

CONTRIBUTION FROM THE RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION,  
MONSANTO COMPANY, ST. LOUIS, MISSOURI 63166**Nitrilotri(methylenephosphonic acid) N-Oxide and Nitrilotriacetic Acid N-Oxide: Acidity and Complexing of Calcium and Magnesium Ions**

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Received August 8, 1966

The synthesis and aqueous stability of nitrilotri(methylenephosphonic acid) N-oxide are reported. Its acidity constants and calcium and magnesium stability constants are reported in addition to those for nitrilotriacetic acid N-oxide. Available information, including  $^1\text{H}$  and  $^{31}\text{P}$  nmr measurements as a function of the number of bound protons, indicates these ligands exist as dipolar ions in solution.

In recent years, considerable interest has developed in the complexing properties of molecules containing phosphonate moieties.<sup>1,2</sup> However, the synthesis and complexing properties of an  $\alpha$ -aminomethylphosphonic acid N-oxide have not been reported. This paper reports the synthesis, acidity, and complexing of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for nitrilotri(methylenephosphonic acid) N-oxide (ONTMP).

The stepwise replacement of N-acetate by N-methylenephosphonate groups in nitrilotriacetic acid (NTA) results in an increase<sup>2-4</sup> in the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  stability constants, although the increase over NTA does not follow a linear relationship.

The comparison of nitrilotriacetic acid N-oxide (ONTA) and nitrilotri(methylenephosphonic acid) N-oxide (ONTMP) was desirable in order to determine the effect of the N-oxide group on complex formation and to ascertain whether replacement of an acetate N-oxide by a methylenephosphonate N-oxide group would cause similar changes.

ONTA was, therefore, also synthesized and its acidity and complexing of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  studied. An independent synthesis of ONTA has been reported.<sup>5</sup>

In an attempt to define the individual deprotonation steps, changes in the  $^1\text{H}$  and  $^{31}\text{P}$  nmr chemical shifts were measured as a function of the number of protons per ligand. This approach, in conjunction with acidity data on various aqueous N-acetates,<sup>6</sup> was useful in establishing the dipolar nature of such ions in solution, as well as their ionization patterns.

**Experimental Section**

**Synthesis.**—Nitrilotri(methylenephosphonic acid) N-oxide (ONTMP) was prepared by the reaction of pure nitrilotri(methylenephosphonic acid) (NTMP)<sup>7</sup> with  $\text{H}_2\text{O}_2$  under controlled conditions. A 0.50-mole sample of recrystallized NTMP was placed in a stirred reactor and 1.6 moles of  $\text{H}_2\text{O}_2$  (30%) added. The initial mixture was a slurry which slowly dissolved

to form a clear solution as the reaction proceeded. Stirring was continued for 11 hr.

The liquid reaction product was transferred to an evaporation dish and left at ambient temperature under a stream of dry air for 36 hr. The resulting slush was filtered and washed three times with methanol and then ground under methanol. Finally, the solid was washed with acetone, filtered, and the last traces of solvent removed under vacuum. The crystalline product was obtained in 49% yield; mp (uncor) 171° dec. *Anal.* Calcd for  $\text{C}_2\text{H}_{12}\text{O}_{10}\text{NP}_3$ : C, 11.44; H, 3.84; N, 4.45; P, 29.49. Found: C, 11.26; H, 3.78; N, 4.44; P, 29.52.

Nitrilotriacetic acid N-oxide (ONTA) was prepared by reaction of reagent grade nitrilotriacetic acid with 30%  $\text{H}_2\text{O}_2$  in a manner not substantially different from that reported by Coeur and Alary.<sup>5</sup> The product was isolated as the trisodium salt. *Anal.* Calcd for  $\text{C}_6\text{H}_8\text{O}_7\text{Na}_3$ : C, 26.39; N, 5.13. Found: C, 26.07; N, 4.87.

**Acidity and Stability Constants.**—Acidity constants of ONTMP in 1.0 M  $\text{KNO}_3$  and ONTA in 0.1 M  $\text{KNO}_3$  were determined potentiometrically at 25°.

The experimental procedures and calculations were identical with those described in the preceding paper.<sup>4</sup>

The various metal ion stability constants, defined by the equation

$$\beta_{\text{MH}_i\text{L}} = \frac{[\text{MH}_i\text{L}]}{[\text{M}][\text{H}_i\text{L}]}$$

where M stands for either  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  and L represents the appropriate ligand, are therefore relative values which are strictly valid only in 0.1 and 1.0 M  $\text{KNO}_3$  media. Choice of these conditions permits comparison with existing data on the parent compounds.

