July, 1987] © 1987 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 60, 2701—2703 (1987) 2701

Some Unusual Phase Transitions of Nickel(II) Diamine Complexes

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(Received December 26, 1985)

Synopsis. [$NiX_2(tn)_2$], (tn=1,3-propanediamine; X_2=Br_2, SO_4, or SeO_4) undergoes phase transitions upon heating and reverts to their original structure upon cooling. These transitions have been investigated by differential scanning calorimetry and infrared spectroscopy.

Earlier, we reported the thermally induced phase transitions of nickel(II) diamine complexes.[1-5] Most of these phase transitions are time dependent reversible type and the extent of reversibility are found to be catalyzed by humid atmosphere. [$Ni(tn)_3$]X_2[6] and [$NiX_2(tn)_2$]·H_2O[7,8] (X_2=Cl_2, Br_2, SO_4 etc.) were found to decompose through bis and monodiamine steps. We isolated and characterized all the possible intermediates. But we did not carry out thermal studies of these intermediates from the room temperature. This communication reports some new and interesting reversible phase transitions of [$NiX_2(tn)_2$] (X_2=Br_2, SO_4, or SeO_4).

Experimental

Preparation of the Complexes: The complexes [$NiBr_2(tn)_2$] (**1**) and [$Ni(SO_4)(tn)_2(H_2O)$] (**3**) were prepared following the method reported earlier.[6,7]

The complex [$Ni(SeO_4)(tn)_2(H_2O)$] (**8**) was prepared by mixing $NiSeO_4$ and the diamine in 1:2 molar ratio in water and subsequent precipitation by adding ethanol. This complex was recrystallized from water–ethanol (2:1) mixture.

Elemental analyses of these samples are in good conformity with their compositions. Infrared spectra were recorded in KBr matrices (pellets) on a Perkin Elmer 783 IR spectrophotometer. Temperatures of the samples were varied using a variable temperature cell with a temperature controller. C, H, and N were analyzed using a Perkin-Elmer 240C elemental analyzer. Electronic spectra were recorded in a Pye Unicam SP8-150 and Hitachi 330 spectrophotometer. Thermal measurements were carried out with a Perkin-Elmer DSC-2 differential scanning calorimeter. The enthalpy of melting of indium was used for the calculation of enthalpy changes associated with the phase transition.

Results and Discussion

Earlier, we reported the synthesis of [$NiBr_2(tn)_2$)] from [$Ni(tn)_3$]Br_2·H_2O in solid state and its spectral properties.[6] This complex is slightly hygroscopic. It is very difficult to distinguish the cis or trans form of the nickel(II) octahedral complexes by usual spectral data. We have taken the electronic spectra (Table 1) of *trans*-[$Ni(NCS)_2(tn)_2$],[1] [$NiBr_2(tn)_2$], [$Ni(SO_4)(tn)_2(H_2O)$],[7] and found hardly any difference. But the IR spectra of these three are quite different. Splitting of $\rho(CH_2)$ and $\delta(NH_2)$ of the latter two complexes suggest probably cis-structure (C_2 symmetry) of [$NiBr_2(tn)_2$] (**1**).[9,10] Figure 1 and Table 2 show the thermal behavior of [$NiBr_2(tn)_2$] (**1**) which shows one phase transition upon heating accompanied by no color change. The species **2**, after phase transition reverts to **1** upon cooling. IR spectra of **1** and **2** are taken at 380 K (room temperature IR spectrum of this complex is faulty owing to its hygroscopic nature) and 450 K, respectively (Table 3). It is found that **2** shows a simpler spectrum than **1**. Splitting of $\delta(NH_2)$, ν(C–N), ν(C–C), and $\rho_r(CH_2)$ bands occurs in **1**. This is absent or reduced in **2** (Table 3). This suggests **2** exists in more symmetrical form than **1**.

Table 1. Electronic Spectral Data

Compound	λ_{max}/nm
[$NiBr_2(tn)_2$]	≈965 wbr,[a] 563, 362
[$Ni(SO_4)(tn)_2(H_2O)$]	≈955 wbr,[a] 680 sh,[b] 560, 360
trans-[$Ni(NCS)_2(tn)_2$]	≈965 wbr,[a] 563, 362

a) wbr=weak and broad. b) sh=shoulder.

Earlier, we reported[7] thermal behavior of [$Ni(SO_4)(tn)_2(H_2O)$] (**3**) where we presumed that water molecule in **3** was not coordinated to nickel as we were unable to record the IR spectrum of the dehydrated complex due to its hygroscopic nature. With the new technique of IR measurements, it was found that water molecule is coordinated in **3** as it shows $\rho_r(H_2O)$ at 731 cm^{-1} and $\rho_w(H_2O)$ at 700 cm^{-1}. These bands are found to be absent in the anhydrous species. With the help of IR the prediction about the mode of coordination of SO_4 in [$Ni(SO_4)(tn)_2(H_2O)$] (**3**) and its dehydrated form **4** is not possible due to the serious overlapping of diamine and SO_4 bands.

