

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27515

Substituted Pyridine N-Oxide Complexes of Copper(II) Halides. II. Magnetic Properties of Complexes with 3-Picoline N-Oxide, 2,6-Lutidine N-Oxide, and 2,4,6-Collidine N-Oxide¹

BY WILLIAM E. HATFIELD AND JOHN C. MORRISON

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The magnetic properties of copper(II) halide complexes of 3-picoline N-oxide, 2,6-lutidine N-oxide, and 2,4,6-collidine N-oxide have been determined as a function of temperature. The complexes with the general formula CuL_2X_2 have magnetic moments in the range 1.9–2.0 BM and probably have monomeric structures, whereas the complexes with the general formula CuLX_2 have low moments and probably have di- or polymeric structures similar to that exhibited by $[\text{Cu}(\text{C}_5\text{H}_5\text{-NO})\text{Cl}_2]_2$. For the condensed systems the magnetic susceptibilities of the bromo complexes are invariably lower than those of the corresponding chloro complexes, and the susceptibilities decrease as the degree of methyl substitution on the pyridine ring increases. These observations indicate that the singlet states of the dimeric molecules are stabilized by the electron-donating methyl groups and support a mechanism for spin-spin coupling operating through the orbitals of the bridging oxygen atoms.

Introduction

Pyridine N-oxide reacts with copper(II) chloride in ethanol to give a complex with a 1:1 mole ratio of ligand to metal salt.² On the basis of the low magnetic moment at room temperature and, later, in view of the temperature dependence of the magnetic susceptibility^{3,4} a bi- or polynuclear structure was postulated. A complete X-ray examination of single crystals revealed that the dimeric molecule consisted of two distorted tetrahedra sharing an edge with the oxygen atoms from the pyridine N-oxide ligands acting as the bridging units.⁵ The magnetic susceptibility data for a series of 4-substituted pyridine N-oxide complexes of copper(II) chloride suggested that the spin-spin coupling in these compounds occurred by a superexchange mechanism operating through the orbitals of the bridging oxygen atoms.⁶ The superexchange mechanism is consistent with the observed copper-copper internuclear distance of 3.3 Å. In connection with this work, the properties of a number of copper(II) complexes with pyridine N-oxides substituted at other positions on the aromatic ring have been determined, and the results of these investigations are reported herein.

Experimental Section

Preparation of the Compounds.—The organic compounds used as ligands in this study were obtained from commercial sources and were used without further purification. The complex compounds were prepared by mixing a stoichiometric quantity of the pyridine N-oxide in ethanol with the copper halide in ethanol. The compounds either precipitated immediately or crystallized from solution upon standing a short time; they were purified by

recrystallization from ethanol. Analyses were performed by conventional techniques by Micro-Tech, Skokie, Ill. The analytical data are given in Table I.

Spectral Investigations.—Diffuse reflectance spectra were measured with a Beckman DU spectrophotometer equipped with a standard reflectance attachment using a block of MgCO_3 as a reflectance standard.

Magnetic Susceptibility Determinations.—Magnetic susceptibilities were determined by the Faraday method using a Cahn Model G microbalance and a Varian V4004 electromagnet. The equipment and procedures have been described elsewhere.⁷ Since most of the compounds described in this report were only slightly paramagnetic, forces were determined in the temperature range of 25–150°.

The heater used for the measurements above room temperature was constructed from a 12-in. section of brass pipe with a 2.5-cm o.d. and a wall thickness of 0.3 cm. The pipe was noninductively wound with furnace wire and then wrapped with asbestos tape. The control thermocouple from an F & M Model 2240 temperature programmer was placed under the asbestos tape near the sample position, and an iron-constantan thermocouple was placed between the wall of the heater and the glass sample compartment exactly adjacent to the sample. Only the isothermal mode of the temperature programmer was used. The sensing thermocouple from the F & M programmer served only to provide a constant temperature which was measured by the calibrated iron-constantan thermocouple located between the sample compartment wall and the heater. The integrity of the latter thermocouple was checked by placing the bulb of a calibrated mercury thermometer in the sample position and comparing the results of the thermocouple with those of the thermometer after a 20-min equilibration period. The two temperature-sensing devices always agreed within 0.5°, and although the thermal characteristics of the samples differ considerably from those of a mercury-in-glass thermometer, it is believed that the temperatures measured with the thermocouple reflect those of the samples within the limits of at least 1°.

Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,⁸ and diamagnetic corrections were estimated from Pascal's constants.⁹

Results

Magnetic susceptibilities were determined as a func-

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TABLE I
ANALYTICAL DATA

Compd	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
CuCl ₂ ·C ₆ H ₇ NO ^a	29.58	29.52	2.90	2.97	5.75	5.73
CuBr ₂ ·C ₆ H ₇ NO ^a	21.67	21.80	2.12	2.20	4.21	4.15
CuCl ₂ ·C ₇ H ₉ NO ^b	32.64	32.08	3.52	3.38	5.44	5.30
CuCl ₂ ·2C ₇ H ₉ NO ^b	44.16	44.16	4.76	4.78	7.36	8.18
CuBr ₂ ·C ₇ H ₉ NO ^b	24.26	24.66	2.62	2.67	4.04	3.99
CuBr ₂ ·2C ₇ H ₉ NO ^b	35.80	35.60	3.86	3.60	5.97	5.82
CuCl ₂ ·C ₈ H ₁₁ NO ^c	35.38	35.42	4.08	4.13	5.16	4.87
CuCl ₂ ·2C ₈ H ₁₁ NO ^c	47.00	46.98	5.42	5.53	6.85	6.91
CuBr ₂ ·C ₈ H ₁₁ NO ^c	26.65	26.63	3.06	3.19	3.89	3.42
CuBr ₂ ·2C ₈ H ₁₁ NO ^c	38.61	38.60	4.46	4.50	5.63	5.03

^{a-c} The ligands are: ^a 3-picoline N-oxide; ^b 2,6-lutidine N-oxide; ^c 2,4,6-collidine N-oxide.

TABLE II
MAGNETIC SUSCEPTIBILITY DATA

Compd	T, °K	10 ⁶ χ _m ^{cor} , cgs units	μ _{eff} , BM
	307	266	0.99
	318	288	1.05
	331	298	1.09
	344	330	1.17
	376	387	1.33
[Cu(C ₆ H ₇ NO)Br ₂] ₂ ^a	300	176	0.80
	322	183	0.84
	338	230	0.97
	353	250	1.03
	370	273	1.11
	404	326	1.26
[Cu(C ₇ H ₉ NO)Cl ₂] ₂ ^b	297	127	0.68
	316	134	0.72
	334	140	0.75
	355	142	0.78
	382	147	0.83
	407	178	0.94
[Cu(C ₇ H ₉ NO) ₂ Cl ₂] ^b	298	1511	1.90
[Cu(C ₇ H ₉ NO)Br ₂] ₂ ^b	295	119	0.65
	320	131	0.71
	341	140	0.76
	363	149	0.81
	383	160	0.86
	401	174	0.92
	422	188	0.98
[Cu(C ₇ H ₉ NO) ₂ Br ₂] ^b	298	1727	2.04
[Cu(C ₈ H ₁₁ NO)Cl ₂] ₂ ^c	295	111	0.63
	324	116	0.67
	382	142	0.84
	414	187	0.97
[Cu(C ₈ H ₁₁ NO) ₂ Cl ₂] ^c	298	1521	1.91
[Cu(C ₈ H ₁₁ NO)Br ₂] ₂ ^c	295	100	0.60
	312	106	0.63
	327	110	0.66
	344	117	0.70
	364	133	0.77
	383	138	0.80
	403	151	0.86
[Cu(C ₈ H ₁₁ NO) ₂ Br ₂] ₂ ^c	298	1483	1.89

^{a-c} The ligands are: ^a 3-picoline N-oxide; ^b 2,6-lutidine N-oxide; ^c 2,4,6-collidine N-oxide.

