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N,N-Diethylamino-oxy Derivatives of Dialkyltin(IV)

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Diethylamio-oxy derivatives of dialkyltin(IV) have been synthesized and characterized on the basis of elemental analysis, molecular weight determination and IR data.

IN continuation of our previous work on N,N-diethylhydroxylamine derivatives of titanium[1], boron and aluminium[2], the derivatives of dialkyltin (IV) are reported in this note.

Dimethyl-, diethyl- and dibutyltin diisopropoxides and dibutyltin diethoxide, prepared by the sodium method, react with diethylhydroxylamine to give products, $R_2Sn(OR')_{2-x}[ON(C_2H_5)_2]_x$ (Table 1). The reactions can be represented as follows:

$$R_2Sn(OR')_2+x(C_2H_5)_2NOH \longrightarrow R_2Sn(OR')_{2-x}[ON(C_2H_5)_2]_x+xR'OH$$

($R = CH_3$, C_2H_5 and C_4H_9; $R' = C_2H_5$ and $C_3H_7^i$ and $x = 1$ and 2).

The general method of preparation of the compound is as follows: Dialkyltin dialkoxides and diethylhydroxylamine were mixed in benzene in stoichiometric ratios and left overnight. Reaction mixtures were heated at a bath temperature of 80-90° for 4-8 hr. In reactions (1-3) the benzene was removed and the products distilled under reduced pressure. In other cases, insoluble products were separated by filtration and washed subsequently. Dibutyltin derivatives (Table 1, Nos. 1-3) are liquids, miscible with organic solvents. These are volatile and can be distilled with slight decomposition under reduced pressure.

The molecular complexity of soluble diethylamino-oxy derivatives of dibutyltin(IV) was found to be about three as revealed by mol. wt determination. Compounds derived from dimethyl- and diethyltin diisopropoxides are insoluble and can be considered to be polymeric.

IR spectra of the compounds exhibit ν_{as} and ν_s N-O around 950 and 910 cm^{-1} respectively[3]. The characteristic absorptions[4] of isopropoxy group occur at 1140, 1055-1050 cm^{-1} and that of ethoxy group at 1180-1103 and 1010 cm^{-1}. The bands in the regions 620-609 and 521-510 cm^{-1} have been assigned to ν_{as} and ν_{as} Sn-C respectively. ν_{as} and ν_s Sn-O appear around 572-560 and 475-466 cm^{-1} respectively[5].

Table 1 — Products of the Reactions of Dialkyltin Dialkoxides with Diethylhydroxylamine

Sl No.	Molar ratio of reactants	Product	Found (%) (calc.) Sn	N
1	1 : 1	$(C_4H_9)_2Sn(OC_2H_5)[ON(C_2H_5)_2]$, b.p. 113-16°/1 mm; 27%	32·39 (32·46)	3·85 (3·83)
2	1 : 2	$(C_4H_9)_2Sn[ON(C_2H_5)_2]_2$, b.p. 103-6°/1 mm; 40%	29·27 (29·04)	6·83 (6·84)
3	1 : 1	$(C_4H_9)_2Sn(OC_3H_7^i)[ON(C_2H_5)_2]$, b.p. 110°/0·5 mm; 35%	31·29 (31·33)	3·60 (3·64)
4	1 : 1	$(CH_3)_2Sn(OC_3H_7^i)[ON(C_2H_5)_2]$, insoluble and infusible; 99%	39·93 (40·05)	4·70 (4·73)
5	1 : 2	$(CH_3)_2Sn[ON(C_2H_5)_2]_2$, insoluble and infusible; 97%	36·72 (36·53)	8·60 (8·62)
6	1 : 1	$(C_2H_5)_2Sn(OC_3H_7^i)[ON(C_2H_5)_2]$, soluble in hot benzene and infusible; 98%	36·81 (36·64)	4·46 (4·33)
7	1 : 2	$(C_2H_5)_2Sn[ON(C_2H_5)_2]_2$, insoluble and infusible; 96%	33·98 (33·67)	7·93 (7·94)

Products 1-3 are yellow liquids and of 4-7 are white solids.

