Inorganica Chimica Acta, *173* (1990) 223–227

Spectral Characterization of Bimetallic Complexes of Monoacetylferrocenethiosemicarbazone (MAFTSC) with Co(II) Salts

B. S. GARG* and LALIT KAPUR

Department of Chemistry, University of Delhi, Delhi 110007 (India)

(Received July 28, 1989; revised February 1, 1990)

Abstract

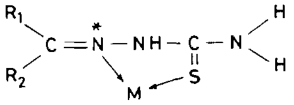
Monoacetylferrocenethiosemicarbazone (MAFTSC) has been investigated for its complexation behaviour towards Co(II) salts. Two types of bimetallic complexes, CoL_2X_2 and CoL_2, where L = MAFTSC; $X = Cl^-$, Br^-, I^-, NO_3^-, SO_4^{2-} have been prepared and characterized through elemental analysis, conductivity measurements, UV, IR and ^1H NMR spectral techniques and by magnetic susceptibility measurements at room temperature. Conductance measurement in DMF indicated the complexes to be non-electrolytic in nature. Contrary to previous opinion, potentially bidentate thiosemicarbazones (general formula $NH_2{\cdot}CS{\cdot}NH{\cdot}N{:}CR^1R^2$) may also act as unidentate ligands, when R^1 and/or R^2 is an aryl group. During spectral characterization, differences between low symmetry tetrahedral and five-coordinate cobalt(II) complexes have been observed and possible stereochemistry has been assigned to the complexes.

Introduction

Although thiosemicarbazones, ($NH_2C(S)NHN{=}CR_1R_2$) have long been known to give stable complexes with transition metal ions [1], only recently have the stereochemistry and reactions of these complexes been investigated [2]. The reason for this renewed interest is the proved antitumour activity and their uses in biological systems [3]. This is believed to be related to their complexation with metal ions.

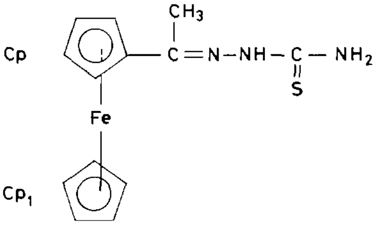
Some substituted ferrocenes like benzoylferrocene have been shown [4] to retard the actinic degradation of polymer films and photodecomposition of ferrocenes in hydroxylic [5] and alkyl halide solvents [6].

Thiosemicarbazones (TSC) usually act as chelating ligands with transition metal ions by bonding through the sulphur and hydrazino nitrogen (asterisk) atom [7–9].



Structural studies on very few TSC complexes have been carried out. Some are four coordinate, some five coordinate and others are six coordinate. The same ligand with different metal salts of the same metal can give different geometries [10].

In this paper we report the characterization of thiosemicarbazone complexes which contain two metal ions and their use as a protective ultraviolet absorber. Potentially bidentate monoacetylferrocenethiosemicarbazone (MAFTSC) behaves as a monodentate ligand, the structure of which in the solid state is tetrahedral of chromophore CoS_2X_2.



Monoacetylferrocenethiosemicarbazone (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

The 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, mixed together and a few drops of glacial acetic acid were added. The contents were refluxed for 1 h. The resulting contents were cooled and poured in ice.

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

The granular product was filtered, recrystallized from absolute ethanol and dried in a vacuum desiccator over P_2O_5 (melting point of MAFTSC = 129–131 °C).

