complexing by ONTMP in comparison to NTMP. The log β_{ML} values for NTMP[4] are 6.68 and 6.73 (1.0 M KNO_3, 25°), respectively, while corresponding values for ONTMP are 5.67 and 8.29. This reflects a small decrease in calcium complex stability and a sizable increase for magnesium relative to the parent acid.

The interaction between cationic size and charge *vs.* anionic size, configuration, and charge must play an important role in establishing the relative values of the Ca^{2+} *vs.* Mg^{2+} stability constants with the various ligands. Participation by nitrogen as a coordinating site is apparently of major importance in NTA complexes, but not in NTMP complexes since nitrogen itself is geometrically excluded as a coordinating site in N-oxides. With NTMP and ONTMP the electrostatic attraction of the six negative charges probably provides the primary binding force.

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Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas

Properties of Some Copper(II) and Zinc(II) N-Oxide and β-Diketone Complexes

By M. R. KIDD, R. S. SAGER, and W. H. WATSON

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The unit cell dimensions, space group, and molecular weight have been determined for a number of copper(II) and zinc(II) N-oxide and β-diketone complexes. Pyridine N-oxide, 2-picoline N-oxide, 3-picoline N-oxide, 4-picoline N-oxide, and 2,6-lutidine N-oxide were used as ligands and all except 2-picoline N-oxide formed 1:1 binuclear copper(II) complexes with abnormally low magnetic moments. The 2-picoline N-oxide is postulated to be trinuclear of formula Cu_3Cl_6 (2-picoline N-oxide)$_2\cdot 2H_2O$. All N-oxides except 2-picoline N-oxide yielded two 2:1 complexes with copper(II). The green form of dichlorobis(4-picoline N-oxide)copper(II) is required by space group considerations to be *trans* square-planar. The yellow form of dichlorobis(2,6-lutidine N-oxide)copper(II) is distorted and is approximately halfway between *cis* square-planar and tetrahedral. It is postulated that all green 2:1 complexes can be described by an approximate *trans*-square-planar geometry and all yellow 2:1 complexes by a distorted tetrahedral configuration. The magnetic properties of the 2:1 complexes are normal. The N-oxide ligands form only a 2:1 complex with zinc(II). Zinc(II) and copper(II) complexes were prepared with trifluoroacetylacetone (TFA), hexafluoroacetylacetone (HFA), and benzoyltrifluoroacetone (BTFA). The complexes $(TFA)_2Cu^{II}$, $(TFA)_2Cu^{II}(DMSO)$, $[(TFA)_2Zn^{II}]_3$, $(TFA)_2Zn^{II}(DMSO)_2$, $(HFA)_2Cu^{II}\cdot 2H_2O$, $(HFA)_2Zn^{II}\cdot 2H_2O$, and $(BTFA)_2Cu^{II}$ were prepared and characterized. The geometry of a number of these complexes is determined by space group considerations. The molecular weight and X-ray data indicate the $(TFA)_2Zn^{II}$ complex must exist as a trimer.

Introduction

There have been a number of studies on copper(II) N-oxide complexes. The magnetic susceptibility of many of these complexes has been reported[1-6] and the crystal structures of dichloro(pyridine N-oxide)copper(II),[7] $C_5H_5NOCuCl_2$, and dichlorobis(pyridine N-oxide)copper(II),[8] $(C_5H_5NO)_2CuCl_2$, have been reported. Most of these studies have been concerned with the existence of binuclear complexes with strong metal–metal interactions. Spectral studies have been used to make predictions concerning the structure and bonding in 1:1 and 2:1 N-oxide complexes. We have been interested in the types of interactions that are possible in N-oxide systems and in finding suitable complexes for single-crystal electron spin resonance studies. Because of the existence of strong dipole–dipole interactions, it is necessary to dilute magnetically the copper complexes in an isomorphous diamagnetic host.

We have collected physical data on a number of N-oxide compounds and wish to report the results for some copper(II) and zinc(II) complexes. The data on a few β-diketone complexes have also been included.

We have completed a three-dimensional refinement of the structure of bis[dichloro(pyridine N-oxide)-copper(II)] and the yellow form of dichlorobis(2,6-lutidine N-oxide)copper(II). We are initiating structural studies on several other complexes in this series. Epr studies of dichlorobis(2,6-lutidine N-oxide)copper(II) diluted in dichlorobis(2,6-lutidine N-oxide)zinc(II) show well-resolved hyperfine structure and indicate a significant concentration of spin density on the N-oxide ligand. These results will be reported when studies are complete.

Experimental Section

Materials.—Pyridine N-oxide and 2,6-lutidine N-oxide were obtained from K & K Chemical Laboratories and Reilly Tar & Chemical. Practical grade picoline N-oxides were obtained from Reilly Tar & Chemical and Matheson Coleman and Bell. The picoline N-oxides were purified by vacuum distillation and

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recrystallization. Trifluoroacetylacetone, hexafluoroacetylacetone, and benzoyltrifluoroacetone were obtained from Pierce Chemical Co. Copper(II) chloride dihydrate and zinc(II) chloride were obtained from Allied Chemical Co. Analytical grade dimethyl sulfoxide (DMSO), J. T. Baker Chemical Co., and absolute ethanol, U. S. Industrial Chemical, were used without further purification. Analytical reagent grade toluene was dried over calcium hydride.

