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Thermally induced isomerization and decomposition of *N*-(2-aminoethyl)-1,3-propanediamine complexes of nickel(II) in the solid state

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Abstract

$[Ni(aepn)_2]X_2 \cdot nH_2O$, $Ni(aepn)Y_2 \cdot nH_2O$ and $[Ni(aepn)Z_2]$ (where aepn is *N*-(2-aminoethyl)-1,3-propanediamine; $n = 0$ when X is Cl, Br, NO_3 and ClO_4; $n = 4$ when X or Y is $0.5SO_4$ or $0.5SeO_4$ and Z is Cl, Br and NO_3) have been synthesized and investigated thermally in the solid state. $[Ni(aepn)_2]X_2$ (X is $0.5SO_4$ or $0.5SeO_4$) undergoes exothermic irreversible phase transitions on heating (238-261°C and 220-244°C for $[Ni(aepn)_2]SO_4$ and $[Ni(aepn)_2]SeO_4$ respectively, $\Delta H = -7.3\ kJ\ mol^{-1}$ for $[Ni(aepn)_2]SeO_4$); and $[Ni(aepn)_2](ClO_4)_2$ shows an endothermic irreversible phase transformation on heating (228-240°C, $\Delta H = 4.2\ kJ\ mol^{-1}$). All the complexes possess octahedral geometry and the latter transformation is explained in terms of conformational changes of the individual chelate ring.

INTRODUCTION

Several complexes [1-4] of nickel(II) and zinc(II) with dien (diethylenetriamine), aepn (*N*-(2-aminoethyl)-1,3-propanediamine) and dpt (*N*-(3-aminopropyl)-1,3-propanediamine) are known. Recently, we reported the synthesis, characterization and thermal investigations of several metal-dien complexes in the solid state, where the metals were Ni(II), Zn(II) and Cd(II) [5-8]. These complexes show a number of novel thermally induced phase transformation phenomena in the solid phase, which occur due to conformational changes of the individual chelate rings [5-7] or to geometrical arrangements of the ligand around the metal [8]. However, to our knowledge, a similar study with aepn complexes has not yet been undertaken. Therefore, the present paper reports the thermal investigations of nickel(II) aepn complexes in the solid phase.

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EXPERIMENTAL

High purity *N*-(2-aminoethyl)-1,3-propanediamine was purchased from Aldrich Chemical Company Inc. and used as received. All the other chemicals used were of AR grade. The equipment employed for recording IR and electronic spectra, elemental analysis, magnetic susceptibility, X-ray powder diffraction and thermal measurements (TG–DTA and DSC) are the same as described in an earlier report [5]. The far-IR spectra were

TABLE 1

Analytical, magnetic and electronic (mull) spectral data of *N*-(2-aminoethyl)-1,3-propanediamine (aepn) complexes of nickel(II)

