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Original Scientific Paper

Magneto-Spectral Studies on Some Trivalent Metal Complexes: Chromium, Iron and Cobalt Complexes Derived from 4-Benzylamidothiosemicarbazide and its Thiosemicarbazone.

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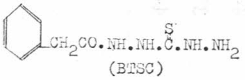
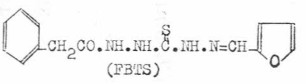
Complexes of chromium(III), iron(III) and cobalt(III) with 4-benzylamidothiosemicarbazide (BTSC) and 1-(α-)furyl-4-benzylamidothiosemicarbazone (FBTS) have been prepared and characterized by conventional chemical and physical measurements. Tetragonal symmetry has been proposed for these complexes on the basis of electronic spectral data. The various ligand field parameteres have been evaluated, wherever possible. The infrared spectral studies indicate the S-N- bidentate nature of both ligands.

INTRODUCTION

Thiosemicarbazides and thiosemicarbazones have long been known for their pharmacological[1], anti-bacterial[2], fungicidal[3] and versatile chelating[4–8] properties. In our previous communications[6–8] 4-benzylamidothiosemicarbazide and 1-(α-)furyl-4-benzylamidothiosemicarbazone have been reported as chelating agents for a number of transition metals. The present paper deals with the isolation and characterization of the chromium(III), iron(III) and cobalt(III) complexes of these ligands.


(BTSC)


(FBTS)

MATERIALS AND METHOD

Both ligands (BTSC and FBTS) were prepared by the general method outlined by Stempel et al.[9]

(i) *Dihalobis(BTSC)Chromium(III) Chloride and Dihalobis(FBTS)Chromium(III) Chloride*

When 50 ml of an ethanolic solution (95%) of chromium(III) chloride (1.0 mmol) were mixed with 125 ml of an equimolar solution of the ligand in the same solvent, a green colour developed. This green coloured solution was refluxed for about one hour and finally concentrated to a small volume, when a greyish green coloured precipitate was produced. This precipitate was filtered off, washed with ethanol and ether and dried at 110 °C. The analyses correspond to general formula $[Cr(L)_2Cl_2]Cl$, where L = BTSC and FBTS. Yield ~ 55%.

TABLE I

Analytical and Magnetic Data of Chromium(III), Iron(III) and Cobalt(III) Complexes of Both Ligands (BTSC and FBTS)

Complex	Observed percentage of					Calculated percentage of					μ_{eff} (B. M.)
	C	H	N	M	X	C	H	N	M	X	
$[Cr(C_9H_{12}N_4OS)_2Cl_2]Cl$	35.72	3.98	18.39	8.59	17.59	35.62	3.96	18.47	8.58	17.54	3.71
$[Cr(C_{14}H_{14}N_4O_2S)_2Cl_2]Cl$	44.23	3.69	14.72	6.83	14.05	44.07	3.67	14.69	6.82	13.95	3.68
$[Fe(C_9H_{12}N_4OS)_2Cl_2]Cl$	36.17	4.12	18.54	9.27	17.17	35.93	3.99	18.63	9.29	17.69	5.79
$[Fe(C_{14}H_{14}N_4O_2S)_2Cl_2]Cl$	44.01	3.95	14.56	7.53	9.47	43.85	3.65	14.62	7.29	9.25	5.81
$[Co(C_9H_{12}N_4OS)_2(H_2O)_2](OH)_3$	37.37	5.42	18.32	9.92	—	37.14	5.48	18.60	9.80	—	—
$[Co(C_{14}H_{14}N_4O_2S)_2(H_2O)_2](OH)_3$	44.93	4.60	14.30	7.82	—	44.84	4.62	14.76	7.78	—	—

M = Metal and X = Cl

(ii) *Dihalobis(BTSC)iron(III) Chloride and Dihalobis(FBTS)iron(III) Chloride*

A dark brown colour was observed to develop when 50 ml of anhydrous ferric chloride (1.0 mmol) in ethanol were added to 125 ml of an equimolar ethanolic solution of the ligand, the pH of the reaction mixture being 2.0. The colour of the reaction mixture deepened on being refluxed for a couple of hours. After concentrating the mixture to half of its volume, a deep brown precipitate was obtained. This was filtered off and washed and dried as in procedure (i). The chemical analyses (Table I) correspond to the general formula $[Fe(L)_2Cl_2]Cl$. Yield ~ 65%.

