

NOTES

TABLE 1 — COLOUR, MAGNETIC MOMENT AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	m.p. (°C)	Magnetic moment (B.M.)	Found (calc.), %		
				M	N	S
VO(SPTSC-2H)	Black	> 350	1.02	13.9 (14.4)	11.5 (11.8)	8.6 (9.1)
Mn(SPTSC-2H)	Ash colour	> 350	6.00	15.9 (16.6)	12.5 (12.7)	9.7 (9.4)
Fe(SPTSC-2H)OH	Black	185	3.48	16.3 (16.0)	12.4 (12.0)	9.2 (9.0)
Co(SPTSC-2H)	do	> 350	2.14	16.4 (16.9)	11.99 (12.2)	9.6 (9.3)
Ni(SPTSC-2H)	Dirty green	> 350	Diamagnetic	16.3 (16.9)	12.13 (12.14)	8.9 (9.3)
Cu(SPTSC-H)Cl*	Ash colour	345	1.08	14.8 (15.3)	10.49 (10.90)	8.5 (8.3)
Cu(SPTSC-2H)	Dirty green	252	1.36	17.6 (18.1)	12.4 (12.0)	9.5 (9.2)
Zn(SPTSC-2H)	White	> 350	—	18.4 (18.6)	13.7 (14.2)	8.9 (9.2)

*Analysis for Cl; Found, 8.9%; Calc. 9.2%.

observed for Fe(II), oxovanadium(IV) and Cu(II) complexes may be explained by assuming hydroxyl-bridging⁶ interactions of the type V=O...V (ref. 7) and metal-metal interactions⁸ respectively.

The 3350 cm⁻¹ band in the IR spectrum of SPTSC (nujol) is assigned to the νO-H (phenolic) which disappears in the spectra of all the complexes except Cu(SPTSC-H)Cl, indicating coordination through phenolic oxygen. The νN-H band at 3300 cm⁻¹ in the solution spectrum of the ligand suffers a negative shift in all the complexes indicating the involvement of one or more >N-H groups in coordination. The νC=O band at 1660 cm⁻¹ in the spectrum of SPTSC remains unaltered in Cu(SPTSC-H)Cl indicating that the carbonyl group is not taking part in coordination in this complex. This band, however, disappears in all the other complexes, suggesting the enolization of keto group.

The νC=S occurring at 1338 cm⁻¹ in the spectrum of SPTSC disappears in Cu(SPTSC-H)Cl but suffers a negative shift in all the other complexes indicating the involvement of the thioketo group in coordination.

νN-N occurring at 900 cm⁻¹ in the spectrum of SPTSC shifts to the higher frequency side in all the complexes. The magnitude of the positive shift suggests the involvement of only one of the hydrazinic nitrogens^{9,10} in bonding.

The non-ligand bands occurring in the regions 450-400, 385-308, 330-280 and 850 cm⁻¹ in the spectra of complexes may be tentatively assigned to νM-O (ref. 11-13) νM-S (ref. 11, 14) νM-N (ref. 12, 15, 16) and ν_{as} Fe-O-Fe (ref. 6) modes respectively.

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Organotin(IV) & Organoxytitanium(IV)
Diphenyl Phosphinates*

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Organotin(IV) phosphinates of the formula R₂SnL₂ and R₃SnL (R = butyl, phenyl, benzyl; LH = diphenyl phosphinic acid) have been prepared from the respective chlorotin compound and sodio-derivative of the ligand. Organic chelating ligands (salicylaldehyde, acetyl acetone, 8-hydroxyquinoline) replace the alkoxy groups of diisopropoxy titanium bis-diphenyl phosphinate giving new chelated titanium compounds in which both the isopropoxy groups are replaced by the ligands.

ORGANOMETALLIC compounds containing Sn-O-P and Ti-O-P linkages have attracted considerable attention¹⁻³. A number of titanium

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derivatives of benzene phosphinic acid⁴ and some alkyl phosphates⁵ have also been reported. Diphenyl phosphinic acid derivatives of some di- and tri-organotin(IV) compounds, isopropyl titanate and chelated Ti(IV) compounds are reported here.

The reaction between an organotin chloride and diphenyl phosphinic acid was found to give products containing chlorine and were of indefinite composition. But when the reaction was carried out using the sodium salt of diphenyl phosphinic acid, the reaction proceeded smoothly to give organotin diphenyl phosphinates in excellent yield (Table 1). The compounds were slightly soluble in benzene, chloroform and carbon tetrachloride. All of them decomposed before melting ($>200^\circ$).

The IR spectra of the organotin diphenylphosphinates show the disappearance of $\nu_{P=O}$ of the free ligand at 1200 cm^{-1} due to either coordination of the ligand to the metal atom through the phosphoryl oxygen or to the polymerization of these compounds through phosphoryl oxygen. The appearance of strong bands near 1190 and 1060 cm^{-1} indicate that the P—O bonds are approximately equivalent when they form phosphinate bridges. The lack of sufficient solubility of these compounds in benzene precluded molecular weight determinations. Similar complexes are reported to be oligomers with degree of association ranging from two to six³.

