the compounds not containing the nitro group. The decreased stability arises from the electron-withdrawing influence of the nitro group. The extent of destabilization of the chelates of 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid appears to differ markedly among the several metal ions studied. The order of destabilization as measured by the stability decrease on the introduction of the nitro group is Zn(II) > Co(II) > Ni(II), which is reflected in the stability order as Cu(II) > Ni(II) > Zn(II), Co(II). This stability order is in better agreement with the order observed for 8-quinolinol and 8-quinolinol-5-sulfonic acid than any other 2-methyl derivative thus far studied.

A similar comparison of the chelates of 7-nitro-8-quinolinol-5-sulfonic acid was not possible because the chelates were significantly formed prior to titration, in most cases. However, sufficient stability data were obtained to establish that steric hindrance was still a factor in the formation of the chelates of 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid. The stability order obtained for 7-nitro-8-quinolinol-5-sulfonic acid is Cu(II) > Ni(II) > Co(II) > Zn(II). The formation constant of the zinc chelate was in satisfactory agreement with the previous study.[17] The formation of a 3:1 nickel chelate was indicated for the first time in the present study.

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Metal-Containing Compounds of the Anion $(C_2H_5)_2NN_2O_2^-$

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The following compounds of the anion $(C_2H_5)_2NN_2O_2^-$ have been prepared: $K(C_2H_5)_2NN_2O_2$, $Ca((C_2H_5)_2NN_2O_2)_2\cdot 2H_2O$, and $Cu((C_2H_5)_2NN_2O_2)_2\cdot CH_3OH$. Evidence is presented to indicate that the anion is a bidentate, chelate ligand in the copper compound. Complexes with Co^{+2}, Ni^{+2}, Mn^{+2}, Fe^{+3}, and Cr^{+3} form in solution. The infrared spectrum of the ethylated product $(C_2H_5)_2NN_2O_2C_2H_5$ is compared with those of the metal derivatives.

Introduction

Reactions of nitrogen(II) oxide with various primary and secondary amines are reported[2,3] to form compounds of the type $R_2NH_2^+R_2NN_2O_2^-$. It is suggested that the structure of $(C_2H_5)_2NN_2O_2^-$ is similar to that for the anion $SO_3N_2O_2^{-2}$, which is established by an X-ray study.[4] The two oxygens would then be *cis* to one another and $(C_2H_5)_2NN_2O_2^-$ should be capable of forming neutral chelate complexes with metal ions, similar to those formed by acetylacetonate. These considerations led us to study some metallic derivatives of the ligand $(C_2H_5)_2NN_2O_2^-$. Ionic sodium, potassium, and calcium compounds are formed.

Spectroscopic and conductometric studies demonstrate the existence of the neutral copper and cobalt complexes in solution. The neutral complexes appear to be solvent-stabilized, forming readily in solution but decomposing upon removal of solvent; however, a solvated copper complex can be isolated. Elemental analysis, infrared spectra, and molecular weight data are presented for the copper complex to indicate that the $(C_2H_5)_2NN_2O_2^-$ ion behaves as a bidentate ligand.

Experimental

Instrumentation.—Infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. The instrument was frequency calibrated using the absorptions of ammonia, water vapor, and polystyrene, and the appropriate corrections were applied to the spectral data reported.

Nuclear magnetic resonance spectra were obtained at room temperature in carbon tetrachloride solution (with 1% tetramethyl silane) with a Varian Model A-60 spectrophotometer employing a 60 Mc. probe.

Conductivity data were obtained with an Industrial Instruments, Inc., conductivity bridge, Model RC 16 B2.

Molecular weights were determined in toluene with a Mechrolab, Inc., Model 301A vapor pressure osmometer.

Ultraviolet and visible spectra were obtained with a recording Bausch and Lomb Spectronic 505 spectrophotometer employing hydrogen and tungsten lamp sources.

Preparative Techniques.—Unless otherwise indicated, commercial, reagent grade materials were used.

Diethylammonium Salt.—This compound was prepared by the high pressure technique and purified as previously described.[3]

Sodium and Potassium Salts.—The synthesis of the sodium salt has been reported.[2] An analogous procedure (except for the use of KOC_2H_5) yields the potassium salt. Purification was effected by washing the crude material with cold ethanol, chloroform, and anhydrous diethyl ether. Both compounds were very hygroscopic, and were dried in a vacuum desiccator

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[1] American Cyanamid Fellow, 1961–1962. Abstracted in part from the Ph.D. Thesis of Raymond Longhi, University of Illinois, 1962.