Dichloro(N-oxide)copper(II) Complexes.—These complexes were prepared by mixing ethanol solutions of the N-oxide and copper(II) chloride dihydrate in a 1:1 mole ratio. The complexes precipitated immediately. Melting and decomposition temperatures are uncorrected. Unless thermal analysis data were used to distinguish between the processes, they are listed as melting points.

Dichloro(pyridine N-oxide)copper(II), (PyNO)CuCl$_2$.—Yellow-green crystals were obtained, mp 241°. *Anal.* Calcd for Cu(C_5H_5NO)Cl_2: Cu, 27.68; C, 26.16; H, 2.20; N, 6.10. Found: Cu, 27.98; C, 26.22; H, 2.22; N, 6.07.

$Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$ (?).—When 2-picoline N-oxide was mixed with copper(II) chloride dihydrate in a 1:1 mole ratio, yellow-green crystals were obtained. These crystals decomposed at 232–235°. Chemical analyses on three different preparations did not check with the formulation of a 1:1 complex. The analytical data were more consistent with a formulation of three copper(II) chloride units, two 2-picoline N-oxide units, and two waters of hydration. Thermal analysis gave a small endothermic peak at 150–160° (dehydration) and two exothermic peaks (decomposition) centered at 235°. *Anal.* Calcd for $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$: Cu, 28.9; C, 22.0; H, 2.73; N, 4.27. Found: Cu, 27.62; C, 22.12; H, 2.71; N, 4.14.

Dichloro(3-picoline N-oxide)copper(II), (3-PicNO)CuCl$_2$.—Yellow-green crystals were obtained and were recrystallized from ethanol. The crystals decomposed at 238°. *Anal.* Calcd for $Cu(C_6H_7NO)Cl_2$: Cu, 26.09; C, 29.59; H, 2.90; N, 5.75. Found: Cu, 25.92; C, 29.33; H, 3.10; N, 5.48. Thermal analysis gave an exothermic peak beginning at 230° indicating decomposition occurs rather than melting.

Dichloro(4-picoline N-oxide)copper(II), (4-PicNO)CuCl$_2$.—Green crystals were obtained and were recrystallized from absolute methanol, mp 214°. *Anal.* Calcd for $Cu(C_6H_7NO)Cl_2$: Cu, 26.09; C, 29.59; H, 2.90; N, 5.75. Found: Cu, 26.68; C, 29.56; H, 2.89; N, 5.63.

Dichloro(2,6-lutidine N-oxide)copper(II), (2,6-LuNO)CuCl$_2$.—Yellow crystals immediately formed but were soon replaced by dark green crystals. The complex was recrystallized from absolute ethanol, mp 215°. *Anal.* Calcd for $Cu(C_7H_9NO)Cl_2$: Cu, 24.67; C, 32.64; H, 3.52; N, 5.44. Found: Cu, 24.75; C, 32.83; H, 3.55; N, 5.40. The molecular weight determined at a concentration of 0.393 g/l. indicates the complex exists as a dimer in solution.

Dichlorobis(N-oxide)copper(II) Complexes.—These complexes were prepared by dissolving the dichloro(N-oxide)copper(II) complexes in ethanol and adding an excess of ligand. The solutions were then evaporated and the crystals recovered.

Dichlorobis(pyridine N-oxide)copper(II), (PyNO)$_2$CuCl$_2$.—A yellow crystalline compound was obtained, mp 172–174°. *Anal.* Calcd for $Cu(C_5H_5NO)_2Cl_2$: Cu, 19.57; C, 36.99; H, 3.10; N, 8.63. Found: C, 36.94; H, 3.11; N, 8.63. Thermal analysis indicated no decomposition below 160°.

Dichlorobis(2-picoline N-oxide)copper(II), (2-PicNO)$_2$CuCl$_2$.—Light green crystals immediately precipitated, but after a period of several hours were replaced by dark green crystals, mp 149–150°. *Anal.* Calcd for $Cu(C_6H_7NO)_2Cl_2$: Cu, 18.01; C, 40.86; H, 4.00; N, 7.94. Found: Cu, 17.82; C, 40.81; H, 4.10; N, 7.84. The molecular weight was determined at a concentration of 5.512 g/l.

Dichlorobis(3-picoline N-oxide)copper(II), (3-PicNO)$_2$CuCl$_2$.—Yellow crystals were obtained which turned green at 100–110° and then melted at 145–146°. After several days the yellow crystals turned green, mp 145–146°. *Anal.* Calcd for $Cu(C_6H_7NO)_2Cl_2$: Cu, 18.02; C, 40.86; H, 4.00; N, 7.94. Found: C, 40.81; H, 4.03; N, 7.86. Thermal analysis gave an endothermic peak at 146° indicating melting rather than decomposition.