Complex	Elemental analyses (%) [a]				μ_{eff} (BM)	λ_{max} (nm)
	Ni	N	C	H		
$[Ni(aepn)_2]Cl_2$ (**1**)	15.9 (16.3)	23.3 (23.1)	32.4 (33.0)	8.6 (8.3)	3.1	552, 347
$[Ni(aepn)Cl_2]$ (**2**)	24.0 (23.8)	16.8 (17.0)	24.0 (24.3)	6.0 (6.1)	3.3	612, 382
$[Ni(aepn)_2]Br_2$ (**3**)	12.7 (13.0)	18.3 (18.5)	26.6 (26.4)	6.8 (6.6)	3.1	556, 354
$[Ni(aepn)Br_2]$ (**4**)	17.1 (17.5)	12.7 (12.5)	18.1 (17.9)	4.5 (4.5)	3.3	610, 384
$[Ni(aepn)_2]SO_4 \cdot 4H_2O$ (**5**)	13.0 (12.7)	17.9 (18.2)	25.8 (26.1)	8.5 (8.3)	3.2	530, 341
$[Ni(aepn)_2]SO_4$ (**5a**)	14.9 (15.1)	21.3 (21.6)	31.2 (30.9)	7.3 (7.7)	3.2	548, 353
$Ni(aepn)SO_4 \cdot 4H_2O$ (**5b**)	16.8 (17.1)	11.9 (12.2)	17.6 (17.5)	6.9 (6.7)	3.4	574, 378
$Ni(aepn)SO_4$ (**5c**)	21.8 (21.6)	15.3 (15.5)	21.9 (22.1)	5.6 (5.5)	3.4	587, 381
$[Ni(aepn)_2]SeO_4 \cdot 4H_2O$ (**6**)	11.3 (11.6)	16.4 (16.5)	23.8 (23.6)	7.1 (7.5)	3.3	535, 375
$[Ni(aepn)_2]SeO_4$ (**6a**)	13.6 (13.5)	19.0 (19.3)	27.0 (27.5)	7.0 (6.9)	3.3	544, 383
$[Ni(aepn)_2]SeO_4$ (**6b**)	13.6 (13.5)	19.1 (19.3)	27.2 (27.5)	7.1 (6.9)	3.3	542, 382
$Ni(aepn)SeO_4 \cdot 4H_2O$ (**6c**)	14.7 (15.0)	11.0 (10.8)	15.6 (15.4)	6.3 (5.9)	3.2	558, 367
$Ni(aepn)SeO_4$ (**6d**)	18.6 (18.4)	13.4 (13.2)	18.5 (18.8)	5.0 (4.7)	3.2	567, 361
$[Ni(aepn)_2](NO_3)_2$ (**7**)	13.7 (14.1)	27.0 (26.9)	30.0 (28.8)	7.0 (7.2)	3.2	545, 351
$[Ni(aepn)(NO_3)_2]$ (**8**)	19.5 (19.6)	23.1 (23.4)	19.7 (20.0)	4.8 (5.0)	3.2	567, 359
$[Ni(aepn)_2](ClO_4)_2$ (**9**)	12.1 (11.9)	17.0 (17.1)	24.1 (24.4)	6.0 (6.1)	3.1	550, 348
$[Ni(aepn)_2](ClO_4)_2$ (**9a**)	12.0 (11.9)	16.9 (17.1)	24.2 (24.4)	5.9 (6.1)	3.1	549, 353

[a] Percentages in parentheses are theoretically calculated values.

TABLE 2

Thermal analyses of *N*-(2-aminoethyl)-1,3-propanediamine (aepn) complexes of nickel(II)

Complex	Dehydration temperature (°C)	Wt. loss (%) [a]	Isomerization temperature (°C)	Pattern	ΔH (kJ mol^{-1})
$[Ni(aepn)_2]SO_4 \cdot 4H_2O$ (**5**)	72–158	10.9 (10.9)	–	–	–
$[Ni(aepn)_2]SO_4$ (**5a**)	–	–	238–261	Exotherm	[b]
$Ni(aepn)SO_4 \cdot 4H_2O$ (**5b**)	60–143	18.0 (18.1)	–	–	–
$[Ni(aepn)_2]SeO_4 \cdot 4H_2O$ (**6**)	75–159	6.5 (6.2)	–	–	–
$[Ni(aepn)_2]SeO_4$ (**6a**)	–	–	220–244	Exotherm	−7.3
$Ni(aepn)SeO_4 \cdot 4H_2O$ (**6c**)	67–145	18.5 (18.4)	–	–	–
$[Ni(aepn)_2](ClO_4)_2$ (**9**)	–	–	228–240	Endotherm	4.2

[a] Calculated values are in the parentheses. [b] ΔH value could not be calculated due to overlapping of decomposition peaks.