[2] R. S. Drago and F. E. Paulik, *J. Am. Chem. Soc.*, **82**, 96 (1960).

[3] R. S. Drago and B. R. Karstetter, *ibid.*, **83**, 1819 (1961). The structures, relative stabilities, and physical properties of these materials are discussed and other references pertinent to nitric oxide reactions are contained in these articles.

[4] E. G. Cox, G. A. Jeffrey, and H. P. Stadler, *J. Chem. Soc.*, 1783 (1949); *Nature*, **162**, 770 (1948); G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1467 (1951).

over anhydrous P_2O_5. Once obtained in the anhydrous form, these salts had a very limited solubility in ethanol.

Anal. Calcd. for $K^+(C_2H_5)_2NN_2O_2^-$: C, 28.05; H, 5.89; N, 24.54. Found: C, 28.23; H, 6.17; N, 24.31.

Calcium Salt.—The sodium salt prepared *in situ* was used directly in this synthesis. If equimolar quantities of sodium hydroxide and the diethylammonium salt were allowed to react in a minimum amount of distilled water (15 cc. of H_2O/g. of NaOH) and the mixture was extracted with ethyl ether to remove diethylamine, a clear, colorless, aqueous layer was obtained to which powdered anhydrous calcium chloride was added directly in an amount corresponding to one-half the molar theoretical yield of sodium salt. A white solid formed immediately and was filtered, washed with excess absolute ethanol, and vacuum-dried over P_2O_5. The product evolved nitric oxide when treated with hydrochloric acid.

Anal. Calcd. for $Ca[(C_2H_5)_2NN_2O_2]_2 \cdot 2H_2O$: C, 28.23; H, 7.10; N, 24.69. Found: C, 28.15; H, 6.88; N, 24.57.

Copper Complex.—One mole of $CuCl_2$ in a minimum amount of distilled water was cooled to 0–5° in an ice–salt bath and added in small portions to a cold (0–5°) solution of 2.5 moles of $Na^+(C_2H_5)_2NN_2O_2^-$ in a minimum amount of 1:1 methanol–distilled water. After each addition the green reaction mixture was extracted with diethyl ether. Attempts were made to keep the reaction flask cool throughout this procedure. The deep blue ether extracts were combined and dried over anhydrous sodium sulfate. The ether solution was filtered, and the solvent removed under vacuum (at 5–10°) in a stream of pure, dry nitrogen. The resulting blue crystalline solid decomposed with NO evolution without melting when warmed to just above room temperature. The solid evolved nitric oxide when treated with concentrated hydrochloric acid, and slowly precipitated metallic silver when treated with aqueous $AgNO_3$. Molecular weights determined in toluene (at 37° on solutions in the concentration range of 9.1 to 5.3 mg./cc.) on different preparations were 360, 357, and 359, compared to a theoretical value of 360. A typical analysis is reported.

Anal. Calcd. for $Cu[(C_2H_5)_2NN_2O_2]_2 \cdot CH_3OH$: C, 30.04; H, 6.72; N, 23.36; Cu, 17.65; mol. wt., 360. Found: C, 29.84; H, 6.53; N, 23.16; Cu, 17.77; mol. wt. in toluene, 359.

Attempts to remove the methanol from the compound under vacuum (0.5–1 mm.) at −78 or 0° produced no change, whereas vacuum treatment at room temperature resulted in decomposition.

$(C_2H_5)_2NN_2O_2C_2H_5$.—The procedure employed is similar to that reported by Reilly.[5] One mole of solid $(C_2H_5)_2NH_2^+(C_2H_5)_2NN_2O_2^-$ was added slowly to a solution prepared by dissolving 1.35 moles of NaOH in a minimum amount of distilled water. After the resulting paste was extracted several times with diethyl ether, the remaining pasty aqueous residue was dissolved in methanol, and, while stirring, 1.50 moles of $(C_2H_5)_2SO_4$ was added. The reaction mixture was allowed to stand for 1 hr. at room temperature and then heated on a steam bath (for more than 1 hr.) until no further vapor evolution was noted and a tan "wet" solid remained. The entire residue was extracted with anhydrous diethyl ether until the solid appeared white, and the combined extracts were dried over anhydrous Na_2SO_4 and anhydrous $CaCl_2$, and filtered. The solvent was removed at room temperature under vacuum, and the resulting viscous deep brown liquid was distilled at reduced pressure. The clear light yellow liquid product was obtained in 75% yield and had a b.p. of 54.5° at 0.05 mm. and $n^{24.3}D$ of 1.4501.