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Mn(II), Fe(II), Co(II), Ni(II) & Cu(II) Complexes with Benzoylhydrazine

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Benzoylhydrazine (BH) complexes of the types $M(BH)_3SO_4.3H_2O$ where M=Ni(II), Co(II) or Fe(II); $M'(BH)_2SO_4.2H_2O$ where M'=Cu(II) or Mn(II); $M''(BH)_3Cl_2.3H_2O$ where M''=Ni(II), Co(II) or Mn(II) and $Ni(BH)_3X$ where $X=HgCl_4^{2-}$, $HgCl_2I_2^{2-}$, HgI_4^{2-}, $CdCl_2I_2^{2-}$ or CdI_4^{2-} have been synthesized and characterized by analysis and physicochemical studies. The complexes are spin-free and octahedral where BH acts as a bidentate coordinating ligand. Molar extinction coefficient (3) and approximate oscillator strength (*f*) of the electronic bands have been calculated for complexes of the type $M''(BH)_3Cl_2$. Sulphate group is bonded to metals directly or to BH by hydrogen bonding.

IN continuation of our work[1,2] on benzoylhydrazine (BH) complexes of Ti(IV) and some non-transition metal ions, the preparation and characteri-

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zation of BH complexes with metal ions of first transition series are reported in this note.

Metal salts (BDH) of LR grade were used and benzoylhydrazine (BH) was prepared as described by Curtius[3]; m.p. 112° (lit. m.p. 111°). Metal complexes were synthesized by mixing ethanolic solutions of metal chlorides or aqueous solutions of metal sulphates and ethanolic solutions of BH in appropriate molar ratios. The metal chloride complexes were recrystallized from hot ethanol and the metal sulphate complexes, obtained as precipitates, were washed with dilute ethanol and dried in a desiccator.

For the syntheses of $Ni(BH)_3X$ complexes, $Ni(BH)_3Cl_2 \cdot 3H_2O$ was dissolved in ethanol and an aqueous solution or ethanolic solution of K_2HgCl_4, $K_2HgCl_2I_2$, K_2HgI_4, $K_2CdCl_2I_2$ or K_2CdI_4 (prepared by mixing appropriate amounts of the salts) added to it. The precipitated complexes were washed with dilute ethanol and dried as mentioned above. Similar complexes were also prepared by reacting hot ethanolic solutions of $Ni(BH)_3Cl_2$ and Hg(II) or Cd(II) salts in 1: 1 molar ratio, cooling and crystallizing or precipitating the complexes with the addition of water.

Literature procedures[4] were followed for gravimetric estimation of metals and anions. BH was estimated volumetrically using potassium iodate[4] after acid hydrolysis. Estimation procedures were suitably modified to permit the estimation of BH in the presence of Fe(II), Cu(II) and I^- and the analysis of Ni(II) in the presence of Hg(II) and Cd(II).

Conductometric studies were carried out with Philips conductivity bridge (model 4494) using a dip type of cell. Spectrophotometric studies in solution and electronic spectra of some of the isolated products were carried out on a Perkin-Elmer spectrophotometer model 227. Nujol spectra of some insoluble complexes were recorded on Cary spectrophotometer model 14 and infrared (KBr) spectra on Perkin-Elmer grating spectrophotometer model 337. Faraday magnetic balance was used for the measurement of room temperature magnetic susceptibility.

It is evident from Table 1 that ionic complexes decompose above 240° without melting. Those having greater covalency due to either change in metal character or anion character melt with decomposition or melt below 200°.

The complexes, in general, are insoluble in organic solvents like benzene, chloroform, carbon tetrachloride, ether, nitrobenzene, etc. The metal sulphate complexes are insoluble in ethanol. Metal sulphate

