]$	3496w, 3290m, 3240m, 3210vw, 3190m, 3150vw, 3070wbr, 3020wbr	2965m, 2930m, 2880w, 2860w	—	1580 s, 1570m, 1545sh	1458m, 1438m, 1430sh	1395vw, 1363w, 1355sh	1335w, 1272w, 1255m, 1160sh, 1130 s	1120sh, 1100m, 1045sh, 1038m, 1020vw, 1010vw, 960sh	955 s, 905w, 890vw, 858m, 750vbr	—	630m, 605w, 540 s
$[NiL_2(NCS)_2]$	3308m, 3260m, 3240sh, 3218m, 3129w	2945sh, 2930m, 2915sh, 2870m, 2840w	2095vs	1580 s, 1576sh, 1550sh	1450m, 1445sh, 1435vw, 1425sh	1360sh, 1350m	1235vw, 1250m, 1150sh, 1120vw	1120 s, 1075m, 1032 s	945 s, 920w, 895vw, 722w	770w	595 s, 555 s
$[NiL(NCS)_2]$	3318m, 3260m, 3225sh, 3138w	2950m, 2937m, 2920sh, 2875m, 2840w	2160wsh, 2130 s, 2120 s, 2080sh, 2060sh	1575sh, 1560 s, 1550m,	1452m, 1445sh, 1432vw, 1425sh	1360m, 1350w,	1245m, 1220vw, 1140sh	1100 s, 1072sh, 1067sh, 1045m, 1040sh, 1015w	955 s, 935w, 910vw, 898vw, 722w	763w	590sh, 520 s

vs=very strong, s=strong, ms=medium strong, m=meduim, br=broad, w=weak, vw=very weak, sh=shoulder. a): Compound gives bands at 3240 ms and 3360 ms for ν(OH) and at 1630 sh for δ(HOH). b): Compound gives bands at 3400 sh and 3370 sh for ν(OH) and at 1655 ms and 1645 sh for δ(HOH).

tion character of the ligand.[8-13] Literature shows less number of IR bands due to $\nu(NH_2)$ and $\nu(CH_2)$ for the complexes, where diamine acts as bridging bidentate ligand.[2] Morever, the IR spectrum of complex (**1**) is quite similar to the IR spectrum of $[Ni(tn)_3]Cl_2 \cdot 2H_2O$ (tn=1,3-propanediamine),[9] which also indicates the chelation character of the ligand in the complex.

We are not able to isolate the bis(diamine) species from complex (**1**) by temperature arrest technique owing to its thermal instability. So it is very difficult to suggest the actual configuration of the bis species. But the isolation of *cis* bis(diamine) complexes from $[M(en)_3]Cl_3$ [M=Co(III) and Cr(III)],[14,15] $[Ni(en)_3]Cl_2$ and $[Ni(tn)_3]Cl_2$[9] hint the formation of *cis* bis-(diamine) species here. Decomposition of $[NiL_3]Cl_2$ is different from the corresponding tris chelate complexes of 1,2-ethanediamine and 1,3-propanediamine as it generates $[Ni_2L_3Cl_4]$ (**1A**) upon heating. The IR spectrum (Table 3) of complex (**1A**) shows some additional bands in the regions of stretching (ν), bending (δ), wagging (ρ_w), twisting (τ) vibrations of NH_2 and CH_2 and stretching vibrations of skeleton ν(C–N) and ν(C–C) along with the other bands responsible for chelation character of diamine in comparison to the IR spectrum of complex (**1**). This observation suggests the chelating as well as bridging character of the ligand in complex (**1A**). Two probable structures are suggested (Structures 1* and 1; Scheme 1) for the complex (**1A**). It is rather difficult to say which structure actually displays here. Spectral and magnetic data of the complex cannot distinguish the structures clearly. However, electronic spectral band positions (Fig. 3) in 800—300 nm and their relative intensity difference may suggest the formation of *tbp* geometry.[16] If O_h geometry would be considered for the complex (**1A**), the relative intensity of $\nu_2[^3A_2 \rightarrow {}^3T_1(F)]$ and $\nu_3[^3A_2 \rightarrow {}^3T_1(P)]$ bands in mull spectra would not differ much.[8,9,13]

