better atom for promoting the type of spin coupling studied here than oxygen. We are presently engaged[22] in the study of a nitrogen-bridged species.

Acknowledgments.—We wish to acknowledge continued support by the National Science Foundation under Grant No. GP22887 and by the Materials Research Center of the University of North Carolina at Chapel Hill under Contract No. SD-100 with the Advanced Research Projects Agency. We also wish to thank Professor D. van der Helm for providing additional details concerning the structure prior to publication.

(22) J. F. Villa and W. E. Hatfield, to be submitted for publication.

CONTRIBUTION FROM THE WM. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Lewis Basicity of a Free-Radical Base. II

BY Y. Y. LIM[1] AND R. S. DRAGO*

Received September 13, 1971

Calorimetric measurements of the interaction of the free-radical base 2,2,6,6-tetramethylpiperidine-*N*-oxyl with the Lewis acids boron trifluoride and bis(hexafluoroacetylacetonato)copper(II) are reported. Using data previously reported,[2] the *C* and *E* numbers of the base were determined to be 6.21 and 0.915. The *C*/*E* ratio is much larger than other typical diamagnetic oxygen donor molecules, *e.g.*, ethyl acetate, dimethyl sulfoxide, and pyridine *N*-oxide, etc. The 1:1 adduct of Cu(hfac)$_2$ with the free-radical base was isolated and its magnetic properties were investigated. It was found that the adduct exhibited large intramolecular antiferromagnetic coupling. Various mechanisms of spin-spin interaction are proposed to explain its magnetic behavior. By comparing the enthalpy predicted for the formation of this adduct from the *E* and *C* correlation with that measured experimentally, the contribution to the stability of this adduct from spin-spin interaction can be estimated. The implication of these results to the bonding in systems involving coordinated O$_2$ are discussed.

Introduction

In a previous article from this laboratory,[2] it was demonstrated on the basis of epr spectral studies that in adduct formation with the stable free-radical base 2,2,6,6-tetramethylpiperidine-*N*-oxyl (hereafter designated as TMPNO) the donor MO is largely a lone-pair oxygen orbital. In order to understand better the chemistry of this new class of donors, we have extended the calorimetric investigation of the Lewis basicity of TMPNO with a series of Lewis acids, including bis(hexafluoroacetylacetonato)copper(II). The copper complex has one unpaired electron (in the $d_{x^2-y^2}$ orbital) which would be expected to undergo spin-spin exchange with the unpaired electron of TMPNO on adduct formation. The exchange of the two spins with each other is of interest, from the standpoint of the theory of both spin exchange and oxygen coordination.

An additional objective of the present study was to investigate the deviation of the enthalpy of adduct formation in a system in which spin pairing occurred from the enthalpy predicted from our *E* and *C* equation.[3] This equation has been successfully applied to many donor-acceptor systems where steric effects are absent[4] and where there is no possibility of spin pairing between the donor and the acceptor.

Experimental Section

(a) **Solvents.**—Reagent grade cyclohexane was stored over Linde 4A Molecular Sieves for several days prior to use. 1,2-Dichloroethane (Fischer Certified ACS grade) was stored over Linde 4A Molecular Sieves for at least 24 hr and used without further purification. The sieves were discarded and replaced with a fresh portion after several days due to the discoloration of the sieves.

(b) **Preparation and Purification of Acids and Bases.**—The free-radical base was prepared and purified as previously described.[2] The hydrated bis(hexafluoroacetylacetonato)copper(II) was prepared as described previously.[5] The anhydrous form obtained by sublimation under reduced pressure could be stored over P$_2$O$_5$ (*in vacuo*) for several days.

Anal. Calcd for CuC$_{10}$H$_2$O$_4$F$_{12}$: C, 25.13; H, 0.42; Cu, 13.31. Found: C, 24.97; H, 0.42; Cu, 13.12.

The boron trifluoride-diethyl ether adduct was purified as previously described.[6]

(c) **Preparation of the 1:1 Adduct of Cu(hfac)$_2$ with TMPNO.**—Stoichiometric amounts of Cu(hfac)$_2$ were mixed with the free radical in methylene chloride in a drybag and the solvent was removed by filtration. The resulting complex is not hygroscopic and the crude product was recrystallized from CH$_2$Cl$_2$ by cooling the solution to Dry Ice temperature. The product was immediately filtered and stored over anhydrous P$_2$O$_5$.

