$$2CuCl_2^- + 2NO + 2H^+ \rightarrow N_2O + 2CuCl_2 + H_2O \quad (5)$$

The oxidation of CO by Pd^{2+} (reaction 2) which is first order[3] with respect to CO, Pd^{2+}, and Cl^-, is more rapid than the N_2O forming reactions 4 and 5. The reaction of NO with $CuCl_2^-$ is relatively slow,[4] but the rate of this reaction is considerably enhanced in the presence of Pd^{2+}. A palladium(II)-copper(I) chloride bridged species may be the reactive entity for reaction with NO, analogous to the tin(II)-copper(I) species suggested for the rapid copper(I) catalyzed reduction of NO with tin(II).[4] A UV-visible spectral study of the NO-CO-$PdCl_2$-$CuCl_2$ systems reveals the formation of a new band at 450 nm which we attribute to such a palladium(II)-copper(I)-NO species. This absorption band which is also observed in an aqueous solution containing $PdCl_2$-CuCl-NO-HCl decays with concomittant growth in intensity of absorption due to copper(II) at 800 nm. Palladium forms nitrosyl complexes such as $Pd(NO)_2Cl_2$ and insoluble PdNOCl, the latter which reacts with HCl to give N_2O, palladium(0) and palladium(II).[5] Under the present experimental conditions, the reaction of $PdCl_2$ with NO leading to PdNOCl and subsequent N_2O formation was found to be unimportant. The reaction of NO with a mixture of 50.0 mg of palladium(0) in 2 M HCl gave only a small yield of N_2O (5%) after stirring for 72 h. The results thus far appear to be consistent with a suggestion that the reactive entities for N_2O production are chloride bridged species containing palladium(II)-copper(I) and palladium(II)-palladium(0). The reduced rate of N_2O formation at high copper(II) concentration may be due to reduced palladium(0) concentrations (reaction 3) or formation of a copper(II)-NO complex[6] which, however, is unstable in aqueous solutions. The decreased rate of NO consumption at high copper(II) concentrations indicates that metal-NO complex formation is not an important factor.

Preliminary infrared spectral studies of the aqueous $PdCl_2$-$CuCl_2$-NO-CO systems have not provided useful results thus far. It would be appropriate at this stage to propose that a significant intermediate in the N_2O forming reaction is likely to be a palladium hyponitrite species with a cis-bidentate oxygen-bonded hyponitrite ligand such as reported for the complex resulting from the reaction of NO with the platinum(0) complex $Pt(PPh_3)_3$.[7] Further studies are being pursued to elucidate the mechanisms of reactions in the CO-NO-$PdCl_2$-$CuCl_2$ system and to seek even more efficient systems for the CO-NO reaction.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, The Research Corporation, and the Lilly Foundation for support of this research. J.C.M. acknowledges support from the National Science Foundation Undergraduate Research Program.

References and Notes

(1) J. D. Butler and D. R. Davis, *J. Chem. Soc., Dalton Trans.*, 2249 (1976).
(2) (a) C. D. Meyer and R. Eisenberg, *J. Am. Chem. Soc.*, **98**, 1364 (1976); (b) D. E. Hendriksen and R. Eisenberg, *ibid.*, **98**, 4662 (1976); (c) J. Reed and R. Eisenberg, *Science*, **184**, 568 (1974); (d) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).
(3) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, N.Y., 1971, p 120.
(4) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1912 (1970).
(5) J. Smidt and R. Jira, *Chem. Ber.*, **93**, 162 (1960).
(6) M. P. Doyle, B. Siegfried, and J. J. Hammond, *J. Am. Chem. Soc.*, **98**, 1627 (1976).
(7) S. Bhaduri, B. F. G. Johnson, A. Pickard, P. R. Raitby, G. M. Sheldrick, and C. I. Zuccaro, *J. Chem. Soc., Chem. Commun.*, 354 (1977).

