

A STUDY OF SOME RHODIUM(II) ACETATE ADDUCTS

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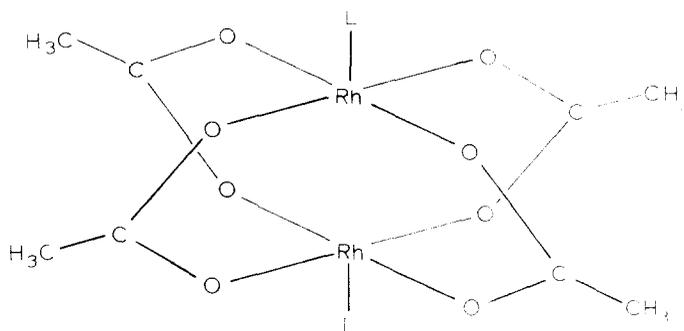
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Abstract—Several rhodium(II) acetate adducts have been prepared and their spectral and thermal properties investigated. The ligands used to form the adducts were water, diethylsulfide, dimethylsulfoxide, pyridine, triethylarsine, ammonia, and the ethyl and methyl amines. The spectral transitions of the adducts in the visible region were dependent on the nature of the ligand forming the adduct. The thermal properties of the adducts were studied using thermogravimetric analysis and differential scanning calorimetry.

INTRODUCTION

DIMERIC compounds of hydrated copper(II) and chromium(II) acetate have been known and studied for the past several years[1, 2]. These compounds are of particular interest because of their unusual magnetic properties caused by a metal-metal interaction in the dimeric species. More recently molybdenum(II) acetate has been prepared[3] and determined to have essentially the same dimeric structure as copper(II) acetate hydrate[4]. In 1962 Chernyaev *et al.*[5] prepared rhodium(II) acetate hydrate by the action of acetic acid on ammonium hexachlororhodate(III) in ethanol solution. X-ray analysis by Porai-Koshits and Antsyshkina[6] has shown that this complex also possesses a dimeric structure and has a metal-metal distance of about 2.45 Å. More recently compounds of Rh(II) of the formulas $[\text{Rh}(\text{RCOO})_2(\text{C}_2\text{H}_5\text{OH})]_2$ ($\text{R} = \text{CCl}_3, \text{CHCl}_2, \text{CH}_2\text{Cl}$,



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CF_3 , CF_2Cl , CH_2Br][7] and $[\text{Rh}(\text{CH}_3\text{COO})(\beta\text{-diketonato})\text{H}_2\text{O}]_2$ (where $\beta\text{-diketonato}$ is the anion of the enol form of acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone)[8] have been prepared.

Johnson, Hunt, and Neumann have prepared anhydrous rhodium(II) acetate by the action of glacial acetic acid on freshly precipitated rhodium(III) hydroxide [9]. These authors found that the anhydrous complex reacts with various donor-type ligands to form a 1:2 adduct. The adducts exhibited a wide variation in colors depending on the nature of the ligand. The resulting, often large blue shifts observed in these adducts offer an interesting system to study how changes in properties of the ligand alter the energy levels in the anhydrous complex. A number of additional studies have been reported on the preparation and properties of many of these adducts[10, 11, 12]. In this study ligands which show a large variation in basicity and π -bonding ability were chosen to see what effect these variations would have on the spectral and thermal properties of the rhodium complex.

EXPERIMENTAL

Preparation of adducts

For the most part the adducts were prepared by placing a few drops of the potential ligand on finely powdered anhydrous rhodium(II) acetate. The excess solvent was then pulled off in a vacuum system. The water, diethylsulfide, dimethylsulfoxide, pyridine and mono-, di- and triethylamine adducts were prepared in this manner.

The ammonia adduct was prepared by passing anhydrous ammonia over finely powdered anhydrous rhodium(II) acetate. The mono-, di-, and trimethylamine adducts were made by passing vapors of the dry amine over powdered anhydrous rhodium(II) acetate. The gaseous amine was generated by dripping a saturated sodium hydroxide solution onto the solid hydrochloride salt of the appropriate amine, and then dried by passing through calcium chloride.

