

Complexes of Lanthanide Nitrates & Perchlorates with 1-Carbamido-3-methylpyrazol-5-one

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Fourteen new complexes of lanthanide nitrates and perchlorates with 1-carbamido-3-methylpyrazol-5-one (CMP) having the general formula $[\text{Ln}(\text{CMP})_2\text{X}_3]_n$ (where Ln = La, Pr, Nd, Sm, Gd, Dy and Y; X = NO_3 or ClO_4 ; $n = 2-6$) have been prepared and characterized. The complexes are insoluble in common solvents and are polymeric in nature. The IR spectral data show that the nitrate and perchlorate ions are coordinated unidentately, while the ligands are coordinated tridentately through the ring carbonyl oxygen and the carbamido oxygen to one metal ion and nitrogen of the $-\text{NH}_2$ (carbamido) to another metal ion in a polymeric structure with a coordination number of six to each of the lanthanide ions.

As a part of our programme on the synthesis and characterization of solid lanthanide complexes with pyrazolone-type ligands^{1,2}, in this note we report the synthesis and characterization of solid complexes of lanthanide nitrates and perchlorates with 1-carbamido-3-methylpyrazol-5-one (CMP). This ligand is of particular interest, as it contains in addition to carbonyl group at 5-position as the donor site, two more donor sites namely, oxygen of the $>\text{C}=\text{O}$ group and nitrogen of the $-\text{NH}_2$ group of the carbamido group.

The nitrate and perchlorate salts of La, Pr, Nd, Sm, Gd, Dy and Y were prepared³ from the respective oxides (99.9% pure). The ligand was prepared by the literature method^{4,5} and its purity ascertained by elemental and spectral analyses and its m.p. which tallied with that reported in literature.

The nitrate and perchlorate complexes were prepared by a similar method. Solutions of lanthanide nitrate or perchlorate (2 mmol) and CMP (6 mmol) in minimum amount of hot ethanol were mixed and the resulting solution was refluxed for 1.5 to 2 hr. After cooling, ether was added to the reaction mixture in small portions with vigorous stirring when the complex precipitated out. It was filtered, washed repeatedly with ether and hot ethanol and dried *in vacuo* over P_4O_{10} . The prepared complexes were analysed for metal, nitrogen or perchlorate by standard methods⁶⁻⁸.

The magnetic susceptibilities of the complexes were measured at room temperature by the Gouy

method using mercury (II) tetrathiocyanatocobaltate(II) as the calibrant. The IR spectra of the ligand and complexes in the range $400-4000\text{ cm}^{-1}$ were recorded in KBr on a Perkin-Elmer 397 double beam IR spectrophotometer. The molecular weights of the complexes were determined by the Rast method using biphenyl as the solvent⁹.

The analytical data (Table 1) show that all the 14 complexes have the general formula $\text{Ln}(\text{CMP})_2\text{X}_3$ (where Ln = La, Pr, Nd, Sm, Gd, Dy and Y; X = NO_3 or ClO_4). The complexes are non-hygroscopic solids, insoluble in common solvents such as water, methanol, acetonitrile, benzene, nitrobenzene, ether, petroleum ether, etc. Hence the conductances of the complexes could not be determined. All the complexes decompose without melting on heating. The above observations indicate that the complexes may be polymeric in nature.

The room temperature magnetic data of the complexes (Table 1) indicate that the complexes of La and Y are diamagnetic as expected, while measured magnetic moments of other complexes agree well with those calculated using the Van Vleck formula¹¹. The molecular weights of the complexes reveal them to be polymeric consisting of 2-6 units.

The IR spectrum of the free ligand (CMP) exhibits a strong doubly split band around 3450 cm^{-1} , attributable to νNH_2 . This band is shifted to 3370 cm^{-1} in the IR spectra of the complexes indicating that the $-\text{NH}_2$ group is involved in coordination. Two strong free ligand bands around 1700 and 1640 cm^{-1} have been assigned to $\nu\text{C}=\text{O}$ of the amide group and carbonyl at position-5, respectively. In the complexes, these bands are shifted and appear respectively around 1660 and 1600 cm^{-1} indicating that both the oxygen atoms of the amidecarbonyl and the carbonyl at position-5 are coordinated to the metal ion.