TABLE 1 — ANALYTICAL*, COLOUR, M.P. AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Compound	Colour	Melting/decomposition point (°C)	Analysis (%)			Magnetic moment (BM)
			Metal†	Halide/sulphate	BH	
$Mn(BH)_3Cl_2.3H_2O$	Yellow brown	71	9·5 (9·3)	12·0 (12·0)	69·3 (69·4)	6·1
$Co(BH)_3Cl_2.3H_2O$	Light red	149	10·0 (9·9)	11·7 (11·9)	68·8 (68·9)	5·2
$Ni(BH)_3Cl_2.3H_2O$	Blue	>240	10·0 (9·9)	11·9 (11·9)	69·3 (68·9)	3·2
$Mn(BH)_2SO_4.2H_2O$	Shining pale white	>240	12·2 (11·9)	20·8 (21·3)	59·8 (59·9)	7·2
$Fe(BH)_3SO_4.3H_2O$	Yellow	Not clear	9·5 (9·1)	15·8 (15·8)	66·9 (66·6)	5·9
$Co(BH)_3SO_4.3H_2O$	Light red	>240	9·7 (9·5)	15·2 (15·5)	65·7 (66·1)	5·3
$Ni(BH)_3SO_4.3H_2O$	Light blue	>240	9·4 (9·5)	15·6 (15·5)	65·8 (66·1)	3·2
$Cu(BH)_2SO_4.2H_2O$	Blue	>240	13·3 (13·5)	20·6 (20·5)	57·9 (58·1)	2·2
$Ni(BH)_3HgCl_4$	Light blue	>240	7·0 (7·2)	17·7 (17·5)	49·4 (50·4)	3·2
$Ni(BH)_3HgCl_2I_2$	do	193	5·8 (5·9)	32·2 (32·7)	40·7 (41·1)	3·1
$Ni(BH)_3HgI_4$	Light green	135	4·7 (4·9)	43·2 (43·1)	34·7 (34·7)	3·2
$Ni(BH)_3CdCl_2I_2$	Light blue	200	6·4 (6·6)	36·0 (35·9)	44·8 (45·1)	3·2
$Ni(BH)_3CdI_4$	Light green	165	5·3 (5·5)	46·2 (46·8)	37·9 (37·6)	3·1

*Figures in parentheses are calculated values.

†% nickel in $Ni(BH)_3X$ complexes.

complexes, namely Cu(II) and Mn(II) complexes are insoluble, Ni(II) complex is slightly soluble while Co(II) and Fe(II) complexes dissolve freely in water. Metal chloride complexes, however, dissolve both in water and ethanol. $Ni(BH)_3CdI_4$ and $Ni(BH)_3HgI_4$ dissolve in ethanol but are insoluble in water. The other $Ni(BH)_3X$ complexes are practically insoluble in the above solvents.

The conductometric titration curves of metal sulphates against BH show a sharp inflexion at 1: 2 molar ratio in the case of Cu(II), a broad bulge at 1: 3 molar ratio for Ni(II) and a slight inflexion at about 1: 3 molar ratios for Co(II) and Fe(II). A similar titration of nickel chloride hexahydrate and BH in aqueous medium yields only a linear curve. In ethanol medium, however, inflexions at 1: 1, 1: 2 and 1: 3 molar ratios show stepwise exchange of two water molecules by one BH molecule.

Visible spectra of the above ethanolic solutions show blue shift of λ_{max} with increasing concentration of BH. For example, metal-ligand in 1: 1 ratio shows λ_{max} at 390 and 644 nm, in 1: 2 ratio λ_{max} shift to 320 and 606 nm respectively while in 1: 3 ratio the absorption maxima undergo a further blue shift, appearing at 356 and 586 nm respectively. The solutions of ratios higher than 1: 3 do not show any shift. From these observations and 1: 3 composition of the Ni(II) complex, it can be safely inferred that the Ni(II) complex has a coordination number 6 with the ligand acting as a bidentate ligand.