The synthesis of the triethylarsine adduct was performed by adding a drop of triethylarsine to an ethyl ether solution saturated with rhodium(II) acetate under a dry nitrogen atmosphere. As the adduct was formed it dissolved in the ether resulting in a red-orange solution. The solution was allowed to sit for about 10 min until no further reaction took place. The ether solution was then decanted from the rhodium(II) acetate which always remained in excess and was allowed to evaporate to dryness. The adduct was recrystallized from absolute ethanol. The preparation of the triethylphosphine adduct was attempted in the same manner as the triethylarsine. The result was a yellow-orange oil which could not be crystallized and which gradually turned olive green.

The reaction of rhodium(II) acetate with most ligands has been found to be a reversible one which yields the anhydrous complex upon heating as evidenced by analysis, spectral, thermal, and magnetic properties. Therefore, the percent ligand analysis was performed by means of thermogravimetric analysis using the Dupont TGA 950. All thermograms were run at a heating rate of $20^\circ\text{C}/\text{min}$ and under a flowing nitrogen atmosphere except that of triethylarsine which was run under a vacuum. Table 1 gives a list of adducts prepared and their per cent composition. Those adducts being reported for the first time in this paper are starred (*). Thermogravimetric analysis proved to be a rapid method of analysis which also yielded information about the procedural decomposition temperature and the

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formation of intermediates. Typical thermograms obtained are shown in Fig. 2. The first decomposition results in loss of the adduct ligands to anhydrous rhodium(II) acetate. At a higher temperature the anhydrous rhodium(II) acetate decomposes resulting in a residue of rhodium metal as evidenced by its magnetic properties and X-ray analysis. More evidence concerning the decomposition of anhydrous rhodium(II) acetate will be published at a later date.

Table 1. Adducts of dimeric rhodium(II) acetate

Ligand	Color of adduct	Per cent ligand in adduct		Per cent Rh in adduct	
		Calcd.	Found	Calcd.	Found
H ₂ O	Green	7.5	7.2	43.1	43.6
S(CH ₂ -CH ₃) ₂	Burgandy	29.0	28.8	33.1	32.5
DMSO	Orange	26.1	26.1	34.4	34.2
NH ₃	Wine-Red	7.1	7.1	43.2	44.1
*NH ₂ CH ₃	Rose-Red	12.3	11.6 → 13.9	40.8	42.2 → 43.0
*NH(CH ₃) ₂	Rose-Red	16.95	16.7	38.7	38.9
N(CH ₃) ₃	Rose-Red	21.1	20.1	36.7	39.1
*NH ₂ CH ₂ -CH ₃	Rose-Red	16.95	20.4 (10.1 + 10.3) 15.3, 15.7	38.7	40.7 → 41.0
*NH(CH ₂ -CH ₃) ₂	Rose-Red	24.9	24.1	35.0	36.4
*N(CH ₂ -CH ₃) ₃	Purple	31.4	31.3	31.9	31.6
Pyridine	Rose-Pink	26.4	25.3	34.3	35.3
*As(CH ₂ -CH ₃) ₃	Orange-Red	42.3	42.7	26.9	†

†The sample is blown out of the boat in the vacuum.

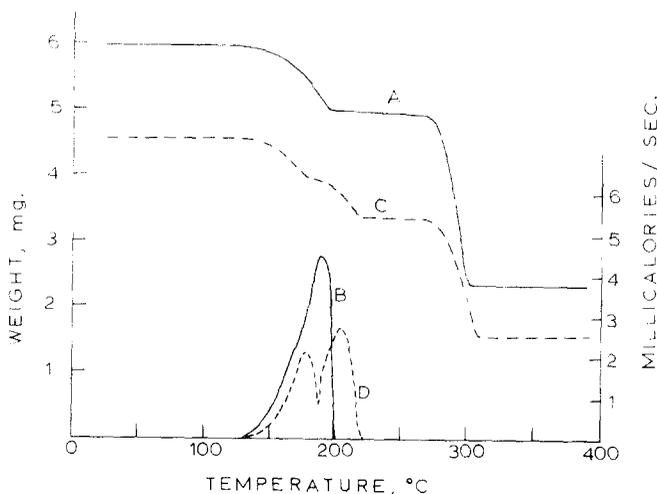


Fig. 2. A, B Thermogram and DSC curve that were obtained for the dimethylamine adduct. C, D Thermogram and DSC curve that were obtained for the dimethylsulfoxide adduct.

