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### Studies on Hydrazones, Semicarbazones & Thiosemicarbazones as Ligands : Part I—Some Divalent Metal Complexes of Benzil Phenyl Hydrazone

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Complexes of the compositions  $MLX_2$  and  $ML_2X_2$ , where M is Mn(II), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II); X is  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SCN^-$  or  $ClO_4^-$  and L is benzil phenyl hydrazone have been isolated and characterised on the basis of analysis, conductance, magnetic moment, infrared and electronic spectral studies.

NICKEL(II) complexes containing noncyclic and macrocyclic ligands derived from benzil monohydrazone have been studied by Kerwin<sup>1</sup>. Melson *et al.*<sup>2</sup> have also prepared complexes of some  $\alpha$ -diketone hydrazones and benzil monohydrazone and showed that the latter behaved as a bidentate ligand bonding through the oxygen and nitrogen atoms. However, complexes of benzil phenyl hydrazone have not been studied. It was thought worthwhile to carry out a comparative study of the complexing abilities of hydrazones, semicarbazones and thiosemicarbazones towards transition metal ions. As a part of this programme, this note

reports complexes of benzil phenyl hydrazone with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

All the chemicals used were of AR grade. Benzil phenyl hydrazone was synthesised by a known method<sup>3</sup>. Its purity was checked by nitrogen estimation and melting point determination [Found : N, 9.58, Calc. N, 9.33%; M. P. 138°C (lit. 134°C)]. Ethanolic solutions of divalent metal salts were refluxed with ethanolic solution of the ligand in 1:2 molar proportion for 30-60 min. The resulting solutions were evaporated *in vacuo*. On cooling the solutions overnight, crystalline compounds separated out. In some cases ether was added and the solution kept overnight in a refrigerator to induce precipitation of compounds. These were filtered *in vacuo*, washed with small amounts of ethanol and ether and dried *in vacuo*. Metal ions, halogen and thiocyanate were estimated by standard gravimetric or volumetric methods. Nitrogen in the nitrate and perchlorate complexes was estimated by micro-analysis. Conductances of the  $M/1000$  solutions of the complexes in acetone were measured using a Toshniwal conductance bridge. Magnetic measurements were made on solid specimens by Gouy method. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer and visible electronic spectra were recorded in  $M/100$  chloroform solution of the complexes using a Hilger Watt Uvispeck spectrophotometer. The relevant analytical data are presented in Table 1.

All the complexes reported in the present investigation have the general composition  $MLX_2$  excepting the manganese (II) perchlorate, nickel chloride and perchlorate and cobalt(II) chloride, nitrate and thiocyanate complexes which have the general formula  $ML_2X_2$ . The complexes are soluble in common organic solvents. Acetone solutions of the compounds, except those of the nickel and manganese perchlorate complexes, have low molar conductance values indicating their non-electrolytic nature. The Ni(II) ( $248 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) and Mn(II) ( $245 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) perchlorate complexes show 1:2 electrolytic behaviour<sup>3a</sup>.

Infrared spectra of benzil phenyl hydrazone has main absorption bands at 3100, 1640, 1620 and  $920 \text{ cm}^{-1}$  assignable<sup>4</sup> to  $\nu(N-H)$ ,  $\nu(C=O)$ ,  $\nu(C=N)$  and  $\nu(N-N)$  modes respectively. In the complexes the band due to  $\nu(N-H)$  remains unaffected whereas bands due to  $\nu(C=O)$  and  $\nu(C=N)$  shift to lower frequency region indicating bonding through the carbonyl oxygen and azomethine nitrogen atoms. Consequent upon bonding through the nitrogen atom of  $C=N$  group.  $\nu(N-N)$  shifts to higher frequency region as expected. In the case of the thiocyanato complexes,  $\nu(C\cdots N)$  is observed around  $2100 \text{ cm}^{-1}$  suggesting<sup>5-8</sup> the presence of N-bonded terminal thiocyanato group; whereas in the case of the cadmium complex this band is noticed at  $2135 \text{ cm}^{-1}$  suggesting coordination through the terminal sulphur atom. This type of bonding has been further substantiated by the observation of  $\nu(C-S)$  at  $700 \text{ cm}^{-1}$  in the case of cadmium thiocyanate complex and around  $790-800 \text{ cm}^{-1}$  in other metal complexes.

