

SYNTHESIS AND CHARACTERISATION OF NOVEL COORDINATION COMPOUNDS OF Cr(III), Fe(III), WITH α -BENZILMONOXIMETHIOCARBOHYDRAZIDE

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Received: June 11, 2018

Accepted: July 25, 2018

ABSTRACT

The reaction of α -Benzilmonoximethiocarbohydrazide (HBMOTCH) with metal salts in ethanol gives the mononuclear complexes. The complexes were characterized on the basis of their elemental analysis, physico-chemical techniques, FTIR, ¹HNMR, electronic spectra. The FTIR studies were useful in assigning the coordination mode of the title ligand to metal(III) ions. FTIR spectral data indicated that ligand coordinated to metal ions through nitrogen atoms only and also the oximino group deprotonated during complex formation. Magnetic moment and electronic spectral data suggests that all complexes are octahedral geometry.

Keywords: Chromium(III), Iron(III), α -Benzilmonoximethiocarbohydrazide, Electronic spectra.

Introduction:

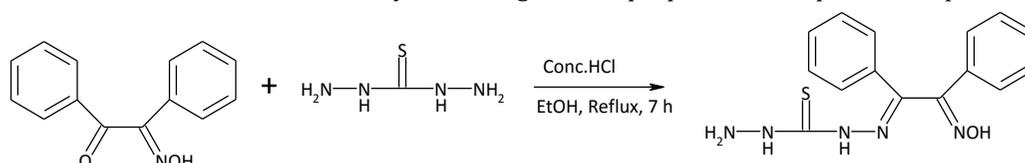
α -Benzilmonoxime are known as chelating agents and frequently used in extractive and analytical chemistry¹⁻². α -Benzilmonoximes are of special interest owing to their biological activities and semi-conducting properties³⁻⁴. On the other hand Cr(III), Fe(III) are an essential trace mineral that are involved in the regulation of carbohydrate and lipid metabolism and insufficient dietary intake of it is associated with increased susceptibility to diabetes and cardiovascular diseases⁵⁻⁶ while the role of Cr(III) in normal glucose metabolism is well recognized, its use as a therapeutic agent in diabetes is controversial because of conflicting human clinical data⁷. Many derivatives of α -Benzilmonoximes recently reported and also studied its metal complexes⁸⁻¹⁰. In view of these and our continuing interest on the synthesis of new complexes of α -Benzilmonoximethiocarbohydrazide, we wish to report the synthesis and characterization of their Cr(III), Fe(III), complexes. The properties of the complexes were investigated by spectroscopic methods.

Experimental:

All chemicals were used AR grade. The metal contents were estimated by complexometric titration. The FT(IR) spectra were recorded on a Perkin-Elmer spectrum-100. The conductivity measurements were carried out on a CM-82T Elico conductivity bridge in nitrobenzene. Magnetic susceptibility measurements were done by Gouys balance at room temperature. The Electronic spectra were recorded JASCO V60 spectrophotometer. PMR spectra in d₆ DMSO records on a Bruker AV300 NMR instrument with TMS as internal standard. Molecular weight determination by Rast method (Vogel, 1996). Elemental analysis (C, H, and N) were carried out with a Carlo Erba EA-1108 Analyzer.

Preparation of the ligand and its complexes:

The α -Benzilmonoximethiocarbohydrozide ligand was prepared as our previous reported work¹⁴.



Preparation of the complexes:

Tris(α -Benzilmonoximethiocarbohydrazidechromium(III), [Cr(BMOTCH)₃]:

A solution of CrCl₃·6H₂O (0.537g, 2mmol) in 20ml methanol was added to a solution of HBMOTCH (1.87g, 6mmol) in 25ml of hot methanol. The mixture was heated under reflux for 3h until a clear solution was obtained. The solution was then placed in ice-water container to give a dark green precipitate, which was filtered off, washed with hot water and ethanol and dried. The product was further purified by

recrystallization from chloroform (yield: 81%, m.p.:211°C). Anal Calcd for $C_{45}H_{42}N_{15}O_3S_3Cr$: C:54.65, H:4.25, N:21.25, O:4.86, S:9.72, Cr:5.26; found C:54.11, H:4.09, N:21.22, O:4.61, S:9.49, Cr:5.80.

Tris(α -Benzilmonoximethiocarbohydrazideferric(III), [FeCBMOTCH]₃):

A reaction between 0.935g (3mmol) of HB MOTCH in 1M Sodium Hydroxide solution with an aqueous solution of 0.126g (1mmol) ferric chloride with constant stirring, then red colored precipitated was appeared. The precipitated was digested in a boiling water bath for 30 minutes and then filtered through Buckner funnel. The product was washed with hot water and recrystallized from chloroform, dried at 110 °C. Anal Calcd for $C_{45}H_{42}N_{15}O_3S_3Fe$: C:54.44, H:4.23, N:21.17, O:4.84, S:9.68, Fe:5.63; found C:54.18, H:4.03, N:21.09, O:4.60, S:9.41, Fe:5.71.