Spectra

Absorption spectra were obtained on the Cary Model 15 Recording Spectrophotometer in the cases where the adducts were soluble enough in the ligand to form a solution. In the other cases the spectra were obtained on the Beckman DK-2A Ratio Recording Spectrophotometer with reflectance attachment. The spectra are summarized in Table 2 and Fig. 3.

Table 2. Visible absorption and reflectance spectra of dimeric rhodium(II) acetate

Adduct	Maxima			
	λ m μ	ϵ	λ m μ	ϵ
Anhydrous	617	R*	442	
H ₂ O	584	197	441	102
S(CH ₂ -CH ₃) ₂	541	258	Sh†	
DMSO	497	317	Sh	
NH ₃	528	R	442	
NH ₂ CH ₃	519	R	Sh	
NH(CH ₃) ₂	518	R	Sh	
N(CH ₂) ₃	521	R	Sh	
NH ₂ CH ₂ -CH ₃	523	R	Sh	
NH(CH ₂ -CH ₃) ₂	530	R	Sh	
N(CH ₂ -CH ₃) ₃	540	245	458	118
Pyridine	514	R	Sh	
As(CH ₂ -CH ₃) ₃	512	R	—	

*Refers to the reflectance spectra, therefore, no ϵ values were obtained.

†Sh = shoulder.

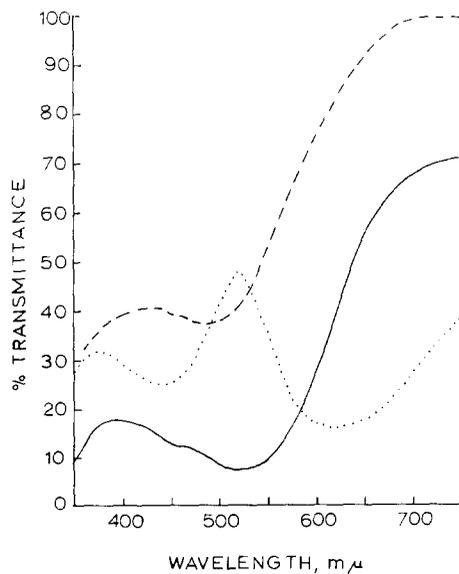


Fig. 3. ... Reflectance spectra of anhydrous rhodium(II) acetate. — Reflectance spectra of dimethylamine adduct. ----- Reflectance spectra of DMSO adduct.

Calorimetry

The heats of reaction for the endothermic decomposition of the adducts were obtained on a Perkin-Elmer DSC-1B. A heating rate of 20°C/min and a flowing nitrogen atmosphere were used in all cases except the triethylarsine which was under a vacuum. The calorimeter was standardized with the heat of fusion of indium metal (6.79 cal/g) under the same experimental conditions. The areas were measured by means of a planimeter. Figure 2 and Table 3 show the types of curves and data obtained by this method.

Table 3. Calorimetry data for adducts of dimeric rhodium(II) acetate

Adduct	ΔH kcal/mole	Ave. deviation (kcal/mole)	Procedural decomposition temperature (°C)
H ₂ O	23.2	±0.3	85
S(CH ₂ -CH ₃) ₂	27.4	±0.6	84
DMSO	29.1	±0.8	147
NH ₃	23.8	±0.4	130
NH ₂ CH ₃	—	—	120 → 155
NH(CH ₃) ₂	26.5	±0.5	135
N(CH ₃) ₃	24.7	±0.2	139
NH ₂ CH ₂ -CH ₃	—	—	115
NH(CH ₂ -CH ₃) ₂	33.1	±0.3	75
N(CH ₂ -CH ₃) ₃	27.2	±0.5	76
As(CH ₂ -CH ₃) ₃	*		~ 75
Pyridine	36.7	±0.5	170

*This sample was run under a vacuum. The heats obtained were not repeatable and are therefore not reported.