Dichlorobis(4-picoline N-oxide)copper(II), (4-PicNO)$_2$CuCl$_2$.—A mixture of yellow and green crystals was obtained upon evaporation of an ethanol solution containing dichloro(4-picoline N-oxide)copper(II) and an excess of 4-picoline N-oxide. The yellow crystals were converted to the green form between 73 and 113°. The green form decomposed at 176°. *Anal.* Calcd for $Cu(C_6H_7NO)_2Cl_2$: Cu, 18.02; C, 40.86; H, 4.00; N, 7.94. Found (green form): Cu, 18.36; C, 40.36; H, 3.89; N, 7.82. No analytical data are available for yellow form.

Dichlorobis(2,6-lutidine N-oxide)copper(II), (2,6-LuNO)$_2$CuCl$_2$.—A green solution at room temperature yielded yellow crystals after a few minutes. On recrystallization from absolute ethanol, yellow and yellow-green crystals were obtained. The two compounds melted around 199°, but X-ray data indicate they belong to different crystal classes. Thermal analysis of the two compounds showed no transition below their melting points. The yellow form gave an endothermic (melting) peak at 198° and an exothermic peak (decomposition) beginning at 230°. The green form gave an endothermic peak at 201° and an exothermic peak beginning at 240°. *Anal.* Calcd for $Cu(C_7H_9NO)_2Cl_2$: Cu, 16.69; C, 44.16; H, 4.77; N, 7.36. Found: yellow form: Cu, 16.57; C, 43.87; H, 4.74; N, 7.32. Green form: Cu, 16.57; C, 44.11; H, 4.76; N, 7.29. The molecular weights of the two forms were determined at concentrations of 2.030 and 2.225 g/l., respectively.

Dichlorobis(N-oxide)zinc(II) Complexes.—The zinc complexes were prepared by mixing ethanol solutions of the metal chloride and the ligand in a mole ratio of 1:2. The complexes were filtered, usually washed with ethanol and acetone, and dried over calcium chloride. The same zinc complexes were obtained when the zinc(II) and ligand were mixed in a 1:1 mole ratio.

Dichlorobis(pyridine N-oxide)zinc(II), (PyNO)$_2$ZnCl$_2$.—The compound was isolated as a white crystalline material, mp 160–162°. *Anal.* Calcd for $Zn(C_5H_5NO)_2Cl_2$: Zn, 19.52; C, 36.79; H, 3.09; N, 8.58. Found: Zn, 20.03; C, 36.58; H, 3.02; N, 8.46. The molecular weight was determined at a concentration of 5.264 g/l.

Dichlorobis(2-picoline N-oxide)zinc(II), (2-PicNO)$_2$ZnCl$_2$.—The compound was isolated as a white crystalline compound, mp 139–140°. *Anal.* Calcd for $Zn(C_6H_7NO)_2Cl_2$: Zn, 18.44; C, 40.65; H, 3.98; N, 7.90. Found: Zn, 18.11; C, 39.19; H, 3.90; N, 7.38.

Dichlorobis(3-picoline N-oxide)zinc(II), (3-PicNO)$_2$ZnCl$_2$.—This compound was isolated as a white crystalline compound, mp 126–128°. *Anal.* Calcd for $Zn(C_6H_7NO)_2Cl_2$: Zn, 18.44; C, 40.65; H, 3.98; N, 7.90. Found: Zn, 18.00; C, 40.53; H, 4.01; N, 7.88. The molecular weight was determined at a concentration of 0.800 g/l.

Dichlorobis(4-picoline N-oxide)zinc(II), (4-PicNO)$_2$ZnCl$_2$.—This compound was isolated as a white crystalline material, mp 193–195°. *Anal.* Calcd for $Zn(C_6H_7NO)_2Cl_2$: Zn, 18.44; C, 40.65; H, 3.98; N, 7.90. Found: Zn, 17.84; C, 40.58; H, 3.91; N, 7.92. The molecular weight was determined at a concentration of 3.550 g/l.

Dichlorobis(2,6-lutidine N-oxide)zinc(II), (2,6-LuNO)$_2$ZnCl$_2$.—This compound was isolated as a white crystalline material, mp 254–255°. *Anal.* Calcd for $Zn(C_7H_9NO)_2Cl_2$: Zn, 17.90; C, 43.95; H, 4.74; N, 7.32. Found: Zn, 16.60; C, 43.61; H, 4.74; N, 7.24. The molecular weight was determined at a concentration of 4.488 g/l.

Bis(trifluoroacetylacetonato)copper(II), (TFA)$_2$Cu.—A concentrated solution of ammonium hydroxide, 0.55 ml, was added to an aqueous suspension of 1.25 g of 1,1,1-trifluoroacetylacetone (TFA). The slate-blue complex precipitated immediately on adding an aqueous solution of 0.549 g of copper(II) chloride. The complex was recrystallized from hot toluene, mp 197° (lit. 189°[9]

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and 200°[10]). *Anal.* Calcd for $Cu(C_5F_3H_4O_2)_2$: Cu, 17.19; C, 32.48; H, 2.18. Found: Cu, 17.05; C, 32.42; H, 2.19. The molecular weight was determined at a concentration of 13.245 g/l.