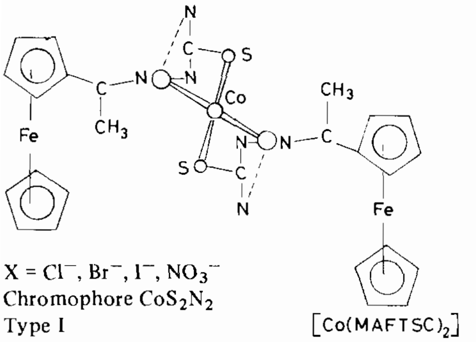
The purity of the ligand was checked by TLC and characterized by elemental analysis, IR and ^1H NMR. The relevant ^1H NMR data for the ligand are as follows. ^1H NMR signals in $CDCl_3$ (ppm): 2.3 (s, 3H, $-CH_3$); 4.23 (s, 5H, Cp_1); 4.45 (s, 2H, Cp(H^2, H^5)); 4.6–4.85 (m, 2H, Cp(H^3, H^4)); 5.7 (s, 2H, $-NH_2$); 8.7 (s, 1H, N–NH–C).

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

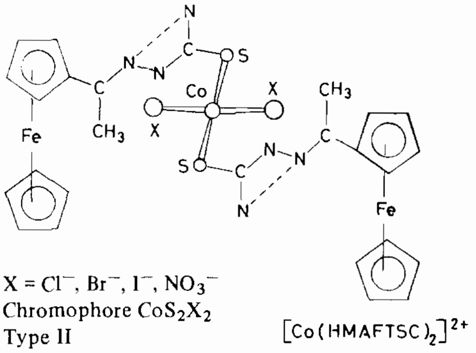
MAFTSC (0.6 g, 0.002 mol) was dissolved in absolute ethanol (30 cm^3) by heating. The hot solution was filtered into a solution of metal salts (0.001 mol). The resulting mixture was refluxed for 1 h. The solvent was vacuum evaporated. The residue was recrystallized from absolute ethanol and dried *in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



X = Cl^-, Br^-, I^-, NO_3^-
Chromophore CoS_2N_2
Type I

Type II

This set of complexes was prepared by dissolving and stirring MAFTSC (0.6 g, 0.02 mol) and the corresponding metal salt (0.001 mol) in tetrahydrofuran. Complexes were separated by filtration. The precipitates were dried *in vacuo*. The general formula of the complex is $Co(HMAFTSC)_2X_n$, where X = Cl^-, Br^-, I^-, ONO_2^- ($n = 2$); X = SO_4^{2-} ($n = 1$).



X = Cl^-, Br^-, I^-, NO_3^-
Chromophore CoS_2X_2
Type II

Characterization of the Complexes

IR spectra were recorded on Perkin-Elmer 1710 and 598 FT spectrometers as direct film and in KBr disks. Electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer. ^1H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer in $CDCl_3$ and deuterated DMSO. Conductance measurements were carried out on a Leeds-Northrup conductivity bridge (4959) using a Elico conductivity cell calibrated with aqueous 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). 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 anion concentration in the complex wherever possible was estimated gravimetrically by reported methods [14]. Analytical data are given in Table 1.

Results and Discussion

The reaction between Co(II) salts, CoX_2 (X = Cl^-, Br^-, I^-, ONO_2^- or CoX′ (X′ = SO_4^{2-}) and MAFTSC in different molar ratios proceeds according to the following reaction:

