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Synthesis and Characterization of Complexes of Neodymium(III) with Piperazines*

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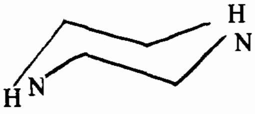
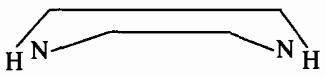
Piperazines, the diheterocyclic nitrogen bases, which exist in the chair form (**A**) in the free state can form complexes with metal ions either in the chair form or in the boat form (**B**), giving polymeric bridged or chelated structures respectively. We have been working in this area of research for many years to explore the mode of coordination of piperazines and have found that with the exception of uranyl chloride complexes, where at least some of them coordinate in the boat conformation [1], these ligands normally prefer to retain a chair conformation in the majority of complexes.



A



B

In this paper the synthesis and characterization of complexes of the general formula $NdX_3{\cdot}xL{\cdot}yROH$ where $X = Cl$ and NO_3; $x = 0.5$, 1 and 1.5; L = piperazine, 1-methyl-, 2-methyl-, 1-phenyl-, 1,4-dimethyl-, 2,5-dimethyl- and 2,6-dimethyl-piperazine and $R = CH_3$ and C_2H_5 have been described.

For the preparation of the chloride complexes, the ligand (0.70–1.30 g; 8 mmol) and metal salt (1.00 g; 4 mmol) were reacted together in absolute ethanol (50 ml) with constant shaking. The precipitated bluish violet complexes were washed successively with ethanol and diethyl ether 5–6 times, filtered in a G_4 filtration unit and finally dried under vacuum. In the case of the nitrate complexes, a solution of neodymium nitrate (1.00 g; 2.19 mmol) in a mixture (30 ml) of 2,2′-dimethoxypropane and methanol was refluxed until a red solution was obtained. To this red solution was added, after cooling to room temperature, a solution of the ligand (0.40–0.70 g; 4.38 mmol) in methanol (10 ml) with shaking. The red colour disappeared and a violet compound separated, which was washed, filtered and dried. The complexes are slightly hygroscopic and were stored under vacuum in sealed ampoules. They do not melt up to 300 °C and are insoluble in most organic solvents; molecular weight determinations were thus precluded. Table I gives some of the properties of these complexes.

Broad IR bands in the region 3600–3100 cm^{-1} with a break at 3250 cm^{-1} result from the overlapping of the bands due to $\nu(NH)$ and $\nu(OH)$ [2]. These modes appear around 3600 cm^{-1} in the free ethanol and methanol and around 3300 cm^{-1} in the free ligands [2]. This indicates the coordination of piperazines through NH nitrogen and also the coordination of alcohol molecules. The CH stretching mode of NCH_3, which appears at 2750 and 2810 cm^{-1} in the IR spectra of 1-methyl- and 1,4-dimethylpiperazine, is not observed in the complexes. It presumably shifts to higher frequencies and mixes with the other CH bands occurring around 2900 cm^{-1} on coordination of the nitrogen atom of the $N-CH_3$ group [3].

The IR spectrum [4] of $PdCl_2$(1,4-dimethylpiperazine) in which the piperazine has been shown by X-ray diffraction studies to be coordinated in a boat form [5] exhibits a large number of new bands of low and medium intensity in addition to changes in the IR spectral bands characteristic of the free ligand. No new bands assignable to the boat conformation of piperazines appear in the IR spectra of the complexes, thus showing that ligands prefer to retain the chair conformation even in the complexes and afford polymeric non-chelated species which is also indicated by their insolubility and non-melting nature.

The appearance of a strong band around 1310 cm^{-1} and the absence of bands characteristic of ionic nitrate (1390 and 830 cm^{-1}) indicate the presence of coordinated nitrates only [6]. On the basis of the magnitudes of separations between the nitrate group combination bands, $(\nu_2 + \nu_{3hc}) - (\nu_2 + \nu_{3lc})$* and $(\nu_2 + \nu_3) - (\nu_2 + \nu_5)$, which are about 220 and 50 cm^{-1}, chelating bidentate nitrates are indicated in these compounds [6–10].