Anal. Calcd. for $(C_2H_5)_2NN_2O_2C_2H_5$: C, 44.74; H, 9.38; N, 26.07; mol. wt., 161. Found: C, 44.90; H, 9.31; N, 25.88; mol. wt. in acetone, 163.

$K_2SO_3 \cdot 2NO$.—The synthesis of this compound has been reported.[6]

Results and Discussion

Although many first row transition metal ions appear to form complexes with the anion $(C_2H_5)_2NN_2O_2^-$ in solution, attempts to isolate stable solid products were successful only with Cu(II).

A number of experimental procedures were employed in which solutions of the sodium and diethylammonium salts were used as anion sources in reactions with anhydrous transition metal chlorides in a variety of solvents, mixed solvents, or in the solid state. Marked color changes occur in the reactions with Cu^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2}, Fe^{+3}, and Cr^{+3} in solution at stoichiometries suggestive of complexation by the $(C_2H_5)_2NN_2O_2^-$ ion. Attempts to prepare the Pd(II) complex in absolute ethanol resulted in the production of metallic palladium.

A variety of isolation procedures was employed without success in attempts to isolate solid complexes. Only the procedure described in the Experimental section was successful for the copper salt.

Cobalt(II) Complex.—Continuous variation studies of the conductivity and ultraviolet and visible spectra of mixtures of $Na(C_2H_5)_2NN_2O_2$ and $CoCl_2$ were performed in absolute ethanol. Figure 1 illustrates the data obtained for this system (both compounds at 0.1 *M* concentration). Mole fraction of the sodium salt is plotted *vs.* the "change in conductance." The latter refers to the difference in conductance readings between the actually observed value and a straight line connecting the points obtained for pure $CoCl_2$ and pure $Na(C_2H_5)_2NN_2O_2$ representing no interaction. The vertical lines illustrate the limits of experimental error, which are ±5%. Since sodium chloride is a reaction by-product, we have corrected each reading by subtracting from it the conductance of a saturated sodium chloride solution in absolute ethanol. The primary point of interest is the very distinct break in the curve at a 2 anion to 1 cobalt ratio. This corresponds to a minimum conductivity in the study and is suggestive of the formation of an uncharged compound.

The system $CoCl_2$–$Na(C_2H_5)_2NN_2O_2$ at concentrations of 5×10^{-3} *M* in absolute ethanol also was studied spectroscopically at 320 mμ by the continuous variation procedure. Figure 2 illustrates the curve obtained when Δ absorbance *vs.* mole fraction of $Na(C_2H_5)_2NNO_2$ is plotted. The "change in absorbance" values are obtained from a difference plot similar to that used for the conductivity experiment. This curve also shows a distinct break at a 2 anion to 1 cobalt mole ratio.

Copper(II) Complex.—Since a solvated copper complex could be isolated, its properties were examined in detail. The copper complex has solubilities similar to the metal acetylacetonates; it is soluble in a wide variety of polar and non-polar hydrocarbon solvents (including CCl_4), but only sparingly soluble in water, where it appears to decompose within a short period of time at room temperature. Infrared spectra show that this complex is stable for several weeks at −78° under dry nitrogen, but it decomposes within a few hours when

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[5] E. L. Reilly to E. I. du Pont de Nemours and Co., French Patent No. 1,171,532, Jan. 27, 1959.

[6] R. S. Drago, *Inorg. Syn.*, **5**, 120 (1957).