Reaction between isopropyl titanate and diphenyl phosphinic acid gave diisopropoxytitanium bis-diphenyl phosphinate as a yellow solid, slightly soluble in benzene, and decomposing on heating. This compound readily reacted with organic chelating ligands such as salicylaldehyde, acetylacetone and 8-hydroxyquinoline eliminating isopropanol (Table 1). The NMR spectra of the products indicate that both the isopropoxy groups were lost during the reaction. The products obtained were analysed as bis-chelated titanium bis-diphenyl phosphinates. In the IR spectrum of the salicylaldehyde compound, the shift in ν_{CO} from 1660 cm^{-1} in the free ligand to 1625 cm^{-1} indicates weak coordination of the carbonyl group to the metal. In the acetylacetone complex, the ν_{CO} was found at

1580 cm^{-1} in place of a doublet at $1715 \pm 10\text{ cm}^{-1}$ in the free ligand, again indicating weak coordination. In the 8-hydroxyquinoline derivative, two bands at 1587 and 1600 cm^{-1} instead of only one (at 1587 cm^{-1}) in the ligand probably indicate coordination of the nitrogen atom with the metal and consequent separation of the C=N frequency from the C=C frequency in the ring⁶. The limited solubility of these compounds in benzene did not permit accurate molecular weight determinations, but indicated that they were polymeric in nature.

Triphenyltin diphenyl phosphinate — Triphenyltin chloride (3.85 g; 0.01 mole) was dissolved in benzene (50 ml) and refluxed with sodium diphenyl phosphinate (3.60 g; 0.015 mole) for 2 hr; the solvent was evaporated under reduced pressure and the residue washed with distilled water to remove the sodium chloride formed. The product which was insoluble in water was washed several times with pet. ether and dried *in vacuo*, yield 4.82 g; 85%. This white powdery compound, insoluble in benzene, decomposed without melting above 200° [Found: C, 63.35; H, 4.57; mixed oxide, 38.71. $(C_6H_5)_3Sn(C_6H_5)_2PO_2$ requires C, 63.53; H, 4.41; mixed oxide, 39.13%].

Diisopropoxytitanium bis-(diphenyl phosphinate) — Isopropyl titanate (2.84 g; 0.01 mole) was mixed with benzene (50 ml) and diphenyl phosphinic acid (4.36 g; 0.02 mol) added to it and refluxed for 2 hr with continuous azeotropic removal of the alcohol formed. The product was evaporated under reduced pressure, washed with pet. ether and dried *in vacuo*, yield 5.4 g; 90%. The pale yellow powder was slightly soluble in benzene, and decomposed without melting above 200° [Found: C, 59.51; H, 5.44; Ti, 8.1. $(C_3H_7O)_2Ti[(C_6H_5)_2PO_2]_2$ requires C, 59.95; H, 5.66; Ti, 8.0%].

Bis-salicylaldehyde titanium bis-(diphenyl phosphinate) — Diisopropoxytitanium bis-(diphenyl phosphinate) (6 g; 0.01 mole) and salicylaldehyde (2.68 g; 0.022 mole) were mixed in benzene (50 ml) and refluxed for 2 hr with continuous removal of the liberated isopropanol. The product was isolated as above, yield 6.5 g, 90%, orange powder, slightly soluble in hot benzene, and decomposed on heating

TABLE 1 — ORGANOTIN AND ORGANOXYTITANIUM DIPHENYL PHOSPHINATES

Sl. No.	Organometallic used	Molar ratio	Product*
REACTION WITH SODIUM DIPHENYL PHOSPHINATE			
1	$(C_6H_5)_3SnCl$	1 : 1.5	$(C_6H_5)_3Sn(C_6H_5)_2PO_2$
2	$(C_6H_5)_2SnCl_2$	1 : 3	$(C_6H_5)_2Sn[(C_6H_5)_2PO_2]_2$
3	$(C_4H_9)_2SnCl_2$	1 : 3	$(C_4H_9)_2Sn[(C_6H_5)_2PO_2]_2$
4	$(C_6H_5CH_2)_2SnCl_2$	1 : 3	$(C_6H_5CH_2)_2Sn[(C_6H_5)_2PO_2]_2$
5	$(C_6H_5CH_2)_3SnCl$	1 : 1.5	$(C_6H_5CH_2)_3Sn(C_6H_5)_2PO_2$
REACTION WITH DIPHENYL PHOSPHINIC ACID			
6	$Ti(OPri)_4$	1 : 2	$[(C_6H_5)_2PO_2]_2Ti(OPri)_2$
REACTION WITH SALICYLALDEHYDE			
7	$[(C_6H_5)_2PO_2]_2Ti(OPri)_2$	1 : 2.2	$[(C_6H_5)_2PO_2]_2Ti(Sa)_2$
REACTION WITH ACETYL ACETONE			
8	$[(C_6H_5)_2PO_2]_2Ti(OPri)_2$	1 : 2.2	$[(C_6H_5)_2PO_2]_2Ti(Acac)_2$
REACTION WITH 8-HYDROXYQUINOLINE			
"	$[(C_6H_5)_2PO_2]_2Ti(OPri)_2$	1 : 2.2	$[(C_6H_5)_2PO_2]_2Ti(8Oxy)_2$

*Sl Nos. 1-4 were obtained as white solids; 5 and 6 as pale yellow solids; 7 as orange yellow solid; 8 as yellow solid and 9 as orange yellow solid.