Anal. Calcd for CuC$_{19}$H$_{20}$NO$_5$F$_{12}$: Cu, 10.03; C, 35.99; H, 3.16. Found: Cu, 9.99; C, 36.28; H, 3.24. The melting point was found to be 79-80° (uncorrected).

The nmr spectrum of the 1:1 adduct of Cu(hfac)$_2$ with TMPNO in CCl$_4$ was measured with the HR-220 nmr spectrometer by the staff of the Molecular Spectroscopy Laboratory of the University of Illinois. The probe temperature was 23°, and benzene was used as the internal reference.

The solution magnetic susceptibility was measured by the Evans method,[7] using the Jeol-C-6OH. Several samples were run to check the reproducibility of the result. Great care was taken to differentiate the side-band signals from the signal due to the presence of the 1:1 adduct. TMS was used as the reference signal.

The magnetic susceptibility in the solid state (powder form) was measured by Faraday's method, using HgCo(SCN)$_4$ as the calibration standard. Because of the need for temperature studies, the magnetic study was also carried out on a vibrating-

---

(1) Abstracted in part from the Ph.D. Thesis of Y. Y. Lim, University of Illinois, Urbana, Ill., 1971.

(2) R. S. Drago and Y. Y. Lim, *J. Amer. Chem. Soc.*, **93**, 891 (1971), and references therein.

(3) R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).

(4) R. S. Drago, G. C. Vogel, and T. Needham, *ibid.*, **93**, 6014 (1971).

(5) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(6) J. C. Hill, Ph.D. Thesis, University of Illinois, 1968.

(7) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

sample magnetometer (Princeton Applied Research FM-1; property of Professor H. B. Gray at California Institute of Technology; measurements by Professor D. Hendrickson). The output of the magnetometer was automatically plotted on the *Y* axis of a recorder while the *X* axis was linear in millivolts from a thermocouple which is in contact with the sample holder. The signal-to-noise ratio of this equipment was excellent down to 90°K.

The calorimeter used was the same as the one described previously.[8] In the cases involving Cu(hfac)$_2$ and $BF_3 \cdot O(C_2H_5)_2$, the solutions were transferred to the dewar flask in the nitrogen-filled dry glove bag. A stream of dry nitrogen was passed over the Teflon top of the flask during the time of measurement. In this way, no precipitation of the hydrated copper complex or fuming of $BF_3 \cdot O(C_2H_5)_2$ was observed.

Results

The measured heats for the various concentrations of TMPNO and Cu(hfac)$_2$ and the resulting enthalpy of interaction and equilibrium constant are presented in Table I. The enthalpy of formation for the adduct of BF_3 with TMPNO could be measured by the displacement of diethyl ether from $BF_3 \cdot O(C_2H_5)_2$ in the solvent 1,2-dichloroethane.[6,9] The measured calorimetric data are presented in Table II. The comparisons between the enthalpies calculated from the *E* and *C* equation and those determined experimentally are summarized in Table III.

TABLE I[a]

[Cu(hfac)$_2$], *M*	[Base], *M*	Measd heat (h'), cal	[Cu(hfac)$_2$], *M*	[Base], *M*	Measd heat (h'), cal
0.01150	0.001416	1.747[b]	0.01115	0.007820	9.300
0.01109	0.002972	3.740	0.01276	0.008875	10.929
0.01141	0.004982	6.203			

$-\Delta H = 11.7 \pm 0.3$ kcal mol^{-1}; $K = 4200 \pm 1900$ M^{-1}

[a] Measured at 298°K. Total volume of C_6H_{12} solvent 110.0 ml. [b] Corrected for a partial molar ΔH_{soln} of TMPNO in cyclohexane of 4.56 ± 0.07 kcal/mol.