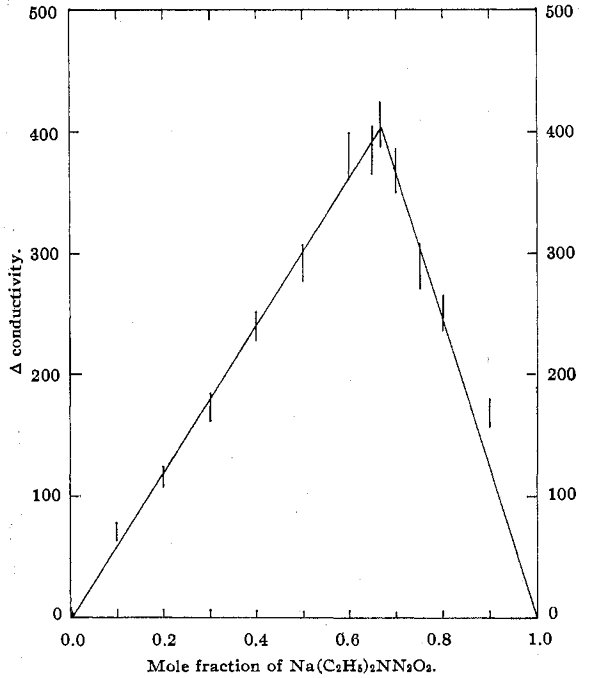

Fig. 1.—Continuous variation study of the system $CoCl_2$–$Na(C_2H_5)_2NN_2O_2$ at a total concentration of 0.1 *M* in absolute anhydrous ethanol. The vertical lines illustrate the limits of experimental error.

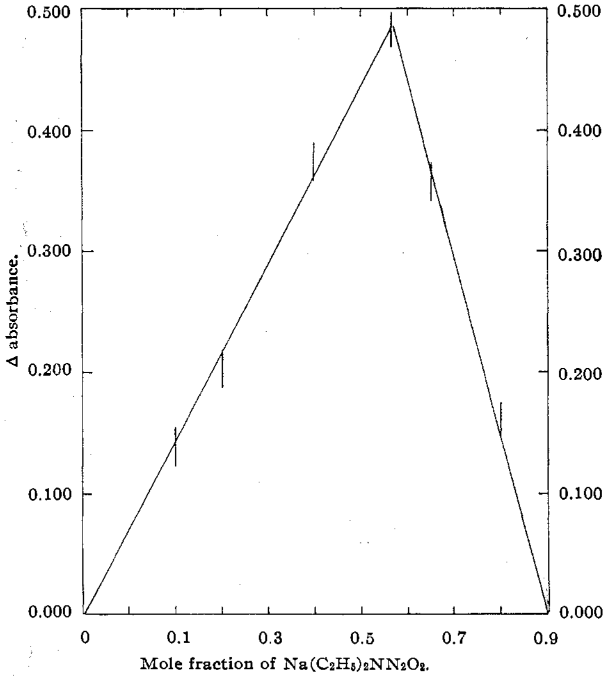

Fig. 2.—Continuous variation study of the system $CoCl_2$–$Na(C_2H_5)_2NN_2O_2$ at a total concentration of 5×10^{-3} *M* in absolute anhydrous ethanol. The vertical lines illustrate the limits of experimental error.

exposed to the air at room temperature to give a green then brown solid. The solvated methanol could not be removed without product decomposition.

The calculated molecular weight for $CuL_2 \cdot CH_3OH$ (where $L = (C_2H_5)_2NN_2O_2^-$) is 360. The measured value of 359 ± 3 indicates that the complex is monomeric and that methanol is in the coördination sphere. It is now necessary to consider whether or not the ligand is bidentate. If it is, several possible structures can be eliminated. Evidence indicating its bidentate nature is obtained from an examination of the N–O stretching frequencies of various compounds (Table I) (Fig. 3).