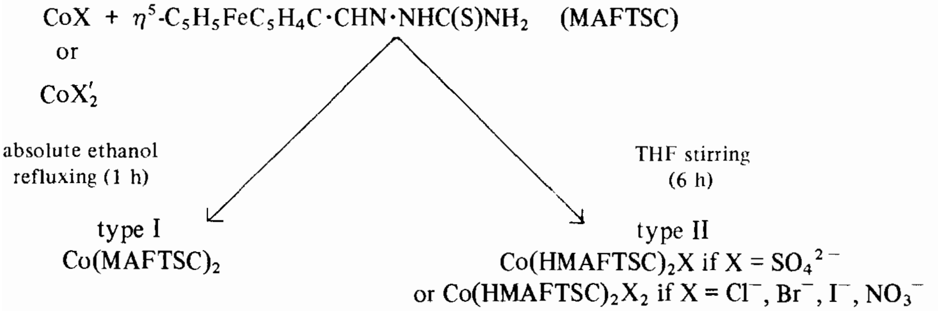


TABLE 1. Analytical data of ligand and its metal complexes

Compound	Nature	Analysis: Found (calc.) (%)				
		C	H	N	Fe	Co
MAFTSC	orange solid	51.4(51.8)	4.7(4.9)	13.7(13.9)	18.9(18.6)	
$Co(MAFTSC)_2$	brown solid	47.1(47.3)	4.08(4.2)	12.6(12.7)	16.6(16.9)	8.7(8.95)
$Co(HMAFTSC)_2Cl_2$	brownish orange solid	46.15(46.3)	4.3(4.45)	12.35(12.48)	16.5(16.65)	8.6(8.76)
$Co(HMAFTSC)_2Br_2$	brown solid	37.95(38.0)	3.7(3.6)	10.15(10.23)	13.4(13.6)	7.05(7.18)
$Co(HMAFTSC)_2I_2$	dark brown solid	39.8(34.09)	3.15(3.27)	9.1(9.18)	12.05(12.24)	6.3(6.45)
$Co(HMAFTSC)_2(NO_3)_2$	saffron solid	39.6(39.7)	3.7(3.8)	10.7(10.7)	14.1(14.2)	7.3(7.5)
$Co(HMAFTSC)_2(SO_4)_2$	brown solid	41.1(41.2)	3.7(3.9)	10.95(11.09)	14.5(14.7)	7.6(7.79)

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} x 10^3)
$Co(MAFTSC)_2$	4.25	18.14	4.5, 5.9, 8.6, 13.3, 16.8, 22.0, 23.5
$Co(HMAFTSC)_2Cl_2$	4.10	18.62	5.6, 6.1, 7.7, 13.7, 14.2, 15.9, 22.1, 31.8
$Co(HMAFTSC)_2Br_2$	4.16	19.60	5.6, 6.0, 8.2, 13.4, 14.0, 15.4, 22.05, 31.5
$Co(HMAFTSC)_2I_2$	4.52	29.44	4.7, 5.7, 7.5, 12.8, 13.0, 15.0, 22.0, 28.9
$Co(HMAFTSC)_2(NO_3)_2$	4.46	26.62	5.2, 6.0, 7.4, 12.7, 13.1, 16.0, 22.05, 32.5
$Co(HMAFTSC)_2(SO_4)_2$	4.36	20.25	4.9, 5.6, 7.1, 13.1, 14.4, 17.1, 22.1, 31.8

The ligand gave only 2:1 complexes with Co(II) salts without apparent oxidation to Co(II) during complexation.

Conductance Measurements

The measured conductances of the complexes are given in Table 2. Conductance measurements showed all the complexes to be non-electrolytic in DMF. The molar conductances of the iodo and nitrato complexes were found to be higher than those of the other complexes which is attributed to partial dissociation and solvation of the complexes by the solvent [15].

Magnetic Susceptibility Measurements

The measured values of the magnetic moments for the complexes are listed in Table 2. All the complexes of Co(II) were found to be paramagnetic. A value ranging from 4.1–4.4 BM corresponds to that of 3 unpaired electrons in Co(II) which is a d^7 system [16, 17]. A high value of magnetic moment indicates a high orbital contribution to the magnetic moment of a high spin Co(II). Such a value of magnetic moment indicates that they are magnetically dilute and there is evidently no magnetic interaction between the Co(II) and the diamagnetic Fe(II) ion of ferrocene [13].

IR Spectra

Pertinent IR bands for the complexes Co-$(HMAFTSC)_2X_2$ (where $X = Cl^-, Br^-, I^-, NO_3^-$), Co-$(HMAFTSC)_2X$ ($X = SO_4^{2-}$) and $Co(MAFTSC)_2$ are listed in Table 3 with their probable assignments. Very little change in the band frequencies with the change of anion is 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 ligands (same as secondary thioamides). The presence of νCo–X absorption band in the far IR region confirms the formation of complexes of type II.

