



Complexes of α -pyridone with divalent transition metals
by Clifford Carlton Houk

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

Six new compounds of α -pyridone (C_5H_5NO) have been prepared. Single crystal x-ray diffraction analysis has shown one of these compounds, $CuCl_2 \cdot C_5H_5NO$, to be a chlorine bridged dimer. X-ray powder diffraction data show that three of these compounds, $MnCl_2 \cdot C_5H_5NO$, $NiCl_2 \cdot C_5H_5NO$ and $CoCl_2 \cdot C_5H_5NO$ are isomorphous and appear to have structures similar to $CuCl_2 \cdot C_5H_5NO$. Magnetic moment, solid and solution spectrophotometric data collectively indicate that all four compounds probably have a distorted tetrahedral configuration in the solid state. $CoCl_2 \cdot 3 C_5H_5NO$ has been prepared; magnetic, solid and solution spectrophotometric data support an octahedral structure for this compound. The sixth compound, $CuCl_2 \cdot 2 C_5H_5NO$ has not been assigned a specific structure; the data for this compound are inconclusive

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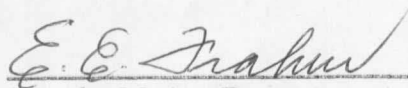
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TABLE OF CONTENTS

	Page
Vita	ii
Acknowledgement	iii
Table of Contents	iv
List of Tables	vi
List of Figures	viii
Abstract	xi
Introduction	1
Analytical Techniques	11
Experimental Procedures and Results	14
Purification of α -pyridone	14
Preparation of Anhydrous Metal (II) Chlorides	14
Solvent Purity	17
Synthesis of Dichloro-mono- α -pyridone Metal (II) Complexes	18
Synthesis of Dichloro-n- α -pyridone Metal (II) Complexes	33
Discussion	41
Dichloro-mono- α -pyridone Metal (II) Complexes	41
Dichloro-mono- α -pyridone Copper(II)	47
Dichloro-mono- α -pyridone Cobalt(II)	50
Dichloro-mono- α -pyridone Nickel(II)	57
Dichloro-mono- α -pyridone Manganese(II)	59
Dichloro-n- α -pyridone Metal (II) Complexes	62
Dichloro-bis- α -pyridone Copper(II)	63
Dichloro-tris- α -pyridone Cobalt(II)	64
Summary	67

Table of Contents (Continued)

	Page
Appendix A	69
Experimental Procedures and Results	70
Purification of Acetamide	70
Preparation and Identification of Sodium Acetamide	71
Attempted Syntheses of Bisacetamido Copper(II) Complexes	73
Direct Combination	73
Soxhlet Extraction Techniques	77
Internal Hydrolysis	78
Closed System Attempts	79
Attempted Synthesis of Bisacetamido Nickel(II) Complex	80
Attempted Synthesis of Bisbenzamido Copper(II) Complex	81
Discussion	82
Literature Cited	90

LIST OF TABLES

Table No.	Title	Page
I.	Cu(II) Compounds with Subnormal Magnetic Moments	2
II.	Cu(II) Compounds with Normal Magnetic Moments	8
III.	Ultraviolet Spectral Bands for α -pyridone	17
IV.	$MCl_2 \cdot 1 C_5H_5NO$ Elemental Analyses	19
V.	$MCl_2 \cdot 1 C_5H_5NO$ Magnetic Susceptibilities and Moments	20
VI.	$MCl_2 \cdot 1 C_5H_5NO$ Powder Diffraction Data	20
VII.	$MCl_2 \cdot 1 C_5H_5NO$ Ultraviolet Absorption Bands and Molar Absorptivities	21
VIII.	$MCl_2 \cdot 1 C_5H_5NO$ Visible Absorption Bands and Molar Absorptivities	27
IX.	$MCl_2 \cdot 1 C_5H_5NO$ Molecular Weight Determinations	32
X.	$CuCl_2 \cdot 2 C_5H_5NO$ and $CoCl_2 \cdot 3 C_5H_5NO$ Elemental Analyses	33
XI.	$CuCl_2 \cdot 2 C_5H_5NO$ and $CoCl_2 \cdot 3 C_5H_5NO$ Powder Diffraction Data	34
XII.	$CuCl_2 \cdot 2 C_5H_5NO$ and $CoCl_2 \cdot 3 C_5H_5NO$ Ultraviolet Spectral Bands	34
XIII.	$CuCl_2 \cdot 2 C_5H_5NO$ and $CoCl_2 \cdot 3 C_5H_5NO$ Visible Spectral Bands	37
XIV.	$CuCl_2 \cdot 2 C_5H_5NO$ and $CoCl_2 \cdot 3 C_5H_5NO$ Magnetic Susceptibilities and Moments	40
XV.	Infrared Band Assignments $MCl_2 \cdot 1 C_5H_5NO$ Complexes	42
XVI.	Visible Spectral Bands of Known Chlorine-Bridged Cu(II) Compounds	49
XVII.	Room Temperature Magnetic Moments for Co(II) Compounds	51
XVIII.	Visible Solution Spectra Bands for Known Co(II) Compounds	53

