

A Preliminary Study of Differential Thermal Analysis, Conductance and Cryoscopic Behavior of Dimethyl Sulfoxide Complexes

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Introduction

When dimethyl sulfoxide (DMSO) became commercially available, several of its physical properties immediately suggested its desirability as a solvent for inorganic compounds. The compound's liquid range (18.5-189°C), moderate viscosity (1.98 centipoise) and high dielectric constant (47) are most important among these properties. Also the convenient freezing point of DMSO (18.45°C) suggested possible utility as a solvent for cryoscopic measurements.

Erhard Saettler⁽¹²⁾, working in this laboratory on a senior project, found that many inorganic salts are quite soluble in DMSO and when these solutions are cooled or the excess solvent removed by pumping, solid complexes or solvates are formed which are analogous to hydrates. These compounds first reported by Saettler are listed in Table 1.

TABLE 1
Analysis of Complexes

Formula	Color	% DMSO		% Metal	
		Theory	Found	Theory	Found
Co(NO ₃) ₂ · 4DMSO	Magenta	63.1	64.1	11.9	11.7
CoCl ₂ · 3DMSO	Deep Blue	64.4	64.4	16.2	16.3
NiCl ₂ · 3DMSO	Blue-green	64.4	63.9	16.1	16.0
FeCl ₃ · 3DMSO	Yellow	59.1	58.8	14.1	14.5
Cu(OAc) ₂ · DMSO	Blue-green	30.1	30.2	24.5	24.2
CuCl ₂ · 2DMSO	Chartreuse	53.8	53.7	21.9	21.1

Since this time, DMSO has been used as a solvent in experiments in the Physical Chemistry laboratory at Wabash College. Experiments where DMSO has been used as a solvent instead of water are: cryoscopic measurements, conductance, polarimetry, spectrophotometry in visible and ultraviolet regions, phase diagrams, and electrochemical cells. It has also been given to students as an unknown for determination of dielectric constant.

Recently, Cotton and Francis⁽¹³⁾ have reported the preparation and characterization of 35 complexes containing DMSO. Also, Sears, Lester and Dawson⁽¹³⁾ have reported conductance measurements of uni-univalent electrolytes in DMSO. The Cotton and Francis report includes four of the six complexes described by Saettler. In the case of FeCl₃, Cotton and Francis report FeCl₃·2DMSO while in this laboratory FeCl₃·3DMSO was found. Cotton and Francis also propose that CoCl₂·3DMSO and NiCl₂·

3DHSO have the following structure in the solid state, $[M(\text{DMSO})_6]^{2+}[\text{MCl}_4]^{2-}$.

The first objective of this research has been to use differential thermal analysis to determine whether these complexes lose DMSO stepwise in the manner of many hydrates and thus explain the two complexes reported for FeCl_3 . The second objective has been to use conductance and cryoscopic measurements to determine the nature of the ions in solution and to compare with the structures suggested by Cotton and Francis for the solids.

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Experimental

1. Preparation of Complexes—Dimethyl sulfoxide was initially obtained from Stepan Chemical Company, and more recently from Crown Zellerbach Corporation. The DMSO was used as received in the preparation of the complexes. The small amount of water in the DMSO or the presence of water in the hydrated salts used had no effect on the composition of the complexes. The complexes listed in Table 1 were prepared by dissolving the corresponding reagent grade hydrated salt in DMSO at 60–80°C and cooling until the solid complex separated out. If no solid was obtained by cooling, the excess solvent was removed by evacuation. In either case the solids obtained were pumped on in a vacuum dessicator until free of excess DMSO. In the case of $\text{Co}(\text{NO}_3)_2 \cdot 4\text{DMSO}$, acetone was used to an advantage as a solvent for recrystallization. Most of the complexes are hygroscopic and as many operations as possible were carried out in a dessicated glove box.

2. Analysis—The complexes were analyzed for DMSO and the metal constituent. DMSO was determined by the method of Douglas⁽⁴⁾. Cobalt, nickel and copper were analyzed by standard electrolytic methods. Iron was analyzed by standard gravimetric procedures. The results are tabulated in Table 2.