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 of type I show relevant shifts in νC–S by 75–90 cm^{-1} and in νCN + δNH (amide II) by 40–50 cm^{-1} due to coordination of the active sites of the 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. This suggests bidentate coordination of the ligand with the metal ion to give the CoS_2N_2 chromophore [18–20]. The bands in the region 570–200 cm^{-1} which are assigned to mixed νCo–N and νCo–S vibrations confirm this fact. The type II complexes show relevant shifts in νC–S by 75–90 cm^{-1} and in

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

Compound	νC–S	Amide II (νCN + δNH)	νNH	νM–X X = Cl$^-$, Br$^-$, I$^-$, ONO$_2^-$	νM–N	νM–S
HMAFTSC	805	1530	3360 3190			
Co(MAFTSC)$_2$	725	1575	3410		345	275
Co(HMAFTSC)$_2$Cl$_2$	710	1535	3340 3160	315		265
Co(HMAFTSC)$_2$Br$_2$	725	1540	3350 3170	320		270
Co(HMAFTSC)$_2$I$_2$	715	1530	3340 3120	310		270
Co(HMAFTSC)$_2$(NO$_3$)$_2$	725	1535	3370 3160			275
Co(HMAFTSC)$_2$SO$_4$	715	1540	3340 3140			270

νCN + δNH (amide II) by 10–20 cm^{-1} and in some complexes there was a split band at ~1530 cm^{-1}. This suggests monodentate coordination of the ligand through the sulphur atom with the metal ion [21]. The bands in the region 570–200 cm^{-1} are tentatively assigned to mixed νCo–S, νCo–N and νCo–X vibrations. νCo–N vibrations are not observed at ~340 cm^{-1} (but in many cases there is overlapping) in type II complexes.

A 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 characteristic of the Cp (cyclopentadienyl) ring were also observed [22].

Electronic Spectra

The electronic spectra of various complexes were recorded in DMF and the data are given in Table 2. The complexes showed two series of bands lying in the ranges 4500–9000 and 13 000–17 000 cm^{-1}. In the intermediate region no bands were observed. These bands may be assigned to $^4T_1(F) - {}^4A_2$ and $^4T_1(P) - {}^4A_2$ transitions. These transitions appear as multiple absorptions in the near infrared and visible regions. The intensities of these bands indicate the presence of tetrahedral Co(II) [23]. The spectra of these complexes are very similar to those of thiourea complexes [24]. The complex Co(HMAFTSC)$_2$I$_2$ shows three weak bands at 4700, 5700 and 7500 cm^{-1} and three bands at 12 800, 13 000 and 15 000 cm^{-1}. (In many complexes there is overlapping and only two bands are observed). We tentatively assign the bands at 4700, 5700 and 7500 cm^{-1} to $^4B_1$, $^4A_2$, $^4B_2$ components of $^4T_1(F)(T_d)$ and 12 800, 13 000 and 15 000 cm^{-1} to the $^4B_2$, $^4A_2$, $^4B_1$ components of $^4T_1(P)(T_d)$ [25].

The average ν_2 and ν_3 positions for these complexes are at too low an energy for bonding by the two nitrogen atoms of the ligand [26]. This suggests a tetrahedral structure with the CoS$_2$X$_2$ chromophore for type II complexes. The ligand is virtually planar. There is a strong hydrogen bond between N(1) and N(4). The CoS$_2$X$_2$ unit is a squashed tetrahedron (with approximately C_{2v} symmetry).

The spectra of the deprotonated complexes (type I) are different from those expected for other, non-mononuclear formulations. An assignment of chromophore CoS$_2$N$_2$ to these complexes then becomes reasonable. This assignment is also supported by the appearance of charge transfer (c.t.) bands in the 21 000–24 500 cm^{-1} region, i.e. at much lower energy than occurs in complexes with unidentate ligands. This is as expected for bonding by a more 'thiolic' sulphur atom, brought by deprotonation at N(2) [27].

