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Spectral Characterization of Bimetallic Complexes of Thiosemicarbazone of Monoacetylferrocene with Cu(II) Halides

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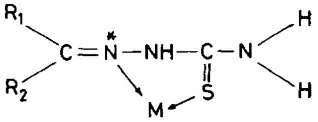
Abstract

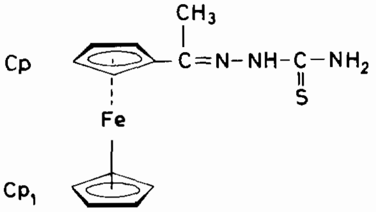
Monoacetylferrocenethiosemicarbazone (MAFTSC) has been investigated for its complexation behaviour towards Cu(II) halides. Two types of bimetallic complexes, MLX_2 and ML_2 (where L = MAFTSC) have been prepared and characterized through elemental analysis, conductivity measurements, UV, IR and ^{1}H NMR spectral techniques and by magnetic susceptibility measurements at room temperature. Conductance measurement in DMF indicated the complexes to be non-electrolytic in nature.

Introduction

Thiosemicarbazones, ($NH_2C(S)NHN{=}CR_1R_2$) usually act as chelating ligands with transition metal ions by bonding through the sulphur and hydrazino nitrogen atom (asterisk) [1–3].



Current interest in the coordination chemistry of thiosemicarbazone has arisen through their uses in biological systems [4]. Metal thiosemicarbazone complexes have been found to be active against protozoa [5] and tumours [6]. They can act as pesticides and fungicides [7]. They are also known to have antitumour activity. Some substituted ferrocenes like benzoylferrocene have been shown [8] to retard the actinic degradation of polymer films and photodecomposition of ferrocenes in hydroxylic [9] and alkyl halide [10] solvents. Very few complexes of thiosemicarbazones which contain two metal ions have been studied. In this paper we have investigated the donor properties of the thiosemicarbazone of monoacetylferrocene (MAFTSC) (I) and its potential effectiveness as an ultraviolet absorber, i.e. photoprotective agent.



MAFTSC (I)

Experimental

All the solvents, metal halides and other reagents used were of AR grade. Solvents (AR) were dried by reported methods [11].

Preparation of Ligand

Thiosemicarbazone of monoacetylferrocene (MAF) was obtained by condensing thiosemicarbazide (Koch. Lab. Light Ltd.) with monoacetylferrocene prepared from ferrocene (E. Merck, F.R.G.) by the 'phosphoric acid method' [12]. MAF (2.28 g, 0.01 mol) and thiosemicarbazide (0.91 g, 0.01 mol) were dissolved separately in absolute ethanol and mixed together. A few drops of glacial acetic acid were added. The contents were refluxed for 1 h. The resulting contents were cooled by pouring in ice. The granular product was filtered and dried in a vacuum desiccator over P_2O_5 (melting point of MAFTSC = 129–131 °C). The purity of the ligand was checked by TLC and characterized by elemental analysis, IR, ^{1}H NMR spectroscopy. The relevant ^{1}H NMR data for the ligand is as follows:

^{1}H NMR signals in $CDCl_3$ (ppm)
2.3(s, 3H, $-C-CH_3$)
4.23(s, 5H, Cp_1)
4.45(s, 2H, Cp (H^2, H^5))
4.6–4.85(m, 2H, Cp (H^3, H^4))
5.7(s, 2H, $C-NH_2$)
8.7(s, 1H, N–NH–C)

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Preparation of Complexes

Preparation of complexes of thiosemicarbazones of MAF often encounter the difficulty of deposition of metallic iron [13]. With repeated trials under different conditions we, however, succeeded in preparing two set of complexes.

Type I. MAFTSC (0.6 g, 0.002 mol) was dissolved in absolute ethanol (30 cm^3) by heating. The hot solution was filtered into a solution of the metal halide (0.001 mol). The resulting mixture was refluxed for 1 h. The solvent was evaporated in vacuum, the residue was recrystallized from absolute ethanol and dried *in vacuo*. With all the copper halides, the final product obtained was Cu(MAFTSC)$_2$.

Type II. This set of complexes was prepared by dissolving MAFTSC (0.3 g, 0.001 mol) and the corresponding metal halide (0.001 mol) in tetrahydrofuran. The resulting contents were stirred for about 6 h and then filtered. The residue was recrystallized from benzene and dried *in vacuo*.