3. Differential Thermal Analysis Apparatus and Procedure—A simple DTA apparatus utilizing thermistors as the temperature sensing elements was designed and built. The apparatus consisted of an aluminum block 2 inches in diameter containing two holes for the sample tubes and a third for the thermocouple, all drilled from the top. The sample tubes were made from $\frac{1}{4}$ inch diameter aluminum tube and were secured to a cap which insured reproducible positioning of the sample tubes within the block. Into one sample tube was placed 120 mg of calcined Al_2O_3 (Merck Reagent) and in the second tube, 60 mg of the sample and 60 mg of Al_2O_3 thoroughly mixed. The matched pair of Fenwal No. GA51P2 thermistors (100,000 ohms at 25°C) were inserted to a fixed depth in the sample and blank. The thermistors were cemented with "plastic aluminum" to a pyrex tube which fitted snugly over the glass body of the thermistor. Leads of No. 26 copper wire were welded to the thermistor leads⁽¹⁵⁾, and brought out through the pyrex tube. The assembled unit was placed in a crucible furnace, and the heating rate of the aluminum block controlled by the

TABLE 2
Equivalent Conductances of Complexes in DMSO

Cx10 ⁴	Λ	Cx10 ⁴	Λ	Cx10 ⁴	Λ
(a) Co(NO ₃) ₂ · 4DMSO (b) CoCl ₂ · 3DMSO (c) NiCl ₂ · 3DMSO					
Eq. wt. = 495.49/2		Eq. wt. = 364.25/2		Eq. wt. = 363.99/2	
7.21	39.89	7.21	35.47	11.13	34.92
14.41	37.83	11.96	28.79	22.25	31.51
28.82	35.63	14.41	28.44	31.43	29.99
61.64	34.42	23.91	22.06	44.51	28.39
		28.83	21.11	62.86	26.80
		47.82	16.52		
(d) FeCl ₃ · 3DMSO (e) CuCl ₂ · 2DMSO (f) Cu(OAc) ₂ · DMSO					
Eq. wt. = 396.61/2		Eq. wt. = 290.75		Specific conduct-	
10.79	23.78	4.75	32.09	ance = 1.8 x 10 ⁻⁶	
21.58	19.95	9.49	26.93	ohm ⁻¹ cm ⁻¹	
29.40	19.56	18.99	22.26		
43.17	17.13	25.11	20.09		
58.80	16.86	50.22	15.17		
117.60	14.93				
(g) KI (h) CaCl ₂					
17.17	36.01	4.78	40.10		
34.34	34.70	9.55	37.01		
68.67	33.56	19.10	33.45		
		38.20	28.81		
		76.40	25.51		

setting of a Powerstat. The difference between the heating rates of the blank and the sample was followed by making the thermistor's legs of a Wheatstone bridge⁽¹¹⁾. The unbalance of the bridge was recorded by a Varian G10 recorder with 100 mv range and chart speed of 16 in./hr. The tracings as obtained are shown in Figures 1 and 2. The temperatures indicated on the individual traces were obtained by a 15 mv Brown Electronik recorder and a copper-constantan thermocouple. The samples were heated to 300°C.

4. Cryoscopic Apparatus and Procedure—The neck of a 50 ml Erlenmeyer flask was modified by sealing on a female part of a 10/30 standard taper joint to accommodate a Sargent Thermometric Element (No. S-81630). A side arm with glass stoppered cap was provided for the introduction of the sample and Teflon covered stirring bar.

The change in resistance of the thermistor during cooling was followed by a Brown Electronik recorder using a modification of the bridge described by Ewing⁽⁶⁾. As the sample began to freeze, the leads of the thermistor were switched to a 5 dial Wheatstone bridge (Rubicon Instruments, Model 1041A) and galvanometer (Leeds & Northrup, Model 2430-A) which permitted measuring the resistance to the nearest 0.1 ohm.