[Found: C, 62.74; H, 4.20; Ti, 6.71. $[(C_6H_4(O)CHO)_2 Ti[(C_6H_5)_2PO_2]_2]$ requires C, 62.99; H, 4.14; Ti, 6.63%].

Other compounds were prepared similarly.

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Adducts of 1-Phenylazo-2-naphthols with Fe(III) Chloride

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1-Phenylazo-2-naphthols form adducts of the type $FeCl_3.L_2$ with iron(III) chloride. Infrared spectral studies show that the ligands act as monodentate, coordinating through their α -nitrogen atoms. The complexes are non-ionic in benzene.

METAL complexes of azo compounds have received considerable attention in the past in view of their application as stable dye-stuffs¹. However, attention was devoted mostly to stable metal complexes, having greatly enhanced fastness properties. Thus, whereas the literature is extensive on o,o' -dihydroxyazo compounds and their metal chelates, very few reports exist on labile complexes of o -monohydroxyazo compounds¹. Hence this investigation on complexes of 1-phenylazo-2-naphthols (I) with iron(III) chloride was undertaken.

Six o -hydroxyazo ligands used by us formed lustrous black crystals with anhydrous iron(III) chloride in boiling dry benzene. These complexes are non-hygroscopic and could be recrystallized several times from benzene. The complexes have the composition $FeCl_3.L_2$ (Table 1). These are non-

ionic in benzene and hence may be represented as $[Fe(L)_2Cl_3]$.

Any deprotonation of the ligands during complex formation is ruled out since no hydrogen chloride could be detected in the effluent vapours from the reaction flask. It is thus evident that the phenylazonaphthols act as neutral ligands. Addition of aqueous caustic soda or mineral acid results in the decomposition of the complexes giving the ligands in almost quantitative yield.

Hydroxyazo compounds exhibit azo-hydrazone tautomerism². In the case of o -hydroxyazo compounds, the tautomers exist as strongly hydrogen bonded structures¹ (I) and (II), the latter predominating³. In accordance with structure (II), the infrared spectra of 1-phenylazo-2-naphthols show a band at $1610+10\text{ cm}^{-1}$, which may be attributed to the hydrogen bonded carbonyl group⁴. In keeping with the hydrogen bonded N—H...O structure, the X-H (X=N or O) band around 2400 cm^{-1} is broadened almost out of recognition. The X-H band remains unaltered in the metal complexes also, showing that the hydrogen bond persists in the complexed state. This is further corroborated by the fact that like the free ligands, the metal complexes also do not form any ammonium salt with dry ammonia in benzene. In view of the hydrogen bonded structure of the coordinated ligands, they may be expected to act only as monodentate ligands. Since the C=O stretching frequency of the ligands remains undepressed in the complexes, it is evident that the oxygen atom does not coordinate⁵.

It appears, therefore, that it is one of the nitrogen atoms of the ligand that is bonded to the

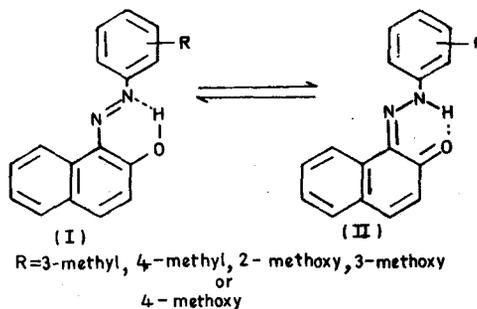


TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Ligand (I) (R =)	m.p. (°C*)	Found (%)†					Ligand
		C	H	N	Fe	Cl	
H	210	—	—	—	8.17 (8.48)	15.90 (16.11)	74.50 (75.68)
3-Methyl	200	59.58 (59.51)	4.39 (4.08)	8.57 (8.16)	8.00 (8.10)	14.95 (15.45)	76.00 (76.38)
4-Methyl	210	60.01	4.46	8.52	8.03	15.15	75.80
2-Methoxy	195	—	—	—	8.04 (7.78)	14.52 (14.72)	76.50 (77.45)
3-Methoxy	205	56.75 (56.82)	4.20 (3.90)	8.51 (7.80)	8.25	14.72	76.87
4-Methoxy	185	—	—	—	8.00	14.60	76.78

*Melt with decomposition; yield about 80%.

†Calculated values are given in parentheses. Calculated values for isomeric compounds are not mentioned.