tion of temperature and are given in Table II. The molar magnetic susceptibilities given in Table II were calculated on the basis of the formula weight as indicated in the table, and magnetic moments were calculated using the expression $\mu_{\text{eff}} = 2.84(\chi_m^{\text{cor}}T)^{1/2}$. The magnetic data reflect the considerable spin-spin

interaction between the unpaired electrons on adjacent copper atoms in the magnetically condensed systems. In no case was it possible to measure directly the Néel temperature by determining the maximum in the susceptibility *vs.* temperature curve. The singlet-triplet splitting energies for the complexes were obtained by fitting the temperature-dependent magnetic data to the expression

$$\chi_m = \frac{2g^2N\beta^2}{3kT} \left(1 + \frac{1}{3} \exp(-2J/kT) \right)^{-1} \quad (1)$$

where g is the Landé factor, N is Avogadro's number, β is the Bohr magneton, k is Boltzmann's constant, and $2J$ is the energy difference between the singlet ground state and triplet excited state.¹⁰

A program written in the GAT language for the Univac 1105 computer was used to give the best fit of the experimental data to the theoretical expression.¹¹ No single choice of J could be found to fit the data precisely, and it was necessary to use a range of J values in order to find agreement between calculated and observed susceptibilities. Several reasons can be put forth to account for the difficulty in the analysis of the data. These are: (i) consistent errors in the very small forces, $\sim 10 \mu\text{g}$, which were observed, (ii) contamination of the samples by traces of paramagnetic impurities, and (iii) departures from the dimeric structure observed for the parent compound of the series, [Cu(C₅H₅NO)Cl₂]₂, in which case eq 1 would not apply. There is no experimental evidence for polymeric structures, and the weighing errors would be expected to be random, and, therefore, average out. However, the presence of paramagnetic impurities could give rise to the deviations observed here. Even though our samples were purified by repeated recrystallization from ethanol, appeared to be homogeneous upon inspection under the microscope, and exhibited acceptable analytical data, the magnetic data indicate that the samples contained traces of perhaps the paramagnetic 2:1 compounds. By assuming a value of 2.2 for g (Smith^{3,5} used 2.17 for CuCl₂·C₅H₅NO), the range of $|2J|$ values needed to fit the experimental data are given in Table III. If one chooses the mean of the

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TABLE III
RANGE OF SINGLET-TRIPLET SPLITTING ENERGIES

Compd	$ 2J $
$[\text{Cu}(\text{C}_6\text{H}_7\text{NO})\text{Cl}_2]_2^a$	680-810
$[\text{Cu}(\text{C}_6\text{H}_7\text{NO})\text{Br}_2]_2^a$	890-1080
$[\text{Cu}(\text{C}_7\text{H}_9\text{NO})\text{Cl}_2]_2^b$	930-1090
$[\text{Cu}(\text{C}_7\text{H}_9\text{NO})\text{Br}_2]_2^b$	940-1100
$[\text{Cu}(\text{C}_8\text{H}_{11}\text{NO})\text{Cl}_2]_2^c$	960-1080
$[\text{Cu}(\text{C}_8\text{H}_{11}\text{NO})\text{Br}_2]_2^c$	960-1120

^{a-c} The ligands are: ^a 3-picoline N-oxide; ^b 2,6-lutidine N-oxide; ^c 2,4,6-collidine N-oxide.

values for the singlet-triplet splitting energy, the calculated susceptibilities are lower than observed at low temperatures and higher than observed at high temperatures. In no case did the deviations between the calculated and observed susceptibilities amount to greater than 50×10^{-6} cgs unit when the mean $|2J|$ was used in eq 1. Whereas this is a large discrepancy, relatively, it is fortunate that paramagnetic impurities have a tendency to suppress the value of $|2J|$, and, consequently, the upper limit of the singlet-triplet splitting energy listed in Table III approaches the correct value.

