# Alkyl Thiosemicarbazone Complexes of Iron(II) Halides

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*Complexes $FeL_2X_2$ (L = chelating thiosemicarbazone of acetone, cyclopentanone, cyclohexanone or cycloheptanone; X = Cl, Br or I) have been prepared and studied by IR, electronic reflectance and Moessbauer spectroscopy. The spectroscopic data suggest a distorted octahedral structure. The isomer shifts, ca. 0.82 mm $sec^{-1}$ at 300 K, similar to those of square planar iron(II) indicate the presence of weak Fe–X bonds. The quadrupole splittings, ca. 3 mm $sec^{-1}$, support a $d_{xy}$, $d_{x^2-y^2}$ or $d_{z^2}$ ground state but slow electronic relaxation at 4 K makes it impossible to identify the ground state by a magnetic perturbation study.*

## Introduction

The formation of complexes with transition metal ions has been proposed as a step in the biological activity of certain thiosemicarbazones [1]. It is therefore essential that we should extend our knowledge of the stereochemistry and electronic properties of such complexes. In previous papers [2, 3] we have reported on complexes $ML_2X_2$ formed between nickel(II) and cobalt(II) halides, $MX_2$, and some alkyl thiosemicarbazones (L). These complexes are found to contain pentacoordinate cations, $ML_2X^+$, of approximately trigonal bipyramidal geometry with the halide ion and the two sulphur donor atoms in the equatorial positions and the two nitrogen atoms in the axial positions [2, 3, 4]. In the present work we report on analogous iron(II) halide complexes, $ML_2X_2$, which have been investigated using infrared, electronic reflectance and Moessbauer spectroscopy.

## Discussion

The room temperature magnetic moments of all the compounds lie in the range 5.1–5.3$\mu_B$ indicative of high spin iron(II) species having an appreciable orbital contribution (spin only value for four unpaired electrons 4.92$\mu_B$). This rules out the possibility of pseudotetrahedral complex species but does not allow us to distinguish between tetragonally distorted octahedral and five-coordinate structures both of which give rise to values in this range.

The diffuse reflectance spectra of all the complexes are very similar and contain two sets of features. Firstly there are some relatively sharp but very weak bands in the visible region of the spectrum which we assign to spin-forbidden transitions from the quintet ground state to excited states of lower spin multiplicity. Secondly there are some broader and more intense bands in the near infrared region consisting of a symmetric band at *ca.* 10500 $cm^{-1}$ and a double peaked band at *ca.* 4000–5000 $cm^{-1}$, which are assigned to spin-allowed $d$–$d$ transitions. The positions of these transitions are compatible with either a five-coordinate or a tetragonally distorted octahedral geometry.

Unfortunately there are no crystallographic data on iron(II) thiosemicarbazone complexes and the only iron(II) thiosemicarbazide complex whose structure is known is bis(thiosemicarbazide)iron(II) sulphate [5]. In this compound the Fe–S distances are exceptionally long, 2.426 Å, suggesting that the iron-sulphur interaction is weak. By contrast most of the thiosemicarbazide and thiosemicarbazone complexes of Co(II), Ni(II), Cu(II) and Zn(II) have relatively short metal–sulphur distances in the range 2.25–2.30 Å. The one notable exception is Ni(thiosemicarbazide)$_2$(NO$_3$)$_2$·2H$_2$O in which as in Fe(thiosemicarbazide)$_2$SO$_4$ long metal–sulphur distances (2.411 Å) are found together with relatively short metal–oxygen distances (2.123 Å) [6]. The infrared spectra of the complexes of each ligand are similar regardless of the anion involved but do show differences from the spectrum of the ligand itself which are compatible with coordination via hydrazinic nitrogen and sulphur. Thus ligand bands in the regions 1600 $cm^{-1}$ ($\delta$(NH$_2$) and $\nu$(CN)) [7, 8, 9] 1530 $cm^{-1}$ ($\nu$(CN) and $\delta$(NH)) [7, 8, 9] 1160 $cm^{-1}$ ($\nu$NN and $\rho$(NH$_2$)) [7, 8, 9] and 800 $cm^{-1}$ ($\nu$(CS) $\omega$(NH$_2$) and $\delta$(NCN)) [7, 8, 9] undergo shifts very similar to those observed for the nickel and cobalt complexes [2, 3].