The IR spectra of the perchlorate complexes show a doubly split, very strong band at 1075 and 1095 , a weak band at 920 and a strong band at 620 cm^{-1} . These are attributed respectively to ν_3 , ν_1 and ν_4 vibrations of the monodentately coordinated perchlorate group¹¹. Thus, the IR spectra of these complexes clearly indicate that the perchlorate groups are coordinated to the metal ion in a unidentate fashion.

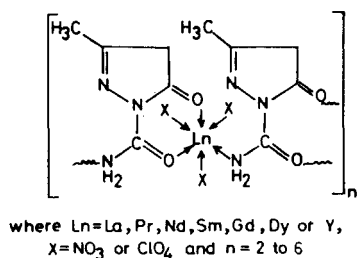
In the IR spectra of the nitrate complexes, two strong bands are present at 1420 and 1310 cm^{-1} , which are not present in the free ligand. These bands are assigned to ν_4 and ν_1 vibrations, respectively of the coordinated nitrate ion. The difference $\nu_4 - \nu_1$ is

Table 1 — Analytical and Magnetic Data of Lanthanide Complexes of 1-Carbamido-3-methylpyrazol-5-one

No.	Complex	Colour	Found (Calc. %)		μ_{eff} B.M.	Mol. weight
			Metal	N/CIO ₄		
1	[La(CMP) ₂ (NO ₃) ₃] ₃	Pale yellow	22.70 (22.88)	21.41 (20.76)	0.00 (0.00)	2022 (1821)
2	[Pr(CMP) ₂ (NO ₃) ₃] ₃	Light yellow	23.12 (23.14)	21.99 (20.69)	3.29 (3.62)	1875 (1827)
3	[Nd(CMP) ₂ (NO ₃) ₃] ₃	Pale yellow	23.89 (23.56)	20.80 (20.57)	3.30 (3.68)	1865 (1836)
4	[Sm(CMP) ₂ (NO ₃) ₃] ₃	Pale yellow	24.43 (24.32)	21.69 (20.37)	1.80 (1.55-1.65)	1695 (1854)
5	[Gd(CMP) ₂ (NO ₃) ₃] ₃	Dull white	24.64 (24.99)	21.42 (20.15)	7.79 (7.94)	3591 (3750)
6	[Dy(CMP) ₂ (NO ₃) ₃] ₆	White	25.34 (25.77)	19.42 (19.98)	10.50 (10.60)	3191 (3150)
7	[Y(CMP) ₂ (NO ₃) ₃] ₅	Pale yellow	15.83 (15.97)	20.72 (22.62)	0.00 (0.00)	2887 (2785)
8	[La(CMP) ₂ (ClO ₄) ₃] ₂	Brownish yellow	19.30 (19.29)	41.06 (41.46)	0.00 (0.00)	1508 (1439)
9	[Pr(CMP) ₂ (ClO ₄) ₃] ₂	Dull white	19.50 (19.54)	41.12 (41.34)	3.30 (3.62)	1710 (1443)
10	[Nd(CMP) ₂ (ClO ₄) ₃] ₂	Pale yellow	19.64 (19.92)	41.15 (40.68)	3.30 (3.68)	1503 (1450)
11	[Sm(CMP) ₂ (ClO ₄) ₃] ₂	Yellowish brown	20.26 (20.58)	40.81 (40.50)	1.57 (1.55-1.65)	1629 (1462)
12	[Gd(CMP) ₂ (ClO ₄) ₃] ₄	Yellow	20.95 (21.32)	40.43 (40.08)	7.33 (7.94)	2783 (2948)
13	[Dy(CMP) ₂ (ClO ₄) ₃] ₄	Pale yellow	21.86 (21.88)	40.14 (39.96)	10.58 (10.60)	2801 (2972)
14	[Y(CMP) ₂ (ClO ₄) ₃] ₂	Light yellow	13.30 (13.29)	44.56 (44.10)	0.00 (0.00)	1671 (1338)

110 cm⁻¹ in these complexes, which shows that the nitrate group is coordinated to the lanthanide ion unidentately¹².

In the light of the above discussion, we have assigned structure (I) to these complexes:



We have not been able to undertake X-ray studies on single crystals and hence the exact geometry cannot be proposed.

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