

## Transition Metal O-Sulphinates Complexes

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Received March 8, 1968

This paper reports on the preparation and characterisation of sulphinates complexes of Mn, Fe, Co, Ni, and Cu. Infrared spectra of these compounds suggest that the sulphinates groups are oxygen-bonded to the metal ions. Magnetic and electronic spectral data are also reported.

## Introduction

Aryl sulphonic acids and their salts have, since 1937, been used in the analytical chemistry of various transition metals.<sup>1</sup> More recently, Deacon and co-workers<sup>2</sup> utilised the ready loss of sulphur dioxide from mercury sulphinates complexes to prepare mercury aryl derivatives. Alternatively, Wojcicki<sup>3</sup> has shown that sulphur dioxide may be reversibly inserted into the iron-carbon bond of  $(\pi-C_5H_5)Fe(CO)_2R$ , where  $R=CH_3, C_2H_5, C_6H_5$ . In these and related complexes infrared studies established the presence of S-bonded sulphinates groupings.<sup>4</sup>

It has also been observed<sup>5</sup> that systems containing sulphonic acids, often in the presence of transition metal salts, readily undergo polymerisation. As part of a study of the role of transition metal complexes in polymerisation we have investigated the polymerising ability of various transition metal sulphinates complexes and find that while some metal sulphinates readily initiate polymerisation of such monomers as methyl methacrylate and acrylonitrile other metal complexes apparently have little or no effect. Accordingly we have investigated the nature of some of the more active metal complexes.

In this paper we report the preparation and characterisation of sulphinates complexes of some transition metals which, under the Arland-Chatt classification, often show class "a" behaviour, in which the sulphinates group behaves as an oxygen donor ligand.

## Results and Discussion

A series of metal complexes  $M(RSO_2)_2(H_2O)_2$  ( $R=C_6H_5$  or  $CH_3C_6H_4$ ;  $M=Mn, Fe, Co, Ni, Cu$ ) have

been prepared by reaction of the corresponding sodium salt with a hydrated metal salt, usually the halide, in aqueous solution. In general the complexes are not very soluble in water or common organic solvents, which has restricted the application of studies in solution. The copper(II) complexes can, however, be recrystallised from acetone or water and does not conduct in dioxane.

Evidence of the mode of bonding of these ligands to the metal ions is proved from their infrared spectra which show that the sulphinates anion is O-bonded in all the complexes prepared. There is well-documented work available for the S—O stretching vibration in sulfoxide complexes which shifts to lower energy on co-ordination via oxygen and to higher energy on co-ordination through sulphur. The benzene and toluene-sulphinates anions show three strong bands in the region 900-1200  $cm^{-1}$  and Hadzi<sup>6</sup> has assigned those at 970 and 1020  $cm^{-1}$  to the symmetric and asymmetric S—O stretching vibrations respectively. In all our complexes strong absorption bands in this region are shifted towards lower energy (Table I).

Table I. Infrared Data

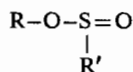
Complex	(S—O) <sub>ass</sub> ( $cm^{-1}$ )	S(S—O) <sub>sym</sub> ( $cm^{-1}$ )
Mn(C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	988	952
Fe(C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	984	940
Co(C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	982	935
Ni(C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	972	949
Cu(C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	962	910
Cu(CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	1011	953

Further proof of this mode of co-ordination is found in the region 580-620  $cm^{-1}$  in which, for systems containing a metal-sulphur bond, there are absorptions assigned to bending modes.<sup>2</sup> No such absorptions were found in our complexes. In the low frequency region, *i.e.* 580-200  $cm^{-1}$ , the spectra are all very similar showing a complex profile containing three bands (540-450  $cm^{-1}$ ). The copper complex shows a more complex profile. These spectra differ both from the original sodium salt and that reported for the mercury sulphur bonded complex, consequently these bands may be associated with metal-oxygen stretching modes.

(6) S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

(1) F. Feigl, *Oester Chemikerzeitung*, 40, 535 (1937).  
 (2) G. B. Deacon, *Aust. J. of Chem.*, 20, 1367 (1967).  
 (3) F. A. Hartman and A. Wojcicki, *J. Amer. Chem. Soc.*, 88, 844 (1966); J. P. Bilber and A. Wojcicki, *J. Amer. Chem. Soc.*, 88, 4862 (1966).  
 (4) B. Chiswell and L. M. Venanzi, *J. Chem. Soc.*, (A), 1246 (1966).  
 (5) Japan Patent 15,986 and 7637.

Sulphinate co-ordination as a monodentate oxygen ligand of the type reported recently<sup>7</sup> for the complex  $\text{Cu}(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2)_2(\text{H}_2\text{O})_4$  would seem to be less favoured for our complexes from spectral comparisons with esters of general formula<sup>6</sup>



when  $\text{R}' = \text{phenyl}$ ,  $\nu(\text{S-O})_{\text{ass}}$  is raised ( $1126\text{--}1136\text{ cm}^{-1}$ ) and  $\nu(\text{S-O})_{\text{sym}}$  is lowered ( $960\text{ cm}^{-1}$ ) relative to the benzene sulphinate anion.