Bis(hexafluoroacetylacetonato)copper(II) Dihydrate, $(HFA)_2Cu\cdot 2H_2O$.—A blue complex was prepared in the same manner as the trifluoroacetylacetonate complex, mp 130°. A second blue-green complex also was obtained, mp 207°. The literature[11] lists a melting point of 95–98° for the purple anhydrous complex and 134–136° for the dihydrate. *Anal.* Calcd for $Cu(C_5HF_6O_2)_2\cdot 2H_2O$: Cu, 12.4; C, 23.4; H, 1.17. Found: blue-green form: Cu, 13.17; C, 23.51; H, 1.68. The blue complex (mp 130°) was identified as the dihydrate reported in the literature, and no further studies were made. The blue-green complex was analyzed further. The molecular weight was determined at a concentration of 4.994 g/l.

Bis(trifluoroacetylacetonato)(dimethyl sulfoxide)copper(II), $(TFA)_2Cu(DMSO)$.—The blue-green complex was prepared by dissolving bis(trifluoroacetylacetonato)copper(II) in warm DMSO, mp 111–113°. The complex loses DMSO at room temperature in the absence of a DMSO atmosphere. *Anal.* Calcd for $Cu(C_5H_4F_3O_2)_2(C_2H_6SO)$: Cu, 14.19. Found: Cu, 13.17. A sample was warmed for a period of several days to drive off the DMSO. The loss in weight corresponds to a DMSO to $(TFA)_2Cu$ ratio of 1.013. The residue was submitted for analysis. *Anal.* Calcd for $Cu(C_5H_4F_3O_2)_2$: C, 32.48; H, 2.18. Found: C, 32.35; H, 2.25.

Bis(benzoyltrifluoroacetonato)copper(II), $(BTFA)_2Cu$.—A small amount of solid ligand was added to an ammonia solution of cupric chloride. The complex was extracted from the solution with benzene. Dark green crystals remained after evaporation of the benzene, mp 235–237° (lit. 243–244°[8] and 241°[9]). *Anal.* Calcd for $Cu(C_{10}H_6O_2F_3)_2$: Cu, 12.87; C, 48.64; H, 2.45. Found: Cu, 13.37; C, 49.23; H, 2.68. The molecular weight was determined at a concentration of 18.72 g/l.

Bis(trifluoroacetylacetonato)zinc(II), $(TFA)_2Zn$.—The white complex was prepared in the same manner as the corresponding copper complex. White crystals were obtained on recrystallization from hot toluene, mp 168–179°. *Anal.* Calcd for $Zn(C_5H_4F_3O_2)_2$: Zn, 17.60; C, 32.33; H, 2.17. Found: Zn, 18.17; C, 30.67; H, 2.76. Molecular weight determined at a concentration of 1.913 g/l. and X-ray data indicate the complex exists as a trimer. A second white complex was obtained during an alternate preparation, mp 186–187°. *Anal.* Calcd for $Zn(C_5H_4F_3O_2)_2\cdot 2H_2O$: C, 29.47; H, 2.97. Found: C, 29.37; H, 2.79. The molecular weight of the latter complex was determined at a concentration of 15.36 g/l. and indicates the complex exists as a monomer in solution.

Bis(hexafluoroacetylacetonato)zinc(II) Dihydrate, $(HFA)_2Zn\cdot 2H_2O$.—The white complex was prepared in the same manner as the corresponding copper complex, mp 148–150° (lit.[12] 153°). *Anal.* Calcd for $Zn(C_5HF_6O_2)_2\cdot 2H_2O$: Zn, 13.63; C, 23.30; H, 1.17. Found: C, 22.36; H, 1.44. The molecular weight was determined at a concentration of 13.90 g/l.

Bis(trifluoroacetylacetonato)bis(dimethyl sulfoxide)zinc(II), $(TFA)_2Zn(DMSO)_2$.—White crystals were obtained upon cooling a solution of bis(trifluoroacetylacetonato)zinc(II) in DMSO, mp 94–98°. *Anal.* Calcd for $Zn(C_5H_4F_3O_2)_2(C_2H_6SO)_2$: Zn, 12.39; C, 31.86; H, 3.82. Found: C, 31.07; H, 3.62.

The two forms of the dichlorobis(N-oxide)copper(II) complexes, the $Cu_3Cl_6(C_6H_7NO)_2\cdot 2H_2O$, and the dichloro(N-oxide)zinc(II) complexes, except for $(PyNO)ZnCl_2$, have not previously been reported. The $(TFA)_2Zn(DMSO)_2$, $(TFA)_2Cu(DMSO)$, and $(TFA)_2Zn\cdot 2H_2O$ complexes have not been reported and, in general, no physical data except melting points have been given for most of the β-diketone complexes.