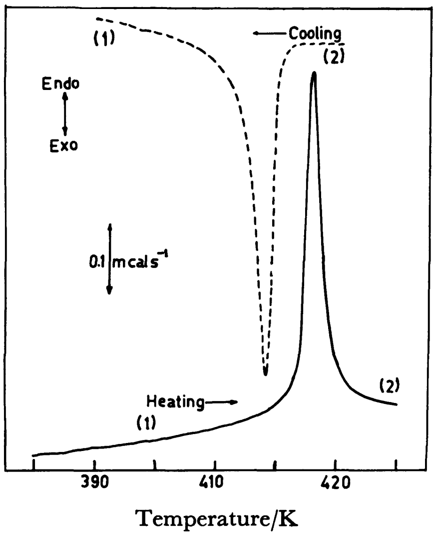

Fig. 1. DSC curves showing the transformations of: complex **1** (wt taken=12.73 mg) into **2**, heating curve (——); **2** into **1**, cooling curve (----).

But SO_4 appears to be unidentate in **3**, which exists in octahedral geometry as is evident from its electronic spectral data (Table 1) and magnetic moment reported by us.[7] However, on comparison of the geometry attained by the analogous species $[Ni(SeO_4)(tn)_2]$,[7] bidentacy of SO_4 may be predicted indirectly in **4**. It is interesting to note that the dehydrated complex $[Ni(SO_4)(tn)_2]$ (**4**) undergoes three successive reversible phase transitions (Table 2; Fig. 2). Earlier,[7] we could not notice these phase transitions in DTA curve because the first two peaks were hidden in the endothermic peak associated with the elimination of water and the third peak was weak in nature which was not possible to detect by DTA. Differential scanning calorimetry traces of the phase transitions (both heating and cooling curve) are shown in Fig. 2. These phase transitions are not associated with any color change. On comparison the IR spectra of **3**,

Table 2. Thermal Data

Phase transition	Heating		Cooling		ΔH
	Temp range K	Peak temp K	Temp range K	Peak temp K	kJ mol^{-1}
$[NiBr_2(tn)_2]$ (**1**) $\underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}}$ $[NiBr_2(tn)_2]$ (**2**)	411.0—438.5	426.5	434.5—393.5	418.0	1.53
$[Ni(SO_4)(tn)_2(H_2O)]$ (**3**) $\xrightarrow[-H_2O]{\text{Heating}}$ $[Ni(SO_4)(tn)_2]$ (**6**) Cooling ↓	353.0—403.0	388.0			
$[Ni(SO_4)(tn)_2]$ (**4**) $\underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}}$ $[Ni(SO_4)(tn)_2]$ (**5**)	353.0—375.5	368.7	362.0—342.5	355.5	0.96
$[Ni(SO_4)(tn)_2]$ (**5**) $\underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}}$ $[Ni(SO_4)(tn)_2]$ (**6**)	376.2—401.0	385.7	396.0—364.0	382.0, 373.5	0.29
$[Ni(SO_4)(tn)_2]$ (**6**) $\underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}}$ $[Ni(SO_4)(tn)_2]$ (**7**)	403.0—433.0	417.8	422.5—401.7	412.5	0.25
$[Ni(SeO_4)(tn)_2(H_2O)]$ (**8**) $\xrightarrow[-H_2O]{\text{Heating}}$ $[Ni(SeO_4)(tn)_2]$ (**10**) Cooling ↓	320.0—375.0	354.0			
$[Ni(SeO_4)(tn)_2]$ (**9**) $\underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}}$ $[Ni(SeO_4)(tn)_2]$ (**10**)	362.0—376.0	372.5	391.0—378.5	360.5	0.67
$[Ni(SeO_4)(tn)_2]$ (**10**) $\underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftarrows}}$ $[Ni(SeO_4)(tn)_2]$ (**11**)	376.0—406.5	392.0	378.5—346.5	383.5	