Scheme 1 clarifies that formation of $[NiLCl_2]$ (**1B**) occurs either from complex (**1A**)(O_h) or from complex (**1A**)(*tbp*). Both the cases seem to be feasible. But if we have octahedrally symmetrical $[Ni_2L_3Cl_4]$, then cleavage of bridging chlorine as well as ligand elimination (Scheme 1) would occur simultaneously during heating, which is rather complicated path. On the contrary, if the complex (**1A**) possesses *tbp* geometry then only ligand elimination would occur for affording $[NiLCl_2]$. In this context single endothermic DTA

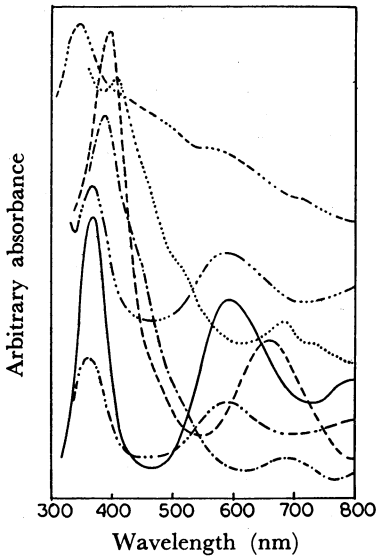
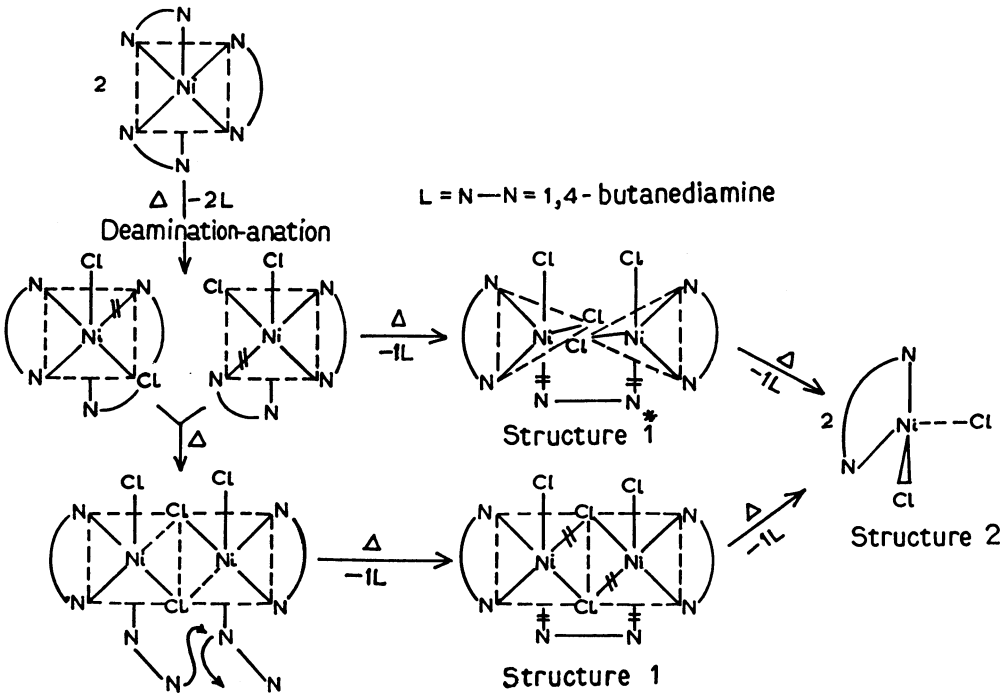


Fig. 3. Electronic mull spectra of $[NiL_3]Cl_2 \cdot H_2O$(**1**) (——), $[Ni_2L_3Cl_4]$ (**1A**) (- - -), $[NiLCl_2]$ (**1B**) (-·-·-), $[NiL_2(H_2O)_2]Br_2$ (**2**) (- -·- -·- - -), $[Ni_4L_3Br_8]$ (**2B**) (·····). $[NiL_2(NCS)_2]$ (**3**) (-·-·-·-) and $[NiL(NCS)_2]$ (**3A**) (- - -·-·-·- - -).



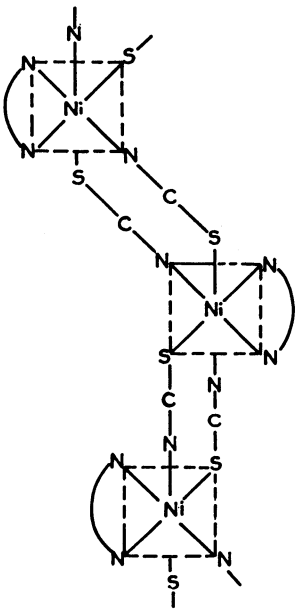
Scheme 1.

peak (Fig. 1) for the solid state reaction of $[Ni_2L_3Cl_4] \rightarrow [NiLCl_2]$ probably corroborates the *tbp* geometry in $[Ni_2L_3Cl_4]$.