Results and Discussions:

The stoichiometric reaction between HB MOTCH and metal salts [$CrCl_3 \cdot 6H_2O$, $FeCl_3$] has yielded to monomeric complexes [$Fe(BMOTCH)_3$], Unfortunately our effort to obtain single crystals of the monomeric complexes has not been successful.

Table-1: Analytical and physical data for HBMOH and its Cr(III) and Fe(III) metal complexes

Compound	Color	Melting Point (°C)	Elemental Analysis: Expected (Found)						Conductance	Magnetic Moment
			C	H	N	O	S	M		
HB MOTCH	White	168	57.51 (57.11)	4.89 (4.42)	22.36 (22.48)	5.11 (5.29)	10.22 (10.00)	-----	-----	
[Cr(BMOTCH) ₃]	Green	190	54.65 (54.11)	4.25 (4.09)	21.25 (21.22)	4.86 (4.61)	9.72 (9.49)	5.26 (5.80)	2.5	3.40
[Fe(BMOTCH) ₃]	Red	195	54.44 (54.18)	4.23 (4.03)	21.17 (21.09)	4.84 (4.60)	9.68 (9.41)	5.63 (5.71)	3.0	4.93

The complexes were initially characterized on the basis of their elemental analysis. The molar conductance data of complexes suggests that they are non-electrolytic¹⁵.

FTIR spectra:

The band due to $\nu(O-H)$ of oxime group at 3288cm^{-1} , is absent in complexes suggesting the deprotonation of the hydroxyl group of the oxime in the complex formation. The band due to the $\nu(C=NN)$ of the azomethine group which is observed at 1600cm^{-1} in HB MOTCH is shifted to higher frequency in the region $1650-1675\text{cm}^{-1}$ in complexes, indicating the participation of the azomethine group in coordination. Also the band at 1580cm^{-1} due to $\nu(C=NO)$ oxime group is observed at a higher frequency at $1603-1627\text{cm}^{-1}$ in the complexes which shows the involvement of the oxime group in the coordination. This fact is further supported by the appearance of new bands in the regions $530-590\text{cm}^{-1}$ in complexes which were assigned to the $\nu(M-N)$ stretching vibrations.

Table- 2: FT(IR) spectral data for HB MOTCH and its metal complexes in cm^{-1}

Compound	$\nu(O-H)$	$\nu(N-H)$	$\nu(C-S-H)$	C=NO	C=NN	$\nu(N-H)$	N - O/ N→O	N-N	M-N
HB MOTCH	3288	3300	2345	1600	1693	1589	1000	1072	---
[Cr(BMOTCH) ₃]	-	3288	2359	1603	1775	1592	1026	1093	590,558
[Fe(BMOTCH) ₃]	-	3290	2328	1627	1750	1590	1025	1099	522,530

Magnetic susceptibility measurements and electronic spectra:

The electronic spectra of HB MOTCH ligand and its complexes are summarized in **Table-3**. A clear analogy is evident among the results for all compounds. In the spectra of free ligand $\pi \rightarrow \pi^*$ transition in the range 239-251nm are not significantly altered on complex formation. The $n \rightarrow \pi^*$ transitions associated with nitrogen of the azomethine and oxime group in free ligand are found in the range 222nm and 271nm. In the complexes results indicate that the nitrogen atoms of the oxime group are coordinated to the metal ions.

Two low intensity transitions ($\log \epsilon \leq 2$) were observed in the spectra of all complexes, and most probably are due to spin allowed d-d transitions. The octahedral complexes of Cr(III) have $(t_{2g})^2$ configuration. It was confirmed by magnetic moments value 3.40 B.M. According to the Tanabe - Sugano diagram for $(t_{2g})^3$ configuration¹⁶ the bands at the regions 535nm and 421nm were assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F) transitions respectively.

When working with electronic spectra, it is often useful to determine the ratio of the energy of the second transition to the first one. In the Cr(III) complex $\nu_2/\nu_1=1.27$, and this ratio correspond to Δ_o/B being equal to 33 on the Tanabe-Sugano diagram. By using this value in the calculation of the Racah parameter, splitting energy, unobserved third transition and nephelauxetic parameter for the Cr(III) complex following results were obtained $B=5600\text{cm}^{-1}$, $\Delta_o = 18484\text{cm}^{-1}$, $\nu_3 = 36960\text{cm}^{-1}$ and $\beta = 061$.