The equation which relates the resistance of a thermistor to temperature over short temperature ranges is:

$$\ln r_2/r_1 = B(1/T_2 - 1/T_1) \quad (\text{Eq. 1})$$

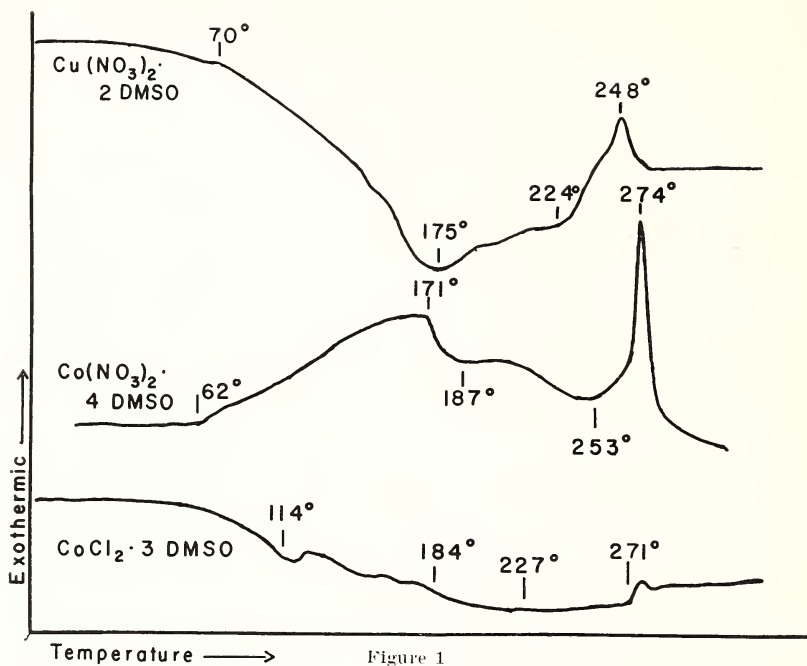


Figure 1. Differential Thermographs. Heating rates were approximately 5°C/minute.

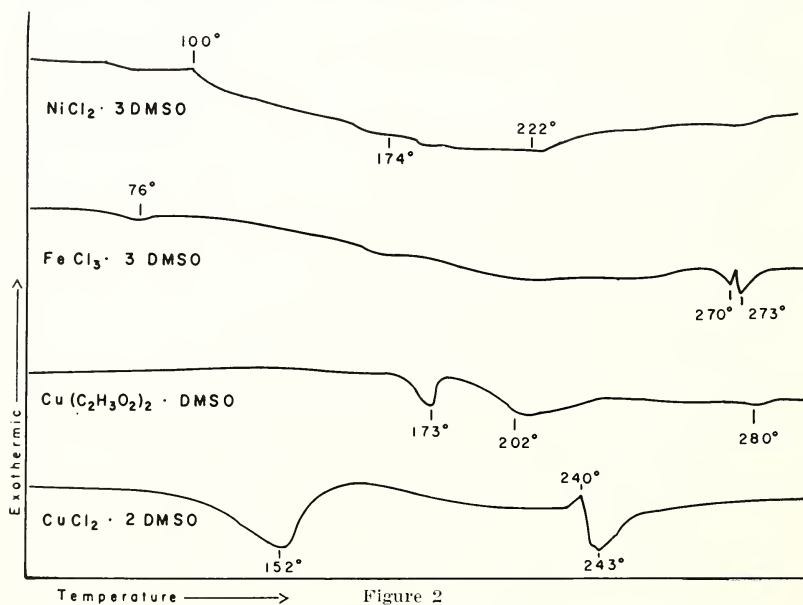


Figure 2. Differential Thermographs. Heating rates were approximately 10°C/minute.

The constant, B, for the thermistor was found to be 3380.2. Values of r and T for the freezing point of benzene (Mallinckrodt Analytical Reagent) and distilled water were substituted in Equation 1.