Bands appearing around 525, 375, 325 and 300 cm^{-1} have been assigned to the NH rocking mode [2], $\nu(Nd-O)$, $\nu(Nd-N)$ and $\nu(Nd-Cl)$ [11–13] respectively. However, it is dangerous to make these assignments with certainty since Koppikar *et al.* have reported a broad range of 180–580 cm^{-1} for (Ln–O), (Ln–N) and (Ln–X) (Ln = lanthanide ion, X = halogen) stretching frequencies [14].

In the electronic reflectance spectra of the complexes it is indicated that the energies at which these

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*High and low energy components of the splittings of ν_3 for ionic nitrate on coordination.

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TABLE I. Elemental Analyses, Decomposition Points, Yields, Probable Coordination Numbers and Magnetic Moments of the Complexes

Compound	Analyses (%)[a]					Decomposition temperature	Yields (%)	Probable coordination number	Magnetic moment
	M	C	H	N	Cl				
$NdCl_3 \cdot 1.5(pipz)C_2H_5OH$[b]	33.87	22.54	4.93	9.86	25.02	310	80	7	3.50
	(33.82)	(22.91)	(4.83)	(9.98)	(25.00)				
$NdCl_3(1\text{-}Me\text{-}pipz)2C_2H_5OH$	29.27	21.91	4.46	5.68	21.61	310	80	7	3.50
	(29.30)	(21.88)	(4.16)	(5.96)	(21.70)				
$NdCl_3(2\text{-}Me\text{-}pipz)2C_2H_5OH$	30.00	22.00	4.03	5.90	21.63	315	85	7	3.52
	(29.30)	(21.88)	(4.16)	(5.96)	(21.70)				
$NdCl_3(1\text{-}Ph\text{-}pipz)C_2H_5OH$	31.44	31.39	4.35	6.10	23.21	315	80	7	3.51
	(31.40)	(31.48)	(4.45)	(6.15)	(23.00)				
$NdCl_3(1,4\text{-}Me_2\text{-}pipz)C_2H_5OH$	35.11	23.37	4.86	6.81	25.92	310	80	7	3.52
	(35.15)	(23.42)	(4.87)	(6.87)	(26.08)				
$NdCl_3(2,6\text{-}Me_2\text{-}pipz)C_2H_5OH$	35.00	23.45	4.12	6.85	26.00	310	80	7	3.52
	(35.15)	(23.42)	(4.87)	(6.87)	(26.08)				
$NdCl_3(2,5\text{-}Me_2\text{-}pipz)C_2H_5OH$	35.20	23.12	4.50	6.90	25.12	310	80	7	3.53
	(35.15)	(23.42)	(4.87)	(6.87)	(26.08)				
$Nd(NO_3)_3 \cdot 1.5(pipz)2CH_3OH$	27.25	18.78	4.34	6.00		310	80	11	3.48
	(27.50)	(18.34)	(4.39)	(6.05)					
$Nd(NO_3)_3(1\text{-}Me\text{-}pipz)2CH_3OH$	32.00	13.80	3.78	16.00		310	85	10	3.42
	(32.46)	(13.50)	(3.15)	(15.75)					
$Nd(NO_3)_3(2\text{-}Me\text{-}pipz)2CH_3OH$	32.40	13.48	3.10	15.80		315	80	10	3.43
	(32.46)	(13.50)	(3.15)	(15.75)					
$Nd(NO_3)_3 \cdot 0.5(1\text{-}Ph\text{-}pipz)2CH_3OH$	30.25	17.80	3.72	11.70		315	85	9	3.45
	(30.35)	(17.67)	(3.15)	(11.78)					
$Nd(NO_3)_3 \cdot 0.5(1,4\text{-}Me_2\text{-}pipz)2CH_3OH$	31.80	13.21	3.30	12.30		310	80	9	3.48
	(31.96)	(13.29)	(3.32)	(12.41)					
$Nd(NO_3)_3 \cdot 0.5(2,6\text{-}Me_2\text{-}pipz)2CH_3OH$	31.90	13.30	3.35	12.20		315	85	9	3.48
	(31.96)	(13.29)	(3.32)	(12.41)					
$Nd(NO_3)_3 \cdot 0.5(2,5\text{-}Me_2\text{-}pipz)2CH_3OH$	31.75	13.88	3.28	12.00		310	85	9	3.45
	(31.96)	(13.29)	(3.32)	(12.41)					