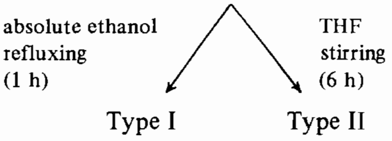
Characterization of Complexes

IR spectra were recorded on a Perkin-Elmer 1710 and 598 FT spectrometer as direct film and in KBr–CsI tablets. Electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer. ^{1}H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer in $CDCl_3$ and deuterated DMSO. Conductance measurements were carried on a Leeds-Northrup conductivity bridge (4959) using an Elico conductivity cell calibrated with aq. KCl (0.01 M) solution at 27 °C using DMF as solvent. Magnetic susceptibility measurements were done on a Vibrating sample magnetometer and Guoy's balance. Metal contents were estimated by the AAS technique on a Perkin-Elmer (2380) machine. Carbon, nitrogen and hydrogen analyses were carried out at the Center for Material Science and Technology, Indian Institute of Technology, New Delhi and at USIC, University of Delhi, Delhi, India. The concentration of halogen atoms was estimated gravimetrically [11]. Analytical results are given in Table 1.

Results and Discussion

The reaction between CuX_2 (X = Cl, Br, I) and MAFTSC in different molar ratios proceeds according to the following reaction:

$$CuX_2 + \eta^5\text{-}C_5H_5FeC_5H_4C{\cdot}CH_3NNHC(S)NH_2$$



Conductance Measurements

Measured conductances of the complexes are given in Table 2. Conductance measurements showed all the complexes to be non-electrolytic in DMF. The molar conductance of the iodo complexes is higher than that of the other halo complexes which is attributed to partial dissociation of the iodo complex in DMF [14].

Magnetic Susceptibility

The measured values of the magnetic moments for the complexes are listed in Table 2. All the complexes of Cu(II) were found to be paramagnetic. A value of ~1.8 BM corresponds to that of one unpaired electron in Cu(II) which is a d^9 system [15, 16]. Such a value of magnetic moment indicates that they are magnetically dilute and there is evidently no magnetic interaction between the Cu(II) ion and the diamagnetic Fe(II) ion of ferrocene [13].

TABLE 1. Analytical data of the ligand and its metal complexes

Complex	Nature	Analysis: found (calc.) (%)					
		C	H	N	Fe	Cu	X = Cl, Br, I
MAFTSC	orange solid	50.7 (51.8)	4.7 (4.9)	13.7 (13.9)	18.9 (18.6)		
Cu(HMAFTSC)Cl_2	brown solid	35.4 (35.8)	3.4 (3.6)	9.3 (9.7)	13.1 (12.8)	14.9 (14.5)	16.9 (16.3)
Cu(HMAFTSC)Br_2	orange–brown solid	29.4 (29.7)	3.1 (2.8)	7.9 (8.0)	11.1 (10.6)	12.4 (12.1)	31.1 (30.4)
Cu(HMAFTSC)I_2	dark brown solid	25.1 (25.2)	2.8 (2.4)	6.6 (6.7)	9.1 (9.0)	10.2 (10.2)	42.1 (41.0)
Cu(MAFTSC)$_2$	brown solid	46.6 (47.0)	4.4 (4.8)	12.2 (12.6)	16.9 (16.8)	9.9 (9.5)	

TABLE 2. Room temperature magnetic moments, molar conductance and electronic spectra of MAFTSC complexes (25 °C)

Complex	μ_{eff} (BM)	Λ (Mho cm^2 mol^{-1})	Band (cm^{-1} × 10^3)
Cu(HMAFTSC)Cl$_2$	1.76	4.08	15, 19, 31.8, 22.0
Cu(HMAFTSC)Br$_2$	1.81	4.45	15, 18.5, 31.6, 22.1
Cu(HMAFTSC)I$_2$	1.92	10.60	15.2, 18.9, 31.8, 22.0
Cu(MAFTSC)$_2$	1.79	3.83	15.4, 19.1, 31.9, 22.2

TABLE 3. Infrared spectral data (cm^{-1}) and tentative band assignments of MAFTSC and its complexes[a]