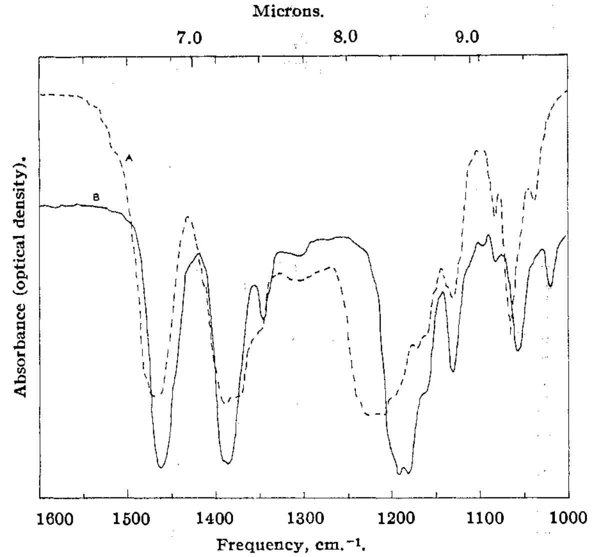

Fig. 3.—Infrared spectra of $Na(C_2H_5)_2NN_2O_2$ (A) and $Cu[(C_2H_5)_2NN_2O_2]_2 \cdot CH_3OH$ (B) in the region 1600–1000 cm.$^{-1}$; spectra obtained in Nujol mulls.

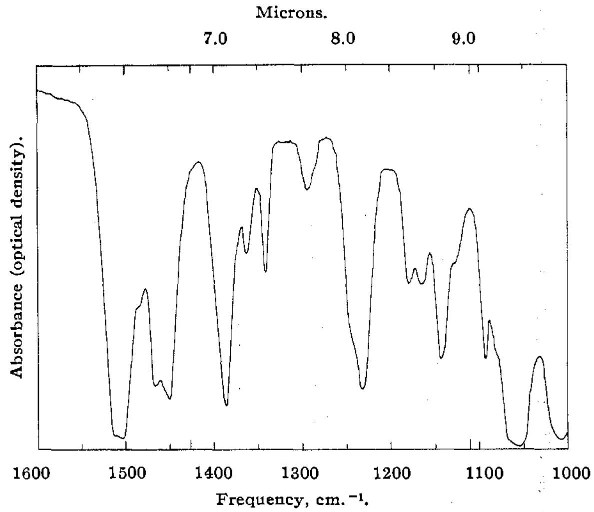

Fig. 4—Infrared spectrum of $(C_2H_5)_2NN_2O_2C_2H_5$ in the region 1600–1000 cm.$^{-1}$; spectrum obtained in CCl_4 solution at a concentration of 10%.

Assignments of the N–O frequencies in $K_2SO_3 \cdot 2NO$ have been reported.[7,8]

The broad band in the infrared spectrum of the sodium salt (curve A, Fig. 3) is attributed to the N–O stretching frequencies. This peak occurs at a lower frequency in the copper complex (curve B, Fig. 3) than in the ionic sodium, potassium, and calcium salts.

Examination of the structure for the anion indicates that the π-electrons in the N_2O_2 group are delocalized, and several resonance structures are indicated in Fig. 5.

If, in the formation of a neutral molecule, copper is coördinated at any one position of the N_2O_2 group, then

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[7] R. S. Drago, *J. Am. Chem. Soc.*, **79**, 2049 (1957).

[8] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 38 (1958).

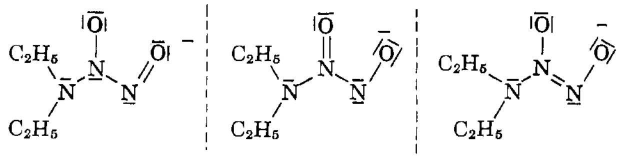

Fig. 5.—Resonance structures for $(C_2H_5)_2NN_2O_2^-$

TABLE I

N–O ABSORPTIONS OF SOME COMPOUNDS CONTAINING THE N_2O_2 GROUP[a]

Compound	N–N stretch in cm.$^{-1}$	N–O stretch in cm.$^{-1}$
$Na(C_2H_5)_2NN_2O_2$	1128	1225–1209
$K(C_2H_5)_2NN_2O_2$	1128	1225–1209
$Ca((C_2H_5)_2NN_2O_2)_2\cdot 2H_2O$	1129	1225–1210
$Cu((C_2H_5)_2NN_2O_2)_2\cdot CH_3OH$	1130	1190–1177
$K_2SO_3\cdot 2NO$	1130	1229 and 1322

[a] Spectral data are obtained from Nujol mulls unless otherwise indicated.

the stretching frequency of at least one of the N–O bonds should increase. This is observed when the anion is alkylated at one of the atoms in the N_2O_2 group, for the two N–O bonds now differ appreciably. Attachment of an alkyl group produces a compound whose infrared spectrum (Fig. 4) contains a band assigned to an N–O stretch at 1506 cm.$^{-1}$. Attachment of a copper(II) ion at any single position in the N_2O_2 group would be expected to give rise to NO absorptions from at least one NO group at higher wave numbers than the value 1225 cm.$^{-1}$ observed in the ionic materials. The absence of appreciable absorption above 1200 cm.$^{-1}$ in the spectrum of mulls or solutions of the copper complex is interpreted to indicate simultaneous attachment of the copper ion to both oxygens in the anion. This would cause the observed decrease in frequency of the entire N–O peak.