The far infrared spectra do not show the presence of any halogen dependent bands above 200 cm$^{-1}$ thus ruling out the possibility of five-coordinate or six-coordinate structures with strong iron—halogen bonds.

The Moessbauer spectra of all the complexes are very similar. It should be noted that in addition to the chlorides and bromides whose analysis figures we give in Table I we also prepared iodides but were unable to obtain samples with a good analysis. However these iodides gave 'clean' Moessbauer spectra very similar to those of the chlorides and bromides with no sign of either iron(III) or iron(II) impurities.

The isomer shift values are characteristic of iron(II) high spin species in tetragonally distorted octahedral environment. Where spectra could be recorded at both 300 and 77 K the isomer shift is seen to be larger at the lower temperature. Relative to other tetragonal complexes, $FeL_4X_2$ with L = py, isoquinoline, the isomer shifts are very low. Indeed the room temperature values of *ca.* 0.82 mm sec$^{-1}$ are only a little higher than that [10] for square planar Fe(II) in the mineral gillespite $BaFeSi_4O_{10}$ which is 0.754 mm sec$^{-1}$. We can tentatively conclude from this that the halides are only very weakly coordinated to the iron.

The quadrupole splittings are sufficiently large, *ca.* 3 mm sec$^{-1}$, for a predominantly $d_{xz}$, $d_{yz}$ ground state to be ruled out. The ground state must therefore be predominantly $d_{x^2-y^2}$, $d_{xy}$ or $d_{z^2}$. The increase in Q.S. on going from 300 K to 77 K may be the result of a thermal equilibrium between an electronic orbital singlet ground state and a doublet excited state. This would be compatible with either of two structures, a tetragonally elongated octahedral structure with a largely $d_{xy}$ ground state and $d_{xz}$, $d_{yz}$ first excited state or a trigonally distorted octahedral structure with a $|d_{z^2}\rangle$ ground state and $|t_{2g}^\pm\rangle$ first excited state. A clear distinction between a predominantly $|d_{xy}\rangle$ and a predominantly $|d_{z^2}\rangle$ ground state can readily be made if the sign of the quadrupole coupling constant is known. Unfortunately in the present case slow electronic relaxation at liquid helium temperatures prevents determination of the sign by means of the usual magnetic perturbation technique. This is in contrast with the behaviour of $FeTSC_2SO_4$ for which electronic relaxation is still fast at 4 K and magnetic perturbation shows $V_{zz}$ to be positive, compatible with a predominantly $|d_{xy}\rangle$ ground state [11].

The Q.S. values for the iodide complexes show a small but significant increase over the values found for the corresponding chlorides. If we assume the crystal field model to be adequate in describing these complexes then this behaviour is compatible with very weak axial bonding by the halide ions. It must however be pointed out that the bromides do not all fit into this pattern.

The most likely stereochemistries for transition metal bis(thiosemicarbazone) complexes, $ML_2X_2$, are tetrahedral, $[ML_2]X_2$, pentacoordinate, $[ML_2X]$ X, or octahedral $[ML_2X_2]$. Some zinc complexes are known to contain tetrahedral species [12], $ZnL_2^{2+}$, and the corresponding nickel and cobalt species are pentacoordinate [3, 4]. We originally anticipated that the iron complexes might also be pentacoordinate but this has proved not to be the case. The evidence we have presented rules out this possibility and is most compatible with a distorted octahedral geometry. The most likely explanation is that the Fe—S bonds are probably longer and weaker than in the corresponding nickel and cobalt compounds.

