

Results and Discussion

The strong ir bands at 1 700 and 1 440 cm^{-1} due to $\nu_{C=O}$ and ν_{C-O} in the spectra of homophthalic acid were shifted to $\approx 1 600$ and $\approx 1 400 \text{ cm}^{-1}$ in the spectra of cobalt(II) complexes and to 1 580 and 1 400 cm^{-1} in the spectra of nickel(II) complexes, respectively. Similarly, the strong bands at 1 650 and 1 400 cm^{-1} in the case of tetrachlorophthalic acid were shifted to 1 600 and 1 350 cm^{-1} , respectively, in the complexes of both the metal ions. This indicated the coordination of these acids through carboxyl groups. The characteristic ring vibrations of the heterocyclic bases in the range 1 600–1 450 cm^{-1} generally show significant changes on complexation as reported by Das and Rao¹ in their studies on Mn^{2+} complexes of pyridine *etc.*, but in our case, these bands could not be distinguished perhaps because of overlapping or mixing with $\nu_{C=O}$ stretching bands. The in-plane ring deformation mode observed at $\approx 500 \text{ cm}^{-1}$ undergoes a positive shift in the mixed ligand complexes confirming thereby a coordination through nitrogen. Paul *et al.*² also reported the same type of observations in their complexes of 8-hydroxyquinoline.

The μ_{eff} values for complexes of cobalt(II) except those with *o*-phenanthroline and dipyriddy were 5.0 B.M. indicating their high-spin octahedral structure. Their electronic spectra in acetone gave two bands in the region 15 000–16 000 (ν_2) and at 18 000 cm^{-1} (ν_3) corresponding to the transitions, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. The transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) could not be observed due to the limited spectral range of the instrument and hence these were calculated using band fitting procedure³ and found to be $\approx 7 400 \text{ cm}^{-1}$. The μ_{eff} values of the *o*-phenanthroline and dipyriddy complexes were found to be ~ 4.5 B.M. indicating their tetrahedral structure. Their electronic spectra gave two intense bands at $\approx 15 000$ and $\approx 24 000 \text{ cm}^{-1}$ corresponding to transitions ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_2) and charge transfer, respectively. The intensity (ϵ) values of ≈ 420 for ν_3 also confirmed their tetrahedral structure, the value for octahedral complexes were found to be ~ 5 only. The variations in the values of μ_{eff} and of molar susceptibilities χ_M with temperature also indicated their octahedral geometry. The μ_{eff} and χ_M values of *o*-phenanthroline and dipyriddy complexes were almost independent of temperature indicating their tetrahedral structure⁴.

Nickel(II) complexes of homophthalic acid except with dipyriddy and *o*-phenanthroline gave three bands in the range 9 000–12 000, 14 000–19 000 and 26 000–30 000 cm^{-1} corresponding to transitions, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. The values of B (Racah parameter) were calculated using the diagonal sum rule⁵ and were found in the range 800–1 000 cm^{-1} . The calculated

energies of ν_2 and ν_3 were in good agreement with the observed values indicating their octahedral structure. The μ_{eff} values were 2.91–3.78 B.M. The near independence of μ_{eff} values with temperature also confirmed A , ground term, and hence the octahedral geometry⁶. Nickel homophthalate complexes of dipyriddy and *o*-phenanthroline were diamagnetic and their electronic spectra in methanol gave three charge transfer bands at $\approx 41 000$, $\approx 33 500$ and $32 200 \text{ cm}^{-1}$ corresponding to the transitions, ${}^1A_{1g} \rightarrow {}^1E_u$, ${}^1A_{1g} \rightarrow {}^1A_{2u}$ and ${}^1A_{1g} \rightarrow {}^1B_{1u}$, respectively, indicating their square-planar structure. Their metal d-orbital energies were calculated assuming $F_2 = 10F_4 = 700 \text{ cm}^{-1}$. The values of Δ_2 and Δ_3 were found to be 8 300 and 5 750 cm^{-1} for dipyriddy complexes and 8 100 and 6 150 cm^{-1} for *o*-phenanthroline complexes, respectively.

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Synthesis and Characterisation of Lanthanide Iodide and Thiocyanate Complexes with 5,6-Benzoquinoline-*N*-oxide

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A number of workers¹⁻³ have isolated a number of lanthanide(III) complexes of aromatic amine-*N*-oxides and found that these ligands occupied six to ten coordination positions of the lanthanide ion. To confirm the view we have isolated a number of complexes of lanthanide iodides and thiocyanates with 5,6-benzoquinoline-*N*-oxide (hereafter Benzquo).

Experimental

5,6-Benzoquinoline was obtained from E. Merck and its *N*-oxidation was carried out by method of Ochiai⁴.

