

Possible existence of the (nitrogen base H)⁺ cations with cobalt(III) chelates of 2-hydroxy-5-methyl acetophenone thiosemicarbazone†

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Abstract. Co(HMAT)₂Cl and Co(HMAT)₂ base H have been synthesized and characterized by elemental analyses, magnetic moments, electronic and infrared spectral measurements. The results show them to be low spin octahedral in nature. Various parameters have been calculated using ligand field theory of spin-allowed transitions.

Keywords. 2-hydroxy acetophenone thiosemicarbazone; ammonia; pyridine; aniline, ligand field parameters.

1. Introduction

Studies on coordination of nitrogen bases with several chelates have been reported (Ablov and Gerbeleu 1964, 1965, 1971). However, Co(III) chelate of the 2-hydroxy-5-methyl acetophenone thiosemicarbazone (HMAT) and their additional compounds with different bases are not known. In this paper, we report the Co(III) chelate of HMAT and its additional compounds with ammonia, pyridine, aniline, *o*-, *m*-, *p*-toluidine. The isolation of these additional compounds suggests that neutral bases are not coordinated to Co(III). It is proposed that these compounds may contain (base H)⁺ unit.

2. Experimental

All the chemicals used were of analytical grade. The ligand was synthesized by the method described in Patel *et al* (1973).

2.1. Preparation of Co(HMAT)₂Cl

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

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centrated and cooled to get a dark brown solid. The product was filtered and washed with alcohol and then with ether.

2.2. Preparation of $\text{Co}(\text{HMAT})_2$ base H

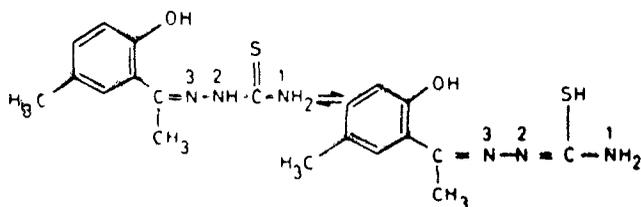
These compounds were also prepared as mentioned above except that the mixture in addition contains 3 g of base. In preparing the NH_4^+ compound ammonium hydroxide (10 ml) was added.

To establish the composition, the Co(III) content in each complex was determined by independent gravimetric and volumetric methods. Carbon-nitrogen-hydrogen analyses were made on a C-H-N analyser (M/s. University, India). The chloride (6.92%) in the parent complex was estimated by Mohr's method. The sulphur was estimated as BaSO_4 by Carius method (Vogel 1958). The conductivities of the complexes in absolute ethanol were measured using a conductometer (M/s. Konduktoskop Metrohm Herisau, Switzerland). Magnetic measurements were made at room temperature (30°C) using a semi-micro Gouy balance (M/s. Sartorius). The visible spectra of the complexes were recorded on a Beckmann-DU spectrophotometer. The infrared spectra were recorded in KBr on IR-20 Beckmann spectrophotometer.

3. Results and discussion

3.1. Nature of the ligand

Potentially HMAT can take the following equilibrium.



A similar tautomeric equilibrium is reported in the case of acetone thiosemicarbazone (Gingras *et al* 1961). The ligand shows a sharp and strong band at 870 cm^{-1} perhaps due to $\nu_{\text{C}=\text{S}}$ with some contribution either δ_{NH_2} or ν_{NCN} (Campbell and Grazeskowiak 1967). The absence of a band at $2560\text{--}70 \text{ cm}^{-1}$ indicates absence of thiol form of the ligand at least in solid state (Poddar and Saha 1975). The sharp and strong band located at 1590 cm^{-1} is attributed to $\nu_{\text{C}=\text{N}}$ (Wiles and Suprunchuk 1969), the strong band at 1300 cm^{-1} to $\nu_{\text{C}-\text{N}} + \delta_{\text{NH}_2}$ (Beecroft *et al* 1974) and the band at 3300 cm^{-1} to $\nu_{\text{O}-\text{H}}$. The bands at 2700 and 3100 cm^{-1} may be due to $\nu_{\text{N}-\text{H}}$ of NH_2 group.

3.2. Nature, bonding and structure of complexes

The elemental analyses (table 1) reveal 1:2 (Co : HMAT) Stoichiometry for the parent complex and 1:2:1 (Co : HMAT : Base) for addition complexes. All

Table 1. Analytical, decomposition temperature and conductivity data.

Compound L = HMAT	Decomposition Temp. °C	Found (Calc.) %			Molar conductance ohm ⁻¹ cm ² mole ⁻¹
		Metal	N	S	
[Co (HL)] Cl	210	10.97 (11.00)	15.45 (15.66)	12.39 (11.93)	36.1
NH ₄ [CoL ₂]	255	11.56 (11.36)	18.57 (18.88)	12.08 (12.33)	27.9
PY. H [CoL ₂]	245	10.50 (10.14)	17.27 (16.89)	11.09 (11.03)	38.1
C ₆ H ₄ NH ₂ · H [CoL ₂]	220	9.56 (9.88)	16.01 (16.48)	10.86 (10.78)	39.2
<i>o</i> -tolu. H [CoL ₂]	238	9.63 (9.68)	16.47 (16.10)	10.71 (10.52)	37.2
<i>m</i> -tolu. H [CoL ₂]	233	9.72 (9.68)	16.35 (16.10)	10.69 (10.52)	37.6
<i>p</i> -tolu. H [CoL ₂]	250	9.73 (9.68)	16.29 (16.10)	10.65 (10.52)	38.3

compounds are found to be diamagnetic indicating oxidation to Co(II) to Co(III) ion on passing air through the mixture. The molar conductivities (table 1) of all compounds in ethanol are in the range required for 1:1 electrolyte (Geary 1971).

