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Equilibrium Studies of Lanthanide(III) Complexes of (1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one) Anthranilic Acid and (1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one) Aminoantipyrine

N. MAHALAKSHMI SITA
Inorganic and Analytical Chemistry Division
Regional Research Laboratory, Trivandrum-695 019, India

The stability constants of lanthanide(III) complexes of (1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one) anthranilic acid $[\mathrm{Ln(PMBAA)_2NO_3}]$ and (1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one) aminoantipyrine $[\mathrm{Ln(PMBAAP)_3}]$ complexes have been determined by potentiometric method and the values obtained practically agree for the whole series of lanthanide for both types of complexes. The IR spectral studies show that in both complexes the ligands are similarly coordinated by carbonyl oxygen atoms. In the $[\mathrm{Ln(PMBAA)_2NO_3}]$ complexes the nitrate ion also takes part in coordination. The multiplet pattern of NMR spectra which partially disappears show a more rigid pattern for PMBAA than for PMBAAP.

INTRODUCTION

β-Diketones are important complex forming agents in biology and medicine[1].

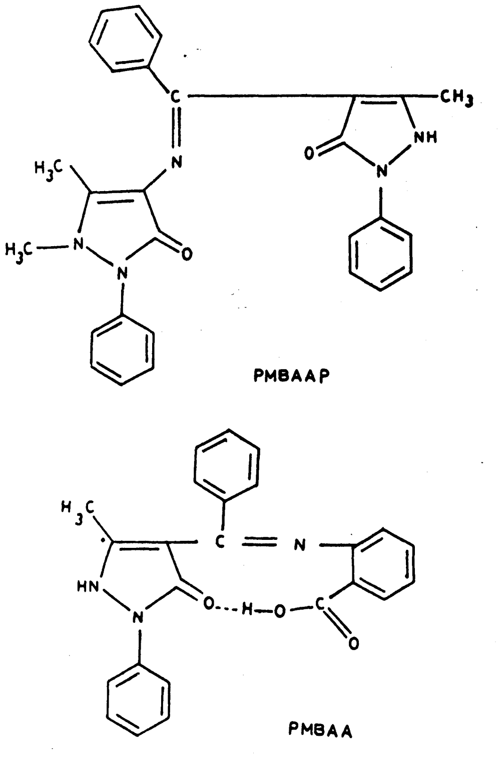

Fig. 1. Structures of PMBAAP and PMBAA.

From a comparison of stability constants of (1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one) anthranilic acid (PMBAA) and (1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one) aminoantipyrine (PMBAAP) (Fig. 1) complexes, it can be seen that the stability constants vary but display similar regularity presenting the 'gadolinium break' phenomena due to lanthanide contraction. However, in the case of lanthanide PMBAA complexes, the stability constants are higher than those of PMBAAP complexes. For an explanation, it can be assumed that PMBAA is tridentate and nitro group is taking part in coordination, whereas PMBAAP is bidentate. In both the complexes, carbonyl oxygen takes part in coordination, the base PMBP (1-phenyl-3-methyl-4-benzoyl-pyrazolone-5-one) being the same in both the ligands. It was interesting to study its coordination capacities in bonding with lanthanides in two different systems, PMBAA and PMBAAP. After detecting the formation of 1 : 2 Ln^{3+} : PMBAAP and 1 : 3 Ln^{3+} : PMBAAP complexes, detailed study of both the systems was carried out in excess ligand to study the maximum number of ligand moieties that could take part in bond formation with the lanthanide ion.

EXPERIMENTAL

The chemicals used were of AR grade. $Ln(NO_3)_3$ solutions were prepared from the appropriate oxides (Fluka) of 99.0% purity. The stability constants of PMBAA and PMBAAP with Ln^{3+} are determined by e.m.f. measurements in methanol ($t = 25 \pm 0.5°C$, $\mu = 0.1$). The ^1H NMR spectra were recorded in a Varian EM360L60 NMR spectrometer using 0.1 M solutions in $CDCl_3$ and TMS as internal standards. IR studies were recorded in a Perkin-Elmer IR spectrometer in KBr. Luminescence studies were recorded in a LS50B Perkin- Elmer spectrofluorimeter.

