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Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn Salts with *o*-Hydroxy Propiophenone and Quinoline

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CHEMISTRY of metal β -diketonates has invoked¹ lot of interest in recent years in such diverse areas as spectral studies, gas chromatography, nmr shift reagents, laser technology and as radical initiators in polymerization reactions. The formation of adducts of metal β -diketone chelates plays an important role in the synergistic enhancement of solvent extraction of metal ions. β -Keto esters and *o*-hydroxy carbonyl compounds closely resemble the β -diketones. It was thought worthwhile to study the reactions of metal salts with *o*-hydroxy propiophenone and quinoline. As a result, this communication reports chelates of *o*-hydroxy propiophenone and their adducts with quinoline.

Experimental

Complexes of the type MLXQ or M' LXQ: Absolute ethanolic solution of metal salts was treated with *o*-hydroxy propiophenone and quinoline in 1:1:1 proportion and the resulting solution refluxed for 30 min. To this solution, dilute ammonium hydroxide was added dropwise under constant stirring till the pH was 7. The resulting precipitates were filtered, washed with ethanol and ether and dried in vacuum.

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Complexes of the type ML₂Q₂ or M'L₂Q: Aqueous solutions of metal acetates were treated with ethanolic solution of *o*-hydroxy propiophenone in 1:2 proportion and the mixture stirred for 30 min at 40°. Metal chelates were filtered, washed with ethanol and ether and dried in vacuum. Ethanolic suspension of different metal chelates was treated with quinoline in 1:2 ratio and the resulting solution refluxed for 30 min. On concentrating the solution in a rotary vacuum evaporator and keeping at 10° overnight crystalline base adducts separated. These were filtered, washed with ethanol and dried in vacuum.

Analyses and physical measurements were done as reported earlier². The relevant analytical data are presented in Table 1 and the spectral data in Table 2.

Results and Discussion

In the infrared spectra of hydroxy propiophenone $\nu(\text{C}=\text{O})$ is observed³ at 1620 and $\nu(\text{O}-\text{H})$ at 3350 cm^{-1} . In monochelate complexes, $\nu(\text{C}=\text{O})$ shifts to lower frequency region and is observed around 1600 cm^{-1} whereas $\nu(\text{O}-\text{H})$ disappears. Thus the ligand anion forms the chelate using both the oxygen atoms. This has been substantiated by the observation⁴ of $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ around 440-460, 320-335 and 230-250 cm^{-1} region, respectively. Thus, these are four coordinated compounds involving the mono chelate, the coordinated anion and coordinated quinoline. In the nitrate complexes, the position of ν_4 and ν_1 (1410 and 1280 cm^{-1}) of NO_3 and their difference of the order of 130 cm^{-1} suggest^{5,6} monodentate nitrate coordination.

In the *bis* chelates $\nu(\text{C}=\text{O})$ is found around 1590-1600 cm^{-1} which shifts to slightly higher frequency region in the base adducts. The formation of the base adducts of the *bis* chelates has been confirmed⁴ by the appearance of $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ around 460 and 320 cm^{-1} region in the far infrared spectra.

In the visible region, cobalt mono chelate complexes give rise to one intense absorption band around 16.0 kK region assignable⁷ to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition. Position of the band, its high intensity and lower magnetic moment value suggest a possible tetrahedral configuration for these complexes. The base adduct of the *bis* chelate complex gives rise to two absorption bands at 18.8 and a shoulder at 19.5 kK assignable to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition. On the basis of the band positions and magnetic moment values an octahedral configuration is proposed for the complex.

Nickel(II) mono chelate complexes are diamagnetic and show one absorption band a 16.5 kK, presumably indicating a square planar configuration for these two complexes, whereas the base adduct of the nickel(II) *bis* chelate gives rise to three absorption bands at 9.5, 13.8 and 24.4 kK

NOTES

TABLE 1—ANALYTICAL DATA OF MIXED LIGAND COMPLEXES

Compound	Colour	ΔM mhos cm^{-2}	Analysis %			μ_{eff} B.M.
			C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	
1. $CoLClQ$	Blue	10.5	57.85 (57.99)	4.03 (4.30)	3.56 (3.76)	4.5
2. $CoL(NO_3)Q$	Blue	8.4	54.19 (54.14)	4.18 (4.01)	6.82 (7.02)	4.6
3. CoL_2Q_2	Pink	11.6	70.02 (70.25)	5.38 (5.20)	4.31 (4.55)	5.0
4. $NiLClQ$	Red	10.2	58.24 (58.03)	4.06 (4.30)	3.65 (3.76)	Diamag.
5. $NiL(NO_3)Q$	Red	8.8	54.25 (54.17)	4.22 (4.01)	6.84 (7.02)	Diamag.
6. NiL_2Q_2	Green	6.5	70.08 (70.27)	5.26 (5.21)	4.22 (4.55)	3.1
7. $CuLClQ$	Brown	10.4	58.22 (58.05)	4.21 (4.30)	3.68 (3.76)	1.82
8. $CuL(NO_3)Q$	Brown	12.5	54.41 (54.2)	4.15 (4.01)	6.76 (7.08)	1.80
9. CuL_2Q_2	Blue	11.8	65.92 (66.04)	4.98 (5.09)	3.68 (3.85)	1.79
10. $ZnLClQ$	White	9.8	57.14 (57.01)	4.11 (4.22)	3.58 (3.69)	—
11. $ZnL(NO_3)Q$	White	9.9	53.2 (53.28)	3.86 (3.96)	6.81 (6.91)	—
12. ZnL_2Q_2	White	7.5	65.66 (65.80)	5.11 (5.07)	2.64 (2.84)	—

L=anion of 2-hydroxy propiophenone, Q=quinoline.

TABLE 2—SPECTRAL DATA OF MIXED LIGAND COMPLEXES

Compound No.	Infrared spectra cm^{-1}				Electronic spectra
	$\nu(C=O)$	$\nu(M-O)$	$\nu(M-N)$	$\nu(M-Cl)$	ν_{max} in kK (ϵ)
1.	1600	440	320	230	16.0(900)
2.	1590	450	325	235	16.1(900)
3.	1595	445	330	235	18.8(95), 19.5
4.	1600	445	325	240	15.5(55)
5.	1605	440	320	235	15.3(50)
6.	1600	450	330	230	9.5(6), 13.8(14), 24.4(16)
7.	1595	460	325	250	17.3(35)
8.	1590	455	320	250	17.0(30)
9.	1590	460	335	245	15.5(60)
10.	1600	460	320	245	—
11.	1605	455	325	250	—
12.	1600	450	330	250	—

attributable^a to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $\rightarrow {}^3T_{1g}(F)$ and $\rightarrow {}^3T_{1g}(P)$ transitions, respectively. Position of spectral bands and magnetic moment value suggest an octahedral configuration for these complexes.

Monochelate complexes of copper(II) give rise to a broad band around 17.3 kK region indicating probably a four coordinated square planar configuration⁹ for these complexes. Mono base adducts of the bis chelate of copper(II) also give rise to one broad band at 15.5 kK. On comparison with the spectra of bis chelate the band has shifted slightly to low frequency region and there is an increase in intensity of the absorption band. Hence the complex may be presumed to be penta-coordinated on the basis of earlier observations¹⁰⁻¹² on the mono base adducts of β -diketonato complexes of copper(II).

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