X-Ray Data.—Precession and cone-axis single-crystal photographs were taken of all complexes. The unit cell dimensions and space groups were determined for all compounds. The bulk materials were then ground, and powder diffraction patterns were recorded. The powder patterns were indexed using unit cell data from the single-crystal photographs. All powder diffraction peaks were identified indicating the single crystals chosen for study were representative of the bulk material collected. In no case were unidentified powder diffraction lines evident. The space group was not uniquely determined for all complexes and alternate speculations concerning some of the structures can be made.

Molecular Weights.—Molecular weights were determined on a Mechrolab osmometer, Model 301A, using distilled nitroethane as a solvent. A number of the most interesting complexes were too insoluble for molecular weight determination. Small variations in measured molecular weights in a series are not significant owing to the low concentrations of sample used. The measured molecular weights are given in Table I, and the concentrations are listed in the Experimental Section under the individual complex.

Thermal Analysis.—A Perkin-Elmer Model DSC-1 differential scanning calorimeter was used to examine the thermal stability of several of the complexes.

Magnetic Susceptibility.—The magnetic susceptibilities were measured by the Faraday method at two different field strengths. $Hg[Co(CNS)_4]$ was used as a calibration standard. The effective magnetic moments were calculated by the formula $\mu_{eff} = 2.84\sqrt{\chi_m^{cor}T}$, where χ_m^{cor} is the corrected magnetic susceptibility per formula weight as indicated in the table. All appropriate diamagnetic corrections were made.[13]

Discussion

The structures of only the 1:1 and 2:1 (pyridine N-oxide)copper(II) complexes have been reported.[7,8] From an examination of magnetic and spectral data of the various N-oxide complexes there appear to be several possible structural variations. The X-ray and molecular weight data in Table I may provide some information about the structures of the copper(II) and zinc(II) complexes.

The complexes $(4\text{-PicNO})_2CuCl_2$ (green), $(TFA)_2Zn(DMSO)_2$, and $(BTFA)_2Cu$ in the crystalline state belong to space group $P2_1/c$ with two molecules per unit cell. This requires the copper and zinc ions to be in special positions at centers of symmetry. This eliminates the possibility of a tetrahedral configuration and requires the like ligands in $(4\text{-PicNO})_2CuCl_2$ (green) to be equivalent and *trans* to each other. This green copper complex of 4-picoline N-oxide must have a square-planar configuration and the normal magnetic moment, Table II, indicates the copper atoms are distant enough to prevent any magnetic interactions. The trifluoroacetylacetonato ligands form a square-planar configuration about the zinc ion and the two DMSO molecules probably occupy the axial positions in a pseudo-octahedral configuration. The $(BFTA)_2Cu$ is required to be square-planar.

There are six complexes which belong to either space group C2/c or Cc with 4 formula weights per unit cell. The molecular weight data indicate that the complexes are monomeric in solution and probably also in the solid. If the space group is C2/c then the metal atoms must be in special positions. Four of the five special positions for this space group are at centers of sym-