TABLE 3

IR spectral data (cm^{-1}) of *N*-(2-aminoethyl)-1,3-propanediamine (aepn) complexes of nickel(II) in nujol

Complex	$\nu(NH_2)$	$\nu(CH_2)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2) + \rho_w(NH_2) + \tau(CH_2) + \nu(C–N) + \nu(C–C)$ stretching vibration of skeleton + $\rho_r(CH_2)$
[Ni(apen)Cl_2] (**2**)[a]	3290s 3262m 3238s 3160w	2948w 2938w 2920sh	1597vs 1578vs	1472m 1463w 1453w 1444s 1427m 1400w 1390vw 1377vw	1358vw 1347m 1322m 1315m 1287s 1280sh 1260w	1160s, 1137s, 1120s, 1095s, 1088s, 1085s, 1042s, 1013s, 972s, 958vs, 928s, 891s, 884s, 855m, 812w
[Ni(aepn)$(NO_3)_2$] (**8**)	3337m 3322m 3282m 3270m 3230s 3180w	[b]	1597m	[b]	[c]	1158s, 1132m, 1100m, 1085m, 1060s, 1050sh, 1045sh, 1042s, 1023s, 997s, 977w, 938w, 890w, 867vw, (825w, 818m)[d], 757w, 740w
[Ni$(aepn)_2$]$(ClO_4)_2$ (**9**)	3320vs 3260vs 3178m	[b]	1595vs	[b]	1410m 1388s 1370s 1348s 1332s 1300s 1290sh	985vs, 932vs, 888vs, 862s, 810s, 730w
[Ni$(aepn)_2$]$(ClO_4)_2$ (**9a**)	3330s 3280m 3180w	[b]	1590m	[b]	1375s 1365sh 1340w 1322m 1294m 1283m	1014s, 980s, 960sh, 937m, 920sh, 887m, 860w, 811w, 795vw, 780vw, 745sh, 730w

Key: sh, shoulder; v, very; m, medium; w, weak; s, strong; vs, very strong; vw, very weak.

[a] IR spectra in KBr. [b] Overlapped with nujol band. [c] Overlapped with NO_3 bands. [d] Bands due to NO_3.

TABLE 4

Prominent lines, *d* (Å), in the X-ray powder patterns of the complexes

$[Ni(aepn)_2](ClO_4)_2$ (**9**)	$[Ni(aepn)_2](ClO_4)_2$ (**9a**) [a]	$[Ni(aepn)_2](ClO_4)_2$ (**9**)	$[Ni(aepn)_2](ClO_4)_2$ (**9a**) [a]
7.89vw	7.49w	2.85vw	4.35vw
7.07vw	7.07vw	2.66m	4.09vs
6.70w	6.36vs	2.36w	3.91vw
5.28s	5.90m	2.31vw	3.63w
4.57m	5.71m	2.27vw	3.50vw
4.48m	5.37m	2.10vw	3.44vw
3.96w	5.27m	1.96vw	3.17vw
3.85w	4.98w		3.09vw
3.53m	4.84m		2.65w
3.45w	4.48s		2.36vw
			2.35vw

Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

[a] Species obtained after the phase transition of (**9**) was cooled in a desiccator; X-ray powder patterns were taken immediately.

recorded in an FTIR spectrometer (Polytech FIR-30). Analytical, thermal, IR spectral and X-ray powder diffraction data are shown in Tables 1, 2, 3 and 4, respectively.

Preparation of the complexes

$[Ni(aepn)_2]Cl_2$ (**1**), $[Ni(aepn)Cl_2]$ (**2**), $[Ni(aepn)_2]Br_2$ (**3**), $[Ni(aepn)Br_2]$ (**4**), $[Ni(aepn)_2]SO_4 \cdot 4H_2O$ (**5**), $Ni(aepn)SO_4 \cdot 4H_2O$ (**5b**), $[Ni(aepn)_2]SeO_4 \cdot 4H_2O$ (**6**), $[Ni(aepn)_2](NO_3)_2$ (**7**), $[Ni(aepn)(NO_3)_2]$ (**8**) and $[Ni(aepn)_2](ClO_4)_2$ (**9**) were prepared following the methods described for the dien complexes [5, 6, 9, 10].