All our metal complexes exhibit absorptions in the  $3500\text{--}3200\text{ cm}^{-1}$  region which remain after refluxing with 2,2'-dimethoxypropane and this is consistent with the presence of co-ordinated water.

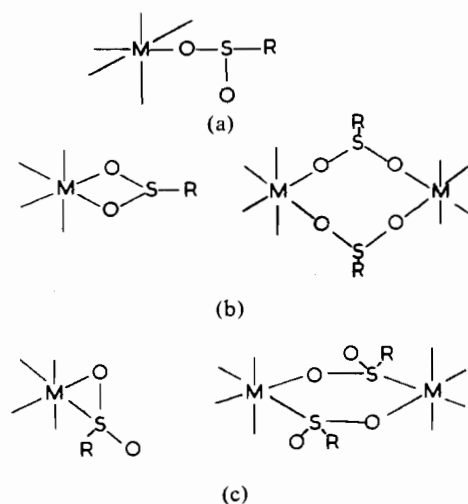


Figure 1.

Thus the infrared data indicate that for the present complexes it is the oxygen atoms of the ligand which are used in co-ordination to the central ion. As illustrated in Figure 1 there are a number of different ligand arrangements which would be consistent with oxygen co-ordination. These might be anticipated to affect the stereochemical arrangement around the metal and accordingly we have investigated the magnetic and electronic spectra of the compounds.

**Magnetic and Electronic Spectra.** The magnetic moments of the complexes are given in Table II.

Table II. Magnetic Data

Compound $\text{MA}_2(\text{H}_2\text{O})_2$	$\mu_{\text{eff}}^a$ (B.M.)
M = Mn	5.93
Fe	5.12
Co	4.93; 4.79; <sup>b</sup> 4.51 <sup>c</sup>
Ni	2.93; 2.82; <sup>d</sup> 2.76 <sup>e</sup>
Cu	1.81
$\text{Cu}(\text{B})_2(\text{H}_2\text{O})_2$	1.96

HA =  $\text{C}_6\text{H}_5\text{SO}_2\text{H}$ ; HB =  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$ ; (a) at  $293^\circ\text{K}$ ; (b) at  $174^\circ\text{K}$ ; (c) at  $90^\circ\text{K}$ ; (d) at  $184.5^\circ\text{K}$ ; (e) at  $97^\circ\text{K}$ .

(7) G. B. Deacon and P. W. Felder, *J. Amer. Chem. Soc.*, **90**, 493 (1968); D. A. Langs and C. R. Hare, *Chem. Comms.*, 853 (1967).

X-ray powder photographs of the manganese, iron, cobalt and nickel complex show that they are isomorphous. In the case of the copper complexes the photographs are very similar, differing from the rest only in occasional splitting of lines. Hence we conclude that the structure of this metal complex is very similar to that of the other four.

The possible stereochemical arrangements for these complexes are tetrahedral, planar or octahedral. Particularly for cobalt and nickel chemistries the methods of differentiating between these various stereochemistries have been summarised<sup>8,9</sup> and as the other metal complexes are isomorphous with these two the nickel and cobalt complexes have been studied in more detail. The room-temperature magnetic moment and the small variation with temperature (Table II) of the nickel complex suggest a six-co-ordinate octahedral stereochemistry around the nickel atom with a  $^3\text{A}_{2g}$  ground state. The room temperature moment of the cobalt complex (4.93 B.M.) falls within the range normally observed for octahedral complexes and the variation of the moment with temperature implies octahedral co-ordination with a  $^4\text{T}_{1g}$  ground state.

Electronic spectral data serve to confirm this stereochemical arrangement for these complexes. The diffuse reflectance spectrum of the cobalt complex  $\text{Co}(\text{C}_6\text{H}_5\text{SO}_2)_2(\text{H}_2\text{O})_2$  has three bands at  $7,700\text{ cm}^{-1}$ ,  $18,800\text{ cm}^{-1}$  and  $20,500\text{ cm}^{-1}$ . Again assignments are tentative but using energy level diagrams given by Liehr and Balhausen<sup>10</sup> the  $7,700\text{ cm}^{-1}$  and  $18,800\text{ cm}^{-1}$  bands may be assigned on the basis of an octahedral stereochemistry as  $^4\text{T}_{2g} \leftarrow ^4\text{T}_{1g}$  and  $^4\text{A}_{2g} \leftarrow ^4\text{T}_{1g}$  respectively. Similarly for the nickel complex the bands at  $8,000\text{ cm}^{-1}$  and  $13,600\text{ cm}^{-1}$  may be assigned to the transitions  $^3\text{T}_{2g} \leftarrow ^3\text{A}_{2g}$  and  $^3\text{T}_{1g} \leftarrow ^3\text{A}_{2g}$  respectively. These, taken together with the copper compounds ( $12,500\text{ cm}^{-1}$  for  $\text{R} = \text{C}_6\text{H}_5$ ;  $12,380\text{ cm}^{-1}$  for  $\text{R} = \text{CH}_3\text{C}_6\text{H}_4$ ), then give a Dq value for the mixed ligand field of sulphinate and water very similar to that of water itself. Such a conclusion can be more readily justified by oxygen rather than sulphur co-ordination of the ligand. These figures are also comparable with the value of  $12,500\text{ cm}^{-1}$  quoted earlier for a similar complex.<sup>7</sup>