$[\text{Ln}(\text{Benzquo})_3(\text{NCS})_3]$: A warm ethanolic solution (20 ml) of lanthanide nitrate hexahydrate (1.0 mmol) was added to warm ethanolic solution (40 ml)

of potassium thiocyanate (8.0 mmol). The solution was evaporated to half its volume and left overnight for complete precipitation of potassium nitrate, which was removed by filtration. The filtrate was mixed with an ethanolic solution (75 ml) of the ligand Benzquo (5.0 mmol) and refluxed for about 0.5 h on a water-bath. The reaction mixture was concentrated on the water-bath until a precipitate was obtained (digested for about 15 min), which was filtered, washed thoroughly with ethanol and ether and dried over P_4O_{10} in a vacuum desiccator (yield ~75%).

$[Ln(\text{Benzquo})_7I]_2$: Lanthanide(III) iodide was first prepared by treating solutions of $Ln(NO_3)_3 \cdot 6H_2O$ (1.0 mmol) and KI (3.0 mmol) in methanol, and the precipitated KNO_3 was removed by filtration. To the filtrate containing LnI_3 , was added ethanolic solution (100 ml) of the Benzquo ligand (7 mmol) and refluxed for about 0.5 h on a water-bath. The complex $[Ln(\text{Benzquo})_7I]_2$ precipitated on cooling was filtered, washed with ethanol and ether and dried as before (yield ~65%).

The analytical procedure and the physical methods used in the present investigation were the same as described earlier⁶.

Results and Discussion

The complexes are soluble in common organic solvents. Electrolytic conductance data in nitrobenzene (Table 1) indicate 1 : 2 electrolyte behaviour for the iodo complexes, while in case of the thiocyanato complexes, the values are too low to account any dissociation in nitrobenzene. Thus all the thiocyanato complexes could be formulated as $[Ln(\text{Benzquo})_8(\text{NCS})_2]$ and the iodo complexes as $[Ln(\text{Benzquo})_7I]_2$, where $Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho$ and Yb . Further, the ir studies reveals the monodentate nature of the ligand and thus an apparent coordination number eight for the tripositive lanthanides has been suggested.

The magnetic moments (μ_{eff}) of the lanthanide complexes measured at room temperature (*ca.* 32°) show little deviation from the Van Vleck values⁶ indicating thereby that 4f-electrons do not participate in bond formation in these complexes. Thus, the magnetic moments of these complexes are within the range predicted and observed in the compounds of the lanthanide ions⁶⁻⁷.

The ir spectra of the complexes indicate the absence of water molecules. In the free ligand Benzquo, the ν_{NO} and δ_{NO} appeared at 1 235 and

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compd.	Colour	M p. °C	Analysis % : Found/(Calcd.)			Λ_m $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} B.M.
			Metal	N	Anion		
$[La(\text{Benzquo})_7I]_2$	Dirty white	125	7.48 (7.37)	5.31 (5.20)	20.40 (20.21)	44.9	Diamag.
$[Pr(\text{Benzquo})_7I]_2$	Greenish black	115	7.55 (7.47)	5.26 (5.19)	20.32 (20.19)	45.6	3.49
$[Nd(\text{Benzquo})_7I]_2$	Light brown	129	7.70 (7.62)	5.26 (5.18)	20.30 (20.16)	47.9	3.57
$[Sm(\text{Benzquo})_7I]_2$	Dark brown	186	7.96 (7.91)	5.23 (5.17)	20.18 (20.09)	51.2	1.61
$[Gd(\text{Benzquo})_7I]_2$	Brown	110	8.39 (8.25)	5.21 (5.15)	20.02 (20.02)	50.9	7.79
$[Tb(\text{Benzquo})_7I]_2$	Dark brown	120	8.41 (8.35)	5.20 (5.14)	20.11 (20.00)	46.9	9.56
$[Dy(\text{Benzquo})_7I]_2$	Brown	118	8.67 (8.51)	5.26 (5.14)	20.10 (19.96)	50.2	10.67
$[Ho(\text{Benzquo})_7I]_2$	Very light brown	135	8.70 (8.63)	5.19 (5.13)	20.06 (19.94)	50.9	10.17
$[Yb(\text{Benzquo})_7I]_2$	Dark brown	192	9.15 (9.01)	5.24 (5.11)	20.01 (19.85)	49.9	4.49
$[La(\text{Benzquo})_8(\text{NCS})_2]$	Brown	—	10.86 (10.79)	8.79 (8.70)	13.62 (13.51)	3.9	Diamag.
$[Pr(\text{Benzquo})_8(\text{NCS})_2]$	Light brown	125	10.99 (10.98)	8.82 (8.68)	13.58 (13.49)	4.1	3.39
$[Nd(\text{Benzquo})_8(\text{NCS})_2]$	Dirty white	90	11.22 (11.14)	8.76 (8.66)	13.55 (13.46)	3.7	3.51
$[Sm(\text{Benzquo})_8(\text{NCS})_2]$	Very light brown	115	11.69 (11.55)	8.71 (8.62)	13.51 (13.39)	4.9	1.59
$[Gd(\text{Benzquo})_8(\text{NCS})_2]$	Pink	110	12.10 (12.02)	8.66 (8.58)	13.40 (13.32)	5.1	7.81
$[Tb(\text{Benzquo})_8(\text{NCS})_2]$	Light brown	130	12.23 (12.16)	8.70 (8.56)	13.42 (13.30)	4.6	9.47
$[Dy(\text{Benzquo})_8(\text{NCS})_2]$	Brown	115	12.50 (12.39)	8.68 (8.54)	13.36 (13.27)	5.2	10.59
$[Ho(\text{Benzquo})_8(\text{NCS})_2]$	Light brown	110	12.66 (12.56)	8.61 (8.52)	13.38 (13.24)	4.8	10.21
$[Yb(\text{Benzquo})_8(\text{NCS})_2]$	Pink	182	13.15 (13.09)	8.59 (8.47)	13.29 (13.16)	4.9	4.51