Spectral Properties.—In Figures 1 and 2 the diffuse reflection spectra of four representative compounds are presented. One compound, $\text{CuBr}_2 \cdot 4\text{-CH}_3\text{C}_5\text{H}_4\text{NO}$, has magnetic properties similar to $\text{CuCl}_2 \cdot \text{C}_5\text{H}_5\text{NO}$ and has been assigned a dimeric structure.¹ The second spectrum in Figure 1, for $\text{CuBr}_2 \cdot \text{C}_7\text{H}_9\text{NO}$, is also for a compound which exhibits antiferromagnetism. In Figure 2, the spectra of two complexes having a ligand-to-salt ratio of 2:1 are shown. In this case the 2,6-lutidine N-oxide complex exhibits a moment of 2.04 BM at room temperature, but the 4-picoline N-oxide complex possesses a moment of 1.33 BM per copper(II) ion at room temperature.

Discussion

For the most part, the complexes prepared in both

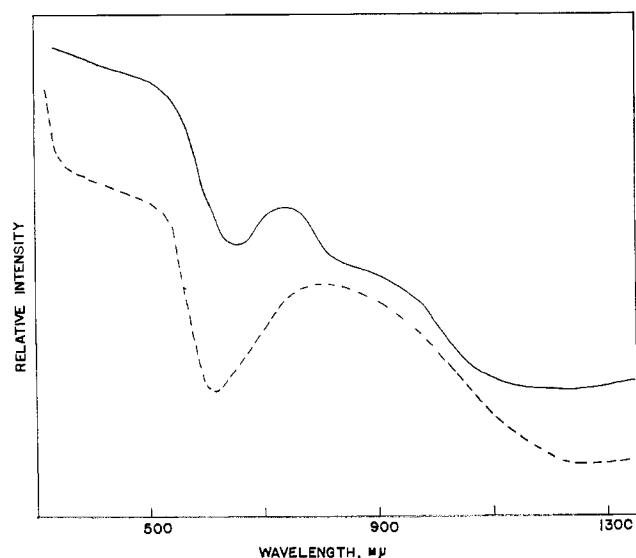


Figure 1.—Spectra of two representative compounds having a ligand-to-salt ratio of 1: —, $\text{CuBr}_2 \cdot \text{C}_7\text{H}_9\text{NO}$; - - -, $\text{CuBr}_2 \cdot 4\text{-CH}_3\text{C}_5\text{H}_4\text{NO}$.

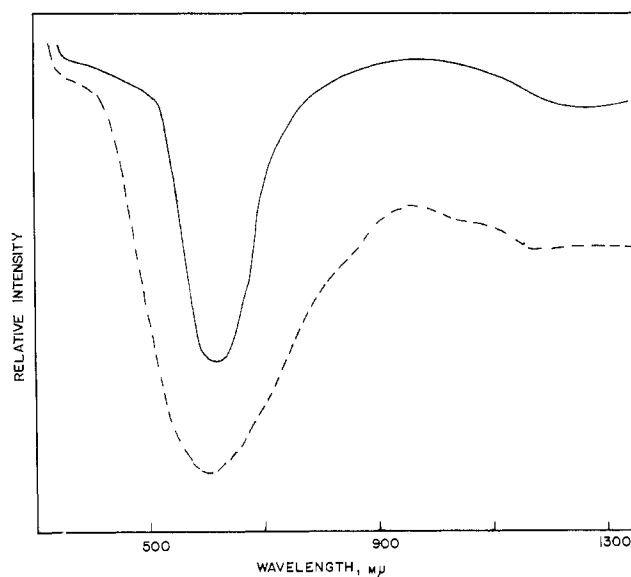


Figure 2.—Spectra of two representative compounds having a ligand-to-salt ratio of 2: —, $[\text{Cu}(\text{C}_7\text{H}_9\text{NO})_2\text{Br}_2]$; - - -, $[\text{Cu}(4\text{-CH}_3\text{C}_5\text{H}_4\text{NO})_2\text{Br}_2]_n$.

this study and the one reported earlier⁸ fall naturally into two classes. The first class includes the compounds with the empirical formula $\text{CuX}_2 \cdot \text{L}$ which usually have low moments and which probably possess a dimeric structure similar to that found by Morrow and co-workers⁵ for the 1:1 complex of pyridine N-oxide with copper(II) chloride. The second principal class includes the compounds with the empirical formula $\text{CuX}_2 \cdot 2\text{L}$ which usually have normal moments, *i.e.*, a moment equal to or greater than 1.7 BM per copper(II) ion, and which probably have monomeric structures in the form of distorted tetrahedra. However, there are important exceptions to these generalizations, and these will be discussed in subsequent sections of this paper.