According to the Tanabe-Sugano diagram for high spin d^5 configuration, the bands to the regions 544nm and 452nm were assigned to the ${}^6A_{1g} \rightarrow {}^4T_{2g}(\nu_1)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(\nu_2)$ transitions respectively (Lobana, 1985). In the iron(III) complex $\nu_2/\nu_1= 1.202$ and the ration correspond to Δ_o/B being equal to 30.5 on the Tanabe-Sugano diagram. By using this value in the calculation of the Racah parameter, splitting energy, unobserved third transition, and nephelauxetic parameter for the iron(III) complex, the following results were obtained $B=706\text{cm}^{-1}$, $\Delta_o=21510\text{cm}^{-1}$, $\nu_3=30333\text{cm}^{-1}$ and $\beta=0.638$. Orange-red Fe (III) complex shows a room temperature magnetic moment of 4.93BM (**Table-1**), which is higher than the spin only magnetic moment of 4.89BM expected for the four unpaired electrons in high spin Ferrous complexes¹⁸. However, term for the high spin octahedral complexes of Fe(III) is expected to contribute significantly to the room temperature magnetic moment and the observed moment for most high spin complexes of Fe(III) is expected to be greater than the spin only moment and are often observed in the range between 5.1-5.7BM. Tetrahedral complexes of Fe(III) are expected to reveal moment in the range between 5.00-5.20BM. Where, the orbital contribution to the observed moment is expected to be lower than for octahedral complexes. Further, for ligands containing 'N' and 'O donor atom, Fe(III) is known to coordinate to give octahedral complexes¹⁸. In HBMOTCH 'N' as donor atom, therefore Fe(III) complex suggests a high spin octahedral geometry. The observation is amply supported by the electronic absorption spectral data from the complex.

Table-3: Electronic spectral data for HIPHT and its metal complexes

No.	Compound	solvent	Band position in nm	Intensity ϵ	Assignment
1	HBMOTCH	Methanol	222	12252	Oximinop \rightarrow p* transition
			271	11181	Azomethinep \rightarrow p* transition
		0.1N NaOH	247	12116	Oximinop \rightarrow p* transition
			322	11288	Azomethinep \rightarrow p* transition
2	Cr(BMOTCH) ₃	Chloroform	535	399	$A_{2g} \rightarrow {}^4T_{2g}$
			421	1269	${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F)
3	Fe(BMOTCH) ₃	Chloroform	544	271	${}^6A_{1g} \rightarrow {}^4T_{2g}$
			452	5444	${}^6A_{1g} \rightarrow {}^4T_{1g}$

¹H NMR Spectra:

The ¹H NMR Spectra of HBMOTCH and its complexes, show the singlet peak due to the N-OH proton at 10.53ppm is absent in complexes, suggesting the deprotonation of the hydroxyl group of the oxime ligand¹⁵. The bands at 8.00, 8.66 and 7.45-7.95ppm were assigned to -NH₂, -NH-, phenyl ring respectively in HBMOTCH ligand. These peaks are also observed in complexes without any change in their positions, indicating no participation in coordination.

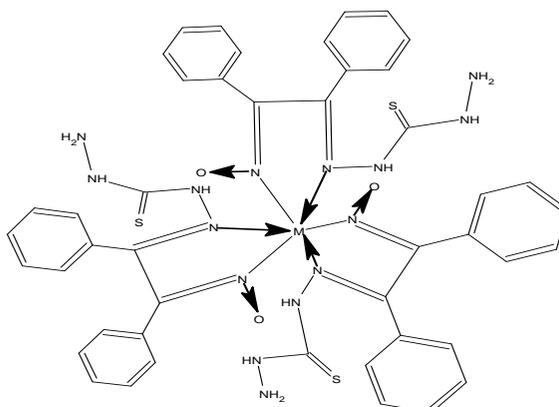
Table-4: PMR data of HBMOTCH and its metal complexes in ppm

Compounds	-OH	-NH ₂	N-H	Phenyl ring
HBMOTCH	12.53	8.00	8.67	7.44 -7.95
[Cr(BMOTCH) ₃]-	7.90	8.65	7.45	-7.90
[Fe(BMOTCH) ₃]-	7.95	8.60	7.44	-7.95

Conclusion:

The title ligand is soluble in most of the organic solvents and dilute alkali, but its ternary metal complexes are insoluble in ethanol, dilute alkali and soluble in methanol, chloroform, DMF etc. All metal

complexes are non-electrolytic nature. Spectral measurements data suggest that all metal ions are bonded with ligand through nitrogen atom for M – N₆ composition and geometries for metal complexes are of octahedral shape. On the basis of physical and analytical data, tentatively assigned the Cr(III) and Fe(III) complexes are;



Where, M = Fe(III) and Cr(III) ion

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