TABLE II

CALORIMETRIC DATA FOR THE $BF_3 \cdot O(C_2H_5)_2$[c] + TMPNO DISPLACEMENT REACTION[a]

Amt of acid, mol	Amt of base, mol	H',[b] cal	$-\Delta H_{disp}$, kcal mol^{-1}
0.06555	0.0008570	12.101	14.12
0.06617	0.001173	15.831	13.50
0.06423	0.001212	16.315	13.46
0.06967	0.0006480	9.443	14.57
0.07008	0.0006962	10.397	14.93
		Av	14.10 ± 0.6

$\Delta H_{dis}(BF_3 \cdot O(C_2H_5)_2) = 12.4$ kcal mol^{-1};[c]

$-\Delta H(BF_3$ *vs.* TMPNO$) = 26.5\ (\pm 0.7)$ kcal mol^{-1}

[a] Measured at 298°K. [b] Corrected for a partial molar heat of solution of the free radical in $C_2H_4Cl_2$ of 3.14 ± 0.05 kcal mol^{-1}. [c] D. E. McLaughlin and M. Tamres, *J. Amer. Chem. Soc.*, **82**, 5618 (1960).

TABLE III

CALCULATED AND EXPERIMENTAL ENTHALPIES OF ADDUCT FORMATION OF TMPNO WITH VARIOUS ACIDS

	$-\Delta H$, kcal mol^{-1}				
Acid	Calcd[a]	Measd	Acid	Calcd[a]	Measd
Phenol	6.7	6.9	BF_3	26.4	26.5
m-Fluorophenol	7.2	7.5	Trifluoroethanol	6.4	6.2
Cu(hfac)$_2$	11.8	11.7	Hexafluoro-2-propanol	8.2	7.9

[a] Calculated from the *E* and *C* equation.[4]

The 220-MHz spectrum of the 1:1 adduct of Cu(hfac)$_2$ with TMPNO in CCl_4 is shown in Figure 1. The peak assignments were made on the basis of integrated area. The 60-MHz spectrum was not resolved. The nmr spectra of TMPNO and the amine 2,2,6,6-tetramethylpiperidine at 100 MHz are reported,[10] and the chemical shifts of the various sets of protons together with those of the 1:1 adduct are summarized in Table IV.

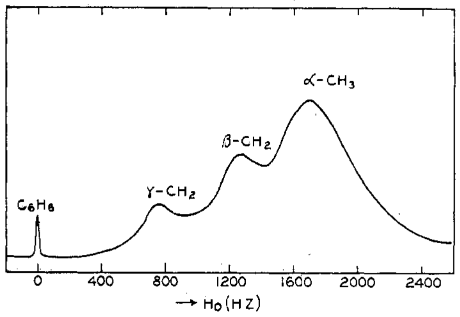

Figure 1.—The 220-MHz nmr spectrum of the 1:1 adduct in CCl_4.

TABLE IV

NMR CHEMICAL SHIFTS (Hz)[a]

	Pure TMPNO[b]	Diamagnetic amine[b]	Adduct[c]
Methyl	+4620	+1353	+770
β-Methylene	+6996	+1294	+1270
γ-Methylene	−1478	+1243	+1710

[a] Shift from benzene; plus implies upfield, and minus, downfield. [b] Measured at 45° with Jeolco 4H-100 nmr spectrometer.[10] [c] Deviation is ±10 Hz; probe temperature was 23°, 220 MHz.

The results of the magnetic susceptibility measurements of the adduct from various methods are summarized in Table V. A variable-temperature study was also carried out on the sample with the vibrating-sample magnetometer over the temperature range of 298–90°K. The plot of χ_M^{uncor} *vs.* *T* is shown in Figure 2.

TABLE V

SUMMARY OF MAGNETIC SUSCEPTIBILITY DATA

State	Method	$10^6\chi_M^{uncor}$, cgsu
Solution[c] (in CCl_4)	Evans (Jeol-C-60H)	292 (299°K)
Solid (powder)	Faraday[a]	−38 (298°K)
	Vibrating-sample magnetometer[b]	−186 (298°K)

[a] At ~5500 G. [b] At ~11,000 G. [c] Molecular weight determination by vapor pressure osmometry indicates the adduct is a monomer.

Discussion

***C* and *E* Numbers of TMPNO.**—The *C* and *E* parameters of TMPNO are based on the enthalpies of interaction of the base with four hydrogen-bonding acids and the Lewis acids Cu(hfac)$_2$ and BF_3. The *C* and *E* parameters are found tentatively to be 6.21 and 0.915, respectively. The fit between the calculated and measured heats (see Table V) is satisfactory for all of the acids studied, and no significant improve-

---

(8) M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 7086 (1970).