Thus these complexes can be formulated as six-co-ordinate and octahedral in which both oxygen atoms of the ligand are used in co-ordination to the central metal atom. This octahedral environment in the solid can readily be achieved in two ways; by polymerisation using the oxygen atoms in a similar way to that which has been postulated to occur in  $[(\text{CH}_3)_2\text{Ga}(\text{SO}_2\text{Ph})_2]$  (Figure 2a) or by chelation to give a monomeric species (Figure 2b).

The limited solubility of these complexes would be more consistent with a polynuclear structure. In such a structure spin-coupling between the copper atoms might be expected to lower the magnetic moment below that observed, but there are many examples where this is not observed, e.g. some copper(II)

(8) B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry", **6**, 37, Ed. F. A. Cotton, Interscience, London.

(9) T. M. Dunn, "Modern Co-ordination Chemistry", Ed. J. Lewis and R. G. Wilkins, Interscience, London (1960).

(10) Liehr and Balhausen, *Ann. Phys.*, N.Y. **2**, 134 (1959).

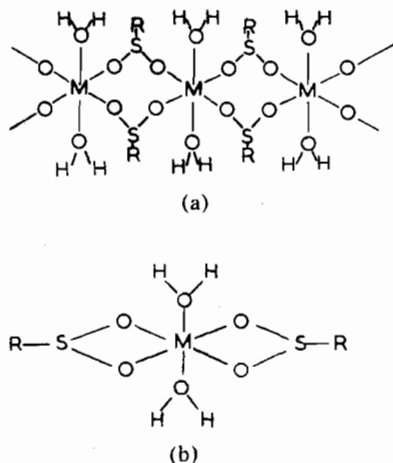


Figure 2.

formates. Consequently at the moment we are unable to accurately distinguish between these two possibilities and it is unlikely that infrared data would serve as a diagnostic tool. Further experiments to investigate the catalytic activity of such complexes are in progress.

### Experimental Section

**Preparation.** The general method was to dissolve a simple hydrated salt of the metal in the minimum quantity of water and treat this with a stoichiometric quantity of sodium aryl sulphinate (in the ratio 1:2 metal ligand) also dissolved in water. The complexes which precipitated either immediately, or on standing

for thirty minutes, were then filtered, washed with water and dried over  $P_2O_5$ .

**Analysis.** Carbon, hydrogen by Wieler and Strauss, Oxford. Metal analyses by standard methods as described in Vogel.<sup>11</sup> The results are shown in Table III.

Table III. Analytical Results

Compound	Found			Calcd.		
	C	H	Metal	C	H	Metal
$MnA_2(H_2O)_2$	38.53	3.61	—	38.61	3.78	—
$FeA_2(H_2O)_2$	38.60	3.62	14.75	38.51	3.77	14.92
$CoA_2(H_2O)_2$	38.57	3.91	—	38.18	3.74	—
$NiA_2(H_2O)_2$	38.24	3.99	—	38.22	3.74	—
$CuA_2(H_2O)_2$	37.34	3.68	16.71	37.76	3.69	16.64
$Cu(B)_2(H_2O)_2$	40.71	4.22	—	41.02	4.43	—

HA =  $C_6H_5SO_2H$ ; HB =  $CH_3C_6H_4SO_2H$ .

**Spectroscopic Measurements.** Infrared spectra were recorded as nujol and hexachlorobutadiene mulls on a Perkin Elmer 457 and 225 spectrometers. The ultraviolet and visible spectra were measured on a Unicam S.P. 700 spectrophotometer.

Magnetic moments were obtained on a Gouy balance at room temperature using a field of 3,500 gauss. Diamagnetic corrections for the  $C_6H_5SO_2^-$  ligand were determined experimentally. X-ray powder photographs were obtained using the Cu- $\alpha$ -line with an exposure of 4-10 hours.

**Acknowledgment.** One of us (C.W.D.) thanks Metal Containers Ltd. for financial support.

(11) "Quantitative Inorganic Analysis", A. I. Vogel.