List of Tables (Continued)

Table No.	Title	Page
XIX.	Diffuse Reflectance Bands of Known Co(II) Compounds	55
XX.	Magnetic Moments of Known Ni(II) Compounds	57
XXI.	Infrared Bands for $\text{CuCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{NO}$ and $\text{CoCl}_2 \cdot 3 \text{C}_5\text{H}_5\text{NO}$. . .	63
XXII.	Sodium Acetamide Analyses	73
XXIII.	Sodium Acetamide Solubilities	73
XXIV.	Solvents Used in Attempted Syntheses	74
XXV.	Results of Selected Bisacetamido Copper(II) \cdot 1 Solvent Synthesis	75
XXVI.	Closed System Results	80
XXVII.	Suspected Reaction Products	82

LIST OF FIGURES

Figure No.	Title	Page
1.	$\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ Structure	3
2.	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 1 \text{H}_2\text{O}$ Structure	5
3.	Observed Carboxylate Bidentate Binuclear Configurations	6
4.	$\text{Cu}(\text{HCOO})_2 \cdot 4 \text{H}_2\text{O}$ Structure	7
5.	Carboxylate and Acetamido Group Similarity	9
6.	Possible Bidentate Ligands	9
7.	Infrared Spectrum of α -pyridone	14
8.	Ultraviolet Spectrum of α -pyridone in H_2O	15
9.	Ultraviolet Spectrum of α -pyridone in $\text{C}_2\text{H}_5\text{OH}$	15
10.	Ultraviolet Spectrum of α -pyridone in CH_3CN	16
11.	Ultraviolet Spectrum of α -pyridone in $\text{HCON}(\text{CH}_3)_2$	16
12.	Visible Absorption Spectrum of $\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in H_2O	22
13.	Visible Absorption Spectrum of $\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in $\text{C}_2\text{H}_5\text{OH}$	22
14.	Visible Absorption Spectrum of $\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in CH_3CN	23
15.	Visible Absorption Spectrum of $\text{CoCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in H_2O	23
16.	Visible Absorption Spectrum of $\text{CoCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in $\text{C}_2\text{H}_5\text{OH}$	24
17.	Visible Absorption Spectrum of $\text{CoCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in CH_3CN	24
18.	Visible Absorption Spectrum of $\text{NiCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in H_2O	25
19.	Visible Absorption Spectrum of $\text{NiCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in $\text{C}_2\text{H}_5\text{OH}$	25
20.	Visible Absorption Spectrum of $\text{NiCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ in $\text{HCON}(\text{CH}_3)_2$	26

List of Figures (Continued)

Figure No.	Title	Page
21.	Diffuse Reflectance Spectrum of $\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	28
22.	Diffuse Reflectance Spectrum of $\text{CoCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	28
23.	Diffuse Reflectance Spectrum of $\text{NiCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	29
24.	Diffuse Reflectance Spectrum of $\text{MnCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	29
25.	Infrared Spectrum of $\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	30
26.	Infrared Spectrum of $\text{CoCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	31
27.	Infrared Spectrum of $\text{NiCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	31
28.	Infrared Spectrum of $\text{MnCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	32
29.	Visible Absorption Spectrum of $\text{CuCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{NO}$ in H_2O	35
30.	Visible Absorption Spectrum of $\text{CuCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{NO}$ in CH_3CN	35
31.	Visible Absorption Spectrum of $\text{CoCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{NO}$ in H_2O	36
32.	Visible Absorption Spectrum of $\text{CoCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{NO}$ in $\text{C}_2\text{H}_5\text{OH}$	36
33.	Visible Absorption Spectrum of $\text{CoCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{NO}$ in CH_3CN	37
34.	Diffuse Reflectance Spectrum of $\text{CuCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{NO}$	38
35.	Diffuse Reflectance Spectrum of $\text{CoCl}_2 \cdot 3 \text{C}_5\text{H}_5\text{NO}$	38
36.	Infrared Spectrum of $\text{CuCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{NO}$	39
37.	Infrared Spectrum of $\text{CoCl}_2 \cdot 3 \text{C}_5\text{H}_5\text{NO}$	40
38.	α -pyridone ($\text{C}_5\text{H}_5\text{NO}$) Structure	42
39.	Unit Cell Relationship Between $\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ and $\text{CoCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	45

List of Figures (Continued)

