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Some lanthanide (III) nitrate complexes of N-(4′-benzoylidene-3′-methyl-1′-phenyl-pyrazol-5′-one)isonicotinylhydrazine

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Nine new complexes of lanthanide (III) nitrates with N-(4′-benzoylidene-3′-methyl-1′- phenylpyrazol-5′-one) isonicotinylhydrazine (BMPIH) have been synthesised. All these complexes have the general formula $[Ln(BMPIH)_2(NO_3)_3]$ where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y. In these complexes BMPIH acts as a neutral bidentate ligand utilizing the azomethine nitrogen and the ring carbonyl oxygen as the donor atoms. The nitrate groups coordinate in a unidentate fashion and, hence, a coordination number of 7 is assigned to the central metal ion.

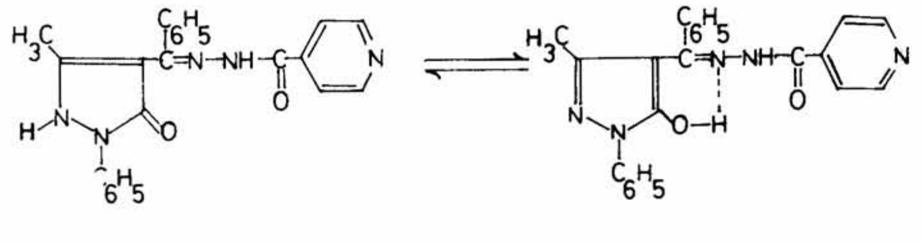
Lanthanide (III) ions form two types of complexes with 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (BMPP)[1,2] under different experimental conditions. In the first type BMPP acts as a univalent bidentate ligand[1] and in the other type it acts as a neutral bidentate ligand [2]. In view of the dependence of the bonding behaviours of BMPP on the experimental conditions, it was thought of interest to study the coordination behaviour of a schiff base derived from BMPP. We report here the synthesis and characterisation of nine lanthanide (III) nitrate complexes of the schiff base derived from BMPP and issonicotinylhydrazine, viz., N-(4′-benzoylidene-3′-methyl-1′-phenylpyrazol- 5′-one)-isonicotinylhydrazine (BMPIH) (structure I).

Experimental

Nitrates of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Y(III) were prepared from their respective oxides (99.9% pure) as reported earlier[3]. BMPP was prepared by benzoylating 3-methyl-1-phenyl-pyrazol-5-one (MPP) by the Jensen method[2,4]. The schiff base, BMPIH, was prepared by condensing equimolar amounts of BMPP (27.8 g) and isonicotinylhydrazine (13.7 g) in ethanol (200 ml each) on a water bath for about 4h. Then the reaction mixture was concentrated to 100 ml, from which on cooling BMPIH crystallized out as red crystals. These crystals were filtered, washed with the minimum quantity of cold ethanol (10 ml) and recrystallized from hot ethanol. The purity of the sample was checked by elemental analysis, IR spectrum, and melting point (230°C).

All the nine complexes were prepared by the following general procedure. Solutions of lanthanide (III) nitrate (0.5 g in 25 ml C_2H_5OH) and BMPIH (1.0 g in 75 ml C_2H_5OH) were mixed together and the resulting solution was kept under reflux on a water bath for 4h. Then the reaction mixture was concentrated when a viscous mass was obtained. It was washed repeatedly with hot benzene (10 ml each) to remove excess ligand. The solid complex was dissolved in hot ethanol (25 ml and the clear solution was stirred after adding diethyl ether (75 ml) when the complex precipitated. The complexes so separated were collected and dried *in vacuo* over phosphorus (V) oxide (yield = ~92%).

Molar conductivities of the complexes at room temperature (28 ± 2°C) were measured in acetonitrile, methanol and nitrobenzene ($\sim 10^{-3}$ *M* solutions) using an Elico conductivity bridge type M82T equipped with a dip type cell having platinum electrodes (cell constant of 1.64 cm^{-1}). Magnetic susceptibilities of the complexes were determined at room temperature by the Gouy method[5]. Electronic spectra of the ligand (BMPIH) and the lanthanide complexes in methanol ($\sim 10^{-4}$ *M* solutions) were recorded on a Hitachi 220A double beam uv-visible spectrophotometer in the range 185-900 nm. The IR spectra of the ligand and the complexes were recorded in KBr using a Perkin-Elmer 397 IR



keto form (I) enol form

spectrophotometer. The lanthanide contents of the complexes were determined by the oxalate-oxide method[6] and the nitrate contents by the nitron method[7]. The carbon, hydrogen and nitrogen analyses of the ligand and the complexes were carried out at the Regional Sophisticated Instrumentation Center, CDRI, Lucknow. Molecular weights of the complexes were determined by the Rast method using biphenyl as the solvent[8].

Results and discussion

All the complexes are non-hygroscopic solids, which are moderately soluble in acetonitrile, ethanol, methanol and nitrobenzene, and insoluble in benzene, carbon tetrachloride, chloroform, diethyl ether, and petroleum ether. From the elemental analysis, molecular weight and molar conductance data (Table 1), all the complexes can be formulated as $[Ln(BMPIH)_2(NO_3)_3]$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y. Molar conductivity values of the complexes in acetonitrile (52-82 ohm^{-1}cm^{2}mol^{-1}) and in methanol (172-219 ohm^{-1}cm^{2}mol^{-1}) indicate considerable solvolysis. However, values in nitrobenzene (1.3-1.9 ohm^{-1}cm^{2}mol^{-1}) indicate non-electrolytic behaviour. Therefore, molar conductivity data suggest that the nitrate ions are within the coordination sphere in these complexes. The room temperature magnetic moments of the complexes are in agreement with the theoretical values calculated by the Van Vleck formula[10]. Thus, the La and Y complexes are diamagnetic, whereas all the other complexes are paramagnetic in nature.

