

TABLE 2—FORMATION CONSTANTS OF LANTHANIDE COMPLEXES WITH COUMARIN-3-CARBOXYLIC ACID

Metal ion	Log K_1	Log K_2
La ³⁺	3.54	2.49
Pr ³⁺	3.62	2.49
Nd ³⁺	3.69	2.59
Sm ³⁺	3.83	2.66
Eu ³⁺	3.57	2.47
Gd ³⁺	3.58	2.66
Dy ³⁺	3.72	2.63
Yb ³⁺	3.81	2.59
Y ³⁺	3.65	2.37

heavier lanthanides loss of water molecules takes place in one step.

It is difficult to assign most of the bands in the IR spectra of the complexes. The discussion has been confined to few pertinent bands. Comparing the spectra of the sodium salt of coumarin-3-carboxylic acid and the acid^{14,15} following observations are made:

(i) The sharp band at 1670 cm⁻¹ in the free ligand is absent in the sodium salt.

(ii) Two new bands appeared in the sodium salt at 1630 (medium) and 1453 cm⁻¹ (strong) are due to $\nu_{as}COO^-$ and ν_sCOO^- respectively.

(iii) A slight shift in $\nu C=O$ of δ -lactone has been observed from 1730 to 1748 cm⁻¹ on changing from the acid to its sodium salt.

It has already been observed by several authors¹⁶⁻¹⁸ that the difference, $\Delta\nu$ between the asymmetric and symmetric COO^- stretching frequencies is greater in complexes than in simple salts. It has been suggested that $\Delta\nu > 225$ cm⁻¹ indicates predominantly covalent character of the carboxylate ion while < 225 cm⁻¹, indicates its ionic nature. Thus the appearance of a new sharp band at about 1640 and a medium band at about 1410 cm⁻¹ in the lanthanide complexes of coumarin-3-carboxylates can be reasonably assigned to the asymmetric and symmetric stretching vibrations of the COO^- .

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Reaction of BCl_3 , $AlCl_3$, $SnCl_4$ & $FeCl_3$ with Phenyl Dichlorophosphine & *t*-Butyl Chloride: Isolation of Solid Complexes

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The title reaction gives solid products of the type $[Bu^t-PhPCl_2]^+ [MCl_x]^-$ (where $x = 4$ or 5). The products have been characterized on the basis of elemental analysis and IR data. Structure of iron(III) complex has been further confirmed by UV and Mössbauer studies.

RECENTLY, Bullock *et al.*¹ have obtained some interesting organophosphorus compounds from the reaction systems $AlCl_3-PCl_3$ -alkyl chlorides and $AlCl_3$ -methyl dichlorophosphine-alkyl chlorides. We report here the preparation and characterization of organophosphorus compounds of the type $(Bu^t-PhPCl_2)^+ (MCl_x)^-$ (where $M = Sn(IV)$, $Al(III)$, $Fe(III)$ or $B(III)$ and $x = 4$ or 5) obtained from the reaction of phenyl dichlorophosphine, metal chloride and *t*-butyl chloride.

Because of hygroscopic nature of the compounds all the preparations were carried out under anhydrous conditions. The reactions were carried out in carbon disulphide medium and the order of addition of reagents was kept the same as reported earlier¹, to prevent the formation of polymeric hydrocarbon compounds. However instead of using nitrogen atmosphere, the reactions were carried out under reduced pressure (150 mm). The solid complexes obtained were washed with carbon disulphide and dried *in vacuo* (1-2 mm) at room temperature, yield $> 90\%$. Experimental conditions and characterization data of the complexes are listed in Table 1. All the complexes melted with decomposition above 180-200°. The IR spectra* were recorded in nujol mull on a Beckman IR 20 spectrophotometer. The far IR spectra were recorded at IIT, Delhi. UV spectra were recorded in the solid state at room temperature. Mössbauer spectra were recorded on a constant velocity type of Mössbauer spectrometer.

The complexes were assumed to be composed of univalent ionic species of the type $[Bu^t-PhPCl_2]^+ [MCl_x]^-$ in agreement with the results obtained for $[Bu^t-PCl_2]^+ [AlCl_4]^-$ and similar compounds^{1,2}. The Mössbauer study of the iron(III) complex in the present investigation also confirmed the presence of univalent anionic species. The infrared spectra of the compounds $[Bu^t-PhPCl_2]^+ [BCl_4]^-$, $[Bu^t-PhPCl_2]^+ [AlCl_4]^-$, $[Bu^t-PhPCl_2]^+ [SnCl_5]^-$ and $[Bu^t-PhPCl_2]^+ [Fe-Cl_4]^-$ show very strong bands around 1000 and

*IR data in cm⁻¹.

