

Studies on Metal Schiff's Base Complexes. Part—I : Some Divalent Metal Complexes of Benzil 2,4-dinitro Phenyl Hydrazone

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A number of complexes of the composition MLX_n , where M is Co(II), Ni(II), Cu(II), Zn(II), Cd(II); X is Cl^- , Br^- , NO_3^- and SCN^- , except nickel(II) thiocyanate complex (which is of the formula NiL_2X_2), and of the type ML_2X_n , where X is ClO_4^- ; M is Ni(II), Cu(II), Cd(II), Mn(II) and L is benzil 2,4-dinitro phenyl hydrazone have been synthesised and characterised on the basis of elemental analyses, conductance, magnetic susceptibility, infrared and electronic spectral studies.

SCHIFF'S bases have drawn considerable attention since such ligands dominate the area of higher coordination polyhedra in scope, number and also from kinetic and thermodynamic stability points of view. Particularly, the compact nature of polydentate Schiff bases make them more effective in attaining high coordination structure. Complexation behaviour of bi, tri and tetradentate Schiff's bases have been reported¹⁻⁶. It was thought worthwhile to study the complexing abilities of Schiff's bases and as a part of this programme, the present communication reports the synthesis and characterisation of complexes of benzil 2,4-dinitro phenyl hydrazone with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions.

Experimental

All chemicals used are of AnalaR grade. Benzil 2,4-dinitro phenyl hydrazone was prepared by a known method⁶. The ethanol solutions of the divalent metal salts were refluxed with ethanol solution of the ligand in 1 : 2 molar ratio for 30 min to 1 hr. The volume of the solutions was reduced in a rotary vacuum evaporator. On cooling the solutions overnight crystalline compounds separated out. In some cases addition of ether was necessary to precipitate out the complex. These were filtered under suction, washed with small quantity of ethanol and ether and dried in a vacuum desiccator (yield 40-50%). Metal ions, halide and thiocyanate were estimated by standard methods. Nitrogen in the nitrate and perchlorate complexes were estimated by microanalysis. The conductance was measured in 10^{-3} M acetone solution of the complexes using a Toshniwal conductance bridge. Magnetic measurements were made

on solid specimens by Gouy method at 25° using $CuSO_4 \cdot 5H_2O$ as calibrant. Infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer. Visible electronic spectra were recorded in 10^{-3} M chloroform solution of the compounds using Hilger-Watt Uvispeck spectrophotometer. The relevant analytical data are presented in Table 1 and spectral data in Table 2.

Results and Discussion

The chloro, nitrate and thiocyanato complexes have the composition MLX_n [except nickel(II) thiocyanato complex], where M is Co(II), Ni(II), Cu(II), Zn(II), Cd(II); X is Cl^- , SCN^- , NO_3^- ; L is benzil 2,4-dinitro phenyl hydrazone. All the perchlorato complexes and nickel(II) thiocyanato complex are of the formula ML_2X_n . All these complexes are soluble in common organic solvents. The acetone solutions of the complexes have low molar conductance values indicating their non-electrolytic nature. Manganese, nickel and cadmium perchlorate complexes show high conductance values (Table 1) suggesting that they are 1 : 2 type electrolytes. The magnetic moment of the manganese complex is 5.8 B.M. and of the cobalt chloride complex is 5.0 while that of the thiocyanate complex is 4.6 B.M. The nickel(II) perchlorate and chloro complexes are diamagnetic in nature and the thiocyanato complex has a moment of 2.8 B.M. indicating a spin free octahedral configuration.

Infrared spectra of the ligand benzil 2,4-dinitro phenyl hydrazone has the important absorption bands in the 3100, 1645, 1620 and 920 cm^{-1} regions, assignable⁷ to $\nu(N-H)$, $\nu(C=O)$, $\nu(C=N)$ and $\nu(N-N)$, respectively. The band due to $\nu(N-H)$

TABLE 1—ANALYTICAL DATA OF COMPLEXES

Compound	Colour	m.p. °C	Λ_M mhos cm ²	μ_{eff} B.M. at 298°K	Analysis% ; Found (Calcd.)	
					metal	halogen, thiocyanate or nitrogen
1. CoLCl ₂	Pink	>250	10.8	5.0	11.05 (11.33)	13.32 (13.65)
2. CoL(SCN) ₂	Green	80	8.5	4.6	10.21 (10.48)	22.02 (22.31)
3. NiLCl ₂	Brown	271	8.8	Diamag.	11.01 (11.29)	13.26 (13.66)
4. NiL ₂ (SCN) ₂	Deep yellow	>250	12.4	2.9	5.85 (6.15)	11.92 (12.15)
5. [NiL ₂](ClO ₄) ₂	do	160	246	Diamag.	5.41 (5.65)	10.51 (10.79)
6. CuLCl ₂	Green	>250	11.8	1.84	11.85 (12.11)	13.22 (13.54)
7. CuL(SCN) ₂	do	>250	9.5	1.78	11.85 (11.16)	20.11 (20.87)
8. CuL(NO ₃) ₂	Blue	122	10.2	1.81	10.75 (11.0)	14.20 (14.54)
9. [CuL ₂](ClO ₄) ₂	do	130	8.8	1.79	5.78 (6.09)	10.51 (10.74)
10. ZnLCl ₂	White	>250	12.5	—	12.11 (12.42)	13.24 (13.49)
11. ZnL(SCN) ₂	do	185	10.4	—	11.14 (11.44)	20.15 (20.30)
12. CdLCl ₂	do	>250	12.8	—	19.32 (19.60)	12.21 (12.38)
13. CdL(SCN) ₂	Yellowish white	>250	11.5	—	17.85 (18.18)	18.56 (18.76)
14. [CdL ₂](ClO ₄) ₂	do	88	248	—	10.04 (10.29)	10.03 (10.29)
15. CdL(NO ₃) ₂	do	120	13.9	—	17.59 (17.94)	13.15 (13.41)
16. [MnL ₂](ClO ₄) ₂	Light brown	180	245	5.8	5.13 (5.81)	10.51 (10.83)

L = Benzil 2,4-dinitro phenyl hydrazone.

