

Thorium(IV) Nitrate Complexes with Some Substituted Pyrazol-5-ones

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Received 31 August 1987; revised 4 February 1988;

accepted 16 February 1988

Nine new complexes of thorium(IV) nitrate with some pyrazol-5-one derivatives such as 3-methyl-1-phenylpyrazol-5-one, 3-methyl-4-phenacyl-1-phenylpyrazol-5-one, 4-benzoyl-3-methyl-1-phenylpyrazol-5-one, 3-methyl-4-nitroso-1-phenylpyrazol-5-one, 3-methyl-4-nitrosopyrazol-5-one, 2,3-dimethyl-4-nitroso-1-phenylpyrazol-5-one, 1-carbimido-3-methylpyrazol-5-one, 2,3-dimethyl-1-phenyl-4-(2,4-dihydroxyphenylazo)pyrazol-5-one and 2,3-dimethyl-1-phenyl-4-(2-hydroxynaphthylazo)pyrazol-5-one have been synthesised and characterised on the basis of elemental analyses, IR spectral, conductance, magnetic moment and molecular weight data.

Pyrazolone and substituted pyrazolones form stable complexes with lanthanides and actinides¹⁻⁸. Herein we report the preparation and characterisation of nine new stable complexes of thorium(IV) nitrate with some pyrazolone derivatives, viz. 3-methyl-1-phenylpyrazol-5-one (MPP), 3-methyl-4-phenacyl-1-phenylpyrazol-5-one (MPPP), 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (BMPP), 3-methyl-4-nitroso-1-phenylpyrazol-5-one (MNPP), 3-methyl-4-nitrosopyrazol-5-one (MNP), 2,3-dimethyl-4-nitroso-1-phenylpyrazol-5-one (DNPP), 1-carbimido-3-methylpyrazol-5-one (CMP), 2,3-dimethyl-1-phenyl-4-(2,4-dihydroxyphenylazo)pyrazol-5-one (DPDP) and 2,3-dimethyl-1-phenyl-4-(2-hydroxynaphthylazo)pyrazol-5-one (DHPH).

Thorium(IV) nitrate (BDH, 99.9% pure) was used as such. The ligand MPP was obtained commercially (BDH, AR) and all other ligands were prepared by literature methods⁹⁻¹⁴. The solvents such as methanol, ethanol, chloroform, acetone, acetonitrile and ether were dried by the usual methods. The complexes were prepared as described below.

A solution of thorium nitrate (2 mmol) and the ligand (4 mmol for DNPP, CMP and DPDP; 6 mmol for other ligands) in methanol (for MPP and MPPP), ethanol (for BMPP and DNPP), acetone (for MNPP, MNP and DHPH) and acetonitrile (for CMP and DPDP) was refluxed for 3 hr. In the case of BMPP sodium acetate (1 g) was also added. The resulting solution was concentrated (i) to a viscous mass in the cases of MPP, MPPP, MNPP, MNP and DHPH, (ii) to half the volume to get crystals of the com-

plexes of BMPP, CMP and DPDP and (iii) to one quarter of its volume to get crystals of DNPP complex. The viscous masses obtained for MPP, MNPP, MNP and DPHP were stirred repeatedly with hot benzene to remove excess ligands leaving behind solid complexes. The MPP complex was recrystallised by dissolving in minimum quantity of methanol and adding ether, while the complexes of MNPP, MNP and DPHP were recrystallised from acetone after adding ether. The complex of MPPP obtained as a viscous mass was washed several times with chloroform to remove excess ligand and the complex was recrystallised from methanol after adding chloroform. All the complexes were filtered and dried *in vacuo* over phosphorus(V) oxide.

Room temperature ($28 \pm 2^\circ\text{C}$) molar conductivities of $10^{-3} M$ solutions of the complexes in acetonitrile, methanol and nitrobenzene were measured using an ELICO conductivity bridge type CM 82 fitted with dip type cell (type-CC-03) having platinum electrodes (cell constant, 1.28 cm^{-1}). Room temperature magnetic susceptibilities were measured by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The IR spectra of the ligands and the complexes were recorded in KBr in the range $4000\text{-}400 \text{ cm}^{-1}$ on a Perkin-Elmer 397 IR spectrophotometer. Molecular weights of the complexes ($\sim 10^{-3} M$ solutions) were determined by the cryoscopic method using nitrobenzene as the solvent¹⁵.