(iii) *Diaquobis(BTSC)cobalt(III) Hydroxide and Diaquobis(FBTS)cobalt(III) Hydroxide*

50 ml of a 0.5 mmol cobalt(II) chloride hexahydrate (dissolved in ethanol) were mixed with 125 ml of an equimolar solution of the ligand in the same solvent. The pH of the reaction mixture was raised to 11.5 by the addition of a dilute ethanolic solution of sodium hydroxide. A vigorous stream of air was passed through the reaction mixture for about 24 hours when a greyish black precipitate was produced. This was filtered off, washed with hot ethanol and ether and dried. The analyses show the formula to be $[Co(L)_2(H_2O)_2](OH)_3$. The same compound was obtained when cobalt(II) bromide and cobalt(II) nitrate were taken as the starting materials instead of cobalt(II) chloride.

All the physical measurements were made as reported earlier[6]. The sparingly soluble nature of these compounds has prevented the determination of molecular weight, conductivity and solution absorption spectral measurements which might have been more helpful in establishing the structure of these complexes.

RESULTS AND DISCUSSION

(i) *Chromium(III) Complexes*

The room temperature magnetic moments for the chromium(III)-BTSC and chromium(III)-FBTS complexes are 3.71 and 3.68 B. M., respectively. The reason for this small reduction in the value of magnetic moments from the spin-only value is due to the positive spin-orbit coupling constant for this ion and also due to the small magnetic anisotropy associated with the chromium(III) ion[10]. The chromium(III)-BTSC complex was subjected to low temperature magnetic measurements and the data obey the Curie-Weiss law ($\vartheta = -10$ °K).

The bands observed in the electronic spectra of the complexes are in accordance with those observed in the spectra of the complexes conforming to D_{4h} symmetry[11]. Griffith and Orgel[12] first spelled out the quantitative aspects of molecular orbital theory for compounds of D_{4h} symmetry. They suggested that for trans-dichlorotetramminechromium(III) one electron e_g ought to split with $E(x^2 - y^2) > E(z^2)$ according to either the crystal field or molecular orbital approach, but the splitting of T_{2g} in the molecular orbital approach should be $E(xz, yz) > E(xy)$ on account of the π-antibonding effect of the chloride ion. This order is the reverse of that predicted by crystal field theory for which the order of splitting is $E(xy) > E(xz, yz)$, since ammonia has a greater crystal field strength than the chloride ion. The transitions which have been cited in Table III are based on the crystal field approach. The first two bands are obtained by splitting the ${}^4T_{2g}$ term (component of O_h) whereas the second two arise from the splitting of the T_{1g} term[13]. The splitting of the first band (T_{2g}) corresponds to 35/4 Dt and the transition ${}^4B_{1g} \rightarrow {}^4B_{2g}$ directly gives the value of 10 Dq[13]. The McClure orbital parameters d_σ and d_π have been evaluated following the equations suggested by Perumareddi[13]. Spectral data also helps to decide whether the chloride ions are in trans- or cis-positions. In complexes where Dq (E) >

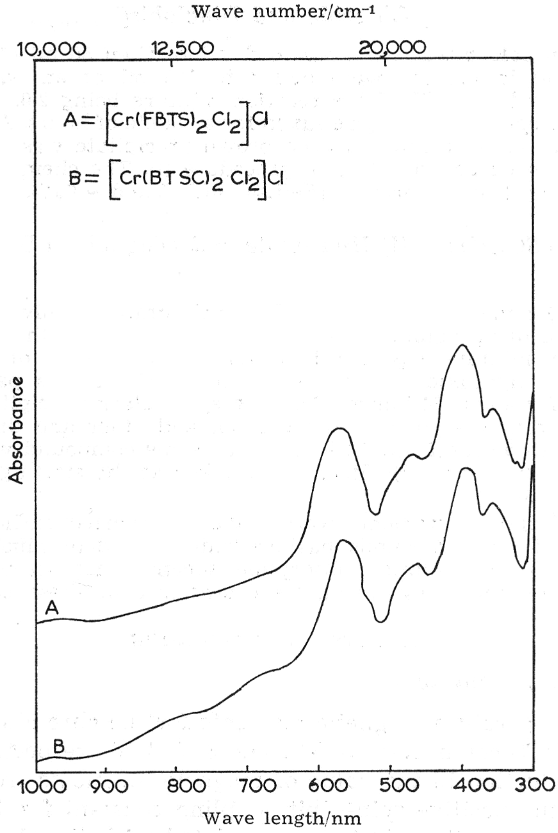


Figure 1. Electronic spectra of cobalt(III) complexes.

