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 \(\nu_C=O\) and \(\nu_{COO}^{-}\) respectively.

(iii) A slight shift in \(\nu C=O\) of \(\delta\)-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 authors\(^{3,16-18}\) that the difference, \(\Delta\nu\) between the asymmetric and symmetric \(\nu COO^{-}\)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 \(\nu COO^-\).}

**References**


**Table 2 — Formation Constants of Lanthanide Complexes with Coumarin-3-carboxylic Acid**

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Log (K_1)</th>
<th>Log (K_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(^{3+})</td>
<td>3.54</td>
<td>2.49</td>
</tr>
<tr>
<td>Pr(^{3+})</td>
<td>3.62</td>
<td>2.49</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>3.69</td>
<td>2.59</td>
</tr>
<tr>
<td>Sm(^{3+})</td>
<td>3.83</td>
<td>2.66</td>
</tr>
<tr>
<td>Eu(^{3+})</td>
<td>3.57</td>
<td>2.47</td>
</tr>
<tr>
<td>Gd(^{3+})</td>
<td>3.58</td>
<td>2.66</td>
</tr>
<tr>
<td>Dy(^{3+})</td>
<td>3.72</td>
<td>2.63</td>
</tr>
<tr>
<td>Yb(^{3+})</td>
<td>3.81</td>
<td>2.59</td>
</tr>
<tr>
<td>Y(^{3+})</td>
<td>3.65</td>
<td>2.37</td>
</tr>
</tbody>
</table>

**Reaction of BCl\(_3\), AlCl\(_3\), SnCl\(_4\) and FeCl\(_3\) with Phenyl Dichlorophosphine & t-Butyl Chloride: Isolation of Solid Complexes**

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*Received 6 December 1975; accepted 23 August 1976*

The title reaction gives solid products of the type [B\(_4\)-PhCl\(_4\)][MCl\(_x\)] (where \(x = 4 \text{ or } 5\)). 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 [B\(_4\)-PhCl\(_4\)]\(^x\) (MCl\(_x\))^\(-\) (where M=Sn(IV), Al(III), Fe(III) or B(III) and \(x = 4 \text{ or } 5\)) 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 earlier,\(^2\) 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°C. 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 [B\(_4\)-PhCl\(_4\)]\(^x\) [MCl\(_x\)]\(^-\) in agreement with the results obtained for [B\(_4\)-PhCl\(_4\)][AlCl\(_4\)]\(^-\) and similar compounds.\(^3\)\(^,\)\(^4\) 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 [B\(_4\)-PhCl\(_4\)]\(^-\) [BCl\(_3\)], [B\(_4\)-PhCl\(_4\)][AlCl\(_4\)]\(^-\), [B\(_4\)-PhCl\(_4\)][SnCl\(_4\)]\(^-\) and [B\(_4\)-PhCl\(_4\)][Fe-Cl\(_4\)]\(^-\) show very strong bands around 1000 and 900 cm\(^{-1}\). The Mössbauer spectrum of the iron(III) complex shows the expected magnetic hyperfine splitting and is typical of a 3d^5 iron(III) complex.
1440-1445 which may be assigned to vP-C vibration of P-Ph moiety in conformity with earlier results. A strong band observed in the region 790-795 is due to vP-C vibration of P-Bu moiety of the phosphonium ion, [Bu'PhPCl]2+. A very strong band around 630-640 may be due to overtone or combination bands around 605-615 and 472-508 may be assigned to vFe-Cl which may be due to a stretching mode at 375 which may be due to FeCl; in [Ti(acac)3]+[FeCl4]- anion and their ability to form adducts with chlorosulphonic acid and their ability to form adducts with pyridine have been investigated.

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

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Complexes of the type [M(Py),(SO3Cl)] 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 an 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, 19.96; S, 22.00; 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%).

### Table 1 — Analytical Data of the Complexes

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product, colour</th>
<th>Time required for the reaction (hr)</th>
<th>Found (calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MClx</td>
<td>PhPCl2</td>
<td>BuCl</td>
<td></td>
</tr>
<tr>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
<td></td>
</tr>
<tr>
<td>2.142</td>
<td>3.40</td>
<td>1.80</td>
<td>[Bu’PhPCl2][MClx+1]+,HOCl→[Bu’PhPCl2]OH+H[MClx+1]</td>
</tr>
<tr>
<td>3.365</td>
<td>4.5</td>
<td>2.4</td>
<td>[Bu’PhPCl2]+[Bu’PhPCl2]+[TCI]</td>
</tr>
<tr>
<td>3.135</td>
<td>2.50</td>
<td>1.3</td>
<td>[Bu’PhPCl2][SnCl4]</td>
</tr>
<tr>
<td>2.323</td>
<td>2.56</td>
<td>1.32</td>
<td>[Bu’PhPCl2][FeCl4]</td>
</tr>
</tbody>
</table>

### References


Notes

Thanks are due to Dr K. S. Sharma and Shri Dinesh Gupta for the far infrared, UV and Mössbauer spectra respectively.

The IR spectrum of [Bu’PhPCl2][FeCl4] shows a stretching mode at 375 which may be due to FeCl; in [Ti(acac)3]+[FeCl4]- anion. The [FeCl4]2- 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, infrared and Mössbauer studies of similar compounds [Si(acac)4]+[FeCl4]-, [Ti(acac)4]+[FeCl4]-, [Zr(bzbz)2]+[FeCl4]- and [(C6H5)3As]+[FeCl4]- in solid state have been made. The UV and visible spectra of these compounds show bands due to the iron(III) complex, which may be due to FeCl; in [Ti(acac)3]+[FeCl4]- anion and their ability to form adducts with 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, 19.96; S, 22.00; 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%).