McMullan and Corbett⁽⁴⁰⁾ have shown that molal concentration, m , can be related to the measured resistance in the following manner:

$$m = K[\Delta r/r_0 - 1/2(\Delta r/r_0)^2] \quad (\text{Eq. 2})$$

where Δr is the change in resistance on addition of the sample to the pure solvent.

Samples of urea and naphthalene (J. T. Baker, C. P. Grade) dissolved in DMSO were used to determine $K = 6.154$.

It was found that the resistance of the thermistor gradually increased during the ten-minute interval the cooling curve was followed with the Rubicon bridge. This corresponded to the lowering of the freezing point of the solution which was being concentrated by the freezing of the solvent. To obtain a value of r which was independent of cooling rate, a plot of time versus resistance was made. A timer was started at the first indication of freezing on the chart of the Brown recorder. Two sets of data on the same sample at different cooling rates gave almost identical values at time zero by extrapolation. This value was used in calculating Δr .

No attempt was made to correct for errors introduced by supercooling of the DMSO. Refinements of this type would be justified if a more accurate bridge for the measurement of resistance were to be used. Since DMSO and the complexes are hygroscopic, the samples were pressed into pellets and transferred into the freezing point vessel inside a desiccated glove box.

The CaCl_2 and HgCl_2 used were Mallinckrodt Reagent grade while KI was J. T. Baker Reagent grade.

5. Conductance Apparatus and Procedure—The conductance apparatus consisted of an Industrial Instruments Model RC-16B bridge and cell. The constant of the latter was 0.115 cm^{-1} .

The DMSO was refluxed over calcium oxide and distilled in a Todd fractionating column at a pressure of 5-10 mm Hg. The specific conductance of the middle fraction was $3.6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

The complexes were pressed into pellets, weighed and dissolved in DMSO without contact with moist air. It is of interest to note that the addition of a drop of water to the solutions did not appreciably change the conductance. The conductance measurements were made at $25 \pm 1^\circ \text{C}$ and at 60 cycles/second.

Results and Discussion

1. Differential Thermal Analysis—The reproductions in Figures 1 and 2 of the recorder tracings are not linear in temperature nor are the heating rates identical. While there will be some base line drift in all thermograms, the breaks correspond to exothermic or endothermic changes in the sample and are of interest.

The same samples were heated on a melting point block where they could be readily observed. The usual pattern of behavior for the complex on heating was melting, bubbling or boiling or liquid in the range $160\text{-}250^\circ$,

and reappearance of a solid phase. The more interesting observations will be correlated with the thermograms in the following abbreviated manner: $\text{NiCl}_2 \cdot 3\text{DMSO}$ —Blue green solid, m.pt. 100° , dark green liquid, bright orange solid at 225° .

$\text{FeCl}_3 \cdot 3\text{DMSO}$ —Yellow solid, m.pt. 76° , yellow liquid; yellow solid changing to brown, $270\text{--}80^\circ$.

$\text{Cu}(\text{OAc})_2 \cdot \text{DMSO}$ —Blue green solid, orange then black solid, charring of acetate, 280° .

$\text{CuCl}_2 \cdot 2\text{DMSO}$ —Chartreuse solid, began melting 110° , complete by 152° , brown liquid, white solid at 243° .

$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{DMSO}$ —This formula is given this complex on basis of work by Cotton and Francis⁽¹²⁾. Blue solid, m.pt. 65° , blue green liquid, black solid at 248° . This latter is an exothermic change probably corresponding to oxidation of DMSO by nitrate.

$\text{Co}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ —Magenta solid, m.pt. 62° , purple liquid, black solid at 274° , oxidation of DMSO by nitrate. Note sharpness of peak at 274° .

$\text{CoCl}_2 \cdot 3\text{DMSO}$ —Deep blue solid, m.pt. 114° , dark blue liquid, pale blue solid by 275° .