TABLE II

Magnetic Data of Chromium(III) and Iron(III) Complexes of BTSC and FBTS at Various Temperatures

Complex	Temp/K	χ_M' (c. g. s. Units)	μ_{eff} (B. M.)
$[Cr(C_9H_{12}N_4OS)_2Cl_2]Cl$	80	19,229	3.59
	98	16,434	3.60
	118.5	13,776	3.63
	152	11,122	3.69
	204	8,282	3.70
	295.5	5,773	3.71
$[Fe(C_9H_{12}N_4OS)_2Cl_2]Cl$	88	45,548	5.74
	109	37,615	5.74
	141	28,997	5.75
	190	21,847	5.78
	295.5	15,635	5.79

TABLE III

Electronic Spectral Data of Chromium(III), Iron(III) and Cobalt(III) Complexes of BTSC and FBTS

Complex	Obs. bands (cm^{-1})	Assignments	Parameters (cm^{-1})	
$[Cr(C_9H_{12}N_4OS)_2Cl_2]Cl$	17,540	$^4B_{1g} \rightarrow {}^4E_g({}^4T_{2g})$	Dq (E) = 2.105	$d_\sigma = -1359$
	21,050	$\rightarrow {}^4B_{2g}({}^4T_{2g})$	Dq (A) = 1.403	$d_\pi = 395$
	25,320	$\rightarrow {}^4A_{2g}({}^4T_{1g})$	Dt = 401	K = 1.01
	27,250	$\rightarrow {}^4E_g({}^4T_{1g})$	Ds = 405	
$[Cr(C_{14}H_{14}N_4O_2S)_2Cl_2]Cl$	17,540	$^4B_{1g} \rightarrow {}^4E_g({}^4T_{2g})$	Dq (E) = 2.128	$d_o = -1460$
	21,280	$\rightarrow {}^4B_{2g}({}^4T_{2g})$	Dq (A) = 1.380	$d_\pi = 408$
	25,320	$\rightarrow {}^4A_{2g}({}^4T_{1g})$	Dt = 427	K = 1.03
	27,400	$\rightarrow {}^4E_g({}^4T_{1g})$	Ds = 439	
$[Fe(C_9H_{12}N_4OS)_2Cl_2]Cl$	17,540	$^6A_{1g} \rightarrow {}^4T_{1g}({}^4E)$	10Dq = 17.330	
	19.800	$\rightarrow {}^4T_{1g}({}^4A)$	B = 1.053	
	24,390	$\rightarrow {}^4T_{2g}$	B = 0.81	
	28,990	→ C. T.		
$[Fe(C_{14}H_{14}N_4O_2S)_2Cl_2]Cl$	17,700	$^6A_{1g} \rightarrow {}^4T_{1g}({}^4E)$	10Dq = 17.520	
	19,610	$\rightarrow {}^4T_{1g}({}^4A)$	B = 1.069	
	25,000	$\rightarrow {}^4T_{2g}$	B = 0.82	
	29,410	→ C. T.		
$[Co(C_9H_{12}N_4OS)_2(H_2O)_2](OH)_3$	16,670	$^1A_{1g} \rightarrow {}^1E_g({}^1T_{1g})$	Dq (E) = 1.887	
	20,830	$\rightarrow {}^1A_{2g}({}^1T_{1g})$	Dq (A) = 1.058	
	25,480	$\rightarrow {}^1T_{2g}$	Dt = 474	
$[Co(C_{14}H_{14}N_4O_2S)_2(H_2O)_2](OH)_3$	16,810	$^1A_{1g} \rightarrow {}^1E_g({}^1T_{1g})$	Dq (E) = 1.902	
	21,060	$\rightarrow {}^1A_{2g}({}^1T_{1g})$	Dq (A) = 1.052	
	25,640	$\rightarrow {}^1T_{2g}$	Dt = 486	

$>$ Dq(A), larger splitting of the first band is expected because of the configuration interaction in the trans-structure. In the present case, since Dq (E) $>$ $>$ Dq(A) and the splitting is larger ($\sim 3600\ cm^{-1}$), one may possibly conclude that the two chloride ions are in trans- position to each other.

(ii) Iron(III) Complexes

Iron(III) complexes reveal normal magnetic behaviour (Table I). The BTSC complex obeys Curie-Weiss law ($\vartheta = -6$ K).