Table 3. IR Data

Compound	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	ν(C-N)+ν(C-C)	$\rho_r(CH_2)$
$[NiBr_2(tn)_2]$ (**1**)	1587 sh, 1583 sh, 1577 s	1462 sh, 1455 w, 1448 vw, 1428 w	1397 m, 1381 m,	1087 w, 1069 ms, 1009 s	910 s, 869 w, 864 w
$[NiBr_2(tn)_2]$ (**2**)	1583 sbr	1467 sh, 1461 w, 1451 vw, 1432 w	1395 wbr	1100 vw, 1073 m, 1014 msbr	913 s, 874 vw
$[Ni(SO_4)(tn)_2(H_2O)]$ (**3**)$^{a)}$	1584 vs, 1560 s, 1554 s	1468 m, 1455 w, 1439 m	1403 m, 1392 m, 1358 vw	1070 s, 1023 s	908 s, 880 w, 805 vw
$[Ni(SO_4)(tn)_2]$ (**4**)	1578 s	1458 m, 1450 w, 1433 w, 1428 w	1396 m, 1383 ms, 1346 vw	1075 s,$^{b)}$ 1019 s	918 s, 878 m, 874 m, 800 vw
$[Ni(SO_4)(tn)_2]$ (**7**)	1576 sbr	1460 w, 1452 w, 1448 w, 1430 w	1394 m, 1386 m, 1382 m, 1347 vw	1075 s,$^{b)}$ 1016 s, 1012 sh	915 s, 876 m, 800 vw

a) (**3**) shows δ(HOH), $\rho_r(H_2O)$, and $\rho_w(H_2O)$ bands at 1628 s, 731 s, and 700 s cm^{-1}. b) Spectra complicated due to overlapping of diamine vibration with ν_3 of SO_4. Some diamine vibrations are masked by SO_4 vibration.

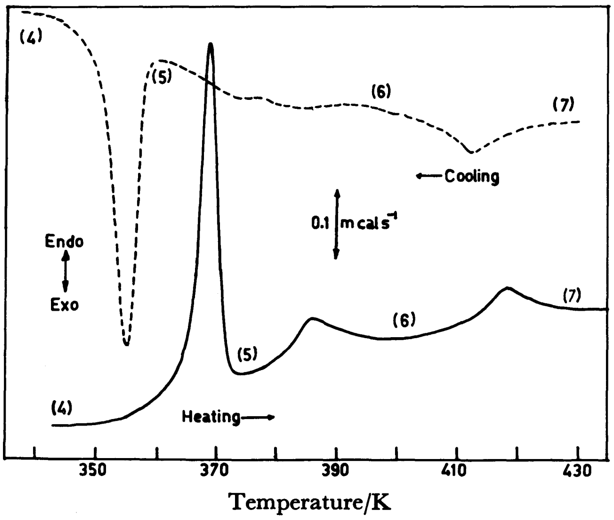

Fig. 2. DSC curves showing the transformations of: complex **4** (wt taken=16.08 mg) into **5**, **6**, and **7**, heating curve (——), **7**, into **6**, **5**, and **4**, cooling curve (----).

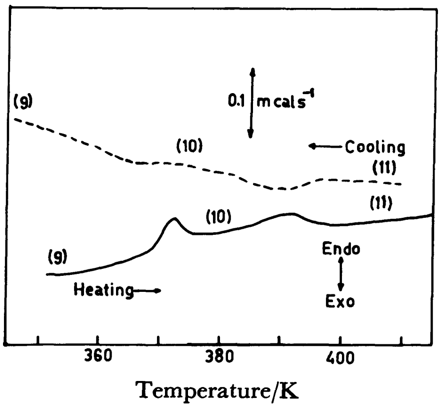

Fig. 3. DSC curves showing the transformations of: complex **9** (wt taken=11.85 mg) into **10** and **11**, heating curve (——), **11** into **10** and **9**, cooling curve (----).

4, and **7** taken at 303, 340, and 435 K respectively (Table 2), it is noticed that complex **3** possesses more infrared active bands than **4** and **7**. IR spectra of **4** and **7** differ in the $\delta(NH_2)$, $\delta(CH_2)$, $\rho_w(CH_2)$, ν(C–N), ν(C–C), and $\rho_r(CH_2)$ regions (Table 3). These data indicate that the six-membered chelate conformations in **4** and **7** are different.

$[Ni(SeO_4)(tn)_2(H_2O)]$ (**8**) shows similar IR and electronic spectra to its corresponding sulfato complex **3**. Its dehydration and phase transition phenomena are tabulated in Table 2. Figure 3 shows the differential scanning calorimetry traces of the phase transitions of $[Ni(SeO_4)(tn)_2]$ (**9**). It shows two overlapping endothermic peaks during heating and transforms to **11** via **10**. Here, the enthalpy changes for the transformation of **9**→**11** is low in comparison to the bromo and sulfato complexes. This is probably due to the presence of large anion SeO_4^{2-} (ionic size of which is larger than SO_4^{2-} and Br^-). Regarding IR spectra of **9** and **11**, we observe only a little difference.

The occurrence of phase changes in $[NiX_2(tn)_2]$ (X_2=Br_2, SO_4, or SeO_4) but not in $[NiCl_2(tn)_2]$ is probably due to the intramolecular interaction of the large anion with hydrogen atoms of the six-membered chelate owing to its unfavorable entropy effect.[11] Experiments have been carried out with large anion like halogenoacetates. But any phase transition phenomena were not noticed due to the decomposition of halogenoacetates at appreciably low temperatures.

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