

Synthesis and physicochemical studies on Co(III) complexes

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Abstract. Complexes of Co(III) with 2-hydroxyacetophenone-thiosemicarbazone, 2-hydroxy-3-methylacetophenonethiosemicarbazone and 2-hydroxy-4-methyl-acetophenonethiosemicarbazone, and the addition complexes of 2-hydroxy-acetophenone thiosemicarbazone with ammonia, pyridine, aniline, *o*-toluidine, *m*-toluidine and *p*-toluidine have been synthesized and characterized on the basis of their conductivities, electronic and infrared spectral data. All complexes are low-spin octahedral in nature. Various parameters have been obtained using ligand field theory.

Keywords. Co(III) complexes ; addition complexes of Co(III) ; 2-hydroxy-acetophenonethiosemicarbazones.

1. Introduction

There are quite a few reports indicating the possible existence of (nitrogen base-H)⁺ containing metal complexes (Patil and Shah 1981). However, very little systematic work seems to have been done on such complexes. In the present study we are reporting the synthesis and characterization of Co(III) chelates of 2-hydroxy acetophenonethiosremicarbazone (HAT), 2-hydroxy-3-methyl-acetophenonethiosemicarbazone (3MeHAT) and 2-hydroxy-4-methyl-acetophenonethiosemicarbazone (4MeHAT) and additional compounds of Co(III) chelate of HAT, with ammonia, pyridine, aniline, *o*-toluidine, *m*-toluidine and *p*-toluidine.

2. Experimental

All reagents used were of AnalaR grade. Absolute ethanol was dried by refluxing with sodium and ethyl succinate. The ligands used in the present study were synthesized following the method of Patel and Patel (1971) and Vogel (1956).

2.1. Preparation of the [CoL₂] Cl complexes

A rapid current of air was passed for 3 hr through the 1 : 2 alcoholic mixture of cobalt(II) chloride and the ligand at 50°C. The resulting solution was then

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concentrated to about half the original volume. The dark brown product was filtered and washed with small portions of absolute ethanol using rapid suction. It was dried in air.

2.2. Preparation of the $[Co(HAT)_2]$ base-H complexes

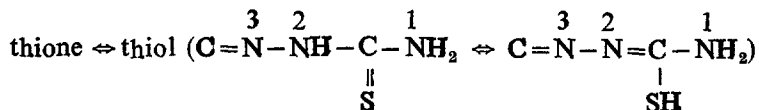
All these complexes were prepared as above except that the mixture in addition contains 3 g of base. In the preparation of ammonium compounds, 10 ml of concentrated solution of ammonium hydroxide were added.

All physico-chemical measurements and analytical studies were made as described by Patil and Shah (1981).

3. Results and discussion

3.1. Nature of the ligands

The ligands used in the present study are known to undergo



tautomerism (Patil and Shah 1980). The infrared spectra of the ligands show bands at $\sim 860 \text{ cm}^{-1}$ which may be assigned to $\nu_{\text{C-S}}$ (Campbell and Grazeskowiak 1967). However, the absence of band due to $\nu_{\text{S-H}}$, suggests the thione form of the ligands at least in the solid state. The band $\sim 1570 \text{ cm}^{-1}$ may be due to $\nu_{\text{C-N}}$ of the azomethine group (Wiles and Suprunchuk 1969).

3.2. Nature, bonding and structure of the complexes

Analytical data (table 1) show the parent complexes to conform to the general composition $[CoL_2]Cl$ and $[CoL_2]$ base-H for the additional complexes. All these complexes are slightly soluble in water, but highly soluble in common organic solvents and also in coordinating solvents. Diamagnetic nature of these compounds suggest the oxidation of Co(II) to Co(III) during their preparation. The molar conductivities (table 1) of the compounds in ethanol indicate their 1:1 electrolyte nature (Geary 1971).

Infrared spectra of all the complexes show the absence of ν_{OH} , suggesting the removal of hydroxy proton on coordination. Downward shifting of $\nu_{\text{C-S}}$ and $\nu_{\text{C-N}}$ indicates the coordination through sulphur and nitrogen. The presence of an additional band at $\sim 960 \text{ cm}^{-1}$ in all the additional complexes is an indication of N^2-N^3 bond elongation and $\text{C}=\text{N}^2$ bond formation and hence the removal of thioenolic proton on coordination. Thus it may be concluded that the ligand would have behaved as a monobasic tridentate for the parent complexes and as dibasic tridentate for the additional complexes.