(9) M. S. Nozari and R. S. Drago, *ibid.*, in press.

(10) R. W. Kreilick, *J. Chem. Phys.*, **46**, 4260 (1967).

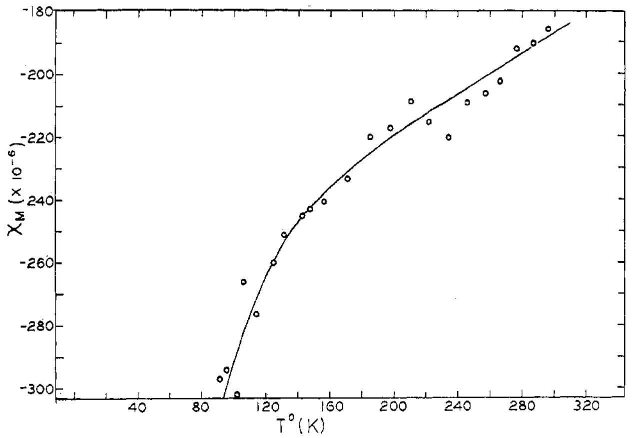

Figure 2.—Plot of $\chi_M{}^{uncor}$ *vs.* T.

ment results when the copper complex is omitted. Thus, the four-parameter enthalpy equation is seen to be applicable to a donor–acceptor system where extensive spin pairing of an electron on the donor and acid was found to occur; *vide infra*. The C and E numbers reported for this donor should be considered tentative because accurate numbers can only be obtained when the enthalpies of interaction involve acids which have C/E ratios which differ considerably. The range of C/E values for the acids in Table III is moderately satisfactory ranging from 0.1 for the alcohols to 0.3 for BF_3 and 0.40 for $Cu(hfac)_2$. We have been frustrated in an effort to find a fourth acid with a larger ratio. Other adducts are reported[11] but they do not have the desired solubility properties. Antimony pentachloride would have been acceptable, but the 1:1 adduct ionizes in 1,2-dichloroethane. The parameters we do have should work well for new acids with C/E ratios in the range 0–0.3. The enthalpies in Table V indicate that there is no significant contribution to the stability of the TMPNO–Cu complex from the extensive pairing in the adduct of the unpaired electrons on the free acid and base. The E and C parameters calculated for the TMPNO–Cu system where spin pairing does occur using parameters from systems where spin pairing does not occur correctly predict the enthalpy on the Cu–TMPNO system where there is extensive spin pairing. Consequently, the spin-pairing enthalpy contribution to the stabilization of the adduct is insignificant. Furthermore, these results indicate that the system need not be described as copper(I) and a cationic ligand or copper(III) and an anionic ligand. We expect E and C numbers for these metal ions and ligands to be different from those used to predict the correct enthalpy. There has been a tendency in studies on oxygen coordination to draw inferences about electron transfer from metal to oxygen from magnetic or esr studies. Clearly, magnetic and esr studies alone do not distinguish the electron-transfer structures from the spin-paired case encountered here.

The C/E ratio of TMPNO is $\simeq 7$, which will put it in the same class of donors as pyridine and dimethylamine. This value is very much different from the other diamagnetic oxygen donor molecules such as ethyl acetate, *n*-butyl ether, pyridine *N*-oxide, etc., which have C/E values ranging from 2 to 4. Thus, TMPNO is a more polarizable donor than most other diamagnetic oxygen donors and is also much more prone to encounter steric repulsions.

Nmr Spectrum of the 1:1 Adduct.—With reference to Table IV, it can be seen that the chemical shift difference between the adduct and the diamagnetic amine is very small (the largest difference being 3.1 ppm in the methyl proton shift) when compared with the difference between the free radical and the amine. Considering that there is a slight degree of dissociation in CCl_4, *vide infra*, the observed shifts are consistent with the results of the magnetic susceptibility measurements (to be discussed later), which indicate that the adduct is diamagnetic (or very slightly paramagnetic) in a 220-MHz magnetic field (*i.e.*, $H = 51{,}670$ G).

