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EDGEWOOD ARSENAL
TECHNICAL REPORT

EATR 4231

METAL ION COMPLEXATION OF MODEL IMIDES

by

Raymond A. Mackay
Edward J. Poziomek

October 1968

U.S. ARMY MUNITIONS COMMAND

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

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EDGEWOOD ARSENAL TECHNICAL REPORT

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Defensive Research Department

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Task 1B622401A10204

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

FOREWORD

The work described in this report was authorized under Task 1B622401A10204, Detection and Warning Investigations (U). The work was started in October 1967 and completed in April 1968. The experimental data are contained in notebooks 7798 and 7908.

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Acknowledgments

Elemental analyses were performed by the Analytical Chemistry Department.

DIGEST

The purpose of this investigation was to study metal ion complexation of model imides. This was accomplished by observing the effect of metal ion complexation on the carbonyl stretching frequencies of two imides, N-cyclohexyl-N-formylacetamide and 3, 5-dioxopyrrolizidine. Two metal complexes were isolated, $(CuCl_2)_3$(N-cyclohexyl-N-formylacetamide)$_2$ and Co(3, 5-dioxopyrrolizidine)$_2$$(ClO_4)_2$.

It is concluded on the basis of analyzing the infrared absorption data that when an imide is fixed in a conformation represented by the one for 3, 5-dioxopyrrolizidine then chelate formation takes place readily. However, when free rotation around the imide C-N bonds is possible then metal complexation takes place only at one carbonyl and then at the oxygen with the highest electron density.

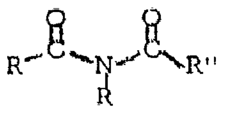
CONTENTS

METAL ION COMPLEXATION OF MODEL IMIDES

I. INTRODUCTION.

Because of current interest by the Detection Research Branch in the nature of intermediates found in metal ion catalyzed reactions of amides with electrophiles, we undertook a study of the metal ion complexation of imides. Imides are formed as a result of allowing formamides to react with acylating agents.

The effect of metal ion complexation on the infrared absorption spectra of amides has been thoroughly investigated.[1-4] The spectra of metal ion-imide complexes have also been recently examined.[5-10] These studies all involved acyclic symmetrical imides (e.g., diacetamides), and we do not believe that such studies have been reported using acyclic unsymmetrical or cyclic imides. The interesting feature is that several metal complexes are possible since four configurations (A-D) can usually be written. The only conformation which is capable of chelate formation with a metal ion is (A). The other conformations should coordinate at only one of the oxygens. (The nitrogen atom is also capable of complexing, but this does not occur for first-row transition metals.) The previous studies have shown that imides can act as both mono- and bidentate ligands, with coordination to the metal via oxygen. In the majority of cases, the imide was bidentate, complexation apparently stabilizing the conformation A. In the cases where the imide was monodentate, both oxygens were usually coordinated but to different metal atoms. We chose to examine the effect of metal ion complexation on the carbonyl stretching frequency of two imides, N-cyclohexyl-N-formylacetamide (I) and 3,5-dioxopyrrolizidine (II). Compound II has configuration A, while (I) may possess any or all of the forms shown.



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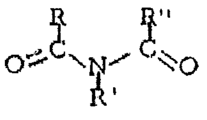

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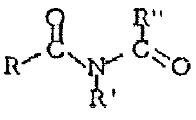

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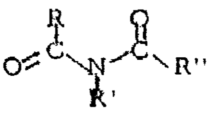

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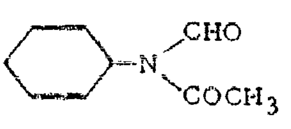

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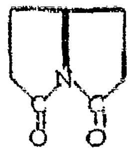


II

II. EXPERIMENTATION.

A. Preparation of Compounds.

1. N-Alkyl-N-formylacetamides.

These compounds were prepared by Hoy and Poziomek.[11]

2. 3, 5-Dioxopyrrolizidine.

A sample of this compound was obtained through the courtesy of Dr. Arnold J. Gordon, Catholic University of America. The particular sample was prepared by Micheel and Flitsch.[12]

3. $(CuCl_2)_3$(N-Cyclohexyl-N-formylacetamide)$_2$.

$CuCl_2 \cdot 2H_2O$ (1.7 grams) was dehydrated by stirring for 1 hour with 10 ml of ethyl orthoformate. The salt did not dissolve but formed an olive green slurry. Upon addition of 7 ml of N-cyclohexyl-N-formylacetamide, the slurry began to form a mustard colored polycrystalline solid. After stirring for 1 hour to insure complete reaction, the solid was filtered off, washed well with ether, and dried in a vacuum desiccator over P_4O_{10}, mp 192° to 193° decomposes.

Anal. Calcd. for $Cu_3Cl_6C_{18}H_{30}N_2O_4$: Cu, 25.6; Cl, 28.8; C, 29.2; H, 4.0; N, 3.8. Found: Cu, 25.3; Cl, 28.7; C, 28.3; H, 4.1; N, 4.0.

