APPLICATIONS OF MASS SPECTROMETRY, MÖSSBAUER SPECTROMETRY AND OTHER PHYSICAL TECHNIQUES TO METAL CHELATE CHEMISTRY*

By

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Introduction

Metal chelate compounds are important because of (1) their many industrial applications (e.g. solvent extraction, catalysis, sequestering etc.), (2) their widespread use in analytical chemistry, and (3) the part they play in many biological systems. The aim of our work has been to prepare and study the structure and reactivity of chelate compounds which have either (a) the metal with an unusual oxidation state and/or coordination number, or (b) a reactive group stabilised by chelation. Such compounds have potential application, or are models in the fields of study mentioned above. A particular feature has been synthesis in non-aqueous media, and this contrasts with the moral usual methods of preparation of chelate compounds.

Thermogravimetric and differential thermal analysis have proved very useful in these studies.

Two of the other physical techniques we have applied to our work are Mössbauer and mass spectrometry. In this paper the use of these techniques is illustrated by reference to two of the systems we have studied:

(1) Tin(IV) and tin(II) halides with 8-quinolinol,
(2) 8-Quinolinolato complexes of iron(III).

1. Reactions of tin(IV) and tin(II) halides with 8-quinolinol

The types of reaction occurring in covalent halide — 8-quinolinol (oxH) systems can be illustrated by reference to reactions of tin(IV) [1] and tin(II) [2] chlorides shown in Table 1. Thermogravimetric analysis was used to establish the stoichiometry of many of these reactions.

The adducts $SnCl_4$, oxH and $SnCl_4$, 2 oxH were insoluble in non-disruptive solvents and so recrystallisation, and molecular weight and conductance measurements were not possible. They also decomposed on heating

and so crystals could not be obtained by sublimation. Mössbauer spectroscopy is applicable to such intractable solids, and the similarity of the spectra and, particularly the absence of quadrupole splitting, was evidence that in both compounds the tin was 6-coordinate [3].
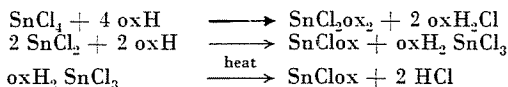
Table 1

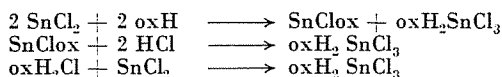The 8-quinolinol — tin(IV) and tin(II) halide system
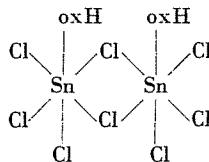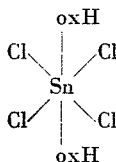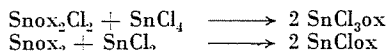
Adduct formation

$$SnCl_4 + oxH \longrightarrow SnCl_4, oxH$$
$$SnCl_2ox + 2\ HCl \longrightarrow SnCl_4, 2\ oxH$$

Chelate formation

$$SnCl_4 + 4\ oxH \longrightarrow SnCl_2ox_2 + 2\ oxH_2Cl$$
$$2\ SnCl_2 + 2\ oxH \longrightarrow SnClox + oxH_2\ SnCl_3$$
$$oxH_2\ SnCl_3 \xrightarrow{heat} SnClox + 2\ HCl$$

8-Quinolinolium salt formation

$$2\ SnCl_2 + 2\ oxH \longrightarrow SnClox + oxH_2SnCl_3$$
$$SnClox + 2\ HCl \longrightarrow oxH_2\ SnCl_3$$
$$oxH_2Cl + SnCl_2 \longrightarrow oxH_2\ SnCl_3$$

Redistribution of ox and X

$$Snox_2Cl_2 + SnCl_4 \longrightarrow 2\ SnCl_3ox$$
$$Snox_2 + SnCl_2 \longrightarrow 2\ SnClox$$

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        oxH                     oxH        oxH
         |                       |          |
  Cl\    |   /Cl          Cl\    |   /Cl\   |   /Cl
      Sn                      Sn        Sn
  Cl/    |   \Cl          Cl/    |   \Cl/   |   \Cl
         |                       |          |
        oxH                     Cl         Cl
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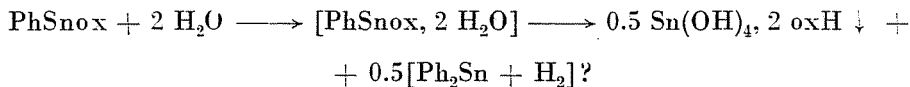
A linear correlation was found between the sum of the Pauling electronegativities of the halogens of SnX_4, noxH and the Mössbauer isomer shift [3]. A similar correlation was found for the series SnY_2ox_2. This work has now been extended and a linear correlation between isomer shifts and core binding energies measured by X-ray induced photoelectron spectroscopy (ESCA) has been found for this series [4].