**Nuclear Magnetic Resonance Spectra.**—The  $^{31}\text{P}$  nmr measurements were obtained at 24.288 Mc with a Varian high-resolution spectrometer,<sup>8</sup> and chemical shifts are reported relative to 85%  $\text{H}_3\text{PO}_4$  as an external reference. A Varian A-60 spectrometer was used to obtain  $^1\text{H}$  data, and chemical shifts are reported relative to the methyl groups of the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid, present as an internal reference. Solutions for nmr measurements were prepared quantitatively in order to maintain constant concentration for each ligand. Solutions for  $^1\text{H}$  measurements were prepared in  $\text{D}_2\text{O}$  and the pH adjusted with DCl or NaOD.

The approximate hydrolytic stability of ONTMP was determined as a function of pH and temperature by following for up to 144 hr the disappearance of the characteristic  $^1\text{H}$  and  $^{31}\text{P}$  spectra of 20% aqueous solutions under conditions of 2.5 M HCl, pH 2, pH 6, pH 10, and 2.5 M NaOH at 25, 80, and 100°.

**Results**

**Hydrolytic Stability of Nitrilotri(methylenetriphosphonic acid) N-Oxide.**—The results of the hydrolytic

(8) M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *Inorg. Chem.*, **1**, 813 (1962).

(1) R. R. Irani and K. Moedritzer, *J. Phys. Chem.*, **66**, 1349 (1962).(2) S. Westerback, K. S. Rajan, and A. E. Martell, *J. Am. Chem. Soc.*, **87**, 2567 (1965), and references therein.(3) G. Schwarzenbach, H. Ackermann, and P. Ruchstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).(4) R. P. Carter, R. L. Carroll, and R. R. Irani, *Inorg. Chem.*, **6**, 939 (1967).(5) A. Coeur and J. Alary, *Bull. Soc. Chim. France*, 2412 (1964).(6) D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, 3645 (1963).(7) K. Moedritzer and R. R. Irani, *J. Org. Chem.*, **31**, 1603 (1966).

stability determination for ONTMP are presented in Table I.

TABLE I  
APPROXIMATE HALF-LIFE OF ONTMP  
IN AQUEOUS SOLUTION AS A FUNCTION OF pH AND TEMPERATURE

Temp., °C	Half-life, hr <sup>a</sup>				
	2.5 M HCl	pH 2	pH 6	pH 10	2.5 M NaOH
25	>650	>650	>2000	>>2000	>>2000
80	0.5	<0.7	~650	~1840	~650
100	0.1	<0.15	115	230	52

<sup>a</sup> Half-lives longer than 144 hr were estimated by extrapolation of linear first-order plots from initial slope.

As all acidity and complexing measurements were run at 25° employing fresh solutions, no difficulty was experienced with contamination by decomposition products.

**Acidity and Complexing.**—The potentiometric titration data are deposited with the American Documentation Institute.<sup>9</sup> Acidity and complexing measurements for ONTMP and ONTA were determined in the presence of K<sup>+</sup>. Like other oxyanions of phosphorus<sup>10</sup> ONTMP is expected to form weak complexes with K<sup>+</sup> having  $\beta_{KL}$  values in the range of 10<sup>1</sup> to 10<sup>2</sup>. The apparent dissociation constant for the least acidic proton of ONTMP is estimated to be smaller than 10<sup>-13</sup> in the absence complexing metal ions. K<sup>+</sup> complexing is probably not as important with ONTA.

The successive acidity constants for ONTMP and its parent acid (NTMP), as well as our ONTA and its parent acid (NTA), are tabulated in Table II along

TABLE II  
ACIDITY CONSTANTS

	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>	pK <sub>4</sub>	pK <sub>5</sub>	pK <sub>6</sub>
ON(CH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> <sup>a</sup>	<2	<2	3.28 ± 0.07	5.26 ± 0.07	6.95 ± 0.07	12.05 ± 0.16
N(CH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> <sup>a,b</sup>	<2	<2	4.30 ± 0.05	5.46 ± 0.05	6.66 ± 0.04	12.34 ± 0.14
ON(CH <sub>3</sub> CO <sub>2</sub> H) <sub>3</sub> <sup>c</sup>	<2	2.57 ± 0.01	7.89 ± 0.01			
N(CH <sub>2</sub> CO <sub>2</sub> H) <sub>3</sub> <sup>c,d</sup>	1.9	2.5	9.73			

<sup>a</sup> In 1.0 M KNO<sub>3</sub>. <sup>b</sup> Reference 4. <sup>c</sup> In 0.1 M KNO<sub>3</sub>. <sup>d</sup> J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," The Chemical Society, London, 1957.

with estimated errors. The latter are reported in terms of statistical 95% confidence limits. Values for the parent acids are included for comparison.