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 free ligand [25].

The above studies suggest that the complexes have a four coordinate tetrahedral structure. Octahedral structures and five coordinate trigonal bipyramidal or square pyramidal structures may be excluded both from the form of the reflectance spectra and from the low magnetic moments.

The structure of type I and type II complexes in the solid state is tetrahedral: in type I, the chromophore being CoS$_2$N$_2$ and the ligand bidentate; in type II, the chromophore being CoS$_2$X$_2$ and the ligand monodentate.

The compounds are all coloured and many of them absorb strongly in the near ultraviolet region. These compounds could be useful as retarders of the photooxidation of polymeric materials. This characterization of Co(II) complexes may possibly aid in the assignment of the stereochemistry of the Co(II) metalloproteins. These complexes are of special interest since they may be used to replace zinc or copper in natural enzymes and can then be used as a probe for the metal site environment.

Acknowledgements

One of the authors (L.K.) is thankful to U.G.C., New Delhi for providing financial assistance and is also indebted to the Department of Chemistry, University of Delhi, India for providing the necessary laboratory facilities.

References

1 Eg. A. V. Ablov and N. V. Gerbeleu, *Russ. J. Inorg. Chem., 9* (1964) 46.
2 M. J. M. Campbell, *Coord. Chem. Rev., 15* (1975) 279.
3 F. A. French, E. J. Blanz, S. C. Shaddix and R. W. Brockman, *J. Med. Chem., 17* (1974) 172.
4 R. G. Schmitt and R. C. Hirt, *J. Polymer Sci., 7* (1963) 1565.
5 M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem., 22* (1957) 903.
6 J. C. Brand and W. Snedden, *Trans. Faraday Soc., 53* (1957) 894.
7 R. B. Singh, B. S. Garg and R. P. Singh, *Talanta, 25* (1978) 619.
8 J. M. Cano Pavon, *Microchem. J., 26* (1981) 155.
9 J. M. Cano Pavon, D. P. Bendito and M. Valacarcel, *Quim. Anal., 1* (1982) 118.
10 M. Mathew, G. J. Palenik and G. R. Clark, *Inorg. Chem., 12* (1973) 446.
11 A. I. Vogel, *A Text Book of Practical Organic Chemistry,* Longmans, London, 1974, p. 163.
12 P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, *J. Am. Chem. Soc.,* (1957) 3416.
13 J. Markopoulos, O. Markopoulou, D. Bethell and D. Nicholls, *Inorg. Chim. Acta, 122* (1986) L15.
14 A. I. Vogel, *A Text Book of Quantitative Inorganic Chemistry,* Longmans, London, 1986.
15 J. A. Walmsley and S. Y. Tyree, *Inorg. Chem., 2* (1963) 312.
16 P. Ray and D. N. Sen, *J. Indian Chem. Soc., 25* (1948) 473.
17 B. N. Figgis, *Introduction to Ligand Fields,* Wiley, New York, 1976.
18 L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Chapman and Hall, London, 1975.
19 M. Mashima, *Bull. Chem. Soc. Jpn., 37* (1964) 974.
20 M. J. M. Campbell and R. Grzeskowiak, *J. Chem. Soc. A,* (1967) 396.
21 C. Bellitto and A. A. G. Tomlinso, *Inorg. Chim. Acta, 27* (1978) 269.
22 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 3rd edn., 1978.
23 R. L. Carlin, *Prog. Inorg. Chem., 1* (1965) 1.
24 O. Piovesana and C. Furlani, *J. Inorg. Nucl. Chem., 30* (1968) 1249.
25 A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 2nd edn., 1984.
26 G. J. Long and D. L. Cotten, *Inorg. Chem., 13* (1974) 270.
27 C. K. Jorgensen, *Inorg. Chim. Acta, 2* (1968) 65.