4. Co(3, 5-Dioxopyrrolizidine)$_2(ClO_4)_2 \cdot H_2O$.

$Co(ClO_4)_2 \cdot 6H_2O$ (0.85 gram) was dehydrated by stirring with 6 ml of ethyl orthoformate and 0.85 gram of 3, 5-dioxopyrrolizidine was then added. Stirring was allowed to continue for 1 hour. The light pink solid obtained was filtered off, washed with a small amount of ethanol, then with ether, and dried in a vacuum desiccator over P_4O_{10}, mp 272° to 276° decomposes.

Anal. Calcd. for $CoCl_2C_{14}H_{20}N_2O_{13}$: Co, 10.6; Cl 12.8; C, 30.3; H, 3.6; N, 5.1. Found: Co, 10.6; Cl, 12.4; C, 31.0; H, 3.8; N, 5.1.

B. Infrared Spectra.

A Perkin-Elmer model 521 grating spectrophotometer was employed to record the infrared spectra. The samples were prepared as neat liquids or Nujol mulls held between KRS-5 (TlI/Br) plates. The carbonyl stretching region was calibrated with polystyrene. The data are given in the table. Results for some N-alkyl amides are also included for purposes of comparison.

Table. Infrared Absorption Data

Compound	Carbonyl stretching frequency cm^{-1}[a]
n-Butylformamide[b]	1670
Sec-butylformamide[b]	1670
Cyclohexylformamide[b]	1665
N-(n-butyl)acetamide[c]	1645
N-(n-butyl)-N-formylacetamide[b]	1720, 1670
N-(sec-butyl)-N-formylacetamide[b]	1730, 1687
N-cyclohexyl-N-formylacetamide[b]	1720, 1672
$(CuCl_2)_3$(N-cyclohexyl-N-formylacetamide)$_2$[c]	1741, 1618
3,5-Dioxopyrrolizidine[c]	1770, 1688
Co(3,5-dioxopyrrolizidine)$_2(ClO_4)_2 \cdot H_2O$[c]	1733, 1642

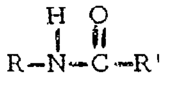
[a] Errors are ca ±3 cm^{-1}.

[b] Neat liquid.

[c] Mull.

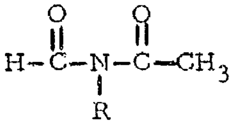
III. DISCUSSION.

The carbonyl stretching frequencies of N-substituted amides (III) are not appreciably affected by changes in R, when R is alkyl. This also holds true for imides of the N-alkyl-N-formylacetamide type (IV).



$R-N(H)-C(=O)-R'$

III



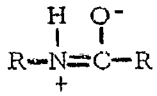
$H-C(=O)-N(R)-C(=O)-CH_3$

IV

However, the carbonyl frequency is influenced by whether R' is H or alkyl. For example, γ C=O occurs at 1670 cm^{-1} for n-butylformamide (R'=H) and 1645 cm^{-1} for N-(n-butyl)acetamide (R'=CH_3) (table). Both carbonyl stretching bands observed in spectra of N-alkyl-N-formylacetamides appear at higher frequencies than in either alkylformamides or acetamides. This is because the pair of electrons from nitrogen are delocalized over two carbonyl groups (structures V and VI) in comparison to one (structure VII) in the alkyl amide.

$H-C(O^-)=N^+-C(=O)-CH_3 \longleftrightarrow H-C(=O)-N^+=C(O^-)-CH_3$

V VI



$R-N^+(H)=C(O^-)-R$

VII

Of the pair of carbonyl absorption bands found for N-alkyl-N-formylacetamides, the higher frequency one is assigned to the formyl carbonyl. The distinction between formyl and acetyl is very evident by comparing N-(n-butyl)-N-formylacetamide with n-butylformamide and N-(n-butyl)acetamide (table). The acetyl carbonyl absorbs at lower frequencies because of the inductive and hyperconjugative effects from the methyl group. The carbonyl absorption of 3, 5-dioxopyrrolizidine is at higher frequency than in the N-alkyl-N-formylacetamides because of ring strain.* It may be noted that while both carbonyl groups are stereochemically equivalent in 3, 5-dioxopyrrolizidine, there are two carbonyl bands. This is due to the strong coupling of the two carbonyl vibrational modes.

---

* It is known that lactam carbonyl absorption is normal in unstrained rings of six carbon atoms, but shifts toward higher frequencies in smaller rings because of ring strain.[13]

For the $(CuCl_2)_3$(N-cyclohexyl-N-formylacetamide)$_2$ complex,[*] the spectrum (figure 1) shows clearly that only the acetyl groups is complexed. The formyl band at 1720 cm^{-1} in the free ligand shifts to somewhat higher frequency (1741 cm^{-1}), while the 1672 cm^{-1} acetyl band drops to 1618 cm^{-1}. Preferential coordination to the acetyl oxygen was expected since the oxygen electron density relative to formyl is higher (methyl inductive and hyperconjugative effects). In the case of Co(3, 5-dioxopyrrolizidine)$_2(ClO_4)_2$ (figure 2), both carbonyl oxygens are bound to the metal as evidenced by the shifts of both carbonyl bands to lower frequency. The absence of chelate formation using $CuCl_2$ and N-cyclohexyl-N-formylacetamide is understandable since electrostatic repulsion between the oxygen atoms would disfavor configuration A. Complexation of N-cyclohexyl-N-formylacetamide with $Co(ClO_4)_2$ gave a product that could not be purified but whose infrared absorption spectrum also indicated the presence of unchelated carbonyl.