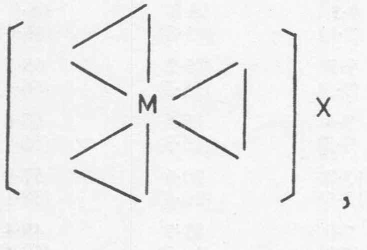
Visible spectrum of Cu(II)-BH complex shows one broad band centred at 718 nm (13930 cm^{-1}) due to transition $^2T_{2g} \longleftarrow {}^2E_g$. Ni(II)-BH complex shows two bands at 586 and 354 nm due to transitions $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ in the region 750-350 nm. These two bands are comparable to those observed for octahedral complexes of Ni(II) with H_2O, NH_3 and $C_2H_4(NH_2)_2$ as ligands[5]. The low values of ϵ_{max} (Table 2) for these bands also indicate octahedral stereochemistry, since the tetrahedral Ni(II) complexes show bands having high ϵ_{max} values[6]. However, a solution spectrum of the Ni(II)-BH complex, obtained on Hitachi Perkin Elmer model 139, shows all the three expected bands due to transitions $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ at 870, 600 and 355 nm respectively for octahedral Ni(II). Visible spectra of $Ni(BH)_3X$ complexes in nujol show bands around 600 nm confirming the presence of octahedral $Ni(BH)_3^{2+}$ complex cation in all of them. Co(II)-BH complex shows a band around 500 nm due to the transition $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ expected for octahedral Co(II) complexes[7]. Oscillator strength values for some of the complexes are also given in Table 2.

Infrared spectra of BH and its metal complexes have been studied and BH has been reported to coordinate through $>C{=}O$ and NH_2 groups[2]. The magnitude of shift in $>C{=}O$ stretching frequency has been related to the order of stability of the metal complexes of amides and ureas[8-10]. The shift in $\nu C{=}O$ in BH complexes of Ni(II), Co(II) and Mn(II) can similarly be used to determine the stability order of $M \leftarrow O{=}C<$ bond. The observed shifts in $\nu C{=}O$ of $M''(BH)_3Cl_2$ complexes (Table 2)

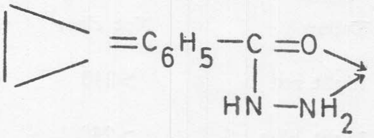
TABLE 2 — SPECTRAL DATA OF $M''(BH)_3Cl_2.3H_2O$ COMPLEXES

Compound	λ_{max} (nm)	ϵ_{max} (litre $mole^{-1}$ (cm^{-1})	Oscillator strength (f)	$\nu_{C=O}$* (cm^{-1})
$Mn(BH)_3Cl_2.3H_2O$	228	—	—	1640
	420	4·42	$1{\cdot}26 \times 10^{-4}$	
$Co(BH)_3Cl._23H_2O$	232	26550	0·50	1636
	252	23300	0·68	
	350	—	—	
	504	1·97	$3{\cdot}46 \times 10^{-5}$	
$Ni(BH)_3Cl_2.3H_3O$	232	28780	0·49	1632
	255	23840	0·72	
	354	3·17	$7{\cdot}97 \times 10^{-5}$	
	586	1·41	$3{\cdot}35 \times 10^{-5}$	

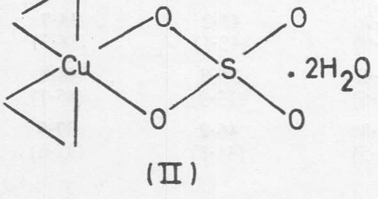
*$\nu_{C=O}$ of BH=1665 cm^{-1}.



(I)



M=Ni(II), Co(II), Fe(II) and Mn(II)
X=$2Cl^-$, SO_4^{2-}, $HgCl_4^{2-}$, $HgCl_2I_2^{2-}$, HgI_4^{2-}, $CdCl_2I_2^{2-}$ or CdI_4^{2-}



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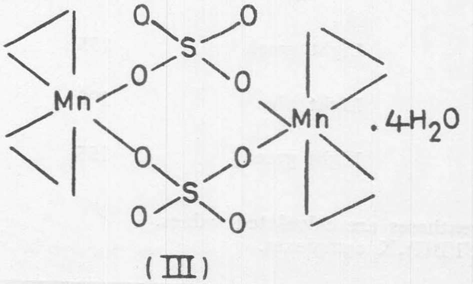

(III)

suggest the following stability order of $M\leftarrow O=C<$ bond: Ni(II)-BH>Co(II)-BH>Mn(II)-BH.