The Condensed Complexes.—The magnetic properties of the 1:1 complexes are explicable in terms of the structure shown in Figure 3 for the parent compound in this series. The structure is made up of two distorted tetrahedra which share an edge with the oxygen atoms from the pyridine N-oxide ligands functioning as the bridging units. As a consequence of this structure, substituents on the pyridine ring have a remarkable effect on the magnetic properties

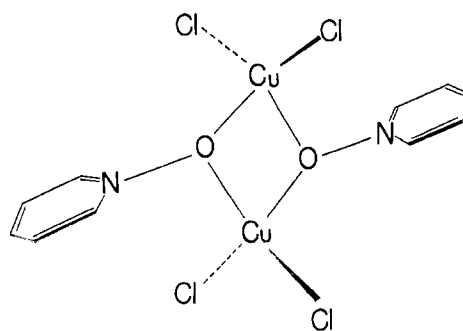


Figure 3.—The structure of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2]_2$.

of the dimeric compounds, and this effect has been correlated⁵ with the σ_R substituent constant.¹² Although the basis for the separation of the electronic substituent constant, σ , into a polar contribution, σ_I , and a resonance contribution, σ_R , is qualitative and perhaps artificial, the division has permitted the correlation and explanation of a considerable body of data.^{13,14} Recently, Eaton and Phillips have considered the utility of the concept in the discussion of the effect of chelate substituents on the contact shifts of some mixed aminotroponimine complexes of nickel.¹⁵

Although the quality of the experimental data will not permit a careful analysis, it is interesting to note that the trend in the singlet-triplet splitting energies parallels notions concerning the electron-donating properties by resonance of the methyl group. Essentially, this may be taken to indicate that electron-donating methyl groups stabilize the singlet states of the dimeric molecules.

One feature of the data for these compounds should be pointed out: the susceptibilities of the bromo complexes are consistently lower than those of the analogous chloro complexes. This probably means that conditions for spin-spin coupling are more readily met with the former, but, conceivably, could arise from such effects as variations in spin-orbit coupling or temperature-independent paramagnetism, TIP. Whereas, in our first paper¹ we assumed a constant value of 60×10^{-6} cgs unit for TIP, the data obtained in this study demonstrated that that value was too high; the susceptibilities of two compounds would have been negative if this "correction" had been applied. Since we have no experimental data bearing on this point we have elected not to adjust the experimental susceptibilities for TIP.

Although all 1:1 pyridine N-oxide complexes of copper halides exhibit low moments, the 4-nitroquinoline N-oxide complex with the empirical formula $\text{CuCl}_2 \cdot \text{NO}_2\text{C}_9\text{H}_6\text{NO}$ has a moment of 1.99 BM.¹⁶ This is a very interesting result since the unsubstituted quinoline N-oxide complex of copper chloride has a low moment³ and, also, in view of the extent the nitro group in the 4-position on the pyridine ring destabilizes the singlet state of $\text{CuCl}_2 \cdot \text{NO}_2\text{C}_5\text{H}_4\text{NO}$ in comparison to the singlet-triplet splitting in $\text{CuCl}_2 \cdot \text{C}_5\text{H}_5\text{NO}$.⁶ This compound is the only example of a 1:1 N-oxide complex with a normal moment that has thus far been characterized. The result suggests that the decreased donor strength of 4-nitroquinoline N-oxide with respect to the unsubstituted quinoline N-oxide and the

increased steric requirements of the ligand with respect to 4-nitropyridine N-oxide combine to force a drastic structural change. A di- or polymeric structure with chloride bridges could account for the magnetic properties of $\text{CuCl}_2 \cdot \text{NO}_2\text{C}_9\text{H}_7\text{NO}$, since Willett and co-workers¹⁷ have pointed out that the binuclear entities formed by bridging copper ions with chloride ions do not tend to be diamagnetic.