The infrared spectra of the ligand and complexes are given in table 3. The ligand band at 1590 cm⁻¹ is shifted to lower frequencies in all the complexes studied here. This suggests that the bonding to metal ion is primarily effected through azomethine of the ligand in the complexes (Sahani *et al* 1977). All the complexes show shifting of the band at 870 cm⁻¹ to a lower region, indicating coordination through sulphur to the metal (Pradhan and Ramanarao 1977). All the complexes show broad band in the ν_{N-H} region. The absence of a band at 3300 cm⁻¹ in all the complexes indicate the possible removal of proton from the ligand. The band at 1330 cm⁻¹ in the parent complex suggests that the ligand would have used its thione form during coordination.

In the additional compounds the band at 1300 cm⁻¹ is found to be shifted to higher frequency. This suggests that the double bond is localised at C-N² (Cavalca *et al* 1962) and hence the presence of thiol form of the ligand.

These observations suggest that in the parent complex the ligand would behave as a singly-charged tridentate, while in the additional compounds, the ligand would behave as a doubly-charged tridentate.

The diffuse reflectance spectra and ethanol solution spectral data are given in table 2, with probable assignments. The spectra are found to be similar and indicate an identical structure. They are found to be spin-paired, indicating six coordinate structure and therefore show two spin-allowed and two spin-forbidden ligand field bands (Lever 1968). However, the reflectance spectra of the complexes show three bands at ~15000, ~20000 and ~24000 cm⁻¹ and indicate

Table 2. Electronic spectral data with probable assignments.

Compounds L = HMAT	Reflectance spectra cm^{-1}			Absorption spectra in ethanol cm^{-1}
	${}^1E_g \leftarrow {}^1A_{1g}$	${}^1A_{2g} \leftarrow {}^1A_{1g}$	${}^1T_{2g} \leftarrow {}^1A_{1g}$	${}^1T_{2g} \leftarrow {}^1A_{1g}$
[Co (HL) ₂] Cl	15750	19600	23810	24100
NH ₄ [CoL ₂]	15380	19600	23520	24390
PY-H [CoL ₂]	15160	19600	23260	24100
C ₆ H ₅ NH ₂ · H [CoL ₂]	15160	19230	23260	24390
<i>o</i> -tolu. H [CoL ₂]	14920	19600	23520	24390
<i>m</i> -tolu. H [CoL ₂]	15160	19600	24390	24390
<i>p</i> -tolu. H [CoL ₂]	15160	19600	24390	24390

Table 3. Important infrared data (cm^{-1})

Compound	$\nu_{(C=N)}$	$\nu_{(C-N)} + \delta \text{NH}_2$	$\nu_{(C=S)}$
L = HMAT	1590s, m	1300s, s	870s, s
[Co (HL) ₂] Cl	1550br	1330sh, m	820s, s
NH ₃ [CoL ₂]	1520sh, m	1450sh, m	800s, s
PY-H [CoL ₂]	1500s, br	1440sh, m	810s, s
C ₆ H ₅ NH ₂ · H [CoL ₂]	1560s, m	1440s, s	800sh, m
<i>o</i> -tolu. H [CoL ₂]	1510sh, m	1420s, br	820s, s
<i>m</i> -tolu. H [CoL ₂]	1550s, br	1450sh, m	810s, s
<i>p</i> -tolu. H [CoL ₂]	1540sh, m	1420s, br	820s, s

s, s = Sharp strong; sh, m = shoulder medium; s, m = sharp medium; s, br = sharp broad.

the possibility of deviation from regular octahedral structure (Rana *et al* 1975). The first spin-allowed transition ${}^1T_{1g} \leftarrow {}^1A_{1g}$ shows splitting and gives rise to two bands corresponding to ${}^1E_g \leftarrow {}^1A_{1g}$ (10 Dq-C-35/4Dt) and ${}^1A_{2g} \leftarrow {}^1A_{1g}$ (10 Dq-C) transitions. The observed two bands at ~ 15000 and $\sim 20000 \text{ cm}^{-1}$ may correspond to the above transitions respectively (Dunlop and Gillard 1963). The band at $\sim 24000 \text{ cm}^{-1}$ may be assigned to ${}^1T_{2g} \leftarrow {}^1A_{1g}$ (10 Dq + 16 B-C) transition (Ballhausen and Maffitt 1956; Kuroda and Gentile 1965; Legg and Cooke 1965; Dey and De 1975). Using these transition energies and assuming $C = 4B$, C was calculated for each complex. The value of 10 Dq for each complex was obtained using the calculated C values. Using the Dq and C values and the observed energy corresponding to ${}^1E_g \leftarrow {}^1A_{1g}$ transition, Dt was calculated for each complex. The parameter of 10 Dq exactly corresponds to that of 10 Dq (XY) (Ballhausen and Maffitt 1956). Using the values given by Wentworth and Piper (1965), the value for $Dt(D_4h) = 4/7 [Dq(XY) - Dq(Z)]$, Dq (Z) was calculated. The calculated values of the C, B, Dt, Dq (XY) and Dq (Z) are in

the range 915–1197, 224–299, 440–534, 20215–20797 and 1123–1295 cm^{-1} respectively. Examination of the above data indicates (i) irrespective of whether it is anionic or cationic, the parameter values of 10 Dq (XY) are similar indicating the identical field strength in the XY-plane. (ii) The Dq (Z) values also show that the ligand field strength perpendicular to the XY-plane is greater in the cationic complex. (iii) The parameter values of Dt suggest that the cationic parent complex is less distorted to anionic complexes. The ethanol solution spectra of the compounds show only one band at $\sim 24000 \text{ cm}^{-1}$ may be assigned to ${}^1T_{2g} \leftarrow {}^1A_{1g}$ transition.

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