Magnetic Susceptibility Measurements.—The 1:1 adduct of $Cu(hfac)_2$ with TMPNO is slightly dissociated in CCl_4 as indicated from esr experiments. Calculations based on a conservative estimate of K_{as} equal to 1000 and the measured susceptibility indicate that in CCl_4 about 90% of the susceptibility comes from the adduct, and the contribution from the dissociated free radical and $Cu(hfac)_2$ is of the right order of magnitude to account roughly for the difference in solid and solution behavior. The standard deviation of $\chi_M{}^{uncor}$ from three measurements on three different samples was estimated to be $\pm 64 \times 10^{-6}$ cgsu. The sources of error in our measurements could come from the weighing, the determination of the density of solution, and the purity of the sample. Diamagnetic corrections have not been applied in Table V for reasons to be discussed later.

The cryomagnetic study indicates that there is large intramolecular antiferromagnetic coupling, showing that the Neel temperature, a maximum in the $\chi_M{}^{uncor}$ *vs.* T plot, should be greater than 298°K (see Figure 2). This result should also hold true in solution, and a preliminary cryomagnetic study of the compound in CH_2Cl_2 by the Evans method from 300 to 243°K in a 14,092-G field does show similar behavior.

For the adduct discussed above, spin–spin interaction can be described by

$$H_{ex} = -2J_{12}\vec{S}_1\cdot\vec{S}_2 \qquad (1)$$

where J_{12} is the spin–spin exchange coupling constant and the rest of the terms have their usual significance. If the coupling is antiferromagnetic (*i.e.*, $J_{12} < 0$), the ground state is a singlet and the triplet state lies $2J_{12}$ higher in energy. It can then be shown that such a system would lead to[12,13] a molar susceptibility expression given by

$$\chi_M = \frac{2g^2N\beta^2}{3kT}\left\{\frac{1}{3}\exp\left(\frac{2J_{12}}{kT}\right) + 1\right\}^{-1} + N\alpha \qquad (2)$$

where $N\alpha$ is the second-order Zeeman contribution to χ_M with the remaining symbols having their usual meaning. The competition between the thermal agitation and the population of the triplet state produces a

---

[11] (a) G. A. Abakumov, *et al.*, *Dokl. Akad Nauk SSSR*, **187**, 571 (1969); (b) G. A. Razuvaev, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1732 (1970); (c) T. B. Earnes and B. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 3141 (1971).

[12] K. Kambe, *J. Phys. Soc. Jap.*, **5**, 48 (1950).

[13] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, **214**, 451 (1952).

maximum in the χ_M *vs.* T curve at[14]

$$J_{12} \simeq -1.247kT_N \qquad (3)$$

This expression is obtained by a simple differentiation of eq 2. Here T_N is the Neel temperature. Hence, using (3) and noting that the Neel temperature is greater than 298°K, the spin singlet–triplet separation as measured by $|2J_{12}|$ should be greater than 450 cm^{-1}.

As stated earlier, the molar susceptibilities measured under different conditions are uncorrected because of difficulty in estimating the diamagnetic susceptibility of the free-radical component of the adduct. Estimation of diamagnetic susceptibility of the ligands by Pascal's constants gives -264×10^{-6} cgsu. However, bearing in mind that the TIP contribution of most copper(II) complexes is around 60×10^{-6} cgsu, a close examination of the cryomagnetic data would show that the diamagnetic correction to be applied must be at least -360×10^{-6} cgsu. The higher observed diamagnetic correction could be due to the effect of the motion of the electron over the two nuclei O and N in the free radical.[15]