HMAFTSC	Cu(MAFTSC)$_2$	Cu(HMAFTSC)Cl$_2$	Cu(HMAFTSC)Br$_2$	Cu(HMAFTSC)$_2$I$_2$	Assignments
3360(sh)	3410(s)	3340(s)	3340(s)	3350(s)	NH and NH$_2$ stretching
3260(sh)	3240	3250	3260	3260	
3190		3140(s)	3160(s)	3170(s)	
3090		3060	3070(m)	3080(w)	
1640(s)	1630(s)	1650(sh)	1635(sh)	1630(sh)	NH$_2$ bend
1620(s)	1595(s)	1605(s)	1605(m)		
1530	1510	1505	1510	1505	Amide II (νCN + δNH)
1320	1360	1365	1360	1370	Amide III
1285	1330(w)	1350(w)	1325(w)	1325(sh)	NH$_2$ rocking
1000(s)	1020(vw)	990(w)	995(w)		NH$_2$ deformation
	965				N–N stretching
805	725	715	730	720	C–S stretching
	430	435			Ring deformation mode
	335	330	350	350	
	345	340	340	345	Cu–N stretching
	275	270	265	265	Cu–S stretching

[a] Only stretching frequencies associated with the ligand are reported; bands due to anion are not included. Relative band intensities are denoted by s, m, w, vw, and sh meaning strong, medium, weak, very weak and shoulder respectively.

IR Spectra

Pertinent IR bands for the complexes Cu(HMAFTSC)X$_2$ (X = Cl$^-$, Br$^-$, I$^-$) and Cu(MAFTSC)$_2$ are listed in Table 3 with their probable assignments. Very little change in the band frequencies with the change of anion are observed.

The two bands in the NH region of the spectrum have been replaced by a single band in the vicinity of 3410 cm^{-1} on complexation in type I complexes. This fact reveals the deprotonation of the ligand in type I complexes. It is reasonable to conclude that complex formation in type I is associated with a reduction in the number of NH groups. In type II complexes we observe two bands in the NH region of the spectrum. The position of these bands is consistent with that observed in the ligand (same as secondary thioamides) showing that there is no reduction in NH groups. In the IR spectra of the ligands, the bands at ~805 and ~1530 cm^{-1} are assigned to νC–S and νCN + δNH (amide II) vibrations respectively. The complexes show relevant downward shifts in νC–S by 75–90 cm^{-1} and in νCN + δNH (amide II) by 25–30 cm^{-1} due to coordination of the active sites of ligands to the metals. These shifts confirm the coordination of metal to the azomethine nitrogen (>C=N) atom and the sulphur atom of the ligand. The bands in the far infrared region 570–200 cm^{-1} are tentatively assigned to mixed νCu–N, νCu–S and νCu–X vibrations [17–30].

The band at 3400 cm^{-1} is assigned to νNH for the terminal –NH$_2$ group. This is unaffected in the complexes, which shows that the terminal –NH$_2$ group is free and does not participate in coordination. In addition to these bands there were bands characteristic of the Cp (cyclopentadienyl) ring [31].

Electronic Spectra

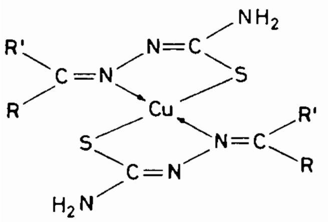
The electronic spectra of various complexes were recorded in DMF and data are given in Table 2.

Two weak bands at ~15 000 and ~19 000 cm^{-1} along with a strong band at ~31 800 cm^{-1} are observed. The two low energy bands are in positions typically found for square planar complexes of Cu(II) (d^9; D_{4h} point group with ground state term ^2D). The two bands may be assigned as (i) $^2A_{1g} \leftarrow {}^2B_{1g}$ and (ii) $^2E_g \leftarrow {}^2B_{1g}$ respectively [16, 32].

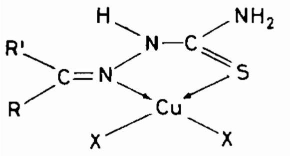
These bands arise from d–d transitions. A high energy band at ~31 800 cm^{-1} is assigned to the M → L charge transfer band. This band was found to shift to lower energies in less coordinating solvents [33]. A broad band centered around 22 000 cm^{-1} is also observed and is assigned to the $^1A_{1g} \rightarrow {}^1E_{1g}$ transition in the iron atom of the cyclopentadienyl ligand; its position is close to that in the free ligand [34].

The compounds are all coloured and many of them absorb strongly in the near ultraviolet region. These substances could be useful as retarders of the photo-oxidation of polymeric materials.

The above studies suggest that the complexes have a four-coordinate square planar structure. Type I complexes are of 1:2 composition and type II are of 1:1. Further it is concluded that there is no magnetic interaction between the Cu(II) ion and the diamagnetic Fe(II) ion. Tentative structures for the complexes may be proposed as:



Type I: $Cu(MAFTSC)_2$



Type II: $Cu(HMAFTSC)X_2$
R' = R = Cp; X = Cl, Br, I

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