$[Ni(aepn)_2]SO_4$ (**5a**), $Ni(aepn)SO_4$ (**5c**), $[Ni(aepn)_2]SeO_4$ (**6a**), $[Ni(aepn)_2]SeO_4$ (**6b**), $Ni(aepn)SeO_4$ (**6d**) and $[Ni(aepn)_2](ClO_4)_2$ (**9a**) were prepared in the solid state by the temperature arrest technique from their respective parent complexes.

RESULTS AND DISCUSSION

Characterization of the complexes

Octahedral bis-complexes with linear triamines such as diethylenetriamine,*N*-(2-aminoethyl)-1,3-propanediamine,*N*-(3-aminopropyl)1,3-propanediamine, etc., can exist as three geometrical isomeric forms, namely s-fac, u-fac and mer. Searle and House [11] characterized all three isomers of $[Cr(dien)_2]^{3+}$ complexes by studying their IR spectral patterns, especially, the $\rho_r(CH_2)$ and $\delta(NH_2)$ bands which appear in the 950–750 and 1600 cm^{-1} region respectively. Recently, we characterized several bis-dien complexes of nickel(II), zinc(II) and cadmium(II) from their IR spectra

[5–7] and also by single-crystal X-ray analysis [8]. In the present case, all the bis-aepn complexes possess one strong band ($\approx 880\,\mathrm{cm}^{-1}$) in the $\rho_r(CH_2)$ region and one broad strong band ($\approx 1590\,\mathrm{cm}^{-1}$) in the $\delta(NH_2)$ region which are very similar to the characteristic bands for the mer isomers of bis-dien complexes. Moreover, a recent study on aepn complexes of zinc(II) with ^{13}C-NMR shows that the most probable configuration for bis-aepn complexes is mer [1]. Although to our knowledge, single-crystal X-ray analysis and molecular mechanics studies on bis-aepn complexes have not been published so far, nonetheless based on ^{13}C-NMR studies of zinc(II) complexes and earlier studies with other linear triamines, i.e. dien [11] and dpt [1, 12], it can be assumed that the bis-aepn complexes of nickel(II) exist as mer isomers, at least in the solid state.

All the mono complexes are octahedral as is evident from their magnetic and electronic spectral data. The far-IR spectrum of $[Ni(aepn)Cl_2]$ (**2**) shows bands at 180, 195 and $230\,\mathrm{cm}^{-1}$ for ν(Ni–Cl); the bands appearing at 180 and $195\,\mathrm{cm}^{-1}$ are interpreted as ν_b(Ni–Cl) whilst the band at $230\,\mathrm{cm}^{-1}$ is interpreted as ν_t(Ni–Cl) [13]. In the case of $[Ni(aepn)Br_2]$ (**4**), these bands shift to $140\,\mathrm{cm}^{-1}$ for ν_b(Ni–Br) and $200\,\mathrm{cm}^{-1}$ for ν_t(Ni–Br). There is no direct structural information on mono-aepn complexes of nickel(II); however, Cannas et al. [14] have shown by single-crystal X-ray analysis that $[Cd(aepn)Cl_2]$ has a pseudo-octahedral dimeric structure with the ligand arranged meridionally and one of the chlorine atoms acting as a bridge and it is interesting to note that the IR spectra of the complexes (**2**) and (**4**) are almost the same as that of $Cd(aepn)Cl_2$. Considering all these facts we propose the structure as shown in Fig. 1 (**I**) as the probable structure for complexes (**2**) and (**4**). However, the complex $[Ni(aepn)(NO_3)_2]$ (**8**) possesses four bands in the region $1800–1700\,\mathrm{cm}^{-1}$ [at approx 1718, 1740, 1760 and 1766(sh) cm^{-1}] in its IR spectra (in nujol); the combination band of the ν_1 symmetric stretching and the doubly degenerated in-plane bending mode of NO_3 ion in a metallic complex are also present [15]. The appearance of these four bands indicates that both the NO_3 ions are bonded [15, 16] with the nickel(II). The large separation between the two peaks at 1718 and $1766\,\mathrm{cm}^{-1}$ ($\approx 48\,\mathrm{cm}^{-1}$) indicates that one of the NO_3 ions is bidentate and the small separation between the other two peaks at 1740 and $1760\,\mathrm{cm}^{-1}$ ($\approx 20\,\mathrm{cm}^{-1}$) is interpreted as the NO_3 ion being present as a monodentate ligand [15, 16]. A similar type of bonding is also observed in the $Ni(dien)(NO_3)_2$ complex [10]. It should be noted here that when the IR spectrum is taken in KBr, the four separated bands for the NO_3 ion are reduced to one strong band at $\approx 1750\,\mathrm{cm}^{-1}$. Very probably this is due to the exchange of NO_3 ions with the Br ions of KBr; such a replacement is also found among other nitrato complexes [16, 17]. The arrangement of the triamine around the nickel(II) ion in complex (**8**) can be either meridional or facial, as shown in Fig. 1 (**II** and **III**). The pattern of triamine vibration bands appearing in the IR spectrum of the complex $[Ni(aepn)(NO_3)_2]$ (**8**)