All the complexes are coloured non-hygroscopic crystalline solids (Table 1). Analytical and molecular weight data of the complexes (Table 1) indicate the general compositions as $\text{ThL}_3(\text{NO}_3)_4$ (L = MPP, MPPP and MNPP), $\text{Th}(\text{BMPP})_3\text{NO}_3$, $\text{ThL}_2(\text{NO}_3)_4$ (L = MNP, DNPP and CMP) and $\text{ThL}_2(\text{NO}_3)_2$ (L = DPDP and DHPH). Amongst the nine complexes, $\text{Th}(\text{CMP})_2(\text{NO}_3)_4$ and $\text{Th}(\text{DPDP})_2(\text{NO}_3)_2$ are insoluble in almost all the common solvents and hence their molecular weights and molar conductivities could not be determined.

Molar conductances of the complexes in acetonitrile, methanol and nitrobenzene (Table 1) are in the ranges expected for nonelectrolytes indicating that nitrate ions are coordinated to the metal ions¹⁶. However, in acetonitrile and methanol slightly higher values than those expected for nonelectrolytes are observed for some of the complexes. This is probably due to partial replacement of the coordinated nitrate groups by the solvent molecules. All

Table 1—Analytical, Molecular Weight and Conductance Data of Thorium(IV) Nitrate Complexes with Some Pyrazol-5-one Derivatives

Complex	Colour	Found (Calc), %				Mol. wt found (Calc)	Λ_M of 10^{-3} M solutions		
		Metal	C	H	N		Aceto-nitrile	Methanol	Nitro-benzene
[Th(MPP) ₃ (NO ₃) ₄]	Pale yellow	23.1 (23.0)	36.1 (35.9)	3.2 (3.0)	13.7 (13.9)	1017 (1002)	42.2	113.2	7.9
[Th(MPPP) ₃ (NO ₃) ₄]	Brown	17.1 (17.0)	47.5 (47.7)	3.5 (3.5)	10.4 (10.3)	1330 (1356)	41.4	97.3	8.7
[Th(BMPP) ₃ (NO ₃) ₃]	Yellow	20.4 (20.6)	54.3 (54.4)	3.5 (3.5)	8.2 (8.7)	1096 (1125)	—	45.8	2.4
[Th(MNPP) ₃ (NO ₃) ₄]	Yellow	21.0 (21.3)	32.9 (33.1)	2.6 (2.5)	16.4 (16.7)	1038 (1089)	15.9	—	2.3
[Th(MNP) ₂ (NO ₃) ₄]	Yellow	31.7 (31.6)	13.0 (13.1)	1.5 (1.4)	19.0 (19.1)	752 (734)	23.6	63.2	2.3
[Th(DNPP) ₂ (NO ₃) ₄]	Brown yellow	25.4 (25.4)	28.6 (28.9)	2.9 (2.4)	15.3 (15.3)	952 (914)	48.2	94.3	6.5
[Th(CMP) ₂ (NO ₃) ₄]	Pale pink	30.3 (30.4)	15.3 (15.7)	1.8 (1.8)	18.2 (18.4)	— (762)	—	—	—
[Th(DPDP) ₂ (NO ₃) ₂]	Red orange	23.0 (23.1)	40.2 (40.7)	2.9 (3.0)	13.6 (13.9)	— (1002)	—	—	—
[Th(DPHP) ₂ (NO ₃) ₂]	Red orange	21.5 (21.7)	47.2 (47.1)	3.3 (3.2)	13.0 (13.1)	1041 (1070)	61.3	113.7	8.5

the complexes, as expected for Th⁴⁺ ion, are diamagnetic.