RESULTS AND DISCUSSION

The dominant reaction of anhydrous rhodium(II) acetate with donor-type ligands is their reversible addition to the coordination sphere. A slower reaction in which the acetate cage is presumably attacked in the presence of an excess of nucleophile has been observed by Johnson *et al.*[9]. We have observed this secondary reaction particularly with group five donor atom ligands. It is this secondary reaction which has prevented the preparation of pure adducts of mono-methyl- and monoethylamine. The thermal properties of these two adducts change drastically depending upon the exposure to excess ligand. The thermograms for several samples of the monomethylamine adduct are shown in Fig. 4. All the samples were prepared in the same manner but with differences of one to two minutes in the time of exposure to the methyl amine gas. Varying degrees of a secondary reaction involving the cage structure result in the formation of intermediates of yet unknown composition.

The reflectance spectra of anhydrous rhodium(II) acetate exhibits two distinct transitions at 617 and 442 m μ . A large shift of the 617 m μ transition results upon the formation of adducts while the 442 m μ transition remains essentially constant. The spectral shifts are related to the donor atoms in the general order.

$$0 < S < sp^3N < sp^2N \approx As < S = 0.$$

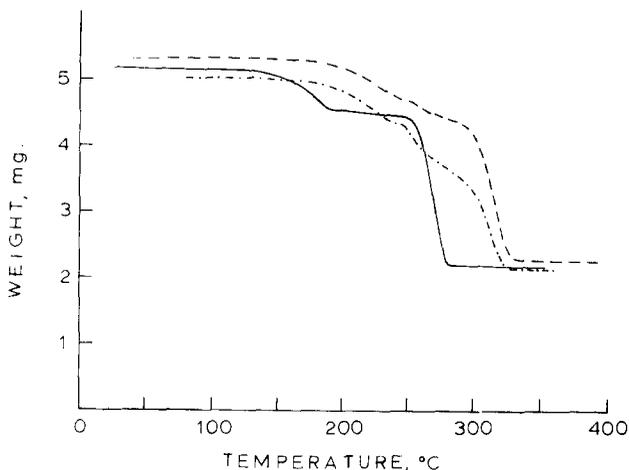


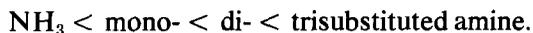
Fig. 4. Thermograms of monomethylamine adduct for different exposure times to excess gas. — Exposed methylamine gas until the green anhydrous rhodium(II) acetate just turned rose-red. ----- Adduct allowed to remain in excess methylamine gas for about 2 min. - · - · - Adduct allowed to remain in excess methylamine gas for about 5 min.

Calorimetric data presented in Table 3 for the reaction



are the average of at least three determinations expressed in kcal/mole of the adduct at the temperature of the reaction. The decomposition temperature reported is for the onset of the reaction. No attempt has been made to correct these enthalpy values to a standard temperature. This correction should be small if the reactions are comparable to the decomposition of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ to the monohydrate. In this reaction the correction $\int_{T_1}^{T_2} \Delta C_p dT$ [13] would be less than one kcal which is a good estimate of the error in the ΔH measurements using a differential scanning calorimeter.

The heats measured should be the sum of two prominent factors—bond dissociation energy and change in crystal structure. If the change in crystal structure is small then the heats measured should correlate with the donating ability of the ligand provided only sigma bonding is involved. To test this hypothesis the nitrogen donor ligand series was used. The expected Lewis basicity would be



This is the general order that is found for the rhodium(II) acetate adducts of this series except for the trisubstituted where steric and crystal effects must be large. Pyridine involves a different hybridization on nitrogen and, therefore, would not be expected to fall in this series.

Most of the adducts decompose in one step without the presence of an intermediate. Exceptions to this trend are diethylsulfide, dimethylsulfoxide, triethylarsine and diethylamine adducts which decompose in two distinct reactions. The stabilization of the mono-adduct intermediate could be due to the pi bonding ability of these ligands.

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