The phosphonate N-oxide titrates as a pentabasic acid having two strongly dissociated protons, with the sixth proton so weakly dissociated that it does not show a break in the pH titration curve. The acetate N-oxide titrates as a tribasic acid having two strong protons and one weak proton.

The stability constants for the 1:1 calcium and magnesium complexes are reported in Table III and errors are reported in terms of statistical, 95% confidence limits.

Log  $\beta_{MH_iL}$  values given in Table III are average

(9) Material supplementary to this article has been deposited as Document No. 9377 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$2.50 for photoprints or \$1.75 for 35-mm microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(10) V. P. Strauss and P. D. Ross, *J. Am. Chem. Soc.*, **81**, 5295 (1959).

values from a series of measurements at various M:H<sub>i</sub>L ratios and represent at least 8 log  $\beta_{MH_iL}$  determinations.

The average log  $\beta_{CaL}$  value for ONTMP includes only those log  $\beta_{CaL}$  determinations for M:L ratios below 0.66, as the existence of higher order complexes was shown by a steady increase in calculated log  $\beta_{CaL}$  values above a M:L ratio of 0.70. The average value for log  $\beta_{MgL}$  includes data taken over M:L ratios below 0.94. Above a ratio of 0.94, a steady increase in the calculated log  $\beta_{MgL}$  was observed, indicative of higher order complexes. No evidence of higher order complexes was obtained with ONTA.

**Nuclear Magnetic Resonance Measurements.**—The changes in <sup>1</sup>H and <sup>31</sup>P chemical shifts with the number of protons bound to the ligand are presented in Figure 1. For comparison, the <sup>31</sup>P and <sup>1</sup>H chemical shift changes for nitrilotri(methylenephosphonic acid)<sup>4</sup> and the <sup>1</sup>H chemical shifts for nitrilotriacetic acid<sup>6</sup> are included.

## Discussions and Conclusions

**Acidity.**—The occurrence of one very weakly acidic proton for ONTMP may be interpreted as due to the removal of the proton from the amine oxygen. Simple electrostatic arguments would not predict the large difference in pK<sub>5</sub> and pK<sub>6</sub> (5.10 units), if protons came only from the phosphonic acid groups. For example, the difference in pK<sub>5</sub> and pK<sub>6</sub> for tetraphosphoric acid,<sup>11</sup> a similarly charged anion, is 1.71 in 1 M tetramethylammonium nitrate.

The large change in the <sup>31</sup>P chemical shift occurring with the removal of the last proton from NTMP has

TABLE III  
LOG  $\beta_{MH_iL}$  FOR ONTMP (IN 1.0 M KNO<sub>3</sub>) AND  
ONTA (IN 0.10 M KNO<sub>3</sub>), 25°

	Log $\beta_{CaHL}$	Log $\beta_{MgHL}$
L <sup>6-</sup> = ON(CH <sub>3</sub> PO <sub>3</sub> ) <sub>3</sub> <sup>a-</sup>	5.69 ± 0.34	8.29 ± 0.16
HL <sup>5-</sup>	2.88 ± 0.11	3.56 ± 0.03
H <sub>2</sub> L <sup>4-</sup>	1.67 ± 0.3	2.06 ± 0.3
H <sub>3</sub> L <sup>3-</sup>	<<1	1.05 ± 0.02
ON(CH <sub>2</sub> CO <sub>2</sub> ) <sub>3</sub> <sup>3-</sup>	2.46 ± 0.06	2.83 ± 0.05

been attributed to the change in the extent of nitrogen hybridization upon removal of this proton. The much smaller corresponding change in <sup>31</sup>P chemical shift occurring with the removal of the last proton from ONTMP is quite consistent since the amine oxide deprotonation site is an additional atom removed from phosphorus and the proton removal does not result in the formation of a tertiary nitrogen.

(11) J. I. Watters, P. E. Sturrock, and R. E. Simonaitis, *Inorg. Chem.*, **2**, 765 (1963).