Mitsuru Kubota,* Kent J. Evans,
Catherine A. Koerntgen, James C. Marsters, Jr.
Department of Chemistry, Harvey Mudd College
Claremont, California 91711

Received August 24, 1977

Nitroxide. 84.
Copper(II)-Bisnitroxide Complex as Evidence for Strong Electron-Exchange Six-Spin System

Sir:

ML_n type transition metal complexes in which L^- is a paramagnetic ligand and M^{n+} a metal ion can give information on electronic interactions.[1-8]

If M^{n+} is diamagnetic, this system is analogous to an organic polyradical.[9,10] If M^{n+} is paramagnetic, in a doublet state for instance, supplementary interactions are expected, leading to different electron spin resonance (ESR) spectra. ESR spectra of compounds containing several paramagnetic centers can be interpreted according to Schlichter's formalism.[9,11-14] For a ML_2 system, the spin hamiltonian can be represented by the six-spin diagram shown in Chart I, where a_M is the hyperfine interaction between the unpaired electron spin and the metal nuclear spin I_M,[15] a_N is the hyperfine interaction between the unpaired electron and one nuclear spin I_N in the ligand,[16] g_M and g_L are the corresponding g factors, and J and J' are the exchange interactions.

If dipolar interactions are small enough, the ESR spectrum in fluid isotropic solution of such a species will depend upon the relative magnitude of the absolute value of J and J' with respect to the absolute value of the hyperfine interactions and to $\Delta g = |g_M - g_L|$ in appropriate units.

Simple spectra are obtained in two limiting cases. In the weak exchange case, $|J|$ and $|J'|$ are both much smaller than $|a_M|$, $|a_N|$, and $|\Delta g\beta H|$ (β Bohr magneton, H applied magnetic induction); the spectrum is the superposition of the spectra of the isolated species. In the strong exchange case, ($|J|$ and $|J'| \gg |a_M|$, $|a_N|$, and $|\Delta g\beta H|$), one expects a signal centered at $g = (g_M + 2g_L)/3$, composed of $(2I_M + 1)(4I_N + 1)$ peaks, the splitting between lines being reduced to $a_M/3$ and $a_N/3$.

A simple example is to be found in complexes of Cu^{2+} ($I_{Cu} = 3/2$) with ligands containing nitroxide free radicals ($g_L \simeq 2.006$, $I_N = 1$, $a_N \simeq 15$ G). Although several examples of this type are known,[1,2,5-7] with g-value evidence for strong exchange,[1,6,7] to our knowledge no example has been reported

Chart I

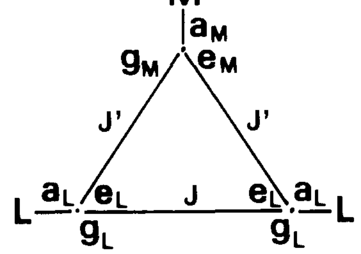
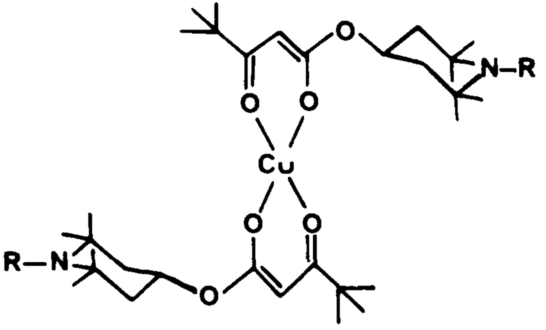