The base PMBP (1-phenyl-3-methyl-4-benzoyl-pyrazole-5-one) prepared by the Jenson's method was used to prepare ligands PMBAA and PMBAAP. Equimolar solutions of PMBP and anthranilic acid/amino antipyrine in ethanol were refluxed for 4 h on a water bath. The resulting solution was concentrated, washed with benzene to remove excess ligand and recrystallized in ethanol. m.p.: PMBAA = 163°C, PMBAAP = 211°C

RESULTS AND DISCUSSION

The formation of 1 : 2 Ln : PMBAA complexes has been detected by luminescence spectroscopy. In the case of Nd^{3+} the ion, low intensity band at 427 nm in the Nd^{3+} aquo ion corresponding to the transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$ is known to be very sensitive to changes in the environment. This band is red shifted by complex formation and the shift is proportional to the number of N and O donor atoms of the coordinated ligand[6, 7]. In the Nd PMBAA, the band maximum is shifted to 429.4 nm. However, when large excess of ligand is added a new blue band appears at 428.3 nm. The intensity of this band increases with rise in excess of PMBAA and pH while that of the band at 429.4 decreased. The excess of ligand being added and pH being varied is to use optimum conditions for band formation. The changes in the spectra prove the formation of a new species, which can only be

1 : 2 Nd^{3+} : PMBAA complex because it is formed in the presence of excess ligand and at pH 2. The blue shift was probably due to a slight increase in metal-donor atom distances, caused by the steric hindrance of the functional groups of the ligand[8] and /or by the increase in coordination number of the metal ion[6].

In the case of PMBAAP complexes, the changes in the spectra prove the formation of a new species which can be 1 : 3 Nd^{3+} : PMBAAP complex since it is formed in the presence of excess ligand. The blue band observed in the presence of excess ligand appears to 428 nm, the intensity of which increases with rise in excess ligand and pH. Here the intensity is less than that of the PMBAA complexes. This might be due to the increase in metal-donor atom distance caused by the steric hindrance of the ligand[8].

It is noticed that the stability constants of the complexes of Ln(III) PMBAA and PMBAAP (Fig. 2) display similar regularity from La to Lu, *i.e.*, log K_{ln}^{3+} presents the 'gadolinium break' phenomena in the order of 'lanthanide contraction' and tends to move upwards from light to heavy lanthanides which may be mainly due to solvation. It is noted that the cooordination capability of the PMBAA is stronger than that of the PMBAAP complex. It follows that tridenticity