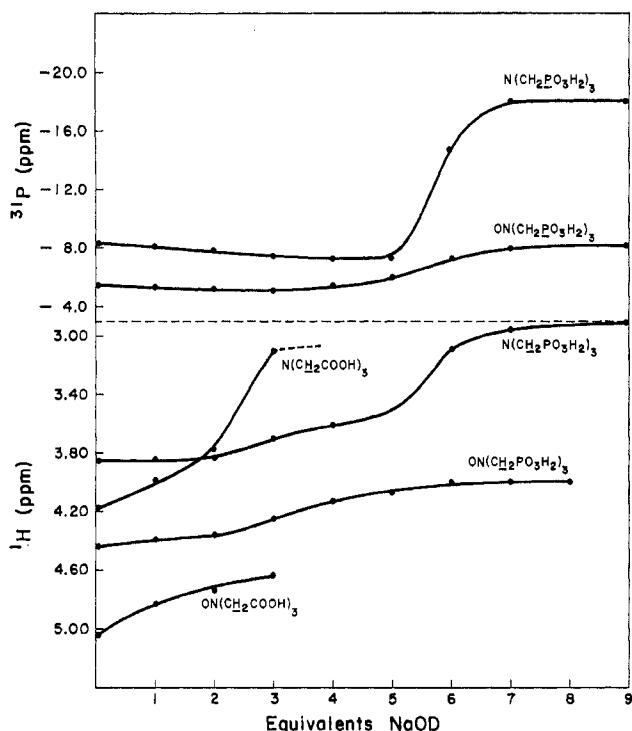


Figure 1.—Variation of  $^1\text{H}$  and  $^{31}\text{P}$  chemical shifts with equivalents of NaOD added for nitrilotri(methylenephosphonic acid) (0.33  $M$ ), its N-oxide (0.10  $M$   $\text{D}_2\text{O}$ ), and nitrilotriacetic acid (0.25  $M$ ) and its N-oxide (0.10  $M$   $\text{D}_2\text{O}$ ), 25°.

The inductive effect of the semipolar  $\text{N} \rightarrow \text{O}$  bond accounts for the general increase in acidity for ONTMP over NTMP although the reversal for  $\text{p}K_5$  is not understood. The possibility of very different stability constants for the respective potassium complexes and the effect of ionic strength on the two  $\text{p}K_5$  values was eliminated as a source of the anomaly by measuring the pH of very dilute solutions of the ligands, at a value of  $\bar{\alpha}^{12}$  of 1.5 in the absence of any supporting electrolyte; the pH of 0.0015  $M$  solutions of each ligand was 8.03 for NTMP and 8.29 for ONTMP, indicating that the difference is real.

The actual value of the  $^{31}\text{P}$  chemical shift increases slowly with successive deprotonations for NTMP, until the removal of the last proton. With ONTMP, however, the  $^{31}\text{P}$  chemical shift increases for the removal of only the first three protons and decreases for the removal of the remainder. This difference in behavior is worthy of comment.

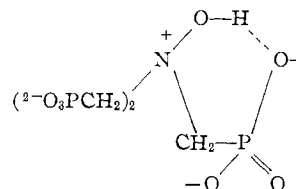
Letcher and Van Wazer<sup>13</sup> have presented a quantum mechanical argument which predicts opposing contributions to  $^{31}\text{P}$  chemical shifts from the inductive effects of proton dissociation as compared to accompanying effects due to changes in  $\pi$  bonding between phosphorus and oxygen. Previously, it has been shown that deshielding effects predominate on deprotonation of phosphates<sup>8</sup> while shielding effects are overriding for simple phosphonates.<sup>14</sup> The chemical shift behavior of NTMP is thus typical of simple phosphonates, while ONTMP

(12)  $\bar{\alpha}$ , defined by eq 5 of ref 4, is the average number of bound protons per ligand.

(13) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).

(14) K. Moedritzer, *Inorg. Chem.*, **6**, 936 (1967).

behaves like a simple phosphonate for the removal of the first three protons and more like a phosphate for the removal of the final three protons. Since the changes in inductive effects are probably quite similar in both compounds, this reversal in the chemical shift behavior of ONTMP probably indicates greater relative changes in  $\pi$  bonding between oxygen and phosphorus during removal of the last three protons from that compound. Hydrogen bonding between undissociated proton(s) and the oxygens of the phosphonate moieties is probably involved. For example, the following type structure may be important.