Chart II



1 R = H
2 R = O•

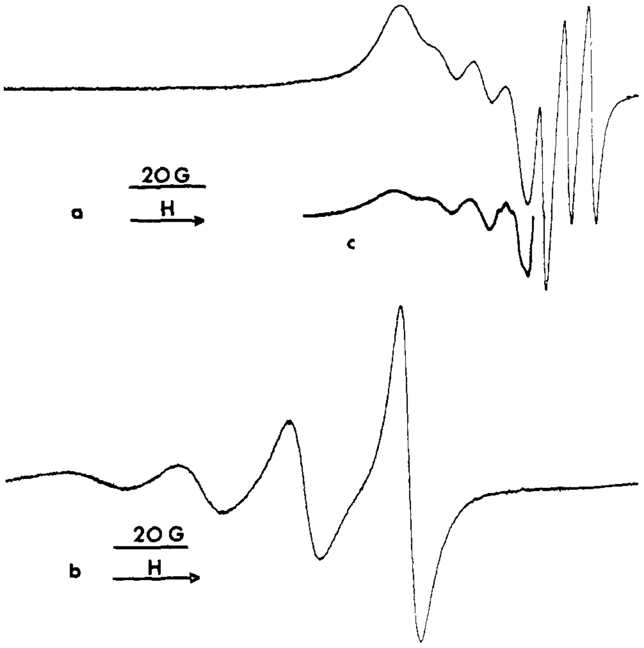


Figure 1. ESR spectrum of a 2 × 10^{-3} M solution in heptane: (a) of **2** at 20 °C; (b) of **1** at 20 °C; (c) of **2** at −60 °C.

of a hyperfine structure corresponding to a strong exchange case. Such evidence is given in the ESR spectrum of compounds **1** and **2**[17] (Chart II).

At 20 °C, a 2 × 10^{-3} M solution of **1** in heptane (Figure 1b) shows a four-line spectrum at $g_M = 2.126$, $a_{Cu} = 65$ G. At 20 °C, a 2.10^{-3} M solution of **2** in heptane (Figure 1a) shows at $g = 2.047$ four peaks assigned to the interaction of the electron spin with one copper nucleus. The weighted average $(g_{Cu} + 2g_L)/3 = 2.046$ is close to the experimental value. Similarly, the 22-G splitting is close to $a_{Cu}/3 = 21.66$ G. At −60 °C (Figure 1c), one of the four lines resolves to show four extra lines separated by 5 G. They may be ascribed to four of the five lines expected for two equivalent nitrogen atoms separated by $a_N/3 = 5$ G. The spectrum (Figure 1a) shows one additional three-peak signal at higher field ($g = 2.0065$) with a splitting of 15 G, the intensity of which increases with time. Such a signal is typical of an isolated nitroxide and can be attributed to either a reversible decomplexation or an irreversible decomposition possibly by electron transfer. The fact that a red powder deposits in the ESR tube upon standing seems to support the latter possibility, but does not exclude a reversible reaction. Such complex may be useful in the study of both phenomena.

To our knowledge, complex **2** is thus the first example of a three-electron, three-nucleus system for which the strong exchange case has been characterized by both the g-factor value and the hyperfine structure.[21]