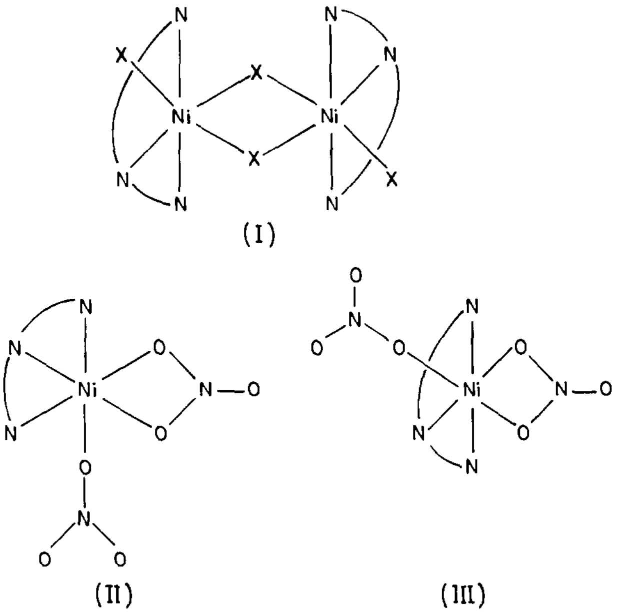

Fig. 1. Proposed structure of $[Ni(aepn)X_2]$ (**I**) (where X is Cl or Br) and $[Ni(aepn)(NO_3)_2]$ (**II**/**III**).

taken in nujol is completely different from that of $[Ni(aepn)Cl_2]$ (**2**), although some of the bands are not distinguishable owing to overlapping with NO_3 bands and with bands for nujol itself. Therefore, the arrangement of aepn around the nickel(II) in the case of (**8**) is not as appears in $[Ni(aepn)Cl_2]$ (**2**), and $[Ni(aepn)(NO_3)_2]$ (**8**) probably possesses either structure **II** or **III** as shown in Fig. 1. However, the mode of coordination of SO_4 and SeO_4 ions in the complexes (**5c**) and (**6d**) respectively, cannot be analysed from their IR spectra due to overlapping of triamine bands.

The mono complexes of chloride and bromide show 1:1 electrolytic behaviour in CH_3OH, indicating the solvation of either bridged halogen or terminal halogen. However, the conductance measurement of these complexes in CH_3NO_2, $C_6H_5NO_2$, etc., could not be performed because of their insolubility in these solvents.