Our studies using two model imides (I and II) appear to indicate that when an imide is fixed in conformation A, chelate formation takes place readily. However, when free rotation around the C-N bonds is possible then metal complexation takes place only at one carbonyl and then at the oxygen with the highest electron density.

IV. CONCLUSIONS.

It is concluded on the basis of analyzing the infrared absorption data that when an imide is fixed in a conformation represented by the one for 3, 5-dioxopyrrolizidine then chelate formation takes place readily. However, when free rotation around the imide C-N bonds is possible then metal complexation takes place only at one carbonyl and then at the oxygen with the highest electron density.

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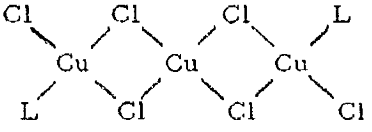
[*] A knowledge of the structure of this complex is not necessary for the purpose of this work. However, the electronic spectrum of the solid indicates a planar or tetragonal configuration about copper. Other copper compounds of the stoichiometry $(CuCl_2)_3L_2$ are known, which generally have the structure, where each copper atom is in a square planar



configuration with a weak tetragonal interaction because of a chlorine atom from another $(CuCl_2)_3L_2$ monomer unit in the layers above and below.[14, 15]

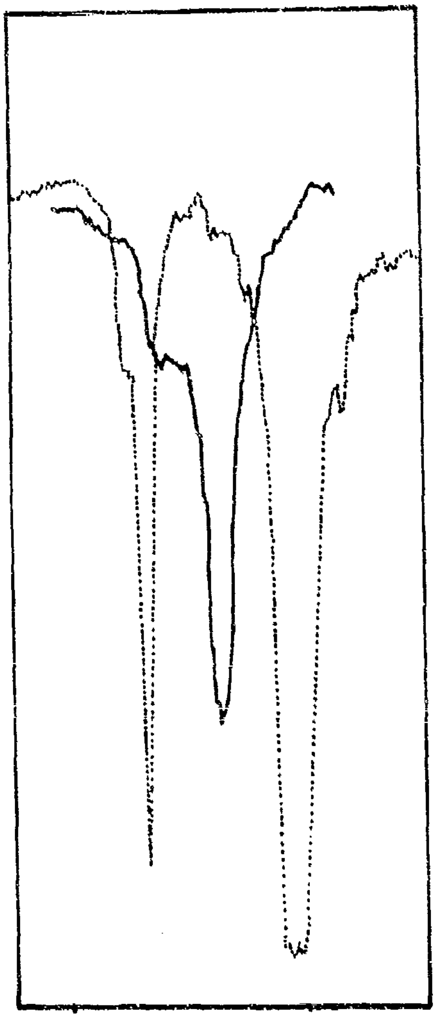


Figure 1. Infrared Absorption Spectra of $(CuCl_2)_3$(N-cyclohexyl-N-formylacetamide$)_2$ (----) and N-cyclohexyl-N-formylacetamide (———).

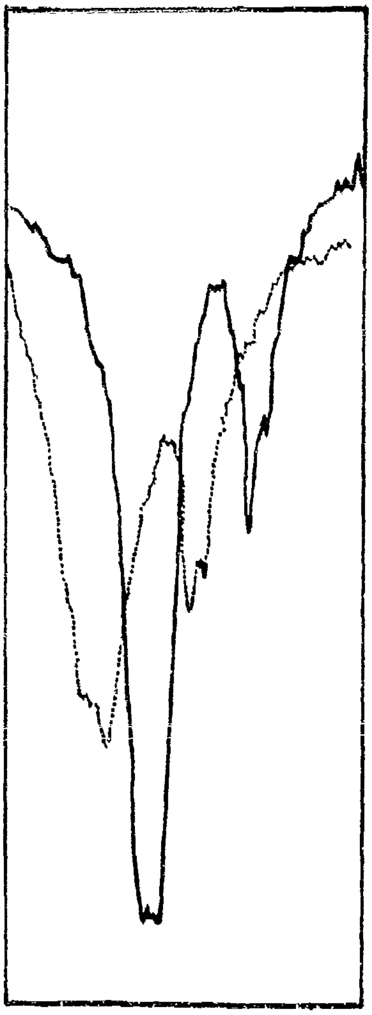


Figure 2. Infrared Absorption Spectra of Co(3, 5-dioxopyrrolizidine)$_2$ $(ClO_4)_2 \cdot H_2O$ (———) and 3, 5-Dioxopyrrolizidine (-----).

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13. ABSTRACT

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14. KEYWORDS

Metal ion complexation
3, 5-Dioxopyrrolizidine
Cobalt perchlorate
Copper chloride
Formamides
Carbonyl
Acetamide
Detection
Imides
Infrared
Chelate
N-Cyclohexyl-N-formylacetamide