With the exception of $\text{CuCl}_2 \cdot 2\text{DMSO}$ very little heat is absorbed in the melting process. Peaks such as the 274° peak for $\text{Co}(\text{NO}_3)_2 \cdot 4\text{DMSO}$ are much sharper at a heating rate of $10^\circ/\text{min.}$ rather than $5^\circ/\text{min.}$ ⁽¹¹⁾

2. Ions in Solution—The results of the conductance measurements are recorded in Table 2. The copper acetate complex only increased the conductivity of the DMSO from 1.1×10^{-6} to 1.8×10^{-6} ohm⁻¹ cm⁻¹ for a 2.24×10^{-3} molar solution and thus may be classed as a non-conductor.

The compounds with the exception of KI do not give a linear plot for Λ versus $\sqrt{C}$. In the case of KI the limiting equivalent conductance obtained from this plot is 38.5 compared with 38.2 ohm⁻¹ eq.⁻¹ cm² reported by Sears et al⁽¹³⁾.

The Shedlovsky equation⁽¹⁴⁾ which follows was found useful:

$$\frac{\Lambda \div \beta \sqrt{C}}{1 - \alpha \sqrt{C}} = \Lambda_o' = \Lambda_o + BC \quad (\text{Eq. 3})$$

The values of the constants, $\alpha = 0.502$ and $\beta = 35.7$ were previously evaluated⁽¹³⁾. A plot of Λ_o' versus C was used for each complex to estimate Λ_o . The plots were extrapolated to zero concentration to obtain the values of Λ_o recorded in Table 3. These plots were not linear but sufficiently close that fair extrapolations could be made.

Other types of treatment of the data such as the Fuoss-Shedlovsky equations⁽¹⁵⁾ were considered but the data is not sufficiently precise or complete to warrant such treatment. A good discussion of the problem involved is found in Chapter 17 of Hamer⁽⁷⁾.

In the above treatment, a choice had to be made in regard to the equivalent weights of solid complexes. These equivalent weights are listed in Table 2 under the empirical formula as a fraction of that formula weight. The choice of this equivalent weight was based on the assumption that the limiting equivalent conductance calculated must be reasonably close to the values obtained for KI and CaCl_2 . Also the equivalent weight

TABLE 3

Limiting Equivalent Conductances and Van't Hoff Factor
for Complexes in Dimethyl Sulfoxide

Empirical Formula	Possible ions	Λ_0	$m_0 \times 10^2$	i	Limiting Value
$\text{Co}(\text{NO}_3)_2 \cdot 4\text{DMSO}$	$\text{Co}^{2+}, 2\text{NO}_3^-$	45.5	1.028	2.61	3
			2.304	2.42	
			5.193	2.29	
$\text{CoCl}_2 \cdot 3\text{DMSO}$	$\text{Co}^{2+}, 2\text{Cl}^-$	42.5	1.303	1.19	3
$\text{NiCl}_2 \cdot 3\text{DMSO}$	$\text{Ni}^{2+}, 2\text{Cl}^-$	41	1.618	2.18	3
$\text{FeCl}_3 - 3\text{DMSO}$	$\text{FeCl}^{2+}, 2\text{Cl}^-$	31	1.921	1.65	3
$\text{CuCl}_2 \cdot 2\text{DMSO}$	$\text{CuCl}^+, \text{Cl}^-$	42.5	2.982	1.10	2
$\text{Cu}(\text{OAc})_2 \cdot \text{DMSO}$	$[\text{Cu}(\text{OAc})_2]_2$	...	1.181	1.11	1
KI	$\text{K}^+ \text{I}^-$	38.5	1.535	1.84	2
CaCl_2	$\text{Ca}^{2+}, 2\text{Cl}^-$	45.7	3.061	1.92	3
HgCl_2	HgCl_2	...	14.65	1.05	1

chosen must be related to the number of ions suggested by the cryoscopic measurements.

The Van't Hoff factor, i , as used here, is defined as the ratio of molality, m , calculated by Equation 2 to the molality, m_0 , obtained from the weights of solute and solvent. The factor, i , in infinitely dilute solutions, should approach a value equal to the number of ions per molecule. This limiting value of i , m_0 , and the Van't Hoff factor, i , are tabulated in Table 3. There is only one simplest choice of formula weight, equivalent weight and number of ions which will satisfy both the conductance and cryoscopic data. For example, a formula weight corresponding to $\text{Cu}(\text{OAc})_2 \cdot \text{DMSO}$ gave a value for i of 0.55. Since the complex is a non-conductor, it must be a dimer in solution. The number of DMSO molecules per metal atom in solution was not determined and therefore omitted in writing the "possible ions" in Table 3.