The pH data show that the weakest proton of ONTA is a stronger acid than the weakest proton of the parent compound NTA. This increase in acidity for the final proton may be explained by the existence of a dipolar ion in solution, similar to that suggested for ONTMP. It is known, for example, that the  $\text{p}K$  for the protonated form of triethylamine oxide is lower, by more than five orders of magnitude, than the  $\text{p}K$  for the protonated form of triethylamine (5.13 vs. 10.77).<sup>15</sup> The smaller decrease for  $\text{p}K_3$  in going from NTA to ONTA ( $\text{p}K$  7.89 vs. 9.73) and  $\text{p}K_6$  in going from NTMP to ONTMP ( $\text{p}K$  12.05 vs. 12.34) probably reflects the increasing effects of hydrogen bonding, as well as increasing total anionic charge.

It is interesting to compare the effect on the methylene chemical shifts of the removal of the weakest proton from ONTA and NTA. The loss of the final proton from NTA coincides with a sudden change in chemical shift, while with ONTA the chemical shift of the methylene group does not respond strongly to ionization of the last proton. The same is true of the methylene protons in ONTMP. These observations are consistent with the existence of dipolar ions in solution with the site for removal of the weakest proton from the N-oxides one additional atom removed from the methylene protons.

**Complexing.**—A striking feature of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  complexing data is the large decrease in the stability constants for ONTA relative to NTA. In 0.1  $M$  KCl at 20°, the values for NTA<sup>16</sup> are  $\log \beta_{\text{CaL}} = 6.41$  and  $\log \beta_{\text{MgL}} = 5.41$ , as compared to  $\log \beta_{\text{CaL}} = 2.46$  and  $\log \beta_{\text{MgL}} = 2.83$  for ONTA at 25° in 0.1  $M$   $\text{KNO}_3$ . This difference can be attributed to the decrease in the chelation effect due to the replacement of a tertiary nitrogen with a quaternary N-oxide group. The lower value is also consistent with the generally accepted criterion that the anion of the weaker acid forms the more stable metal complex.

No large decrease is observed with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$

(15) C. C. J. Culvenor, *Rev. Pure Appl. Chem.*, **3**, 83 (1953).

(16) G. Schwarzenbach, et al., *Helv. Chim. Acta*, **38**, 1147 (1955).

complexing by ONTMP in comparison to NTMP. The  $\log \beta_{ML}$  values for NTMP<sup>4</sup> are 6.68 and 6.73 (1.0 M KNO<sub>3</sub>, 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<sup>2+</sup> *vs.* Mg<sup>2+</sup> 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.

**Acknowledgments.**—The authors wish to thank Dr. R. L. Carroll for helpful discussions.

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## Properties of Some Copper(II) and Zinc(II) N-Oxide and $\beta$ -Diketone Complexes

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Received October 21, 1966

The unit cell dimensions, space group, and molecular weight have been determined for a number of copper(II) and zinc(II) N-oxide and  $\beta$ -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<sub>3</sub>Cl<sub>6</sub> (2-picoline N-oxide)<sub>2</sub>·2H<sub>2</sub>O. 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)<sub>2</sub>Cu<sup>II</sup>, (TFA)<sub>2</sub>Cu<sup>II</sup>(DMSO), [(TFA)<sub>2</sub>Zn<sup>II</sup>]<sub>3</sub>, (TFA)<sub>2</sub>Zn<sup>II</sup>(DMSO)<sub>2</sub>, (HFA)<sub>2</sub>Cu<sup>II</sup>·2H<sub>2</sub>O, (HFA)<sub>2</sub>Zn<sup>II</sup>·2H<sub>2</sub>O, and (BTFA)<sub>2</sub>Cu<sup>II</sup> 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)<sub>2</sub>Zn<sup>II</sup> 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<sup>1-6</sup> and the crystal structures of dichloro(pyridine N-oxide)copper(II),<sup>7</sup> C<sub>5</sub>H<sub>5</sub>NOCuCl<sub>2</sub>, and dichlorobis(pyridine N-oxide)copper(II),<sup>8</sup> (C<sub>5</sub>H<sub>5</sub>NO)<sub>2</sub>CuCl<sub>2</sub>, 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.

(1) Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Japan*, **39**, 58 (1966).

(2) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(3) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3773 (1961).

(4) H. B. Jonassen, Y. Muto, and M. Kato, *U. S. Govt. Res. Rept.*, **39** (9), 20 (1964).

(5) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(6) W. E. Hatfield and J. C. Morrison, *ibid.*, **5**, 1390 (1966).

(7) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(8) J. C. Morrow, National Meeting of the American Crystallographic Association, Gatlinburg, Tenn., June 1965.

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  $\beta$ -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