[a] Calculated values are given in parentheses. [b] pipz = piperazine.

bands appear in the complexes are lower compared to those in the aqua ion. This red shift is due to the nephelauxetic effect which has been interpreted previously as related to a degree of covalency in the bonds [15–17]. The values of β, δ and $b^{1/2}$ calculated from the relations

$$\beta = n^{-1} \sum_{n=1}^{n} \nu_{\text{comp}}/\nu_{\text{aqua}}$$

$$\delta = [(1 - \beta)/\beta] \times 100$$

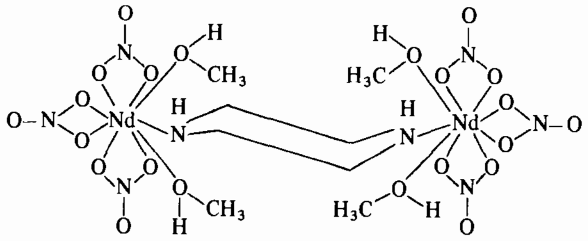
$$b^{1/2} = [\tfrac{1}{2}(1 - \beta)]^{1/2}$$

lie in the ranges 0.09859–0.9899, 1.02–1.50 and 0.0710–0.0860 respectively. These values, together with the room temperature (300 K) magnetic moment values which are somewhat lower (3.42–3.53 BM) than the theoretical value of 3.68 BM, reflect an effect of the M–N bonds on the 4f orbitals.

Molar conductance values in $ohm^{-1}\,cm^{-2}\,mol^{-1}$ of the millimolar solutions of the complexes in DMF and DMSO are very low and thus suggest the complexes are non-electrolytes.

The weight changes noted from the thermograms indicate that the complexes decompose in two steps. The first step involves the loss of alcohol molecules followed by the loss of base molecules.

On the basis of above-mentioned studies, complexes with the general formula $Nd(NO_3)_3 \cdot 0.5L \cdot 2CH_3OH$ have been assigned the following probable structure:



References

1 B. S. Manhas, A. K. Trikha and M. Singh, *Indian J. Chem., 16A*, 431 (1978).
2 M. Avram and G. Mateescu, 'Infrared Spectroscopy', Wiley–Interscience, New York, 1966, p. 257.
3 J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann and N. Sheppard, *J. Chem. Soc. A*, 2780 (1958).
4 P. J. Hendra and D. B. Powell, *J. Chem. Soc. A*, 5105 (1960).
5 O. Hassel and B. F. Pedersen, *Proc. Chem. Soc.*, 394 (1959).
6 J. I. Bullock, *J. Inorg. Nucl. Chem., 29*, 2257 (1967).
7 N. F. Curtis and Y. M. Curtis, *Inorg. Chem., 4*, 804 (1965).
8 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem., 49*, 1957 (1971).
9 B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc. A*, 3965 (1958).
10 A. Seminara, A. Musumeci and A. Chisari, *J. Inorg. Nucl. Chem., 40*, 269 (1978).
11 B. S. Manhas, A. K. Trikha and M. Singh, *Indian J. Chem., 20A*, 196 (1981).
12 B. S. Manhas, A. K. Trikha and M. Singh, *J. Less-Common Met., 68*, 111 (1979).
13 B. S. Manhas, A. K. Trikha and M. Singh, *Indian J. Chem., 20A*, 919 (1981).
14 D. K. Koppikar, P. V. Sivapullaiah, L. Ramakrishnan and S. Soundararajan, *Struct. Bonding (Berlin), 34*, 135 (1978).
15 S. P. Sinha, *Spectrochim. Acta, 22*, 57 (1966).
16 C. K. Jorgensen, *Prog. Inorg. Chem., 4*, 73 (1962); C. K. Jorgensen, 'Modern Aspects of Ligand Field Theory', North-Holland, Amsterdam, 1971, p. 293.
17 D. E. Henrie and G. R. Choppin, *J. Chem. Phys., 49*, 477 (1968).