Of the four absorption bands, three low energy bands are of low intensity whereas the one observed at the highest energy is more intense (perhaps due to the charge transfer). The first two weak bands probably appear[15,16] due to the splitting of the transition ($^6A_{1g} \rightarrow {}^4T_{1g}$), on account of the possible presence of low symmetry elements. The ligand field parameter Dq cannot be evaluated directly by any transition observed in the case of high-spin iron(III) complexes. An alternative approximation suggested by Jørgensen[17] has been adopted for the calculation of 10 Dq, taking 10 Dq = f (ligand) × g (metal ion). The values of 'f' of the two ligands have been calculated by substituting the value of 'g' from the chromium complexes of these ligands described herein. Once 'f' is

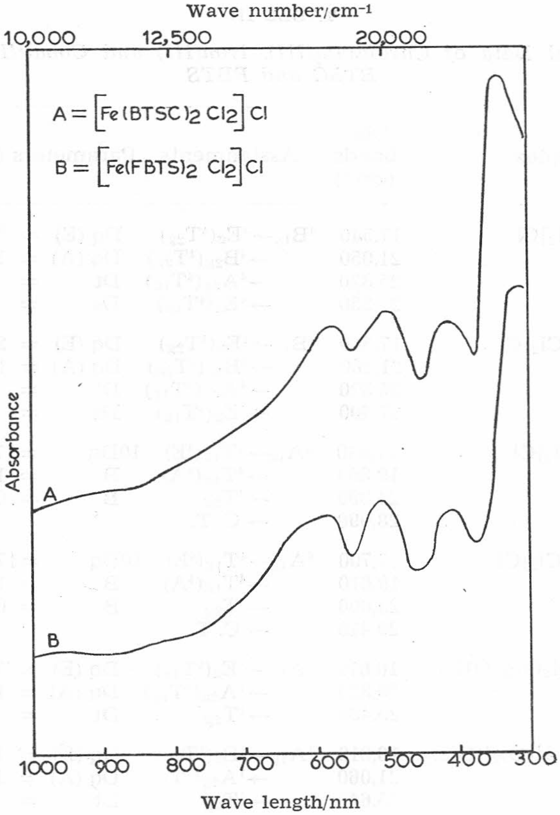


Figure 2. Electronic spectra of iron (III) complexes.

known the value of 10 Dq can be directly computed which comes out to be 17,830 cm^{-1} (BTS complex) and 17,520 cm^{-1} (FBTS complex). The values of the nephelauxetic ratio (β) have also been obtained indirectly by employing the equation suggested by Jørgensen[17].

(iii) Cobalt(III) Complexes

Magnetic measurements indicate the diamagnetic nature of these complexes (X_g = —6.064 × 10^{-6} and —6.103 × 10^{-6} c.g.s. units for BTSC and FBTS complexes, respectively at room temperature). This is indicative that the attempted oxidation of the Co(II) ion during the preparation of these complexes is virtually complete.

A perusal of the electronic spectral data of the cobalt(III) complexes (Table III) suggests the distorted octahedral geometry[10,18] around the metal ion which is anticipated on account of the inequal field strength in xy- and z-plane. The first two bands are observed due to the splitting of the term $^1T_{1g}$ (component of O_h) while the third one (T_{2g}) hardly exhibits any structure. The radial parameters have been evaluated employing the equations suggested by Lever[11]. The values of all the ligand field parameters are given in Table III. The value of Dq(A) (field strength in z- direction), in present complexes for

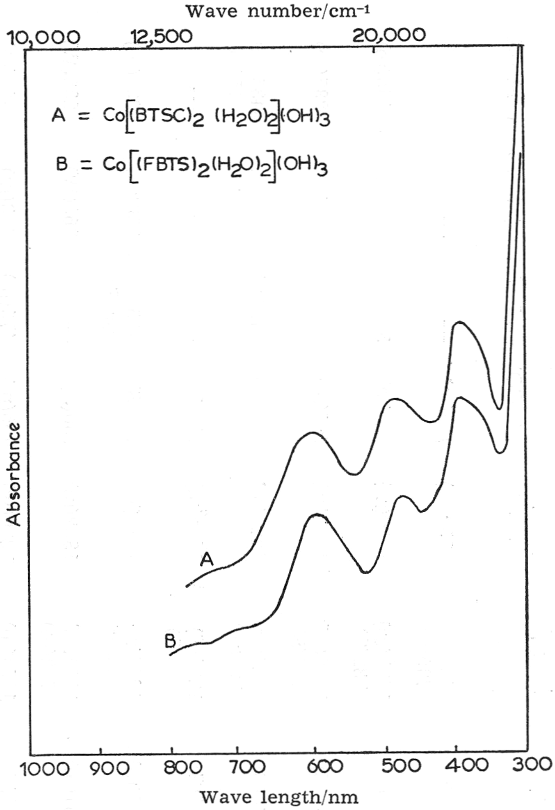


Figure 3. Electronic spectra of chromium (III) complexes.