The IR spectrum of $[NiLCl_2]$ suggests that the ligand is chelated here. Band appearing at 345 and 336 cm^{-1} in IR spectrum (Table 3) is well significant for terminally coordinated Cl atom in T_d geometry.[17] Higher magnetic moment (Table 1) of $[NiLCl_2]$ in comparison to other complexes is due to greater orbital contribution for loss of symmetry. The electronic spectra in mull (Fig. 3) display the characteristic band of the T_d Ni^{II} system (Structure 2, Scheme 1) at ≈670 nm which is tentatively assignable to the $^3T_1 \rightarrow {}^3T_1(P)$ transition (ν_3).[18,19]

In addition to the fundamental modes, we observe other modes of vibration of water molecule $\rho_r(H_2O)$ at ≈700 cm^{-1} and ν(MO) at ≈395 cm^{-1} in IR spectrum of $[NiL_2(H_2O)_2]Br_2$ (2).[20] The bands responsible for $\rho_r(H_2O)$ and ν (MO)are found to be absent in the anhydrous species. The diaquabis(1,4-butanediamine)nickel(II) bromide and dibromobis(1,4-butanediamine)-nickel(II) complexes are undoubtedly *cis* as is evident from IR assignments[21,22] in comparison to the *trans*-$[NiL_2(NCS)_2]$ (**3**). Complex (**2**) after deaquation-anation decomposes less stoichiometrically than that of its chloro analogue (*vide supra*) and generates isolable as well as nonisolable intermediates. This is probably due to anion effect. Complex (**2B**) possesses some additional bands (Table 3) in comparison to the IR spectrum of complex (**1B**) which might be due to the possession of chelating as well as bridging behavior of the diamine. Higher magnetic moment (than that of an O_h complex) and electronic spectrum of complex (**2B**) (Fig. 3) suggest that nickel(II) is probably tetracoordinated having T_d geometry.

Appearance of ν(CN) at 2095 cm^{-1} and ν(CS) at 770 cm^{-1} in the IR spectrum[23–26] (Table 3) of $[NiL_2(NCS)_2]$(**3**) clearly indicates that the compound (**3**) is actually *trans*-diisothiocyanatobis-(1,4butanediamine)-nickel(II). The IR spectrum of complex (**3**) supports the chelation character of diamine. Complex (**3**) generates $[NiL(NCS)_2]$ (**3A**) at 230 °C in single step as observed from its TG curve (Fig. 2) and corresponding DTA profile gives an endotherm followed by an exotherm. The exothermic peak may be due to some rearrangement taking place in complex (**3A**) after its formation. It is interesting to note that isolation of $[Ni(NCS)_2(en)]$ and $[Ni(NCS)_2(tn)]$ was not possible by us from their corresponding bis(diamine) complexes. Similar IR data of $[NiL(NCS)_2]$ (**3A**) with those of $[NiLCl_2]$ and $[NiL_2(NCS)_2]$ indicate that the ligand is also chelated in complex (**3A**). Magnetic moment (Table 1) of the complex (**3A**) suggests that nickel(II) is octahedrally surrounded. Although electronic spectra in mull (Table 1, Fig. 3) are not well resolved due to its dark color, the band maxima are well consistent for pseudooctahedral coordination of nickel(II) ion. ν(CN) of complex (**3A**) exhibits two intense bands at 2130 and 2120 cm^{-1} and three prominent shoulders at 2160, 2080, and 2060 cm^{-1} (Table 3). These data indicate the bridging character of thiocyanato group in the complex.[27,28] The spectroscopic and magnetic data suggest that all thiocyanato groups are bridged having



Structure 3

pseudooctahedral chromophore in complex (**3A**). Structures of $[M(NCS)_2(bipy)]$[M=Co(II) and Mn(II)] have been reported earlier by Dockum *et al.*[28] This observation suggests the probable structure of complex (**3A**) as depicted above. The occurrence of the geometrical difference in $[NiLX_2](X=Cl^-$ and $NCS^-)$ is probably due to more bridging ability of thiocyanato group although examples of similar type chloro-bridged complexes are known.[28]

Thermal studies on en and tn complexes of nickel(II) reported by us and the present investigation reflect that thermal decomposition is very much dependent on the chain length of diamine.

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