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Reactants			Product, colour	Time required for the reaction (hr)	Found (calc.), %		
MCl _x (g)	PhPCl ₂ (g)	Bu ^t Cl (g)			P	M	Cl
2.142	3.40	1.80	[Bu ^t PhPCl ₂] ⁺ [BCl ₄] ⁻ white	2	7.94 (7.97)	—	54.5 (54.7)
3.365	4.5	2.4	[Bu ^t PhPCl ₂] ⁺ [AlCl ₄] ⁻ white	2	7.64 (7.65)	6.50 (6.66)	52.67 (52.59)
3.135	2.50	1.3	[Bu ^t PhPCl ₂] ⁺ [SnCl ₅] ⁻ white	6	5.82 (5.83)	22.36 (22.37)	47.41 (46.61)
2.323	2.56	1.32	[Bu ^t PhPCl ₂] ⁺ [FeCl ₄] ⁻ dark yellow	10	7.20 (7.15)	12.80 (12.87)	49.46 (49.04)

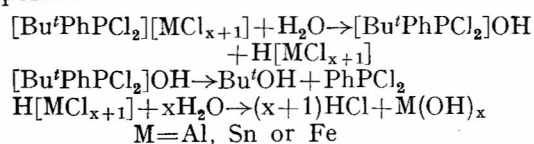
1440-1445 which may be assigned to ν P-C vibration of P-Ph moiety in conformity with earlier results³. A strong band observed in the region 790-795 is due to ν P-C vibration of P-Bu^t moiety of the phosphonium ion, [Bu^tPhPCl₂]⁺. A very strong band around 630-640 may be due to overtone or combination bands. In the far IR region, bands around 605-615 and 472-508 may be assigned to ν P-Cl and ν P-C vibrations. There are some deformation modes also at 208, 210, 225, 227 and 248.

IR bands for AlCl₄⁻ anion are similar to those obtained by Bullock *et al.*¹. BCl₄⁻ shows bands at 1090, 1030, 990, 880, 720, 670, 495, 385, 307 and 285.

The IR spectrum of [Bu^tPhPCl₂]⁺[FeCl₄]⁻ shows a stretching mode at 375 which may be due to ν Fe-Cl of [FeCl₄]⁻ anion in agreement with the reported value of 385 for FeCl₄⁻ in [Ti(acac)₃]⁺[FeCl₄]⁻. The [FeCl₄]⁻ anion is known to exist in many organic solvents, aqueous solution as well as in solid state. It exists as a tetrahedral complex in solutions. UV, visible, infrared⁴ and Mössbauer studies^{4,5} of similar compounds [Si(acac)₃]⁺[FeCl₄]⁻, [Ti(acac)₃]⁺[FeCl₄]⁻, [Zr(bzbx)₃]⁺[FeCl₄]⁻ and [(C₆H₅)₄As]⁺[FeCl₄]⁻ in solid state have been made. The UV and visible spectra of these compounds show bands due to the tetrachloroferrate ion, FeCl₄⁻, at 240, 314, 362 and 447 nm which agree well with the bands observed at 236, 308, 340 and 445 nm for [Bu^tPhPCl₂]⁺[FeCl₄]⁻.

The Mössbauer spectrum of [Bu^tPhPCl₂]⁺[FeCl₄]⁻ shows a line-width of 1.2 mm/sec and an isomer shift of 0.40 mm/sec with reference to stainless steel. Such high values of line-width were also observed in similar compounds [Ti(acac)₃]⁺[FeCl₄]⁻ and [(C₆H₅)₄As]⁺[FeCl₄]⁻ for the tetrachloroferrate anion^{4,5}.

On hydrolysis, the compounds first hydrolyse to give phenyldichlorophosphine and the metal halide. The metal halide further seems to hydrolyse on heating in the presence of a small quantity of ammonia to give the metal hydroxide. Following tentative mechanism for the hydrolysis may be proposed:



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Chlorosulphates of Co(II), Ni(II) & Cu(II) & Their Pyridine Complexes

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Complexes of the type [M(Py)₄(SO₃Cl)₂] where (Py = pyridine, M = Co, Ni and Cu) have been prepared and characterized. Infrared and electronic spectra and magnetic moments have been reported. The complexes have tetragonally distorted octahedral structures with chlorosulphate groups coordinating to metal ions as a unidentate ligand.

THE chlorosulphates of transition metals have so far not been used as electron acceptors to form coordination complexes. In the present note anhydrous Co(II), Ni(II) and Cu(II) chlorosulphates have been prepared by refluxing the respective anhydrous metal acetates with excess of chlorosulphonic acid and their ability to form adducts with pyridine has been investigated.

The chlorosulphates were filtered in a dry atmosphere, washed first with thionyl chloride followed by dry carbon tetrachloride and finally dried *in vacuo*. Co(SO₃Cl)₂, a pink crystalline solid (Found: Co, 20.00; S, 21.98; Cl, 24.56. Req'd: Co, 20.34; S, 22.06; Cl, 24.48%). Ni(SO₃Cl)₂, a green crystalline solid (Found: Ni, 19.96; S, 22.00; Cl, 24.50. Req'd: Ni, 20.26; S, 22.09; Cl, 24.50%). Cu(SO₃Cl)₂, a white crystalline solid (Found: Cu, 21.10; S, 21.47; Cl, 24.14. Req'd: Cu, 21.56; S, 21.73; Cl, 24.10%).