References and Notes

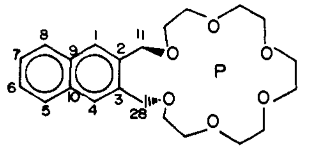
(1) A. Rassat and P. Rey, *Bull. Soc. Chim. Fr.*, **3**, 815 (1967).
(2) A. A. Medzhikov, L. N. Kirichenko, and G. I. Likhtenschtein, *Izv. Akad. Nauk SSSR*, 698 (1969).
(3) A. R. Forrester, S. P. Hepburn, R. S. Dunlop, and H. H. Mills, *Chem. Commun.*, 698 (1969).
(4) L. N. Kirichenko and A. A. Medzikov, *Izv. Akad. Nauk SSSR*, 2849 (1969).
(5) D. Jahr, K. E. Schwarzhans, D. Nöthe, and P. K. Burkert, *Z. Naturforsch., B*, **26**, 1210 (1971).
(6) D. Jahr, K. H. Rebhan, K. E. Schwartzhans, and J. Wiedemann, *Z. Naturforsch., B*, **28**, 55 (1973).
(7) P. Richardson and R. Kreilick, *Int. Symp. Magn. Reson., 6th, 1977*, 62 (1977).
(8) G. A. Braden, K. T. Trevor, J. M. Neri, D. J. Greenslade, and G. R. Eaton, *J. Am. Chem. Soc.*, **99**, 4854 (1977). See also P. M. Boymel, J. R. Chang, D. L. DuBois, D. J. Greenslade, G. R. Eaton, and S. S. Eaton, *ibid.*, **99**, 5500 (1977), and references herein.
(9) R. Brière, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, **11**, 3290 (1965).
(10) A. Hudson and G. R. Luckhurst, *Mol. Phys.*, **13**, 409 (1967).
(11) C. P. Schlichter, *Phys. Rev.*, **99**, 479 (1955).
(12) D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, **33**, 700 (1960).
(13) A. I. Burshtein and Y. I. Naberukhim, *Dokl. Akad. Nauk SSSR*, **140**, 1106 (1961).
(14) H. Lemaire, *J. Chim. Phys.*, **64**, 559 (1967).
(15) I.e. in similar complex where L^- is diamagnetic.
(16) I.e. in the isolated ligand.
(17) Microanalysis are in agreement with the structures. $F = 250°$ (**1**) and $F = 224°$ (**2**). They are prepared by standard method from the corresponding keto ester and copper acetate. Magnetic susceptibility of **2** has been reported.[18] Although keto esters are not so good chelating agents as β-diketones, this new ligand type permits the easy introduction of various groups. The *tert*-butyl substituent[19,20] provides steric protection and solubility in organic solvents. Complexes **1** and **2** are indeed soluble in all organic solvents that we have examined.
(18) C. Veyret and A. Blaise, *Mol. Phys.*, **25**, 873 (1973). We thank these authors for their measurements on our sample.
(19) R. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, **11**, 3196 (1965).
(20) G. D. Mendenhall, D. Griller, and K. U. Ingold, *Chem. Br.*, **10**, 248 (1974), and references therein.
(21) NOTE ADDED IN PROOF. Other three-electron, three-nucleus systems of higher symmetry are known, but they are characterized by one *J*, one *g*, and one a_N only; cf. A. L. Buchachenko, V. A. Golubev, M. B. Neiman, and E. G. Rozantsev, *Dokl. Akad. Nauk SSSR*, **163**, 1416 (1965), and A. Hudson and G. R. Luckhurst, *Mol. Phys.*, **13**, 409 (1967).

R. Brière, A. Rassat,* P. Rey
Laboratoire de Chimie Organique Physique
Equipe de Recherche No. 20 associée au CNRS
Département de Recherche Fondamentale
Centre d'Etudes Nucléaires de Grenoble
85 F.38041 Grenoble Cedex, France
Received August 12, 1977

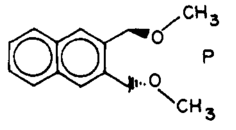
Experimental Observation of the Effect of an Oriented Positive Monopole on Carbon-13 Chemical Shifts of a Naphthalene Derivative. Crown Ether Conformational Changes and Their Effect on an Attached Naphthalene System

Sir:

The variation of ^{13}C chemical shifts of 2,3-naphtho-20-crown-6 (**1**) were noted as increasing mole ratios of alkali



1



2

metal, calcium, and barium salts were added. The data indicate that the naphthalene carbon chemical shifts are generally independent of crown ring conformation changes, independent of the polarizability of the perturbing cation, generally independent of the anion present, but dependent on cation charge, and correlated roughly with cation-induced charge density changes as calculated semiempirically. These results relate to theoretical treatments[1] of monopole effects on ^{13}C NMR chemical shifts, to conformational changes required as crown ethers complex cations, and also to the effects of salts on fluorescence, phosphorescence, and radiationless decay of crown **1** as reported recently.[2]

Experimental determinations of the effects of a noncovalently bound monopole on ^{13}C chemical shifts (or any other property for that matter) are rare.[3] Figure 1 shows the ^{13}C chemical shifts of uncomplexed 2,3-naphtho-20-crown-6 (**1**) in methanol-d_4 and the effect of 1:1 complexation[4] of Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, and Ba^{2+} salts on those shifts. Assignments for the naphthalene carbons are based on ytterbium shift stu-

0002-7863/78/1500-0344$01.00/0