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TABLE I

X-RAY AND MOLECULAR WEIGHT DATA

Compound	Unit cell dimensions		Space group	Formula weights per unit cell	Mol wt		Density	
					Obsd	Calcd	d_o	d_c
$\mathrm{(PyNO)CuCl_2}$[a]	$a = 5.844$ $c = 10.049$	$b = 13.643$ $\beta = 104° 52'$	$P2_1/c$	4	Insoluble		1.9	1.97
$\mathrm{Cu_3Cl_6(2\text{-}PicNO)_2 \cdot 2H_2O}$ (?)	$a = 9.55$ $c = 9.42$ $\beta = 115° 52'$	$b = 7.23$ $\alpha = 92° 50'$ $\gamma = 105° 36'$	P1 or P$\bar{1}$	1	Insoluble		1.94	1.95
$\mathrm{(3\text{-}PicNO)CuCl_2}$	$a = 5.97$ $c = 8.13$	$b = 20.90$ $\beta = 99° 13'$	$P2_1/c$	4	Insoluble		1.77	1.62
$\mathrm{(4\text{-}PicNO)CuCl_2}$	$a = 9.94$ $c = 5.93$ $\beta = 106° 31'$	$b = 9.35$ $\alpha = 98° 48'$ $\gamma = 116° 51'$	P1 or P$\bar{1}$	2	Insoluble		1.85	1.80
$\mathrm{[(2,6\text{-}LuNO)CuCl_2]_2}$	$a = 10.64$ $c = 17.98$	$b = 8.41$ $\beta = 143° 38'$	$P2_1/c$	2	478	516	1.79	1.79
$\mathrm{(PyNO)_2CuCl_2}$[b]	$a = 6.931$ $c = 15.11$	$b = 7.47$ $\beta = 96° 30'$	$P2_1/c$	4	Insoluble		1.72	1.73
$\mathrm{(2\text{-}PicNO)_2CuCl_2}$	$a = 6.73$ $c = 10.73$	$b = 10.39$ $\beta = 101° 22'$	C2/c or Cc	4	278	353	1.65	1.60
$\mathrm{(3\text{-}PicNO)_2CuCl_2}$ (yellow)	$a = 7.75$ $c = 12.04$	$b = 17.23$ $\beta = 111° 8'$	$P2_1/c$	4	*c*	...	1.61	1.56
$\mathrm{(3\text{-}PicNO)_2CuCl_2}$ (green)	$a = 10.67$ $c = 14.77$	$b = 11.01$ $\beta = 120° 26'$	$P2_1/c$	4	Insoluble		1.58	1.57
$\mathrm{(4\text{-}PicNO)_2CuCl_2}$ (yellow)	$a = 10.93$ $c = 7.47$	$b = 20.07$ $\beta = 111° 26'$	$P2_1/c$	4	*c*	...	1.60	1.54
$\mathrm{(4\text{-}PicNO)_2CuCl_2}$ (green)	$a = 6.29$ $c = 11.51$	$b = 10.67$ $\beta = 101° 45'$	$P2_1/c$	2	Insoluble		1.57	1.55
$\mathrm{(2,6\text{-}LuNO)_2CuCl_2}$ (yellow)	$a = 13.89$ $c = 16.23$	$b = 7.68$	$Pna2_1$	4	317	381	1.49	1.48
$\mathrm{(2,6\text{-}LuNO)_2CuCl_2}$ (green)	$a = 15.59$ $c = 14.53$	$b = 7.61$ $\beta = 96° 16'$	C2/c or Cc	4	350	381	1.50	1.48
$\mathrm{(PyNO)_2ZnCl_2}$	$a = 7.31$ $c = 14.60$	$b = 12.39$ $\beta = 104° 10'$	C2/c or Cc	4	304	326	1.72	1.69
$\mathrm{(2\text{-}PicNO)_2ZnCl_2}$	$a = 10.53$ $c = 9.25$ $\beta = 91° 25'$	$b = 8.38$ $\alpha = 109° 29'$ $\gamma = 93° 45'$	P1 or P$\bar{1}$	2	*c*	...	1.61	1.57
$\mathrm{(3\text{-}PicNO)_2ZnCl_2}$	$a = 14.08$ $c = 7.59$ $\beta = 92° 22'$	$b = 8.45$ $\alpha = 117° 34'$ $\gamma = 100° 50'$	P1 or P$\bar{1}$	2	357	355	1.55	1.50
$\mathrm{(4\text{-}PicNO)_2ZnCl_2}$	$a = 23.02$ $c = 14.23$	$b = 7.44$ $\beta = 140° 55'$	C2/c or Cc	4	320	355	1.55	1.53
$\mathrm{(2,6\text{-}LuNO)_2ZnCl_2}$	$a = 14.17$ $c = 14.62$	$b = 8.39$ $\beta = 96° 16'$	C2/c or Cc	4	364	383	1.50	1.48
$\mathrm{(HFA)_2Cu \cdot 2H_2O}$ (blue-green)	$a = 20.77$ $c = 8.84$	$b = 9.07$ $\beta = 100° 53'$	C2/c or Cc	4	596	513	2.03	2.05
$\mathrm{(TFA)_2Cu}$	$a = 4.87$ $c = 8.82$ $\beta = 103° 42'$	$b = 8.38$ $\alpha = 92° 22'$ $\gamma = 106° 36'$	P1 or P$\bar{1}$	1	346	370	1.88	1.83
$\mathrm{(TFA)_2Cu(DMSO)}$	$a = 9.20$ $c = 8.34$ $\beta = 91° 10'$	$b = 12.19$ $\alpha = 96° 5'$ $\gamma = 103° 12'$	P1 or P$\bar{1}$	2	*d*	...	1.62	1.64
$\mathrm{(BTFA)_2Cu}$	$a = 17.19$ $c = 10.41$	$b = 5.71$ $\beta = 92° 55'$	$P2_1/c$	2	580	494	1.66	1.62
$\mathrm{(HFA)_2Zn \cdot 2H_2O}$	$a = 7.46$ $c = 11.18$	$b = 22.13$	Pnma or $Pna2_1$	4	524	515	1.94	1.92
$\mathrm{[(TFA)_2Zn]_3}$	$a = 14.26$ $c = 16.96$	$b = 17.80$ $\beta = 105° 49'$	$P2_1/c$	4	1166	1116	1.82	1.79
$\mathrm{(TFA)_2Zn}$ (?)	$a = 7.59$ $c = 9.28$	$b = 21.20$ $\beta = 91° 38'$	$P2_1/c$	4	492	372	1.72	1.65
$\mathrm{(TFA)_2Zn(DMSO)_2}$	$a = 7.90$ $c = 12.66$	$b = 10.96$ $\beta = 96° 0'$	$P2_1/c$	2	*a*	...	1.63	1.61

[a] Reference 6. [b] Reference 7. [c] No sample available for molecular weight measurements. [d] Sample unstable in solution.