Thermal studies of the complexes

Isomerization of $[Ni(aepn)_2]SO_4 \cdot 4H_2O$ (5), $[Ni(aepn)_2]SeO_4 \cdot 4H_2O$ (6) and $[Ni(aepn)_2](ClO_4)_2$ (9)

Upon heating, the complexes $[Ni(aepn)_2]SO_4 \cdot 4H_2O$ (**5**) and $[Ni(aepn)_2]SeO_4 \cdot 4H_2O$ (**6**) become anhydrous at 158 and 143°C respectively and transform to (**5a**) and (**6a**). On further heating, the complexes (**5a**) and (**6a**) undergo irreversible exothermic phase transitions (238–261 and 220–244°C respectively), whereas the complex $[Ni(aepn)_2](ClO_4)_2$ (**9**), on heating,

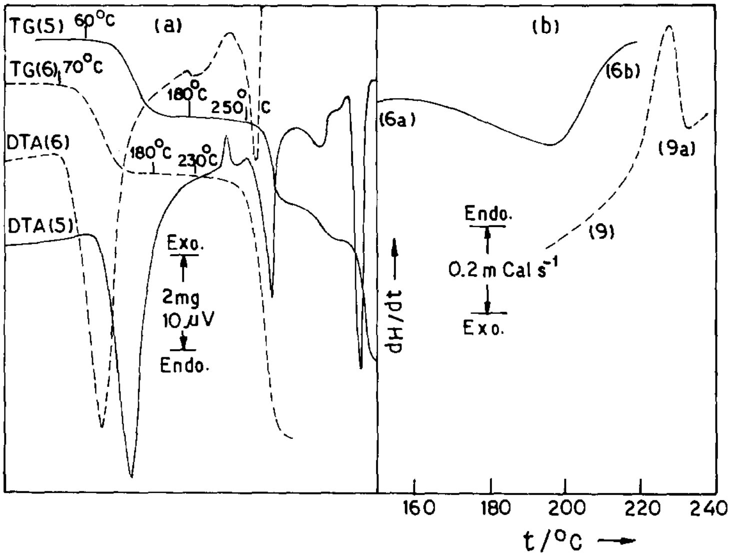

Fig. 2. Thermal analysis curves: (a) TG–DTA curves of $[Ni(aepn)_2]\ SO_4 \cdot 4H_2O$ (**5**) (10.24 mg) (——) and $[Ni(aepn)_2]SeO_4 \cdot 4H_2O$ (**6**) (13.27 mg) (– – –). Heating rate 10°C min^{-1} for both the complexes. (b) DSC curves showing transformations of $Ni(aepn)_2SeO_4$ (**6a**) (10.50 mg) into (**6b**) (——) and $[Ni(aepn)_2](ClO_4)_2$ (**9**) (7.45 mg) into (**9a**) (– – –). Heating rate 10°C min^{-1} for both complexes.

shows an endothermic irreversible phase transition (228–240°C, see Fig. 2). The ΔH values for these transformations were measured by DSC and are shown in Table 2. In the case of complex (**5a**), the ΔH value could not be calculated because the relevant exotherm was partially overlapped by decomposition peaks. Therefore, a pure post-phase species could not be isolated, but on crystallization from ethanol–water mixture (9:1), the impure species showed exactly the same behaviour as complex (**5**).

