ditions employed were those at which the addition is known to take place rapidly.[4b] It was not practicable to attain rapidly the higher reaction temperatures found necessary to effect the addition of methylrhenium pentacarbonyl to tetrafluoroethylene. Apparently $CH_3CF_2CF_2Mn(CO)_5$ once formed does not react further with tetrafluoroethylene.

Attempts to effect the addition of methylrhenium pentacarbonyl to tetrafluoroethylene in pentane using ultraviolet irradiation were not successful. This is in noticeable contrast to the behavior of methylmanganese pentacarbonyl, which undergoes essentially quantitative addition to tetrafluoroethylene on irradiation of mixtures.[17]

[17] J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 218 (1963).

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA,
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Substituted Pyridine N-Oxide Complexes of Copper(II) Halides

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The preparation and characterization of a number of 4-substituted pyridine N-oxide complexes of copper(II) halides are reported. Two series of compounds are formed; one with the general formula $CuLCl_2$ and the second with the formula CuL_2Cl_2. Structural assignments are made on the basis of the similarity of the magnetic and spectral properties of these compounds with those of $[Cu(C_5H_5NO)Cl_2]_2$.

Introduction

In recent years a considerable interest in the donor properties of pyridine N-oxide has been evident. Quagliano, *et al.*,[2] and Carlin[3] have reported the preparation and characterization of a number of coordination compounds of this Lewis base with a wide variety of metal salts; Quagliano and co-workers[4] have studied the infrared spectra of the compounds reported earlier[2]; and Meek, Drago, and Piper[5] have measured the electronic spectra of complexes with nickel(II), chromium(III), and cobalt(II). Harris, *et al.*,[6] have confirmed the abnormally low magnetic moment reported by Quagliano, *et al.*,[2] for the complex with the empirical formula $CuCl_2 \cdot C_5H_5NO$ in a study of the temperature dependence of the magnetic susceptibility. An independent study by Smith[7] is in accord with these results. We now wish to report the results of our magnetic and spectral studies on a series of copper(II) halide complexes with 4-substituted pyridine N-oxides. The results are interpreted in terms of the following structure which has been determined by a complete X-ray crystal structure examination[8] (Figure 1).

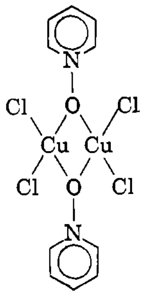

Figure 1.—The structure of $[Cu(C_5H_5NO)Cl_2]_2$.

Experimental

Preparation of the Substituted Pyridine N-Oxides.—Pyridine N-oxide and the 4-substituted pyridine N-oxides were prepared by the method reported by Ochiai[9] or were obtained commercially. The melting points or boiling points of the compounds with a 4-substituent of –H, –Cl, –OH, and $-NO_2$ were in good agreement with those given in Ochiai's paper.

Preparation of the Coordination Compounds.—The complexes were prepared by mixing a solution of the ligand in ethanol with a stoichiometric amount of $CuCl_2 \cdot 2H_2O$ in ethanol or $CuBr_2$ in ethanol. The compounds listed in Table I either crystallized immediately or upon standing for a short time and were purified by recrystallization from ethanol.

Magnetic Susceptibility Determinations.—Equipment for the determination of magnetic susceptibilities by the Faraday method similar to that described earlier[10] has been assembled at Chapel Hill. Mercury(II) tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,[11] and the diamagnetic corrections were estimated from Pascal's constants.[12] In addition to the measurements by the Faraday method, measurements at room temperature by the Gouy method were made at Tulane.

Spectral Studies.—The infrared spectra of Nujol mulls of samples of the complexes were obtained using either a Perkin-Elmer 421 spectrophotometer which was calibrated with polystyrene or a Beckman IR 8 spectrophotometer. Spectra of the substituted pyridine N-oxides were obtained from CS_2 solutions.

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[11] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

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TABLE I

ANALYTICAL DATA

	Analysis, %					
	C		H		N	
Compound	Calcd.	Found	Calcd.	Found	Calcd.	Found
$CuCl_2 \cdot HOC_5H_4NO$	24.46	24.03	2.05	2.61	5.71	5.70
$CuCl_2 \cdot CH_3C_5H_4NO$	29.58	29.60	2.90	2.93	5.75	5.83
$CuBr_2 \cdot CH_3C_5H_4NO$	21.67	21.68	2.12	2.04	4.21	4.17
$CuBr_2 \cdot 2CH_3C_5H_4NO$	32.64	32.10	3.20	3.24	6.34	6.32
$CuCl_2 \cdot 2NO_2C_5H_4NO^{a}$	28.97	29.62	1.94	2.02	13.51	13.08, 12.79
$CuBr_2 \cdot 2NO_2C_5H_4NO^{a}$	23.85	22.72	1.60	2.31	11.13	10.30
$CuBr_2 \cdot NO_2C_5H_4NO$	16.53	17.63	1.11	1.27	7.71	7.41
$CuCl_2 \cdot ClC_5H_4NO$	22.75	23.93	1.53	1.73	5.31	5.66
$CuCl_2 \cdot 2ClC_5H_4NO$	30.52	30.33	2.05	2.19	7.12	6.75
$CuBr_2 \cdot ClC_5H_4NO$	17.02	17.71	1.14	1.36	3.97	4.17
$CuBr_2 \cdot C_5H_5NO$	18.86	19.36	1.58	1.83	4.40	4.56

[a] The experimental assistance of Mr. Fred Bunger in the preparation of these compounds is gratefully acknowledged.