Mechanism of Spin–Spin Interactions.—In the absence of a crystal X-ray structure determination of the adduct, no definitive spin–spin interaction mechanism can be put forward.[16] However, plausible mechanisms can be postulated. Various structures are possible including trigonal-bipyramidal and tetragonal-pyramidal based geometries. For each of these, several isomers dependent on the ligand arrangement can exist. We shall briefly discuss two possibilities selected to summarize the important considerations. A tetragonal-pyramidal structure with the ligand in the apical position was reported for the adduct of bis(2,4-pentanedionato)copper(II) with quinoline[17] (Figure 3) and will be discussed first. It is assumed that, when coordinated, the lone-pair electrons of TMPNO are in essentially oxygen sp^2 hybrids with the unpaired electron in a π^* molecular orbital formed from the remaining oxygen p orbital perpendicular to the sp^2 hybrids, $p_\perp^O$, and the nitrogen orbital, $p_\perp^N$. In square-pyramidal copper(II), the unpaired electron is expected to be in the $d_{x^2-y^2}$ orbital. Antiferromagnetic coupling can occur if the two orbitals containing the unpaired electrons are of correct symmetry to overlap with each other; *i.e.*, there is "incipient" chemical bond formation. Therefore, if the free-radical ligand is axial and is oriented with respect to the square-planar Cu(hfac)$_2$ in such a way that the sp^2 hybrids on oxygen lie in a plane bisecting the x and y axes, the π^* orbital may then have a net overlap with the $d_{x^2-y^2}$ orbital to give rise to antiferromagnetism. This kind of configuration where the plane of the cyclic hydrocarbon ring is perpendicular or slanting at a certain angle with the xy plane is reasonable because it places the bulky methyl groups of the free radical between the oxygen atoms and the CF$_3$ groups of the bidentate ligand. The "sp^2" plane of the ligand N–O group could also bisect the angle O$_2$–Cu–O$_3$ instead of O$_3$–Cu–O$_4$, giving rise to the same mode of spin–spin coupling.

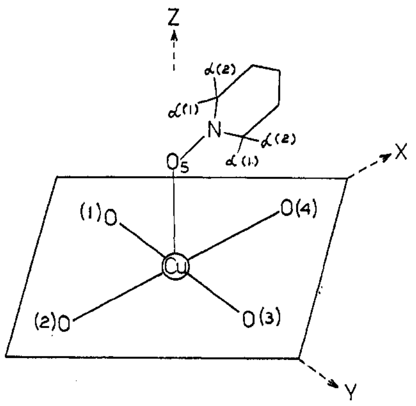

Figure 3.—Proposed structure of the 1:1 adduct of Cu(hfac)$_2$ with TMPNO.

Recently, Wayland and Wisniewski[18] have interpreted esr data to indicate that the added ligand enters the basal plane of the tetragonal pyramid with one of the acetylacetonate groups occupying the axial position. This structure has recently been reported[19] for the 4-aminopyridine adduct of bis(2,4-pentanedionato)copper(II). Such a structure would maintain the N–O π system in an orientation that would be orthogonal to $d_{x^2-y^2}$ if copper were in the basal plane. Thus spin pairing would not be anticipated unless there were substantial distortions from this geometry; *e.g.*, the copper moves into the center of the square pyramid. We should add that if the two different kinds of adducts form in solution when different donors are employed, the E and C numbers reported here may not be correct for all types of donors, but two different sets of E and C numbers would be required for bis(hexafluoroacetylacetonato)copper(II), which would depend on where the Lewis acid site is located. Limited enthalpy data are available, so a definite conclusion cannot be made regarding this possibility at present.

We feel that no reliable $|2J_{12}|$ (antiferromagnetic coupling constant) can be obtained in the solid state in view of the possible existence of intermolecular effects and the difficulty of estimating the diamagnetic correction from the ligands. However, an estimation of $|2J_{12}|$ using (2) and the assumptions $g = 2.15$ and $\chi_{\text{dia}} = -400 \times 10^{-6}$ cgsu would show that $|2J_{12}|$ is not constant but decreases from 736 to 384 cm^{-1} as the temperature decreases from 298 to 91°K. The decrease of J_{12} with temperature could be due to intermolecular ferromagnetic coupling which would make χ_M higher than expected at the lower temperatures thus accounting for the shape of the χ_M *vs.* T curve. Recently, a series of copper(II) complexes with 1,3,5-triketones as ligands has been reported[20] to be anti-

---

[14] R. L. Martin in "New Pathways in Inorganic Chemistry," E. Ebsworth, A. Maddock, and A. Sharpe, Ed., Cambridge University Press, London, 1968, p 175.

[15] L. N. Mulay in "Treatise on Analytical Chemistry," Part I, Vol. 4, I. M. Kolthoff and P. J Elving, Ed., Interscience, New York, N. Y., 1963, pp 1859, 1860.

[16] A crystal structure of this compound was attempted. The space group is $P\bar{1}$ with 4 molecules/unit cell. The Patterson map indicated that the two Cu atoms in the asymmetric unit are (by chance) related by a translation of ($^1/_2$, $^1/_2$, 0). The pseudosymmetry generated by this prevented our solving the structure. Two attempts were made with different direct-method programs, but they also failed.