If $(C_2H_5)_2NN_2O_2^-$ is a bidendate chelate, molecular weights of the copper complex show that in toluene solution the complex exists either as (1) a five-coördinate copper species, (2) a six-coördinate form with toluene in the coördination sphere, or (3) the complex undergoes the following reaction to form four and six-coördinate copper species in solution.[9]

$$[CuL_2\cdot CH_3OH]_x \xrightarrow{C_6H_5CH_3} CuL_2 + CuL_2\cdot 2CH_3OH$$

We prefer (3) as the explanation. The spectrum of the square planar and tetragonal complexes could not be separately distinguished in the ultraviolet and visible regions.

The visible spectra of the complex were examined in a variety of solvents. As with the bis-acetylacetonato copper(II) complex, a spectral shift is observed toward longer wave lengths in basic solvents.[10] The following solvents are in order of spectral shifts to longer wave lengths: $CCl_4 \sim$ acetone $\sim CH_3OH < DMF < CH_3CN \sim$ pyridine. In solvents more basic than methanol the shift probably is due to solvent interaction along d_{z^2}.

The n.m.r. spectrum of the ethylated products shows two distinct $-CH_2-$ and $-CH_3$ absorptions for the ethyl groups. This is interpreted as being due to the existence of $O-C_2H_5$ and $N(C_2H_5)_2$ groups.[11] The relative intensities aid in this assignment. The chemical shifts, δ, for these peak centers relative to tetramethylsilane are: $O-CH_2-$, -4.2 p.p.m.; $N-CH_2-$, -3.0 p.p.m.; $O-CH_2-CH_3$, -1.4 p.p.m.; $N-CH_2-CH_3$, -1.0 p.p.m. There are two possibilities for O-alkylation in the product. A mass spectrum[12] was obtained in an attempt to determine which compound was prepared, but extensive fragmentation occurred and the problem was not resolved.

The assignment of the peak at 1506 cm.$^{-1}$ in the ethylated product to N–O stretch is reasonable. Assignments of NO stretch at this and higher wave numbers have been reported: 1800 cm.$^{-1}$ in NOCl,[13] at 1600–1500 cm.$^{-1}$ in nitroso compounds,[13] at 1527–1515 cm.$^{-1}$ in alkyl N-nitrosated amides,[14] at 1878 cm.$^{-1}$ in nitric oxide,[15] at 1586 cm.$^{-1}$ in nitromethane,[16] at 1486 cm.$^{-1}$ for monomeric $(C_2H_5)_2NNO$ in the vapor phase, and at 1464 cm.$^{-1}$ for the monomer in CCl_4 solution.[17]

Acknowledgments.—The authors wish to express their appreciation to the American Cyanamid Company for the award of a fellowship (to R. L.) and to the Department of the Army Ordnance Corps for financial support of this research under Contract No. DA-11-022-ORD-2772 and Grant No. USDA-G-72.

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[9] $[CuL_2\cdot CH_3OH]_x$ refers to a solid six-coördinate copper complex with bridging CH_3OH molecules.

[10] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[11] A private communication, kindly made available to us by J. P. Freeman, indicates that $O-CH_2-$ and $N-CH_2-$ resonances often overlap in organic compounds containing the $-N_2O_2-$ group. The $O-CH_2-$ resonance in this compound occurs at a much lower field than the overlap region ($\delta = -3.5$ to -2.3) in the compounds studied by Freeman. We have therefore tentatively assigned the quartet at -4.2 p.p.m. to $O-CH_2-$.

[12] The authors gratefully acknowledge the aid of S. Meyerson, American Oil Company, for supplying us with the mass spectrum of this product.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 304.

[14] E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

[15] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

[16] D. C. Smith, C. Y. Pan, and J. R. Nielson, *J. Chem. Phys.*, **18**, 706 (1950).

[17] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).