The spectra were recorded at a scan speed of ~100 cm.$^{-1}$/min. in the spectral range 1000–1500 cm.$^{-1}$. The energies of the intense band near 1200 cm.$^{-1}$ for each of the complexes and the free ligands are given in Table II. This band has been assigned by Quagliano and co-workers[4] to the N–O stretching vibration.

TABLE II

ENERGIES OF THE N–O STRETCHING VIBRATION FOR THE SUBSTITUTED PYRIDINE N-OXIDES AND COMPLEXES[a]

4-Substituted pyridine N-oxide	ν, cm.$^{-1}$	Complex	ν, cm.$^{-1}$
HC_5H_4NO	1265^{b}	$CuLCl_2$	1202^{b}
		CuL_2Cl_2	1223, 1206
		$CuL(DMF)Cl_2{}^{c,e}$	1203
		$CuL(DMSO)Cl_2{}^{d,e}$	1203
		$CuLBr_2$	1200
		$CuL_2Br_2{}^{e}$	1211, 1201
		$CuL(DMF)Br_2{}^{e}$	1202
$CH_3C_5H_4NO$	1249	$CuLCl_2$	1203
		$CuLBr_2$	1203
		CuL_2Br_2	1209
		$CuL(DMSO)Br_2{}^{e}$	1211
ClC_5H_4NO	1256	$CuLCl_2$	1208
HOC_5H_4NO		$CuLCl_2$	1210
$NO_2C_5H_4NO$	1296, 1287	$CuLBr_2$	1238, 1225

[a] The assistance of Mr. H. M. McGuire is acknowledged. [b] Reference 4. [c] DMF is dimethylformamide. [d] DMSO is dimethyl sulfoxide. [e] The preparation and characterization of these compounds has been reported by M. Kishita, Y. Muto, M. Inoui, and M. Kubo at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, March–April 1963.

TABLE III

MAGNETIC SUSCEPTIBILITY DATA

Compound	$\chi_m^{cor} \times 10^6$ c.g.s. units	T, °K.	μ_{eff}, B.M.
$[Cu(C_5H_5NO)Cl_2]_2{}^{a}$	170.2	197.6	0.52
	237.6	215.6	0.64
	258.2	221.6	0.68
	276.6	229.2	0.72
	328.2	247.9	0.81
	472.6	293.9	1.06
	465.6	299.2	1.06
	515.6	316.5	1.15
	566.2	327.5	1.22
	637.8	343.7	1.32
$[Cu(ClC_5H_4NO)Cl_2]_2{}^{b}$	140	300.1	0.58
	180	318.7	0.68
	192	326.8	0.71
	221.4	344.4	0.78
	255.2	357.5	0.86
$[Cu(ClC_5H_4NO)_2Cl_2]^{c}$	1262	297.7	1.75
$[Cu(ClC_5H_4NO)Br_2]_2{}^{d}$	23	297.7	0.23
$[Cu(CH_3C_5H_4NO)Cl_2]_2{}^{e}$	48.2	247.7	0.32
	95.0	273.2	0.46
	106.2	299.4	0.51
	146.2	319.8	0.59
	168.4	335.7	0.68
	226.0	356.8	0.81
$[Cu(CH_3C_5H_4NO)Br_2]_2{}^{f}$	28.1	297.8	0.26
$[Cu(CH_3C_5H_4NO)_2Br_2]_n{}^{g}$	740.5	297.6	1.33
$[Cu(CH_3C_5H_4NO)\{(CH_3)_2SO\}Br_2]_n{}^{h}$	393.3	297.6	0.97
$[Cu(HOC_5H_4NO)Cl_2]_2{}^{i}$	0	297.8	
	14	323	0.04
	24.2	337.2	0.07
	35.8	363.7	0.11
	45.4	374.5	0.14
	73.0	397.7	0.23
$[Cu(NO_2C_5H_4NO)Br_2]_2{}^{j}$	1974	195.7	1.77
	1907	205.9	1.78
	1624	273.2	1.92
	1568	298.2	1.94

[a–j] Diamagnetic corrections × 10^6 c.g.s. units are: *a*, 104.6; *b*, 121.7; *c*, 204.0; *d*, 154.2; *e*, 116.5; *f*, 148.9; *g*, 215.8; *h*, 191.6; *i*, 109.2; *j*, 142.9.

Results.