TABLE 2—INFRARED (cm⁻¹) AND ELECTRONIC SPECTRAL DATA OF COMPLEXES

Compounds	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	ν_{max} in kK(e)
1	1625	1605	925	465	345	18.9(19), 20.1(20)
2	1625	1600	930	460	345	18.0(400)
3	1620	1605	930	470	350	18.2(60)
4	1625	1605	935	470	350	10.0(6), 14.8(6), 25.0(8)
5	1620	1600	935	465	350	18.5(62)
6	1620	1605	930	475	335	14.8(30)
7	1620	1600	930	470	340	14.8(31)
8	1625	1605	935	475	345	15.2(34)
9	1625	1590	925	475	345	15.5(35)
10	1620	1605	925	465	350	—
12	1625	1600	930	470	345	—
14	1620	1600	935	475	350	—
16	1620	1605	930	475	350	20.2(0.9), 22.8(1.0), 23.0(1.0)

remains unaffected in the complexes whereas the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ bands shift to low frequency region indicating the bonding through the carbonyl oxygen and azomethine nitrogen atoms. Consequent upon bonding through the nitrogen atom of $\text{C}=\text{N}$ group, $\nu(\text{N}-\text{N})$ shifts to higher frequency region as expected. In the case of the thiocyanato complexes $\nu(\text{C}\equiv\text{N})$ is observed at 2100 cm⁻¹ suggesting⁹ the presence of N-bonded terminal thiocyanato group whereas in the case of the cadmium complex this

band is observed at 2130 cm⁻¹ suggestive of coordination through the terminal sulphur atom. In the copper(II) nitrate complex the ν_4 and ν_1 bands of NO_3^- are observed at 1480 cm⁻¹ and 1290 cm⁻¹, respectively and the difference $\Delta\nu$ is of the order of 190 cm⁻¹ indicative of bidentate nitrate coordination; whereas in the cadmium complex $\Delta\nu$ is of the order of 125 cm⁻¹ confirming^{9,10} the presence of monodentate nitrate group. Manganese, nickel and cadmium perchlorate complexes have a very

broad hump around 1100 cm^{-1} indicating^{11,12} the presence of ionic perchlorate group which is in conformity with their molar conductance data. The copper(II) complex has three distinct bands at 1150, 1080 and 1000 cm^{-1} suggestive of the presence of coordinated perchlorate group. Bonding through the oxygen of the carbonyl group and the nitrogen of the azomethine group has been confirmed by the observation¹³ of $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ modes around 455-480 and 335-360 cm^{-1} regions in the infrared spectra of the complexes.

The electronic spectra of the manganese perchlorate complex shows three absorption bands at 20.2, 22.3 and 23.0 kK regions assignable to ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1(\text{G})$, $\rightarrow {}^4\text{T}_2(\text{G})$, and $\rightarrow {}^4\text{A}_1(\text{G})$ transitions, respectively. Position of the absorption band and its extinction coefficient value of 1.0 suggest a possible tetrahedral geometry¹⁴ for the complex. Cobalt(II) chloride complex gives rise to two absorption bands at 18.9 (19) and 20.1 (20) kK regions attributable¹⁵ to ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ and $\rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ transitions or may be the consequence of splitting in the ${}^4\text{T}_{1\text{g}}(\text{P})$ state due to spin orbit coupling. The other band due to the transitions to ${}^4\text{T}_{2\text{g}}$ state was beyond the range covered by the instrument. The thiocyanate complex has one intense band at 16.0 (400) kK region due to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition. Considering the band positions, intensities and the magnetic moment data, the cobalt(II) chloride complex may have an octahedral configuration involving bridging chloride group whereas the thiocyanate complex is probably tetrahedral. The nickel(II) halide and perchlorate complexes show one absorption band at 18.2–18.5 ($\xi=60, 62$) kK region. The spectral pattern and the diamagnetic nature of the complexes indicate¹⁶ a square planar configuration. The nickel thiocyanate complex on the other hand gives rise to three absorption bands at 10.0 (6), 14.8 (6) and 25.0 (8) kK regions due to ${}^8\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^8\text{T}_{2\text{g}}(\text{F})$, $\rightarrow {}^8\text{T}_{1\text{g}}(\text{F})$ and $\rightarrow {}^8\text{T}_{1\text{g}}(\text{P})$ transitions, respectively indicating a spin

free octahedral configuration that is also in conformity with its magnetic moment value. All the copper(II) complexes exhibit one broad absorption band at 14.8–15.5 (30-35) kK region indicating a distorted octahedral configuration¹⁷. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope. On the basis of analytical, conductance and infrared spectral data, zinc and cadmium complexes are presumed to be of tetrahedral configuration.

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