Sulphate group may be ionic, coordinated or bridged in metal complexes[11]. The absence of a band around 1220 cm^{-1} indicates the presence of a bridging sulphate group[12,13]. Moreover, sulphate group has a marked tendency to remain in unionized state either by attachment in coordination sphere of metal ion or by ion pairing involving hydrogen bonding with amines[14]. This type of bonding of the sulphate group results in the appearance of a band around 1220 cm^{-1}. The absence of this particular band in $Mn(BH)_2SO_4{\cdot}2H_2O$ shows bridging character of sulphate group. The presence of 1230 cm^{-1} band in Fe(II), Co(II) and Ni(II) complexes may be due to attachment of sulphate group to the ligand by hydrogen bonding. The appearance of 1230 cm^{-1} band in Cu(II) complex may be due to bonding of sulphate group to metal ion.

Water molecules are present in the lattice structures of all the complexes, because, neither there is any change in colour of the complexes on dehydration[15] nor peak-by-peak comparison of the infrared spectra of aquated and dehydrated complexes shows any disappearance of peaks assigned to coordinated water molecules[16].

Magnetic measurements show that all the complexes are spin-free and the magnetic moments fall within the ranges expected for octahedral complexes[17]. The magnetic moment of $Cu(BH)_2SO_4{\cdot}2H_2O$ (2·28 BM) can also be related to the octahedral structure with coordinated sulphate group, because the square planar Cu(II) complexes show magnetic moments around 1·8 BM (ref. 18). The observed magnetic moment of $Mn(BH)_2SO_4{\cdot}2H_2O$ is high, since both tetrahedral and octahedral structures are expected to show magnetic moments very close to the spin-only values (5·92 BM)[19]. Recently, Frazer *et al.*[20] have explained the high value of magnetic moment (3·0 BM) of Cu(II) complexes as due to the presence of some ferromagnetic impurities arising out of dimeric nature of the complexes. The high magnetic moment of Mn(II) complex, in the present case, can similarly be explained. Infrared and magnetic data discussed above indicates a dimeric nature for $Mn(BH)_2SO_4.2H_2O$. The following structures (I, II and III) are, therefore, proposed for the BH complexes.

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Stabilities of Chelates of 2-Phenylacetohydroxamic Acid with Cu(II), Ni(II), Zn(II), Co(II), Mn(II) & Cd(II)

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Thermodynamic stability constants of the 2-phenylacetohydroxamic acid chelates with bivalent transition metal ions, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+} and Cd^{2+}, have been determined in aqueous medium adopting Irving and Rossotti *p*H-titration technique at 25·0° ± 0·1° and μ=0·1*M* ($NaClO_4$). The stability constants are observed to follow the order $Cu^{2+}>Ni^{2+}>Zn^{2+}>Co^{2+}>Cd^{2+}>Mn^{2+}$, in agreement with the Irving-William order.

HYDROXAMIC acids have been widely used[1] as analytical reagents for a variety of metal ions. Though benzohydroxamic acid[2] (BHA), N-phenylbenzohydroxamic acid[3], etc., chelates have been studied, both in solution and solid state, not much work has been reported on 2-phenylacetohydroxamic acid (PAHA) complexes. Thermodynamic stability constants of PAHA chelates with Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+} and Cd^{2+}, in aqueous medium have now been determined adopting Irving and Rossotti[4] *p*H-titration technique at 25·0 ± 0·1° and $\mu = 0{\cdot}1M$.

The ligand was prepared by following one of the general procedures adopted for the preparation of hydroxamic acids[5] recrystallized from dilute acetic acid and repeatedly washed with petroleum ether. Metal perchlorates were prepared and estimated by standard methods[6]. Experiments were carried out using a Leeds and Northrup *p*H meter fitted with glass and calomel electrodes.

Following solutions (total vol. 100 ml) were titrated against carbonate-free 0·1*M* NaOH. (1) 0·005*M* perchloric acid +0·1*M* sodium perchlorate; (2) 0·005*M* perchloric acid +0·001*M* PAHA ±0·1*M* sodium perchlorate; and (3) 0·005*M* perchloric acid +0·001*M* PAHA +0·001*M* metal perchlorate +0·1*M* sodium perchlorate. PAHA was taken ten times in excess to avoid the possible hydrolysis