Magnetic Data.—The temperature dependence of the magnetic susceptibilities of the series of 4-substituted pyridine N-oxide complexes of copper(II) chloride or copper(II) bromide were determined and the results are given in Table III. The molar susceptibilities given in Table III were calculated on the basis of the formula weight as indicated in the table except for $[Cu(CH_3C_5H_4NO)_2Br_2]_n$ and $[Cu(CH_3C_5H_4NO)\{(CH_3)_2SO\}Br_2]_n$. For these two compounds the monomeric formula weight was used. The magnetic moments were calculated using the expression $\mu_{eff} = 2.84[(\chi_m^{cor} - N\alpha)T]^{1/2}$ where a value for $N\alpha$ of 60×10^{-6} c.g.s. unit per copper ion was assumed for the temperature-independent paramagnetism. The magnetic data reflect the considerable spin–spin interaction between the unpaired electrons on the adjacent copper ions in the binuclear compounds. In fact, a structure very similar to that shown in Figure 1 was assigned to $[Cu(C_5H_5NO)Cl_2]_2$ on the basis of the magnetic data.[7] The results of the magnetic investigations have been discussed previously.[13]

Infrared Spectra.—The strong absorption in the region 1200–1300 cm.$^{-1}$ in the infrared spectrum of pyri-

[13] W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.*, **86**, 3888 (1964)

dine N-oxide and its derivatives has been assigned to the characteristic N–O stretching vibration.[4,14,15] Quagliano and co-workers[4] have found that the coordination of pyridine N-oxide to a metal ion results in a lowering of the N–O stretching energy. This was attributed to a decrease in the contribution of the resonance form which contains a nitrogen–oxygen double bond, *i.e.*, there is a decrease in the N–O bond order upon coordination. By and large the absorption energies of the N–O stretching vibration of the 1:1 complexes were lower than the values for the 1:2 complexes. This observation is in agreement with expectation; a larger electron donation from the NO group should be taken to form the Cu–O–Cu linkage of the 1:1 complexes than in forming the single coordinate bond of many of the 2:1 complexes.

Discussion

The structure of $[Cu(C_5H_5NO)Cl_2]_2$ has been established.[8] The binuclear molecule is formed by distorted tetrahedra which share an edge. On the basis of the similarity of the magnetic properties and the infrared spectral data, similar structures can be assigned to the other 1:1 complexes prepared in this study.

Assignment of structures to the 2:1 complexes is more complicated. The presence of two N–O bands in the spectrum of $Cu(C_5H_5NO)_2Cl_2$ suggests the presence of two kinds of pyridine N-oxide ligands in this molecule, and the magnetic data can only be explained on the basis of polynuclear units with Cu–O–Cu bridges. When $Cu(C_5H_5NO)_2Cl_2$ is heated to about 85–90° one pyridine N-oxide (per copper(II) ion) is lost and the high-energy band (at 1223 $cm.^{-1}$) in the infrared spectrum disappears. The simplest structure which encompasses these features retains the binuclear structure and contains a second pyridine N-oxide molecule in the coordination sphere of each copper ion in the dimeric unit. The facility of formation of complexes of the type $[Cu(C_5H_5NO)LX_2]_n$ where L is either dimethylformamide or dimethyl sulfoxide and X is chloride or bromide also supports a structure of this type.

However, not all 2:1 complexes have this structure; a case in point is $Cu(ClC_5H_4NO)_2Cl_2$. The magnetic data indicate the absence of Cu–O–Cu linkages in this compound. Other examples of CuL_2X_2 which are magnetically dilute have been characterized and will be reported in a subsequent publication.

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The Crystal Structure of Di-μ-diphenylphosphinatoacetylacetonatochromium(III)

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The structure of di-μ-diphenylphosphinatoacetylacetonatochromium(III), with sixty atoms in the asymmetric unit, has been determined by Patterson superposition and Fourier techniques. Two molecules crystallize in a triclinic unit cell (space group $P\bar{1}$) with dimensions $a = 12.64$, $b = 15.57$, $c = 13.35$ Å., $\alpha = 112.4°$, $\beta = 112.50°$, $\gamma = 84.2°$. The ligands around the chromium atoms conform to octahedral symmetry and the bridge structure, $(CrOPO)_2$, is a puckered eight-membered ring. Block diagonal least-squares refinement with Cr, P, and O atoms anisotropic resulted in a final R value of 0.09 for 4400 observed reflections.

Introduction

The determination of the crystal and molecular structure of $(AcCHAc)_2Cr(OP(C_6H_5)_2O)_2Cr(AcCHAc)_2$, a dimer and the first member of a series of polymers[2] made up of $Cr(AcCHAc)(OP(C_6H_5)_2O)_2$ units, was carried out by single-crystal X-ray diffraction techniques. Much interest centers on the excellent thermal stability and fairly general insolubility of these inorganically-linked polymers and hence on their structures. It was postulated that the structures involve double diphenylphosphinate bridges between the chromium atoms,[2] similar to a structure given for $UO_2[OP(OC_4H_9)_2O]_2$.[3]

Experimental

Green, plate-like crystals of the dimer were prepared by the reaction of diphenylphosphinic acid with excess chromium(III) acetylacetonate at 240° and recrystallized from diglyme. Precession camera photographs were taken to obtain the space group and approximate lattice parameters. The crystal was triclinic and the space group was determined to be $P\bar{1}$ from an analysis of the Patterson map. Precision measurements of the lattice pa-

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