H_2O, calculated with the help of the equation Dq(A) = 7/4 Dt — Dq(E). The values of Dt, Dq(A) (H_2O) and Dq(E) (BTSC and FBTS) are given in Table III. The calculated values of Dt are positive since the ligand field strength in the xy- plane (BTSC and FBTS) is more than that in the z- plane (H_2O). This inequality in the field strengths results in the tetragonal distortion of the complexes with elongation in z- direction and level ^1E lying lower than $^1A_2$. The splitting of the first band in the complexes understudy is large enough to suggest that these complexes possess trans- configurations, since, in the case of cis- complexes, the splitting of this band has been reported to about half of the values observed[19].

Infrared Spectral Studies

The most relevent bands of the ligands as well as their metal chelates are tabulated in Table IV along with their assignments. These assignments are based on corresponding assignments in thiosemicarbazides, thiosemicarbazones and their metal complexes[20,21].

The coordination through the terminal nitrogen atom of the hydrazinic group and thioketosulphur in BTSC and the unsaturated nitrogen atom of the CN group and thioketosulpher in FBTS to metal ions has been established in

TABLE IV

Important Infrared Spectral Bands of the Ligands (BTSC and FBTS) and Their Assignments

	ν NH and ν NH_2	Amide I and NH_2 bend	Amide II and ν (CN)	ν (CS) and ν (CN)	Amide III	ε (NCO)	ν (M—N)	ν (M—S)	ν (M—X)
BTSC	3290 to 3040(S)	1625(S)	1565(S)	1290(S) 730(S)	1230(m)	755(m)	—	—	
$[Cr(BTSC)_2Cl_2]Cl$	3245 to 3045(S)	1610(S)	1567(S)	1275(m) 732(S)	1220(m)	750(m)	500(m)	365(m)	340(m)
$[Fe(BTSC)_2Cl_2]Cl$	3245 to 3040	1605(S)	1572(S)	1270(W) 727(S)	1225(m)	760(m)	440(m)	260(m)	235(m)
$[Co(BTSC)_2(H_2O)_2](OH)_3$	3230 to 3025(S)	1612(S)	1570(S)	1275(m) 735(m)	1225(m)	757(m)	472(m)	417(m)	3435(m) 515(m)
FBTS	3140 to 3040(S)	1615(S)	1575(S)	1280(S) 735(S)	1235(m)	750(S)	—	—	—
$[Cr(FBTS)_2Cl_2]Cl$	3130 to 3025(S)	1620(S)	1555(m)	1265(m) 730(m)	1230(W)	755(S)	495 (br. S)	350(m)	337(m)
$[Fe(FBTS)_2Cl_2]Cl$	3135 to 3025(S)	1615(S)	1557(m)	1267(m) 732(m)	1332(m)	750(S)	—	265(W)	238(W)
$[Co(FBTS)_2(H_2O)_2](OH)_3$	3125 to 3045(S)	1612(s)	1565(s)	1265(m) 730(m)	1230(w)	755(m)	475(m)	423(m)	3420(m) 525(m)

X = Cl and H_2O

our previous communications[6-8] on the basis of changes in the position and intensity of these vibrations in the infrared spectra of the metal complexes. The S-N bidentate nature of both ligands is further substantiated by the appearance of additional bands of M-N and M-S vibrations in far infrared spectra. The presence of H_2O in the coordination sphere in the cobalt(III) complexes has been proposed[22] on the basis of vibrations observed in the regions 3435—3420 cm^{1-} and 530—510 cm^{-1} in the infrared spectra of the colbalt(III) complexes.

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SAŽETAK

Proučavanje elektronskih i magnetskih spektara kompleksa kroma, željeza i kobalta s 4-benzilamidotiosemikarbazidom i tiosemikarbazonom

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Pripravljeni su kompleksi kroma(III), željeza(III) i kobalta(III) s 4-benzilamidotiosemikarbazidom i 1-(α-)furil-4-benzilamidotiosemikarbazonom. Na temelju elektronskih i infracrvenih spektara predložena je tetragonska simetrija i bidentatni S-N- način koordinacije.

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