The IR spectra of the ligands exhibit $\nu_{C=O}$ modes (ring carbonyl) at 1600 (BMPP), 1605 (for MPP and MPPP), 1610 (DPDP), 1640 (CMP), 1660 (DPHP), 1680 (DNPP), 1690 (MNPP) and 1700 cm^{-1} (MNP). This band is shifted to lower wavenumber in the complexes of seven ligands (except those of MPP and MPPP) indicating that the ring carbonyl group is bonded to the metal ion in these seven complexes. While the solution spectra of MPP and its complex show that the ring carbonyl of MPP is coordinated to the metal ion, those of MPPP indicate that the ring C=O of MPPP is not coordinated. The apparent non-shift of $\nu_{C=O}$ of MPP complex in the solid state is due to the presence of strong hydrogen bonding^{3,17}. The side chain $\nu_{C=O}$ modes of MPPP (1675 cm^{-1}), BMPP (1640 cm^{-1}) and CMP (1700 cm^{-1}) are shifted to 1640, 1610 and 1660 cm^{-1} , respectively on complexation. Therefore, in the complexes of these ligands the side carbonyl group is also participating in coordination. The doubly split band in the region 3500-3450 cm^{-1} observed in the spectrum of CMP due to ν_{NH_2} is not appreciably shifted in the complex indicating noninvolvement of the $-NH_2$ group in coordination.

The $\nu_{N=O}$ modes in the spectra of MNPP, MNP and DNPP appearing in the region 1420-1410 cm^{-1} are shifted in the complexes and appear in the range

1400-1390 cm^{-1} , indicating participation of $-N=O$ group in coordination with the metal ion. The comparatively small shifts (~ 20 cm^{-1}) in $\nu_{N=O}$ modes may be due to coupling of $\nu_{N=O}$ vibration with other stretching vibrations of the ligand.

The ligand BMPP, DPDP and DPHP exhibit a broad band in the regions 2900-2300, 2900-2400 and 3600-2900 cm^{-1} , respectively, assignable to H-bonded ν_{OH} modes. On complexation this band vanishes suggesting that the hydroxy group is coordinated to the metal ion via deprotonation. The deprotonation is further supported by the elimination of the NO_3^- ions in the complexes of BMPP, DPDP, and DPHP. The band at 1220 cm^{-1} in the spectrum of DPDP is assigned to $\nu_{H-O...H}$. This mode is slightly shifted to a higher wavenumber (1230 cm^{-1}) in the complex showing that the Th⁴⁺ ion is substituted for H⁺ ion in the H-O...H system. The $\nu_{N=N}$ modes of DPDP and DPHP appearing at 1480 cm^{-1} are shifted to 1440 cm^{-1} in the complexes of these ligands indicating the participation of π bond of N=N system in complexation with the Th⁴⁺ ion.

IR spectra of all the nine complexes exhibit three additional bands at 1420, 1280 and 1020 cm^{-1} . The bands at 1420 and 1280 cm^{-1} are the two split bands ν_4 and ν_1 , respectively of the coordinated nitrate groups. The third band at 1020 cm^{-1} is attributed to ν_2 mode of NO_3 group. Since the magni-

tude of splitting, $\nu_4 - \nu_1$ is of the order of 140 cm^{-1} , nitrate groups are coordinated monodentately in all the complexes¹⁸, which is supported by the nonelectrolytic behaviour of the complexes.

The above observations and discussion suggest that the present complexes have the formulae shown in Table 1. The ligands MPP and MPPP act as monodentate ones coordinating only through the ring carbonyl group. The ligands BMPP, MNPP, MNP, DNPP and CMP are bonded to the metal ion in a bidentate fashion, while DPDP and DPHP act as tridentate ones. Of the nine complexes, the complexes $[\text{Th}(\text{BMPP})_3(\text{NO}_3)]$, $[\text{Th}(\text{DPDP})_2(\text{NO}_3)_2]$ and $[\text{Th}(\text{DPHP})_2(\text{NO}_3)_2]$ have anionic ligands resulting in the removal of the some of the nitrate ions via deprotonation. Thus, in the first three complexes the metal ion has a coordination number of seven. All the other complexes except $[\text{Th}(\text{MNPP})_3(\text{NO}_3)_4]$ have a coordination number of eight for the metal ion, while in $[\text{Th}(\text{MNPP})_3(\text{NO}_3)_4]$ a coordination number of ten is suggested for Th^{4+} ion.

The authors are grateful to Prof. C G R Nair for his helpful suggestions and also to the UGC, New Delhi for awarding a teacher fellowship under the FIP to one of them (BK).

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