metry. A thorough examination of these positions indicates that the center of symmetry positions are the most probable. This would require $\mathrm{(2\text{-}PicNO)_2CuCl_2}$, $\mathrm{(2,6\text{-}LuNO)_2CuCl_2}$ (green), $\mathrm{(PyNO)_2ZnCl_2}$, $\mathrm{(4\text{-}PicNO)_2ZnCl_2}$, and $\mathrm{(2,6\text{-}LuNO)_2ZnCl_2}$ to be *trans*-square-planar. The blue-green $\mathrm{(HFA)_2 \cdot 2H_2O}$ complex probably contains the HFA ligands in a square-planar configuration with the water molecules occupying the axial

Table II

Magnetic Susceptibility Data

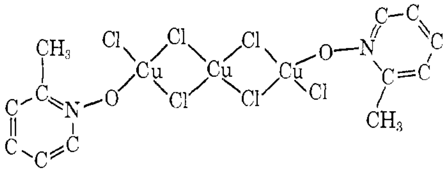
Compound	Temp, °K	Magnetic susceptibility × 10^6 cgs	Magnetic moment, BM
[(PyNO)CuCl$_2$]$_2$	91	78[a]	
	139	87[a]	
	197.6	170.2[b]	0.52
	229.2	276.6[b]	0.72
	343.7	637.8[b]	1.32
Cu$_3$Cl$_6$(2-PicNO)$_2$·2H$_2$O	77	4943	1.75
	87	4509	1.78
	113	3503	1.78
	201	1955	1.77
	273	1193	1.61
[(3-PicNO)CuCl$_2$]$_2$	298		0.55[c]
[(4-PicNO)CuCl$_2$]$_2$	298		0.52[c]
[(2,6-LuNO)CuCl$_2$]$_2$	298		0.22[c]
(PyNO)$_2$CuCl$_2$	298		0.63[d]
(2-PicNO)$_2$CuCl$_2$	77	5439	1.83
	113	3800	1.85
	201	2277	1.91
	273	1610	1.87
(4-PicNO)$_2$CuCl$_2$ (green)	77	5374	1.82
	201	2483	2.00
	273	1806	1.99
(2,6-LuNO)$_2$CuCl$_2$ (yellow)	77	5553	1.85
	87	4914	1.85
	113	4042	1.91
	201	2538	2.02
	273	1998	2.09
(2,6-LuNO)$_2$CuCl$_2$ (green)	77	4892	1.73
	87	4192	1.71
	113	3423	1.76
	201	1716	1.66
	273	1004	1.50
(TFA)$_2$Cu	77	4799	1.72
	87	4103	1.69
	113	3242	1.71
	201	1631	1.62
	273	1013	1.49
(HFA)$_2$Cu·2H$_2$O	77	5724	1.88
	87	5065	1.88
	113	3981	1.90
	201	2189	1.88
	273	1627	1.88

[a] Reference 7. [b] Reference 5. [c] Reference 4. [d] Reference 3.

positions of a distorted octahedron. If Cc is the correct space group, there is no restriction upon the geometry, although a distorted *trans*-square-planar configuration appears most probable.

It is suggested that all 1:1 N-oxide copper complexes are dimeric. The one complex which was soluble enough for molecular weight measurement, (2,6-LuNO)CuCl$_2$, proved to be dimeric in solution. The X-ray data indicated that two of these dimeric units were found in the unit cell. The dimers therefore are required to lie at centers of symmetry as are the (PyNO)CuCl$_2$ and (3-PicNO)CuCl$_2$ complexes. The (4-PicNO)CuCl$_2$ complex belongs to the triclinic system and exhibits the magnetic behavior associated with binuclear complexes.

From the analytical data the unknown 2-picoline N-oxide complex is formulated as Cu$_3$Cl$_6$(2-PicNO)$_2$·2H$_2$O. The magnetic moment of the entire complex is 1.77 BM or an average of 1.03 BM per copper atom. This is consistent with a trinuclear complex with a doublet ground state ($S = {}^1/_2$). The magnetic moment per copper atom would be $\sim\sqrt{{}^1/_3[2(0.0)^2 + 1(1.8)^2]} = 1.04$ BM at room temperature. The proposed structure of the 2-picoline N-oxide complex, I, is similar to that reported for Cu$_3$Cl$_6$(CH$_3$CN)$_2$.[14]



I

The infrared spectra of the unknown complex and the 2:1 complex are identical in the region 600–4000 cm^{-1} except for the water bands and two very weak peaks at 1250 and 1670 cm^{-1} in the unknown spectrum. There was only one band at 1200 cm^{-1} which was indicative of N–O stretching. The N–O stretching frequencies would indicate that the N-oxide is similarly bonded in the 2:1 complex and the unknown complex. Structure I appears to be a reasonable geometric arrangement and is consistent with all experimental data; however, confirmation will require the completion of X-ray studies.

The 2:1 N-oxide copper complexes frequently occurred in two forms. One was a yellow crystalline material and the other green. It was initially thought that these were mixtures of the 1:1 and 2:1 complexes; however, chemical analysis indicated that both forms were 2:1 complexes. Single crystals of the yellow and green forms were used in X-ray studies to determine space group and unit cell dimensions. Samples were then ground and powder diffraction patterns were taken. All lines in each pattern were indexed from the appropriate single-crystal unit cell data. All lines checked and the single crystals were therefore representative of the yellow and green forms.