Figure No.	Title	Page
40.	$\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$ Structure	46
41.	Infrared Spectrum of Acetamide	70
42.	Infrared Spectrum of Sodium Acetamide	72
43.	CuCl_2 Structure	83
44.	Visible Absorption Spectrum of Blue-Green Crystals from $\text{CuCl}_2\text{-NaCH}_3\text{CONH-C}_5\text{H}_5\text{N}$ System	84
45.	Infrared Spectrum of Blue-Green Crystals from $\text{CuCl}_2\text{-NaCH}_3\text{CONH-C}_5\text{H}_5\text{N}$ System	85
46.	Infrared Spectrum of Blue-Green Crystals from $\text{CuCl}_2\text{-C}_5\text{H}_5\text{N}$ Alone	86
47.	Infrared Spectrum of Pyridine	86

ABSTRACT

Six new compounds of α -pyridone (C_5H_5NO) have been prepared. Single crystal x-ray diffraction analysis has shown one of these compounds, $CuCl_2 \cdot 1 C_5H_5NO$, to be a chlorine bridged dimer. X-ray powder diffraction data show that three of these compounds, $MnCl_2 \cdot 1 C_5H_5NO$, $NiCl_2 \cdot 1 C_5H_5NO$ and $CoCl_2 \cdot 1 C_5H_5NO$ are isomorphous and appear to have structures similar to $CuCl_2 \cdot 1 C_5H_5NO$. Magnetic moment, solid and solution spectrophotometric data collectively indicate that all four compounds probably have a distorted tetrahedral configuration in the solid state. $CoCl_2 \cdot 3 C_5H_5NO$ has been prepared; magnetic, solid and solution spectrophotometric data support an octahedral structure for this compound. The sixth compound, $CuCl_2 \cdot 2 C_5H_5NO$, has not been assigned a specific structure; the data for this compound are inconclusive.

INTRODUCTION

The Cu(II) ion ($3d^9$) normally has one unpaired electron in the 3d subshell. Cu(II) has a calculated spin only magnetic moment of 1.73 Bohr Magnetons (B.M.) regardless of the bond type of its compounds. Actually, the observed values of the magnetic moment are 1.9 to 2.2 B.M. for most Cu(II) compounds with ionic or weak covalent bonds and 1.72 to 1.82 B.M. for compounds with strong covalent bonds (1). Thus, Cu(II) compounds with magnetic moments lower than 1.73 B.M. are unusual. Several Cu(II) compounds with unusual magnetic moments have been prepared and investigated (Table I).

Magnetic moments are a measure of the number of unpaired electrons per atom or molecule. Paramagnetic substances contain one or more unpaired electrons per atom or molecule; diamagnetic substances have no unpaired electrons. Therefore, a subnormal magnetic moment means the number of unpaired electrons per atom or molecule has decreased; electron interaction between unpaired d electrons on closely oriented Cu atoms or unpaired d electrons with electrons from the ligand will decrease the number of unpaired electrons. Therefore, Cu(II) compounds with unusual magnetic moments must provide a pathway that permits such electron interaction.

Two possible pathways for electron interaction have been proposed; metal-metal interaction (bond formation) by direct overlap of d orbitals on closely oriented Cu atoms and a super exchange mechanism involving Cu d orbitals and $p\pi$ or $p\sigma$ orbitals of the ligand. If the first pathway were correct, one would expect the magnetic moment to be dependent upon the

Table I

Cu(II) Compounds with Subnormal Magnetic Moments

Ligand	Formula	B.M. Magnetic Moment ^a
Acetate ion	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 1 \text{H}_2\text{O}$	1.43
Acetate ion	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 1 \text{C}_5\text{H}_5\text{N}$	1.43
Formate ion	$\text{Cu}(\text{HCOO})_2 \cdot 4 \text{H}_2\text{O}$	1.64
Benzoate ion	$\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 4 \text{H}_2\text{O}$	1.40
Pyridine-N-oxide	$\text{CuCl}_2 \cdot 1 \text{C}_5\text{H}_5\text{NO}$	0.85
Pyridine-N-oxide	$\text{CuCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{NO}$	0.63
Quinoline-N-oxide	$\text{CuCl}_2 \cdot 1 \text{C}_9\text{H}_7\text{NO}$	0.36
Butyrate ion	$\text{Cu}(\text{C}_3\text{H}_7\text{COO})_2 \cdot \text{H}_2\text{O}$	1.35
Oxalate ion	$\text{Cu}(\text{CO}_2\text{CO}_2)$	1.20
Succinate ion	$\text{Cu}[\text{CO}_2(\text{CH}_2)_2\text{CO}_2]_2 \cdot 2 \text{H}_2\text{O}$	1.40
N,N-Dimethylacetamide	$\text{Cu}(\text{ClO}_4)_2 \cdot [\text{CH}_3\text{CON}(\text{CH}_3)_2]_4 \cdot \text{H}_2\text{O}$	1.57
Triphenylarsine oxide	$\text{CuBr}_2 \cdot [(\text{C}_6\text{H}_5)_3\text{AsO}]_2$	1.56
1,2,4 Triazole	$\text{CuSO}_4 \left(\begin{array}{c} \text{N} - \text{N} \\ // \quad \backslash \\ \text{HC} \quad \quad \text{CH} \\ \backslash \quad / \\ \text{N} \\ \\ \text{H} \end{array} \right) \cdot 4 \text{H}_2\text{O}$	1.62