## Experimental

The thiosemicarbazones were prepared by refluxing thiosemicarbazide (TSC) with the appropriate ketone (acetone, CMe; cyclopentanone, Cpen; cyclohexanone, Chex and cycloheptane, Chep) in ethanol in the presence of acetic acid. All ligands were recrystallised from ethanol.

The complexes were all prepared under an atmosphere of nitrogen. The chloro and bromo complexes were obtained by mixing hot ethanolic solutions of $FeCl_2 \cdot 4H_2O$ and $FeBr_2$ respectively with ethanolic solutions of the ligand in the molar ratio of 1:2. Ethanolic $FeI_2$ was prepared by mixing equimolar quantities of NaI and $FeCl_2 \cdot 4H_2O$ in ethanol and filtering off the precipitated NaCl. Twice the molar quantity of ligand was then dissolved in the hot solution and the complex allowed to crystallise.

The iron content of the complexes was determined by titration against EDTA and also by atomic absorption spectrometry. Carbon, hydrogen and nitrogen analyses were obtained using an F and M Analyser Model 185.

Magnetic moments were determined by the Gouy technique. A Unicam SP700 was used to obtain diffuse reflectance spectra of the solids over the range 30000—5000 cm$^{-1}$ and a Perkin-Elmer 257 spectrophotometer to obtain IR spectra in the range 4000—650 cm$^{-1}$. The far IR spectra were measured using a Beckman-RIIC FS720 Michelson interferometer, with samples cooled to 77 K by means of a TEM-IC temperature controller containing liquid nitrogen. The computations were carried out over the frequency range 500—50 cm$^{-1}$.

Moessbauer spectra were measured using a Harwell Research constant acceleration spectrometer with its associated proportional counter. The $^{57}Co(Rh)$ source was purchased from The Radiochemical Centre. Spectra were measured at 80 K in a bath type cryostat and the results fitted using a least-squares fitting program run on the U.L.C.C. CDC6600 computer.

TABLE I. Analytical Data[a].

| Compound | Fe | C | H | N |
|---|---|---|---|---|
| Fe(TscCMe)$_2$Cl$_2$·H$_2$O | 14.1(13.7) | 23.4(23.6) | 5.7(4.7) | 20.8(20.6) |
| Fe(TscCMe)$_2$Br$_2$·TscCMe | 9.4 (9.2) | 23.6(23.6) | 5.6(4.5) | 20.3(20.7) |
| Fe(TscCpen)$_2$Cl$_2$ | 12.7(12.7) | 33.0(32.7) | 5.1(5.0) | 18.2(19.1) |
| Fe(TscCpen)$_2$Br$_2$·½C$_2$H$_5$OH | 9.8 (9.9) | 27.4(27.4) | 4.1(4.3) | 15.0(14.9) |
| Fe(TscChex)$_2$Cl$_2$ | 12.2(11.9) | 35.1(35.8) | 5.8(5.6) | 18.7(17.9) |
| Fe(TscChex)$_2$Br$_2$·½C$_2$H$_5$OH | 9.6 (9.6) | 32.2(31.0) | 5.6(5.0) | 14.4(14.4) |
| Fe(TscChep)$_2$Cl$_2$·½C$_2$H$_5$OH·H$_2$O | 10.5(10.2) | 38.2(37.8) | 6.8(6.5) | 15.0(15.6) |
| Fe(TscChep)$_2$Br$_2$·½C$_2$H$_5$OH | 9.8 (9.2) | 33.1(33.4) | 5.5(5.4) | 13.2(13.7) |

[a]Values in parentheses are calculated percentages.