Spectra of the 1:1 Complexes.—The manner in which the spectral properties of magnetically "anomalous" compounds should be interpreted has not been resolved. For example, Reimann, *et al.*,¹⁸ have analyzed the spectrum of copper acetate in terms of individual copper(II) ions in the binuclear compound, whereas others have analyzed the spectrum in terms of molecular species.¹⁹ Since the magnetic interactions in the condensed pyridine N-oxide complexes of copper halides are at least twice as great as those in copper acetate monohydrate, it is suggested that the spectra be interpreted in terms of molecular species. As the two representative spectra in Figure 1 show, there are some potentially interesting spectral features. Perhaps the gross difference in the appearance of the near-infrared band (centered at about 800 $m\mu$) reflects the extent of the magnetic interactions in the two compounds and the populations of the singlet and triplet states. A detailed study of the spectra of single crystals is underway in our laboratory.

The Magnetically Normal Complexes.—All of the complexes reported herein with 2 moles of ligand per mole of copper halide have moments on the order of 1.9–2.0 BM. These moments should be compared with the moment of 0.63 BM per copper(II) ion for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2]_n$ ² which indicates that the unsubstituted compound has a di- or polymeric structure. The essential structural features of the parent compound seem to be retained in such diverse compounds as $[\text{Cu}(\text{CH}_3\text{C}_5\text{H}_4\text{NO})_2\text{Br}_2]_n$ and $[\text{Cu}(\text{CH}_3\text{C}_5\text{H}_4\text{NO})\{(\text{CH}_3)_2\text{SO}\}\text{Br}_2]_n$ since they exhibit moments of 1.33 and 0.97 BM, respectively.¹

A close examination of the structure of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2]_2$ yields a clue to the departure of the entire 2:1 series from the behavior exhibited by the 4-substituted pyridine N-oxide complexes. On the basis of the magnetic and infrared data, the 2:1 condensed complexes were assigned a structure which retained the binuclear unit with a second N-oxide ligand in the coordination shell of each copper atom.¹ Now it is unlikely that the steric requirements of the ligands with methyl groups in the 2 and 6 positions could be met under such a structural arrangement. This, of course, does not explain why $\text{Cu}(\text{ClC}_5\text{H}_4\text{NO})_2\text{Cl}_2$ is magnetically normal and probably possesses a monomeric structure. Evidently, in addition to the steric requirements of the ligands, there are important energetic

(12) σ_R is defined as $\sigma - \sigma_I$ where σ is the electronic substituent constant and σ_I is the polar part of the electronic substituent constant. This is the often used division of the electronic substituent constant and, in effect, is an attempt to divide the cause of the electronic effect into two categories, that is, the resonance effect which is thought to be transmitted through the π -electron system and which is designated by σ_R and the polar effect which is thought to act along σ bonds and through space.¹³

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factors to be considered. The data are not extensive enough to permit speculation.

Spectra of the 2:1 Complexes.—The spectrum of the magnetically normal compound dibromobis(2,6-lutidine N-oxide)copper(II) is typical of a great many four-coordinate copper(II) complexes with distorted structures lying somewhere between a square-coplanar arrangement and a tetrahedron.²⁰ Even though the magnetic properties of the 2:1 complex of 4-picoline N-oxide with copper bromide suggests a di- or polymeric structure, the spectrum of the complex is very similar to that of the magnetically normal and presumably monomeric compound. It is unfortunate that all solvents which will dissolve these compounds also decompose them, thus ruling out the use of conductivity or dipole moment measurements.