The diffuse reflectance spectra of all complexes show three bands in the regions required for low spin pseudooctahedral complexes of Co(III) (Legg and Cooke 1965, 1966; Batley and Gradon 1968). The higher energy band may be assigned

Table 1. Decomposition temperature, analyses and conductivity data of Co(III) complexes.

Compound	Decomp. temp. ° C.	Found (calc.) %				Cl	Molar conduc- tance Ohm ⁻¹ cm ² mole ⁻¹
		Metal	C	H	S		
[Co(HAT) ₂]Cl	260	11.20 (11.60)	41.90 (42.76)	4.07 (3.96)	12.47 (12.60)	7.24 (6.99)	42.4
[Co(3MeHAT) ₂]Cl	281	11.20 (11.00)	45.63 (44.74)	4.86 (4.40)	12.05 (12.00)	6.97 (6.68)	34.5
[Co(4MeHAT) ₂]Cl	200	10.67 (11.00)	43.95 (44.74)	4.15 (4.40)	12.38 (12.60)	6.77 (6.68)	34.7
NH ₄ [Co(HAT) ₂]	225	12.16 (12.00)	45.19 (44.10)	5.15 (4.90)	12.95 (13.05)	..	34.59
Py-H[Co(HAT) ₂]	210	10.78 (10.65)	51.05 (50.00)	5.40 (4.71)	11.69 (11.60)	..	31.98
<i>o</i> -tolu. H[Co(HAT) ₂]	217	10.44 (10.38)	49.98 (50.86)	5.45 (4.92)	11.17 (11.60)	..	34.56
<i>m</i> -tolu. H[Co(HAT) ₂]	220	10.34 (10.38)	50.15 (50.86)	5.47 (4.92)	11.92 (11.60)	..	39.24
<i>p</i> -tolu. H[Co(HAT) ₂]	218	10.77 (10.38)	49.75 (50.86)	5.49 (4.92)	11.37 (11.60)	..	36.12
C ₆ H ₅ -NH ₂ ·H[Co(HAT) ₂]	215	10.34 (10.40)	50.12 (50.90)	3.95 (4.77)	11.15 (11.31)	..	35.12

Table 2. Electronic spectral data and spectral parameters of Co(III) complexes.

Compounds	Reflectance spectra (cm ⁻¹)						Dt.	C	B
	${}^1E_g \leftarrow {}^1A_{1g}$	${}^1A_{1g} \leftarrow {}^1A_{1g}$	${}^1T_{2g} \leftarrow {}^1A_{1g}$	$10Dq(xy)$	(Dqz)	(10Dq-C) 35/4 Dt.)			
[Co(HAT) ₃]Cl	15630	19230	25300	20747	1355	411	1517	379	
[Co(3MeHAT) ₃]Cl	15630	19600	25650	21112	1304	461	1512	378	
[Co(4MeHAT) ₃]Cl	15750	19600	25000	20950	1325	440	1350	337	
NH ₄ [Co(HAT) ₃]	15380	19600	25970	21192	1275	482	1592	398	
PyH[Co(HAT) ₃]	15380	20000	25310	21227	1198	528	1327	332	
<i>o</i> -tolu.H[Co(HAT) ₃]	15380	20000	25650	21412	1217	528	1412	353	
<i>m</i> -tolu.H[Co(HAT) ₃]	15380	20000	25650	21327	1217	528	1327	332	
<i>p</i> -tolu.H[Co(HAT) ₃]	15380	20000	25650	21412	1208	528	1412	353	
C ₆ H ₅ NH ₂ H[Co(HAT) ₃]	15380	20000	25310	21327	1208	528	1327	332	

as due to ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition possibly mixed up with metal \rightarrow ligand charge transfer transition and later two due to the split components of ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transitions (Ballhausen and Maffitt 1956). The assignments are listed in table 2 along with their energies. (Ballhausen and Maffitt 1956 ; Lever 1968). Making use of the observed transition energies the values of $10Dq$, B and C have been evaluated and are listed in table 2. The $d-d$ transition energies in terms of tetragonal radial parameter, Dt , have been evaluated by the fact that the splitting of the first excited term ${}^1T_{1g}$ in octahedral symmetry is $35/4 Dt$ and the parameter $10Dq(x\gamma)$ corresponds exactly to $10Dq$. $Dq(z)$ have been obtained (table 2) using (Wentworth and Piper 1965) $Dt(D_{4h}) = 4/7 [Dq(x\gamma) - Dq(z)]$.

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