In the case of the cobalt chloride complex, if one uses $[\text{Co}(\text{DMSO})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$ as the basis for calculations, one calculates a value of about 70 for the equivalent conductance of the most dilute solution and a Van't Hoff factor of 2.38. The first value should be about 35 and the latter could not be larger than 2 for the above ions.

The equivalent conductance calculated on the basis of $\text{CoCl}^+, \text{Cl}^-$ would also be 70 and equally unsatisfactory. However the Van't Hoff factor would be 1.19 which would be satisfactory for 2 ions.

Complete dissociation into $\text{Co}^{2+}, 2\text{Cl}^-$ gives the values in Table 3. The value for i seems unreasonably low for 3 ions. Daniels and Alberty⁽⁹⁾ give values of i in graphical form for aqueous solutions but none deviate so widely from the limiting value.

A plot of $\Lambda - \Lambda_0$ versus $\sqrt{C}$ comparing the complexes with KI and CaCl_2 shows the complexes of NiCl_2 , $\text{Co}(\text{NO}_3)_2$ and FeCl_3 approaching the curve for CaCl_2 , a 2:1 salt. The data for $\text{CuCl}_2 \cdot 2\text{DMSO}$ does not approach the curve for KI as it should if it is a 1:1 salt⁽⁹⁾.

It is widely accepted⁽⁶⁾ that the blue color of Co^{2+} complexes indicates a coordination number of 4 while a pink or magenta color indicates a coordination number of 6. This is the basis for Cotton and Francis⁽⁷⁾ assignment of the structure: $[\text{Co}(\text{DMSO})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$. The blue color of $[\text{CoCl}_4]^{2-}$ is more intense than the pink color of the cation and the solid has a deep blue color. The dilute solutions used in this research still had this blue color and thus suggest the presence of the $[\text{CoCl}_4]^{2-}$ ion even in these solutions. This may indicate the presence of several ionic species in equilibrium.

Complexes, ion pair formation and ion association as discussed in Chapter 25 of Hamer⁽⁷⁾ may need to be considered in a complete explanation of the conductance and cryoscopic behavior.

McMullan and Corbett⁽¹⁰⁾ have shown that K in Equation 2 is related to the heat of fusion in the following manner:

$$K = \frac{1000 \Delta H}{\text{RBM}} \quad (\text{Eq. 4})$$

When the value for B calculated from Equation 1 and known values for the gas constant and molecular weight are taken, the heat of fusion, ΔH , calculated from Equation 4 is 41.3 calories/gram. This throws some doubt on the value of 20 calories/gram currently reported by a manufacturer of DMSO in their technical literature.

The molal freezing point constant calculated for DMSO is 4.09 degree/mole.

Conclusion

In respect to the stated objectives, differential thermal analysis was unsuccessful in detecting the stepwise loss of DMSO from the complexes because the complexes melted too low, and DMSO was not sufficiently volatile. However characteristic curves were obtained and exothermic breaks for nitrate containing complexes probably corresponding to the oxidation of DMSO by nitrate were found.

The cryoscopic and conductance measurements show that the structures suggested by Cotton and Francis for the solids do not exist in solution. The complex derived from copper acetate is a non-electrolyte in solution and is a dimer, $\text{Cu}_2(\text{OAc})_4 \cdot x \text{DMSO}$.

The complexes derived from cobalt nitrate and nickel chloride seem to dissociate completely in dilute solution while those derived from cobalt chloride, ferric chloride and copper chloride show more complicated equilibria.

This preliminary work indicates that future work involving more precise measurements at dilute concentrations coupled with spectrophotometric measurements should indicate the nature of the ions in solution.

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