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NOTES

TABLE 1 — ANALYTICAL DATA OF COMPLEXES

Compounds	Colour	m.p. (°C)	$\mu_{\text{eff}}$ (B.M.)	Found (Calc.) %	
				Metal	Halogen/thiocyanate/ nitrogen
MnLCl <sub>2</sub>	Light-yellow	125	5.8	12.48 (12.89)	16.32 (16.67)
MnL(NO <sub>3</sub> ) <sub>2</sub>	Do	101	5.8	11.24 (11.47)	11.48 (11.69)
[MnL <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Do	120	5.9	9.72 (9.91)	9.98 (10.11)
MnL(SCN) <sub>2</sub>	Do	107	6.0	11.28 (11.66)	24.41 (24.63)
CoL <sub>2</sub> Cl <sub>2</sub>	Deep-brown	171	5.1	7.88 (8.07)	9.45 (9.43)
CoL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Do	109	5.0	7.24 (7.53)	6.85 (7.15)
CoL <sub>2</sub> (SCN) <sub>2</sub>	Do	127	4.9	7.22 (7.60)	14.71 (14.97)
[CoL(ClO <sub>4</sub> ) <sub>2</sub> ]	Do	122	4.6	10.28 (10.56)	4.85 (5.02)
NiL <sub>2</sub> Cl <sub>2</sub>	Yellowish-green	96	3.1	7.82 (8.05)	9.56 (9.73)
NiL(NO <sub>3</sub> ) <sub>2</sub>	Deep-brown	140	Diamag.	11.95 (12.16)	11.32 (11.60)
NiL(SCN) <sub>2</sub>	Do	120	Do	15.41 (15.66)	30.68 (30.95)
[NiL <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Deep-yellow	121	Do	6.46 (6.85)	6.25 (6.53)
CuLCl <sub>2</sub>	Violet	78	1.79	14.31 (14.62)	16.11 (16.34)
CuL(NO <sub>3</sub> ) <sub>2</sub>	Brown	116	1.82	12.80 (13.03)	11.21 (11.49)
CuL(SCN) <sub>2</sub>	Yellow	120	1.81	13.10 (13.25)	24.05 (24.17)
[ZnL(NO <sub>3</sub> ) <sub>2</sub> ]	Yellowish-white	125	—	13.02 (13.36)	11.12 (11.44)
[ZnL(ClO <sub>4</sub> ) <sub>2</sub> ]	Do	105	—	11.25 (11.58)	4.68 (4.96)
ZnL(SCN) <sub>2</sub>	Do	185	—	13.22 (13.58)	23.85 (24.09)
CdL(NO <sub>3</sub> ) <sub>2</sub>	White	85	—	26.08 (20.95)	10.21 (10.44)
[CdL(ClO <sub>4</sub> ) <sub>2</sub> ]	Do	110	—	18.08 (18.38)	4.25 (4.58)
CdL(SCN) <sub>2</sub>	Do	121	—	21.01 (21.27)	21.72 (21.95)

However,  $\delta(\text{NCS})$  band could not be assigned definitely due to the presence of metal-ligand vibration in this region. In the nitrate complexes,  $\nu_4$  and  $\nu_1$  modes of the nitrate group are observed around 1420 and 1290  $\text{cm}^{-1}$  respectively and the difference of the order of 130  $\text{cm}^{-1}$  indicates<sup>9,10</sup> the presence of monodentate nitrate group in all the complexes. Manganese and nickel perchlorate complexes show a broad hump around 1105  $\text{cm}^{-1}$  which is suggestive of the ionic perchlorate group in conformity<sup>11,12</sup> with the molar conductance data. In other perchlorato complexes three distinct bands are noticed around 1000, 1080 and 1150  $\text{cm}^{-1}$  showing the coordinated nature of perchlorate. Bonding through the oxygen of the carbonyl group and nitrogen of the azomethine group has been confirmed by the observation<sup>13</sup> of  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  around 460-485 and 335-350  $\text{cm}^{-1}$  regions respectively in the far infrared spectra of the complexes.

The UV spectrum of benzil phenyl hydrazone shows absorption at 18.52 kK. In the visible region electronic spectrum of manganese (II) complexes

three bands are observed around 20.0-20.4, 22.0-22.5 and 23.0-23.2 kK assignable to  ${}^6A_1 \rightarrow {}^4T_1(G) \rightarrow {}^4T_2(G)$ , and  $\rightarrow {}^4A_1(G)$  transitions respectively. From the band positions and the extinction coefficient values of about 1.0, the complexes are presumed to be of tetrahedral geometry<sup>14</sup>. Cobalt(II) complexes (except perchlorate complex) show two bands around 18.8-19.4 (20) and 20.0-20.5(22) kK attributable<sup>15</sup> to the transitions  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ , and  $\rightarrow {}^4T_{1g}(P)$  respectively. Alternatively, the bands may be the consequence of splitting of the  ${}^4T_{1g}(P)$  state due to spin-orbit coupling. Another band expected due to the transition to the  ${}^4T_{2g}$  state, was outside the range of the instrument. Both the magnetic moment and electronic spectral data suggest an octahedral configuration of the complexes.

The perchlorato complex has an intense band at 16.2(550) kK which is indicative of tetrahedral geometry in conformity with magnetic moment and conductance data. Nickel(II) chloride complex shows three bands at 9.8(4), 14.6(6) and 24.8(8) kK due to transitions,  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  $\rightarrow {}^3T_{1g}(F)$  and

$\rightarrow^3T_{10}(P)$  respectively indicating an octahedral configuration of this complex which is supported by its  $\mu_{\text{eff}}$  value of 3.1 B.M. All the other nickel(II) complexes exhibit one band around 18-18.4 kK with extinction coefficient value of 60-65. The spectral data alongwith the diamagnetic nature of these complexes suggest<sup>16</sup> a square-planar configuration of these complexes. All copper(II) complexes exhibit a broad absorption band around 17.5 kK indicating that the complexes are probably square-planar<sup>17</sup>. On the basis of analysis, conductance and infrared spectral data all the zinc and cadmium complexes may be assigned tetrahedral structures.