As indicated in Table 1, the 8-quinolinolate derivatives of tin(II), (SnXox) have now been prepared and again there is a correlation between the electronegativities of X and isomer shift [2]. The SnXox compounds were prepared as precursors to compounds such as PhSnox. Diphenyl tin is very easily oxidised, and it was desirable to investigate whether chelation in PhSnox would stabilise the Ph—Sn bond. The compound was prepared by the reaction:

$$SnClox + PhLi \xrightarrow[N_2]{benzene} PhSnox + LiCl$$
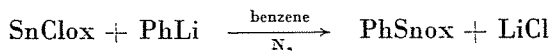
The Mössbauer parameters* are $\delta = 1.70$; $\Delta = 0$ and this is consistent with a polymeric structure containing Sn—Sn bonds. The compound was resistant to oxidation and could be recovered unchanged after oxygen had been passed through a benzene solution for one hour. Under comparable conditions Ph_2Sn would have been readily oxidised.

However PhSnox is not resistant to hydrolysis. A thermogravimetric balance has been used to show that at room temperature PhSnox underwent hydrolytic oxidation on exposure to moist air:

$$\text{PhSnox} + 2\ H_2O \longrightarrow [\text{PhSnox}, 2\ H_2O] \longrightarrow 0.5\ Sn(OH)_4, 2\ \text{oxH} \downarrow +$$
$$+ 0.5[Ph_2Sn + H_2]?$$

The compound $Sn(OH)_4$, 2 oxH has been characterized by elemental analysis and infrared spectroscopy. Further confirmation comes from its Mössbauer parameters which indicate a tin(IV) atom. Furthermore the isomer shift agrees closely with the value predicted from the linear correlation of electronegativity and isomer shift.

Thermogravimetric analysis has also been used to show that on heating to 200° $Sn(OH)_4$, 2 oxH loses water (2 mols/mol of complex) to give the compound $Sn(OH)_2ox_2$ which is thermally stable to 450°.

The tin compounds in Table I have been subjected to mass spectrometry in order to determine vapour phase molecularity, and also to gain insight into potential analytical applications.

Redistribution reactions occurring in the ion source of the spectrometer of the type:

$$2\ \text{PhSnox} \longrightarrow Ph_2Sn + Snox_2$$
$$2\ Ph_2Sn \longrightarrow Ph_4Sn + Sn$$
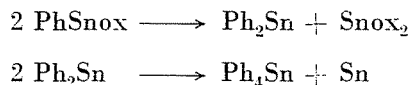
give rise to species such as Ph_3Sn^+ and Ph_2Sn^+ in the mass spectrum of PhSnox [2].

2. 8-Quinolinolato complexes of iron(III)

The solids $FeClox_2$ and $FeCl_2ox$ are insoluble and so molecular weight measurements are not possible [5]. The room temperature magnetic moments (see Table 2) are less than predicted by the "spin-only" formula for a high spin d^5 system. A study of magnetic susceptibility [6] versus temperature (373—88 K) indicates antiferromagnetic interactions, and the actual values

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* (mm/s relative to SnO_2)

of susceptibility agree well with those calculated [7] assuming a model of two magnetically interacting $S = ^5/_2$ iron atoms. The g values obtained by this calculation agree well with those obtained by e.p.r. measurements.

It was decided [6] to examine the solids by Mössbauer spectroscopy (results in Table 2) in order to confirm whether the compounds were dimeric, and also because susceptibility results can be misleading due to their greater sensitivity to the presence of paramagnetic impurities.