The electronic spectrum of the ligand exhibits two bands in the UV region at 40.0 and 47.6 kK. These two bands are present in the spectrum of the complexes also, which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. There is no absorption in the visible region for the ligand and the complexes. However, the spectra of the complexes show an additional broad band at 27.7 kK in the UV region. This broad band is attributed to strong L→M charge-transfer transitions.

The IR spectrum of the ligand (BMPIH) exhibits a medium band at 3300 cm^{-1}, which is assigned to νNH mode. This band is present in the spectra of the complexes also in the same region suggesting that both the imino nitrogen atoms do not participate in coordination. The spectrum of the ligand also exhibits broad band at 2560 cm^{-1} and a strong sharp band at 1630 cm^{-1}. The broad band is attributed to νOH mode of the enol form of the ligand, in which the OH group is strongly hydrogen bonded as shown in (I). The sharp band at 1630 cm^{-1} is assigned to νC=O of the ring carbonyl group present in the keto form. Therefore, BMPIH exhibits keto-enol tautomerism

Table 1—Analytical and molecular weight data of lanthanide (III) nitrate complexes with BMPIH

Complex (colour)	Found (Calc.)					
	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Nitrate (%)	Molecular wt.
$[La(BMPIH)_2(NO_3)_3]$	12.37	49.10	3.28	16.18	17.10	1066
(Orange)	(12.40)	(49.28)	(3.39)	(16.25)	(16.62)	(1120)
$[Pr(BMPIH)_2(NO_3)_3]$	12.50	49.32	3.42	16.28	16.60	1036
(Orange)	(12.60)	(49.24)	(3.39)	(16.24)	(16.59)	(1121)
$[Nd(BMPIH)_2(NO_3)_3]$	12.60	49.02	3.36	16.18	16.32	1183
(Orange)	(12.80)	(49.11)	(3.38)	(16.20)	(16.54)	(1124)
$[Sm(BMPIH)_2(NO_3)_3]$	13.20	48.68	3.34	16.20	16.54	1119
(Orange)	(13.30)	(48.85)	(3.36)	(16.10)	(16.45)	(1130)
$[Eu(BMPIH)_2(NO_3)_3]$	13.49	48.50	3.28	16.14	16.48	1120
(Orange)	(13.42)	(48.76)	(3.35)	(16.08)	(16.43)	(1132)
$[Gd(BMPIH)_2(NO_3)_3]$	13.74	48.66	3.40	15.96	16.58	1197
(Orange-Yellow)	(13.82)	(48.55)	(3.34)	(16.00)	(16.35)	(1137)
$[Tb(BMPIH)_2(NO_3)_3]$	13.94	48.54	3.28	16.02	16.50	1198
(Yellow)	(13.95)	(48.46)	(3.33)	(15.97)	(16.33)	(1139)
$[Dy(BMPIH)_2(NO_3)_3]$	14.19	48.32	3.29	15.84	16.36	1165
(Yellow)	(14.22)	(48.29)	(3.32)	(15.92)	(16.28)	(1143)
$[Y(BMPIH)_2(NO_3)_3]$	8.34	51.45	3.62	16.98	17.54	1009
(Yellow)	(8.32)	(51.64)	(3.55)	(17.03)	(17.40)	(1069)

when it is free. However, in the spectra of the complexes the broad band corresponding to νOH disappears and the band corresponding to νC = O of the ring carbonyl is shifted to 1610 cm^{-1}. These changes indicate that the ligand exists exclusively in the keto form in the complexes bonding through the ring carbonyl oxygen.

A strong sharp band observed at 1680 cm^{-1} in the spectra of the ligand and complexes is attributed to νC = O of the side chain carbonyl group attached to the hydrazine part. Since there is no change in the frequency of νC = O (side chain) on complexation it is suggested that this carbonyl group does not take part in coordination in the present series of complexes. The IR spectrum of BMPIH exhibits two strong bands at 1600 and 1580 cm^{-1}, which are assigned to νC = C and νC = N, respectively. The pyridine ring stretching vibrations appear at 1550 and 1470 cm^{-1} and the out-of-plane bending of CH of the pyridine ring at 830 cm^{-1} in the spectrum of the ligand. In the spectra of the complexes the band due to band due to νC = C and the two bands at 1470 and 830 cm^{-1} due to the pyridine ring remain unaltered, whereas the νC = N mode is shifted to 1560 cm^{-1}. The band at 1550 cm^{-1} of the ligand is shifted to 1540 cm^{-1}. The shift of νC = N mode indicates that the azomethine nitrogen takes part in complex formation. Since the positions of the bands due to the pyridine ring do not change appreciably in the spectra of the complexes, it is suggested that the pyridine nitrogen does not take part in coordination and hence BMPIH acts as a neutral bidentate ligand coordinating through the ring carbonyl oxygen and azomethine nitrogen.

In the spectra of the complexes five new bands appear at 1430, 1320, 1020, 540 and 480 cm^{-1}. The first three bands are assigned to ν_4, ν_1 and ν_2 modes respectively, of the coordinated nitrate ion. Since the separation between ν_4 and ν_1 is of the order of ~ 110 cm^{-1}, the nitrate ions are suggested to be coordinated unidentately in these complexes[11]. The bands at 540 and 480 cm^{-1} are attributed to νM − N and νM − O, respectively[12], nitrogen having a smaller mass than oxygen.

From the foregoing discussion it is concluded that BMPIH acts as a neutral bidentate ligand coordinating through the ring carbonyl oxygen and the azomethine nitrogen. In these complexes the nitrate ions are coordinated unidentately and hence, a coordination number of 7 is assigned to the lanthanide ions.

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