TABLE II. Electronic Spectral Data.

| Complex | Band Maxima ($\times 10^{-3}$ cm$^{-1}$) | |
|---|---|---|
| | spin forbidden | spin allowed |
| Fe(TscCMe)$_2$Cl$_2$·H$_2$O | 21.28, 16.67 | 10.20, 5.62, *ca.* 4.85 |
| Fe(TscCMe)$_2$Br$_2$·TscCMe | 21.98, 20.83, 19.42, 18.52, 16.39 | 10.10, 5.50, *ca.* 4.88 |
| 'Fe(TscCMe)$_2$I$_2$' | 23.00, 21.28, 20.41, 18.69, 17.54, 16.39 | 10.10, 5.40, *ca.* 4.79 |
| Fe(TscCpen)$_2$Cl$_2$ | 20.41, 16.67 | 10.75, 5.75, *ca.* 4.76 |
| Fe(TscCpen)$_2$Br$_2$·½C$_2$H$_5$OH | 21.28, 20.00, 18.52, 16.13 | 10.75, 5.44, *ca.* 5.00 |
| 'Fe(TscCpen)$_2$I$_2$' | 20.83, 19.23, 17.86, 16.13 | 10.99, 5.40, *ca.* 4.81 |
| Fe(TscChex)$_2$Cl$_2$ | 21.51, 19.80, 17.70, 16.81 | 10.96, 5.50, *ca.* 4.83 |
| Fe(TscChex)$_2$Br$_2$·½C$_2$H$_5$OH | 21.98, 21.28, 19.61, 18.52, 16.39 | 10.00, 5.40, *ca.* 4.96 |
| 'Fe(TscChex)$_2$I$_2$' | 17.86, 16.39 | 10.99, 5.46, *ca.* 5.00 |
| Fe(TscChep)$_2$Cl$_2$·½C$_2$H$_5$OH·H$_2$O | 21.74, 20.00, 16.95 | 10.99, 5.51, *ca.* 4.83 |
| Fe(TscChep)$_2$Br$_2$·½C$_2$H$_5$OH | 21.98, 21.28, 19.61, 18.52, 16.26 | 10.31, 5.39, *ca.* 4.90 |
| 'Fe(TscChep)$_2$I$_2$' | 21.28, 20.41, 19.05, 17.86, 16.13 | 10.31, 5.48, *ca.* 4.90 |

TABLE III. Moessbauer Data.

| Compound | Temperature (K) | IS (mm sec$^{-1}$) | QS (mm sec$^{-1}$) |
|---|---|---|---|
| Fe(TscCMe)$_2$Cl$_2$·H$_2$O | 77 | 0.9488 | 3.1035 |
| | 300 | 0.8257 | 2.9755 |
| Fe(TscMe)$_2$Br$_2$·TscCMe | 77 | 0.9355 | 3.2012 |
| 'Fe(TscCMe)$_2$I$_2$' | 77 | 0.9465 | 3.3074 |
| Fe(TscCpen)$_2$Cl$_2$ | 77 | 0.9459 | 3.1032 |
| | 300 | 0.8374 | 2.9676 |
| Fe(TscCpen)$_2$Br$_2$·½C$_2$H$_5$OH | 77 | 0.9489 | 3.0247 |
| 'Fe(TscCpen)$_2$I$_2$' | 77 | 0.9350 | 3.2092 |
| Fe(TscChex)$_2$Cl$_2$ | 77 | 0.9550 | 3.1212 |
| | 300 | 0.8184 | 3.1016 |
| Fe(TscChex)$_2$Br$_2$·½C$_2$H$_5$OH | 77 | 0.9434 | 3.1747 |
| 'Fe(TscChex)$_2$I$_2$' | 77 | 0.9343 | 3.2049 |
| Fe(TscChep)$_2$Cl$_2$·½C$_2$H$_5$OH·H$_2$O | 77 | 0.9293 | 3.0873 |
| | 300 | 0.8117 | 3.0151 |
| Fe(TscChep)$_2$Br$_2$·½C$_2$H$_5$OH | 77 | 0.9373 | 3.2517 |
| 'Fe(TscChep)$_2$I$_2$' | 77 | 0.9308 | 3.1819 |

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