840 cm^{-1} , respectively^{8,9}. Upon complexation the ν_{N-O} centered in the region 1230–1222 cm^{-1} . This lowering of the ν_{NO} was in accordance with O-complexation in all these complexes¹⁰. In most of the complexes, δ_{NO} appearing in the region 830–820 cm^{-1} indicates that it was lowered by some 20–10 cm^{-1} ; this further supported of the coordination through the oxygen. The C—H out-of-plane vibration of the ligand shifted to a higher wave number by 10 cm^{-1} in the complexes due to decrease in the electron density in the aromatic ring as a consequence of ligand to metal charge transfer. The 400–385 cm^{-1} band are tentatively assigned to $\nu_{Ln-O}^{1,18}$. In all the thiocyanato complexes the N-bonded mode of coordination of thiocyanato group^{11,12} was confirmed by the appearance of the bands at \sim 2025, 790 and 470 cm^{-1} , assigned to ν_{CN} , ν_{CS} and δ_{NCB} , respectively.

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Extraction of Titanium(IV) from Acidic Thiocyanate Solution by Tri-isoamyl Phosphate

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AMONG the phosphatic solvents trioctylphosphine oxide (TOPO), diethylhexylphosphoric acid (DEHPA) and tri-n-butyl phosphate (TBP) have been successfully utilised for the extraction of Ti^{IV} from aqueous acidic solutions^{1,2}. Tri-isoamyl phosphate (TAP), an indigenous solvent prepared from fusel oil and a by-product of Indian alcohol industry, has been used for the extraction of Ti^{IV} from its aqueous hydrochloric acid solutions³.

Experimental

Tri-isoamyl phosphate (TAP) was prepared by the standard method as reported earlier³. Stock solution of Ti^{IV} was prepared by digesting potassium titanyle oxalate in concentrated hydrochloric acid and heating with concentrated nitric acid in order to remove the oxalate. Ti^{IV} content of the stock solution was determined spectrophotometrically by the H_2O_2 method⁴. Experimental solutions of Ti^{IV} were prepared by appropriate dilution of the stock solution. All other reagents were of A.R. grade.

The solvent (15 ml) was equilibrated with an equal volume of the aqueous layer having the desired acidity but no Ti^{IV} . The pre-equilibrated solvent (10 ml) was equilibrated with an equal volume of aqueous layer containing requisite amount of sodium thiocyanate and appropriate amount of Ti^{IV} in a stoppered measuring cylinder.

Concentration of hydrogen ion in the aqueous and organic phase (by back-extraction into deionised water) in all the experiments was determined by potentiometric titration with standard alkali. The concentrations of thiocyanate ion and Ti^{IV} in the organic phase were estimated spectrophotometrically⁴. Carbon tetrachloride was invariably used as a diluent because it was completely miscible with TAP. Initial experiments had shown that a 33% solution of TAP gave maximum extraction of Ti^{IV} and a further increase in the concentration of extractant did not increase the distribution ratio.

Results and Discussion

The effect of variation of $[\text{SCN}]^-$ at an arbitrarily fixed $[\text{HCl}]$ of 5.0 M showed that the distribution coefficient increases with increasing thiocyanate ion concentration and was maximum at $[\text{SCN}]^- = 1.8 \text{ M}$; further increase in $[\text{SCN}]^-$ had no effect.