The similarity of the magnetic moment and electronic spectral data (Table 1) of (**9**) and (**9a**) implies the presence of an identical (NiN_6) chromophore in both. Comparison of the IR spectra of (**9**) and (**9a**) shows that both isomers possess almost identical spectral patterns in the regions 1600–1500 cm^{-1} and 950–750 cm^{-1}. Therefore, the meridional ligand arrangement around the metal ion present in complex (**9**) is probably retained on phase transition. However, appreciable differences in the IR spectra of (**9**) and (**9a**) in the $\nu(NH_2)$, $\rho_w(CH_2)$, $\tau(NH_2)$, $\rho_w(NH_2)$ and $\rho_r(CH_2)$ bands indicate that the chelate conformations in (**9**) and (**9a**) are different. Therefore, complexes (**9**) and (**9a**) are probably two different conformers. In addition, a massive difference in *d*-spacing values in the X-ray powder diffraction patterns (Table 4) of the species (**9**) and (**9a**) suggests that a major change in unit cell dimensions occurs during phase transition. This is not inconsistent with the conformational changes in individual chelate rings in $[Ni(aepn)_2](ClO_4)_2$. We have also observed similar types of behaviour in bis-dien complexes [5, 6]. However, comparison of the IR spectra of (**6a**) and (**6b**) shows no detectable difference between them; X-ray powder patterns of (**6a**) and (**6b**) could not be taken due to their extreme hygroscopic nature. The transition could not, therefore, be characterized.

It is to be noted here that the humidity of the atmosphere and solvent have the same effect on reversion from post-phase to pre-phase, as reported earlier [6, 7].

Decomposition of the complexes

All the complexes, except (**7**), (**8**) and (**9a**), decompose on heating in the solid state to their corresponding metal salts. In the case of (**7**) and (**8**) the decompositions are very complicated and the end products are not characterized. The temperature range and the nature of the reactions are shown in Table 2 (Fig. 2). The decomposition of $[Ni(aepn)_2]SO_4$ (**5a**) is very interesting as it shows the breaks for the formation of $Ni(aepn)_{1.25}SO_4$ and $Ni(aepn)SO_4$ (Fig. 2). It is also interesting to note that on aging these breaks merge with each other and show an one-step decomposition, i.e. $[Ni(aepn)_2]SO_4 \rightarrow NiSO_4$.

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REFERENCES

1 S.P. Dagnall, D.N. Hague and A.D. Moreton, J. Chem. Soc. Dalton Trans., (1988) 1989 and references cited therein.
2 D.N. Hague and A.D. Moreton, J. Chem. Soc. Dalton Trans., (1987) 2889.
3 S.K. Srivastava and H.B. Mathur, Indian J. Chem., 11 (1973) 936.
4 R. Barbucci, L. Fabbrizzi and P. Paoletti, Inorg. Chim. Acta, 7 (1973) 157.
5 S. Koner, A. Ghosh and N. Ray Chaudhuri, Transition Met. Chem., 13 (1988) 291.
6 S. Koner, A. Ghosh and N. Ray Chaudhuri, Transition Met. Chem., 15 (1990) 394.
7 S. Koner, A. Ghosh and N. Ray Chaudhuri, Thermochim. Acta, 159 (1990) 55.
8 S. Koner, Ph.D. Thesis, Jadavpur University, Calcutta-700 032, 1990.
9 N.F. Curtis and H.K.J. Powell, J. Chem. Soc. A, (1968) 3069.
10 N.F. Curtis and Y.M. Curtis, Inorg. Chem., 4 (1965) 804.
11 G.H. Searle and D.A. House, Aust. J. Chem., 40 (1987) 361 and references cited therein.
12 S. Biagini and M. Cannas, J. Chem. Soc. A, (1970) 2398.
13 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley–Interscience, New York, 1977, pp. 318, 322.
14 M. Cannas, G. Marongiu and G. Saba, J. Chem. Soc. Dalton Trans., (1980) 2090.
15 A.B.P. Lever, E. Mantovani and B.S. Ramaswamy, Can. J. Chem., 49 (1971) 1957.
16 D. Gomez de Anderez, A.K. Mukherjee, S. Koner and N. Ray Chaudhuri, Polyhedron, 10 (1991) 2225.
17 L. Menabue, G.C. Pellacani, L.P. Battaglia, A.B. Corradi, F. Sandrolini, A. Motori, R.J. Pylkki and R.D. Willett, J. Chem. Soc. Dalton Trans., (1984) 2187.