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Nd(III), Pr(III), Ce(III) & La(III) Complexes with 3-Formyl-4-hydroxy- & 3-Oximinomethyl-4'-nitroazobenzenes

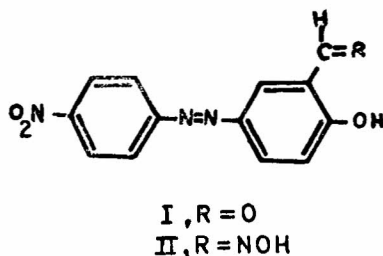
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Nd(III), Pr(III), Ce(III), and La(III) form 1:2 complexes with 3-formyl-4-hydroxy-4'-nitroazobenzene HF4NB, and 1:3 with 4-hydroxy 3-oximinomethyl-4'-nitroazobenzene (HO4NB). The complexes have been studied using Calvin-Bjerrum pH titration technique in 60% (w/w) ethanol-water medium at $28 \pm 1^\circ\text{C}$. The free energies of formation of the complexes have been evaluated. The order of stability is found to be: Nd > Pr > Ce > La. HO4NB forms stabler complexes with these metal ions.

WE have reported previously¹ the effect of methyl substitution on the stepwise stability of Nd(III), Pr(III), Ce(III) and La(III) complexes with 3-formyl-4-hydroxyazobenzene. In this note we report the synthesis of 3-formyl-4-hydroxy-4'-nitroazobenzene (HF4NB, I) and its oxime, 4-hydroxy-3-oximinomethyl-4'-nitroazobenzene (HO4NB, II). The stabilities of Nd(III), Pr(III), Ce(III) and La(III) complexes with these ligands have been studied.

HF4NB was prepared by a method similar to that reported earlier². The oxime, HO4NB, was prepared from HF4NB by standard methods. The identities of the ligands (I) and (II) were confirmed by their melting points and IR data which agreed with those reported in literature¹.



Experimental procedure was the same as reported earlier². The metal ion solutions were prepared from metal nitrates in conductivity water and a Systronic pH meter type 322 (accuracy 0.05) was used for pH measurements.

The protonation constants of the ligands HF4NB and HO4NB were found to be 7.15 and 8.84 respec-

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TABLE 1 — STABILITY CONSTANTS OF THE COMPLEXES

Metal	HF4NB log β_3	HO4NB log β_3
Nd(III) (a)	8.63 ± 0.04	15.32 ± 0.04
(b)	8.20	14.85
Pr(III) (a)	8.35 ± 0.04	14.92 ± 0.04
(b)	8.00	14.60
Ce(III) (a)	8.25 ± 0.04	14.67 ± 0.04
(b)	7.95	14.20
La(III) (a)	8.05 ± 0.04	14.47 ± 0.04
(b)	7.95	14.10

(a) Bjerrum values

(b) Correction-term method

tively as calculated by the Irving and Rossotti method³ and by direct calculations.

Formation curves for the metal-ligand systems were drawn between \bar{n} and pA which in turn were calculated by the method of Bjerrum⁴ and Calvin⁵. The log K values for the systems were taken directly from the formation curves and were refined by computational method described by Rossotti and Rossotti⁶. All metals precipitate beyond pH 7.0 in the case of HF4NB and 8.0 in the case of HO4NB. These form 1:2 complexes in the case of HF4NB and 1:3 complexes in the case of HO4NB.

Replacement of the formyl group of HF4NB by an oximinomethyl group increases the complexing tendency of the ligand considerably as seen from pK values. Both the ligands behave as monoprotic and bidentate ligands in complex formation. Instead of the oxygen of the formyl group in HF4NB, nitrogen of the oxime group in HO4NB takes part in coordination. Similar structures for some oxime complexes have been confirmed by X-ray analysis⁷. As seen from Table 1, both the 1:2 and 1:3 complexes follow the stability order Nd(III) > Pr(III) > Ce(III) > La(III). La(III), Ce(III), Pr(III) and Nd(III) possess ionic radii 1.061, 1.034, 1.013 and 0.995 Å respectively and the stability of metal complex increases with increase in ionic radius. This is also justified by considering Z^2/r values for these metal ions. The complexing tendency of the ligands may be expressed in the order HO4NB > HF4NB.

The values for the free energy changes during complexation have also been calculated ($-\Delta F \approx 12.0$ kcal/mole for complex formation with HF4NB and ≈ 21.0 kcal/mole for complex formation with HO4NB). These are in good agreement with the stability constants of the complexes.

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