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### Some Cyclopentadienyl- & Indenyl-niobium(V) Dioximates

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Dimethylglyoximate,  $\alpha$ - and  $\gamma$ -benzildioximate derivatives of dicyclopentadienylniobium(V) and diindenylniobium(V) have been prepared by reacting  $(C_5H_5)_2NbCl_3$  or  $(C_9H_7)_2NbCl_3$  with the respective dioximes. Products of the type  $D_2Nb(R-H)_2Cl$  are obtained when the reaction is carried out in 1 : 2 molar ratio in cold (D = cyclopentadienyl or indenyl, R = dioxime). On refluxing the reactants, however, products of the type  $D_2Nb(R-2H)$  (R-H) are obtained.  $\gamma$ -Benzildioxime, when reacted in 1 : 1 molar ratio, gives products of the type  $D_2Nb_2(R-2H)Cl$ . The complexes have been characterised on the basis of elemental analyses, IR and electronic spectral, conductance and molecular weight studies.

NI OBIUM pentachloride is reduced by sodium cyclopentadienide in ether or benzene to give  $(C_5H_5)_4Nb^1$ ; in diamethoxyethane,  $(C_5H_5)_2NbCl$  is obtained and in inert solvents  $(C_5H_5)_2Nb$  is formed<sup>2</sup>. But  $(C_5H_5)_2NbCl_3$  is formed by the interaction of  $NbCl_5$  and sodium cyclopentadienide in tetrahydrofuran<sup>3</sup>. A number of cyclopentadienyl compounds containing Nb(III) and Nb(IV) are mentioned in literature but only a few Nb(V) compounds have been reported. In continuation of our earlier work on cyclopentadienyl and indenyl compounds of Nb(V)<sup>4</sup>, we report here the synthesis and characterization of some cyclopentadienyl- and indenyl-niobium (V) dioximates.

All the reactions were carried out in dry atmosphere using standard quickfit apparatus with interchangeable ground glass joints. Freshly distilled cyclopentadiene and indene were used for the preparation of their sodium salts. A good quality niobium pentachloride was used for the preparation of  $(C_5H_5)_2NbCl_3$  and  $(C_9H_7)_2NbCl_3$ . Tetrahydrofuran was purified and dried by keeping it over solid KOH and distilling overlithium aluminium hydride. Dimethylglyoxime was of AR grade;  $\alpha$ - and  $\gamma$ -benzildioximes were prepared from a pure sample of benzil as described in the literature<sup>5,6</sup>. Niobium was estimated as  $Nb_2O_5$ . Carbon and hydrogen were estimated by micro analytical methods. Nitrogen was estimated by Kjeldahl's method and chlorine was estimated as AgCl at semimicro level (Table 1). Infrared spectra of the complexes were recorded on a Perkin-Elmer spectrophotometer model 621 in KBr in the range 4000-200  $cm^{-1}$ .

*Preparation of (chloro)bis(dimethylglyoximate) dicyclopentadienylniobium (V) — I*—About 1.0 g (0.003 mol) of  $(C_5H_5)_2NbCl_3$  was dissolved in 80 ml of THF and 0.7 g (0.006 mol) of dimethylglyoxime was added to the solution. The reaction mixture was stirred for 15 hr and then filtered through a sintered glass disc (G-4). The clear brownish filtrate was evaporated to dryness *in vacuo*. The residue was extracted several times with petroleum ether. A light brown solid was obtained which was purified by reprecipitation from a concentrated solution of the compound in THF by adding ether. The elemental analysis of the purified product corresponded to the formula  $(C_5H_5)_2Nb(C_4H_7N_2O_2)_2Cl$ . The corresponding  $\alpha$ -benzildioximate derivative was similarly synthesized. The corresponding diindenylniobium (V) compounds were also prepared by the same procedure. The compounds are light-brown to brown solids, insoluble in water but soluble in THF. They are stable in inert atmosphere but are sensitive to moisture. They do not melt but decompose on heating to  $\sim 150^\circ C$ . They are readily hydrolysed by hot water, dilute acids or alkalis.

*Preparation of bis(dimethylglyoximate) dicyclopentadienylniobium (V) — II*—To a solution of about 1.0g (0.003 mol) of  $(C_5H_5)_2NbCl_3$  in 90 ml of THF 0.75 g (0.006 mol) of dimethylglyoxime was added. The reaction mixture was refluxed for 18 hr and then filtered. The clear filtrate was evaporated to dryness *in vacuo* and the residue was washed with petroleum

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