^aRoom temperature

distance between interacting Cu atoms. If there were bond formation between Cu atoms, it would be one of three types: σ ($d_{z^2} - d'z^2$), π ($dxz - d'xz$, $dyz - d'yz$) or δ ($d_{xy} - d'xy$, $dx^2 - y^2 - d'x^2 - y^2$). In a tetragonally distorted system (copper(II) acetate), π bonds are not likely because the orbitals in

question are lowest in energy of the 3d orbitals. The dx^2-y^2 level has the highest energy, but overlap between dz^2 orbitals should be greater and therefore the bonding will be determined by competition between $dz^2(\sigma)$ and $dx^2-y^2(\delta)$ orbitals. Ross and Yates (2), Ross (3) and Royer (4) favor δ bond formation. Forster and Ballhausen (5) favor σ bond formation. If a super exchange mechanism were correct, one would expect the magnetic moment to be dependent upon the electron density of the $p\pi$ and $p\sigma$ orbitals of the ligand. Schluetter (6), Kokozka (7,8) and Hansen and Ballhausen (9) state that interacting Cu atoms are only weakly coupled by d orbital overlap and suggest a super exchange pathway instead.

Super exchange was also favored in a study by Hatfield and Pascal (10) who synthesized and investigated homologs of $CuCl_2 \cdot 1C_5H_5NO$ (C_5H_5NO is pyridine-N-oxide). $CuCl_2 \cdot 1C_5H_5NO$ has been prepared and shown to be an oxygen bridged binuclear (dimeric) compound, with the structure shown in Figure 1, by Morrow, Schaefer and Smith (11). The Cu

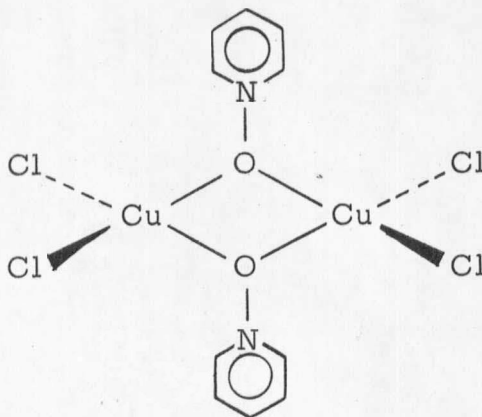


Figure 1. $CuCl_2 \cdot 1C_5H_5NO$ Structure

atoms and bridging oxygen atoms lie in the same plane; the distance between bridge Cu atoms is $3.23 \pm (0.01 \text{ \AA})$. The environment of each Cu atom is a distorted tetrahedron. Some studies listing M-M distances do not give standard deviations (uncertainties) for bond lengths. M-M distances that appear in the discussion without accompanying uncertainties may vary as much as $\pm 0.1 \text{ \AA}$. This compound has a magnetic moment of 0.85 B.M. at room temperature. The 3.23 \AA distance between the Cu atoms makes direct d orbital interaction less likely and suggests a super exchange mechanism might be functioning. Hatfield and Pascal have substituted functional groups with different electron withdrawing and electron releasing properties in the four position of pyridine-N-oxide. The new ligands were then used to prepare a series of $\text{CuCl}_2 \cdot 1\text{R-C}_5\text{H}_4\text{NO}$ compounds (R = substituted group). They assumed the products were isostructural (oxygen bridged dimers) to $\text{CuCl}_2 \cdot 1\text{C}_5\text{H}_5\text{NO}$. The magnetic moments of their compounds decreased as the electron releasing ability of the substituent increased. The decrease of the magnetic moment indicated the electron density in the π orbitals of the bridging oxygen atoms increased and permitted increased interaction between the unpaired Cu d electrons and the oxygen π electrons. They concluded that a super-exchange mechanism was favored because the amount of overlap of the d orbitals should not be affected by ring substituents. Muto and Jonassen (12) have used mono, di and trisubstituted pyridine-N-oxides to prepare copper (II) halide complexes. Their results confirm those of Hatfield and Pascal; the magnetic moments of the compounds were dependent