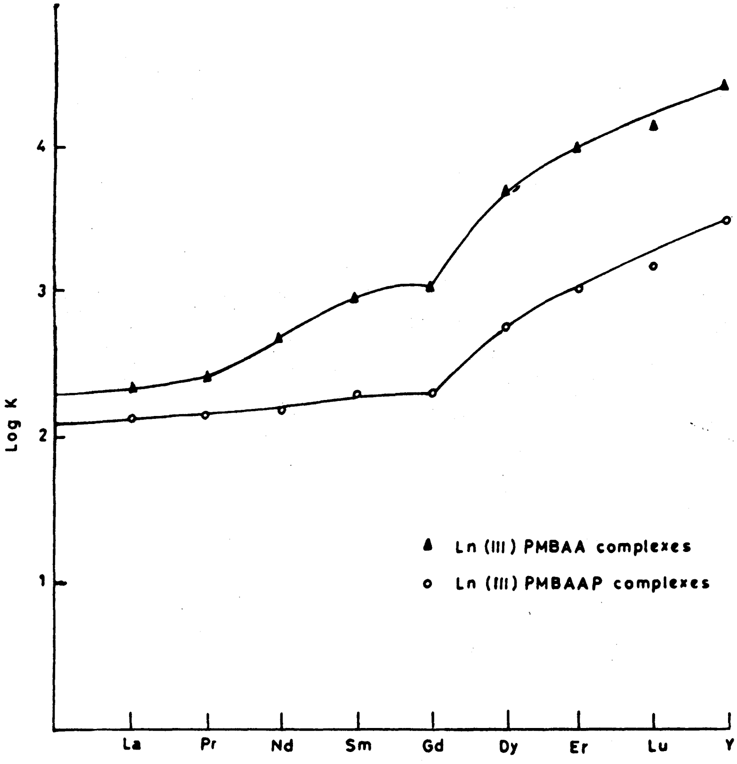

Fig. 2. Stability constants of Ln(III) PMBAA and Ln(III) PMBAAP complexes.

of the ligand and presence of nitro group in the coordination sphere increases the coordinating ability of the PMBAA ligand in its Ln(III) complexes. To get additional information on the structure, the complexes ^{1}H NMR spectra and IR spectra were recorded in the presence and absence of ligands. The IR spectra of the PMBAA complexes show that the band at 3100 cm^{-1} due to ν(OH) in the ligand is absent in the complexes. The two bands at 1600 and 1380 cm^{-1} due to ν_{asym}(OCO) and ν_{sym}(OCO) in the complexes and their differences being 220 cm^{-1} show that the carboxylate ion is bonded unidentately. The shift in the bands of ν(C=O) and ν(C=N) at 1680 and 1580 cm^{-1} further shows that the ligand PMBAA exhibits tridenticity. Three additional bands at 1430, 1310 and 1020 cm^{-1} due to ν_4, ν_1 and ν_2 of the coordinated nitrate ions are observed. The splitting of ν_4 and ν_1 being 120 cm^{-1} indicates that nitrate ion coordinates unidentately. The IR spectra of PMBAAP complexes show shift in the bands of ν(C=O). The change in the shape of the band, and a slight shoulder indicates that both the carbonyl oxygens are taking part in bond formation. Also both the complexes exhibit band at 410 cm^{-1} due to ν(Ln—O). In PMBAA complexes the additional band at 540 cm^{-1} is due to ν(Ln—N) indicating that PMBAA acts as a neutral tridentate ligand whereas PMBAAP acts as a neutral bidentate ligand in their lanthanide complexes.

The ^{1}H NMR spectra (Table-1) show interesting features. The spectra of the ligand PMBAA show a peak at 10.08 due to OH which is absent in the spectra of its complexes indicating bonding by deprotonation. The spectra groupings are due to *o*-(phenyl), *o*-(benzoyl) and *m,p*-(phenyl) protons. In complexation the *o*-(phenyl) and *m,p*-(phenyl) protons do not show much change. As expected the *o*-(benzoyl) protons are deshielded in the PMBAAP complexes; they occur at 8.38 δ, whereas in PMBAA complexes they occur as a single peak at 8.71. The reason could be that the *o*-(benzoyl) protons are adjacent to the bonding site and/or also due to the O—C=O group; the *o*-(benzoyl) protons coalesce suggesting an increase in the rate of intramolecular processes and as a consequence there will be a slight increase in the metal-donor distances leading to deshielding.

TABLE-1

NMR SPECTRA OF PMBAA AND PMBAAP AND THEIR Ln(III) COMPLEXES δ (ppm)

	o-protons		*m,p*-protons (benzoyl and phenyl)	Methyl protons
	o-(benzoyl)	*o*-(phenyl)		
PMBAA	8.12	8.09	7.66	2.57
[Ln(PMBAA)$_2$·NO$_3$]	8.71	8.06	7.64	2.56
PMBAAP	8.14	8.06	7.68	2.59
[Ln(PMBAAP)$_3$]	8.38	8.10	7.66	2.57

Thus, the ligand PMBAA coordinates to the lanthanide ions tridentately with a coordination number 7 much strongly that PMBAAP which coordinate bidentately having a coordination number of 6.

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