Table 2

Mössbauer* (mm/s at 80 K) and magnetic (B.M. at 274 K) data

| Compound	δ	Δ	μ_{eff}
FeClox$_2$	0.49	0.77	5.27
FeCl$_2$ox	0.41	0.46	4.58

* relative to iron

The following conclusions can be made:

1. The δ and Δ values are in the range normally associated with high spin iron(III).

2. The spectra at low temperatures and in zero applied field consist of quadrupole doublets in which the component peaks have normal widths and equal areas, therefore all the iron atoms are equivalent and this is consistent with the dimeric formulation.

3. There are now δ values (mm/s) for the series Feox$_3$ (0.46) [6], FeClox$_2$, FeCl$_2$ox and FeCl$_3$ (0.53) [8]. The first and last members of the series have six coordinate iron and similar coordination for FeClox$_2$ is reasonable on the basis of the similar value of δ. On the other hand, the lower value for FeCl$_2$ox may indicate five coordinate iron. Furthermore, the value for FeCl$_2$ox lies between that of Feox$_3$ and four coordinate Fe in FeCl$_4^-$ (0.29). [9]. Six and five coordination for FeClox$_2$ and FeCl$_2$ox respectively is further support for dimeric formulations.

Possible structures are:
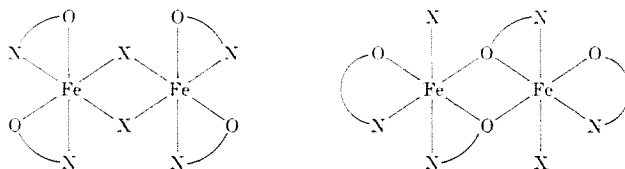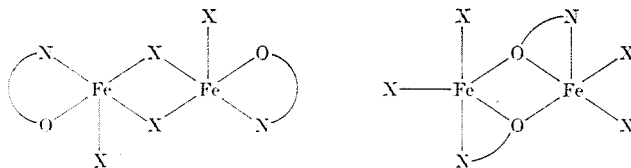
4. At 4.2 K hyperfine splittings are small and this is consistent with a non-magnetic ground state arising from antiferromagnetic interactions.

Similar magnetic and Mössbauer results have been obtained for $FeBrox_2$ and $FeBr_2ox$.

The mass spectra of the compounds $Feox_3$, $FeXox_2$ and FeX_2ox exhibit two important features [10].

1. Redistribution reactions can occur in the ion source of the spectrometer leading to unexpected species in the mass spectrum. Thus the spectrum of FeX_2ox contains the ions $FeXox_2^+$ and $Feox_2^+$; and that of $FeXox_2$ contains FeX_2ox^+ and $Feox_3^+$. These species could arise respectively by ionization and fragmentation of the product of the redistribution reactions.

$$2\ FeX_2ox\ \rightarrow\ FeXox_2 + FeX_3$$

$$2\ FeXox_2\ \rightarrow\ FeX_2ox + Feox_3$$
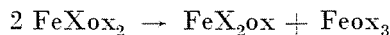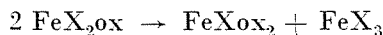
2. The comparative abundances of fragments are primarily related to the common oxidation states of the metals. For example in the series Mox_3 [M = Al, Ga, In, Sc, Cr and Fe] all the spectra show the ions $[Mox_3]^+$ and $[Mox_2]^+$. The ions $[Mox]^+$ and $[M]^+$ are present when M = Ga, In, Cr or Fe but for the elements with only one oxidation state (Al or Sc) $[M]^+$ is absent and $[Mox]^+$ has only very low abundance. When M = Cr or Fe metal containing ions arising from loss of species such as CO H_2O HX C_2H_2 H· and ȮH by fragmentation of the ox ligand are also present. This behaviour can be rationalised in terms of unit changes in oxidation state of the metal.

Summary

Mass spectrometry, thermogravimetric and differential thermal analysis, Mössbauer spectrometry together with X-ray induced photoelectron spectroscopy (ESCA) and magnetic susceptibility measurements were applied for the preparation and study of the structure and reactivity of various metal chelate compounds. The use of these techniques was illustrated by referring to two of the studied systems: (1) Tin (IV) and tin (II) halides with 8-quinolinol, (2)8-quinolinolate complexes of iron (III).

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