At least three structures must be considered before an assignment for the 2:1 complexes can be made. On the basis of the structure exhibited by $[\text{Cu}(\text{C}_6\text{H}_5\text{NO})\text{Cl}_2]_2$ and the similarity of the spectra of the compounds, the planar *cis* or *trans* structures with the fifth and/or sixth coordination positions filled by chloride ions from an adjacent molecule may be less likely than a distorted tetrahedral arrangement of nearest neighbor ligand atoms. A positive structural assignment must

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be deferred until the completion of some single-crystal X-ray studies which are underway in Professor Morrow's laboratory.

Mechanism for Spin-Spin Coupling.—The data collected in this study support the earlier proposal that the spin-spin coupling in binuclear pyridine N-oxide complexes of copper halides occurs by a mechanism which operates through the orbitals of the bridging oxygen atoms.⁶ The effect of the substituent is most easily seen in terms of a valence bond model for the substituted pyridine N-oxides. The methyl group donates electron density by resonance to the nitrogen atom adjacent to the bridging oxygen atom, thereby reducing the positive charge on the nitrogen atom which in turn diminishes the importance of canonical forms with nitrogen-oxygen double bonds. In this way the methyl groups enhance the electron density in the p_z orbitals of the bridging oxygen atoms and stabilize the singlet state of the dimeric molecules in the same manner that has been described for a series of binuclear Schiff's base complexes of copper(II).¹¹

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TECHNOLOGICAL CENTER, KING OF PRUSSIA, PENNSYLVANIA 19406

Titanium(IV) Chelates Containing Binegative Ligands

BY G. H. DAHL AND B. P. BLOCK

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The reaction of titanium(IV) alkoxides in 1:1 stoichiometry with 2-methyl-2,4-pentanediol, pyrocatechol, salicylic acid, or P,P'-diphenylmethylenediphosphinic acid yields chelates of the form $\text{Ti}(\text{BB})(\text{OR})_2$, where BB represents the binegative bidentate ligands involved and R is ethyl or isopropyl. A similar reaction with 1,3-propanediol does not produce $\text{Ti}(\text{OC}_2\text{H}_5\text{O})(\text{OR})_2$, but instead $\text{Ti}(\text{OC}_2\text{H}_5\text{O})_2$ and $\text{Ti}(\text{OR})_4$ are recovered. The $\text{Ti}(\text{BB})(\text{OR})_2$ derivatives are all associated in solution. Replacement of the alkoxy groups with acetylacetonate groups in the pyrocatecholate derivative gives the monomeric mixed chelate $[\text{Ti}(\text{o}-\text{C}_6\text{H}_4\text{O}_2)(\text{C}_5\text{H}_7\text{O}_2)_2]$. P,P'-Diphenylmethylenediphosphinic acid was prepared *via* the reaction of diisopropyl phenylphosphonite with methylene iodide.

In connection with our polymer studies we had a need for compounds of the type $\text{Ti}(\text{BB})\text{X}_2$ in which BB represents a doubly charged chelating group and X is a readily replaced anion. Examination of the literature failed to reveal any good candidates for our purposes, so we undertook the synthesis of a few compounds of this type. As the reactive group X we selected alkoxides and for the chelating agent pyrocatechol, salicylic acid, and P,P'-diphenylmethylenediphosphinic acid. We also repeated the reaction of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ with 2-methyl-2,4-pentanediol, the only alkoxy derivative of the $\text{Ti}(\text{BB})\text{X}_2$ type which we found

described in the literature,¹ and attempted to make $\text{Ti}[\text{O}(\text{CH}_2)_3\text{O}][\text{OCH}(\text{CH}_3)_2]_2$.

Experimental Section

The sensitivity of many of the titanium compounds to moisture required the use of carefully dried solvents and reagents as well as manipulation in the absence of moist air.

Materials.—Technical grade 2-methyl-2,4-pentanediol (Matheson Coleman and Bell) was dried by refluxing with a small amount of sodium and then vacuum distilled, n^{25}_D 1.4266 (lit.² n^{17}_D 1.4298).

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