The yellow form of (4-PicNO)$_2$CuCl$_2$ changed to the *trans*-square-planar green form at 73–113°. The unit cell dimensions are similar except the *b* axis in the yellow form is doubled. These could be just two crystalline modifications involving the same molecular structure; however, it is more likely that the yellow form represents a distorted square-planar or distorted tetrahedral structure. It is doubtful that a *cis–trans* ligand shift involving a bulky group could occur.

The two forms of the 2,6-lutidine N-oxide complexes melted at approximately 200° to a green liquid which decomposes around 230–240°. Thermal analysis showed no transformation in either form below the melting point. The green form has been assumed to have a *trans*-square-planar conguration (C2/c). The structure of the yellow form has recently been determined[15] and is almost halfway between a tetrahedral and a square-planar configuration. It can be approximated by rotating two *cis* ligands by 45° about an axis bisecting them and passing through the copper atom or

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(14) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

(15) Unpublished results.

by rotating two tetrahedral ligands by 45° around an axis bisecting them and passing through the copper atom. This distortion does not appear to be due to steric factors and might result from an interaction between the copper ion and the π system of the ligands and the copper ion.

The 3-picoline N-oxide yellow form converts to the green form at 100–110°. It is proposed that the yellow form is distorted square-planar or distorted tetrahedral and the green form is approximately *trans*-square-planar. It is possible that diffuse reflectance spectra can be used to confirm some of these assignments.[16]

The zinc and copper β-diketone complexes were not in general easily characterized. The $(TFA)_2Zn$ complex, mp 168°, was a trimer in solution and the unit cell contained 4 trimeric units. The structure may be similar to that of bis(acetylacetonato)nickel(II).[17] A second white complex, mp 186–187°, was obtained during some of the preparations. The second complex was monomeric in solution and the analytical data are consistent with the formulation of a dihydrate.

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Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas

Refinement of the Crystal Structure of Di-μ-(pyridine oxide)-bis(dichlorocopper(II))

By R. S. Sager, R. J. Williams, and W. H. Watson

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The crystal and molecular structure of di-μ-(pyridine oxide)-bis(dichlorocopper(II)) has been refined using three-dimensional single-crystal X-ray data. The crystals are monoclinic, $P2_1/b$, with unit cell dimensions $a = 5.844 \pm 0.005$ A, $b = 10.049 \pm 0.005$ A, $c = 13.643 \pm 0.005$ A, and $\gamma = 104° 52' \pm 10'$. Two dimeric molecules are found per unit cell. The ligands about the copper ion are best described as forming a distorted square-planar configuration, and π bonding is postulated to be important in the superexchange mechanism.

Introduction

A number of complexes between transition metals and pyridine N-oxide, C_5H_5NO, and its derivatives have been prepared and characterized.[1-4] The abnormally low magnetic moments of most 1:1 complexes of copper(II) halides[1,3,5] have led to the prediction of a dimeric or polymeric oxygen-bridged structure. It was suggested that the low magnetic moment could be accounted for by a superexchange mechanism operating through the bridging oxygen atoms of the N-oxide ligands.[6,7]

The crystal structure of $[(C_5H_5NO)CuCl_2]_2$ was determined by two-dimensional, single-crystal X-ray diffraction techniques and indicated an oxygen-bridged dimer.[4] We have collected three-dimensional X-ray data and have refined the positional and thermal parameters using a full-matrix, least-squares procedure. We wish to report the details of the refined structure.

Experimental Section

Pyridine N-oxide was obtained from K & K Chemical Laboratories and copper(II) chloride from the Allied Chemical Co. Both were used without further purification.

Di-μ-(pyridine oxide)-bis(dichlorocopper(II)), $[(C_5H_5NO)CuCl_2]_2$, was prepared by the method of Quagliano, *et al.*[1] Green, needle-shaped crystals suitable for X-ray study were recrystallized from an ethanol solution. A single crystal, 0.87 × 0.17 × 0.13 mm, was used in the collection of all data.

Crystals of $[(C_5H_5NO)CuCl_2]_2$ are monoclinic belonging to space group $P2_1/b$ with unit cell dimensions[4] $a = 5.844 \pm 0.005$ A, $b = 10.049 \pm 0.005$ A, $c = 13.643 \pm 0.005$ A, and $\gamma = 104° 52' \pm 10'$. There are two dimeric molecules per unit cell.

Three-dimensional intensity data were collected at room temperature by the multiple-film (three films), equiinclination Weissenberg technique. Reflections 0*kl*–6*kl* were recorded using filtered molybdenum radiation, Mo $K\alpha = 0.71069$ A. A total of 1144 nonzero reflections were recorded and were visually estimated by comparison with a calibration strip. The data were corrected for absorption using Bond's values[8] with $\mu R = 0.30$. Precession data were used initially to place all data on a common scale. Scale factors were later refined during the least-squares calculations.

Structure

The atomic positions and isotropic temperature factors of Schafer, *et al.*,[4] were used as the starting parameters in a full-matrix, least-squares refinement.[9] The

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