[17] P. Jose, S. Ooi, and O. Fernando, *J. Inorg. Nucl. Chem.*, **31**, 1971 (1969).

[18] B. B. Wayland and M. D. Wisniewski, *J. Chem. Soc. D*, 1025 (1971).

[19] G. W. Bushnell, *Can. J. Chem.*, **49**, 555 (1971).

[20] D. P. Murtha and R. L. Lintvedt, *Inorg. Chem.*, **9**, 1532 (1970).

ferromagnetic and to have intermolecular ferromagnetic contributions. An additional possibility for the observed variation of $2J_{12}$ could be a very slight contamination by excess free radical or copper complex or both. Our main interest, however, is the predominant intramolecular antiferromagnetic coupling which has been conclusively shown.

Acknowledgment.—The authors are grateful for the generous support of the Paint Research Institute and the National Science Foundation for support of this research. We also acknowledge a National Science Foundation grant to the University of Illinois for the purchase of the HR-220 nmr spectrometer. We are also thankful to Professor D. Hendrickson for the magnetic susceptibility measurements.

CONTRIBUTION FROM THE DEPARTMENTS OF THEORETICAL AND PHYSICAL CHEMISTRY,
UNIVERSITY OF NIJMEGEN, NIJMEGEN, THE NETHERLANDS

Extended Hückel Calculation of the Electron Paramagnetic Resonance Parameters of Copper(II) Bis(dithiocarbamate)

BY C. P. KEIJZERS, H. J. M. DE VRIES, AND A. VAN DER AVOIRD*

Received August 2, 1971

The g tensor and ^{63}Cu hyperfine coupling tensor in bis(N,N-diethyldithiocarbamato)copper(II) have been calculated with the aid of the iterative extended Hückel LCAO–MO method. Two empirical parameters which were varied, the Wolfsberg–Helmholz parameter and the charge dependency of the Hamiltonian matrix elements, could be chosen such that fair agreement with the observed values was obtained. The molecular orbitals, calculated with this parameter set, illustrate that strong covalency occurs in this complex. With these parameters other experimental quantities (*e.g.*, the electric field gradient) can also be calculated for similar complexes.

Introduction

For some time we have been studying the electronic properties of the dithiocarbamato and diselenocarbamato complexes of certain transition metals.[1] Using epr we have investigated the Cu(II), Ag(II), and Au(II) complexes, and with Mössbauer spectroscopy, Fe(II) and Fe(III) complexes. In this article we will give a molecular orbital explanation for the measured g and hyperfine coupling (hfc) parameters of bis(diethyldithiocarbamato)copper(II), Cu(dtc)$_2$.

In order to obtain information from epr experiments about the bonding properties of a transition metal complex, one often attempts to estimate the contribution of the metal and the ligand orbitals to the molecular orbitals (MO's) from the measured g tensor and hfc tensor. This procedure necessitates a simplification of the MO picture. For complexes of low symmetry even then too many MO coefficients are left to be determined from the experimental data, so that an artificial addition of symmetry is usually needed.[2]

In this paper we avoid these simplifications by directly comparing the measured epr quantities of Cu(dtc)$_2$ with those calculated by means of the iterative extended Hückel method. Since this method is semiempirical and some uncertainty exists about the best choice of the empirical constants, we have varied two important parameters in order to check their effect on the calculated g and hfc tensors of Cu(dtc)$_2$.

The Molecular Orbital Calculation

The MO's of Cu(dtc)$_2$ were calculated by means of the LCAO–MO extended Hückel method.[3] The computer program[4] used was based on the self-consistent charge method. In this method a set of secular equations

$$\sum_j(\mathcal{H}_{ij} - ES_{ij})C_j = 0 \tag{1}$$

is constructed in a semiempirical way. In these equations $\mathcal{H}_{ij}$ and S_{ij} are elements of the Hamiltonian and overlap matrix, respectively

$$\mathcal{H}_{ij} = \langle\phi_i|\mathcal{H}_{\text{eff}}|\phi_j\rangle \tag{2}$$

$$S_{ij} = \langle\phi_i|\phi_j\rangle \tag{3}$$

where ϕ_i are atomic orbitals and $\mathcal{H}_{\text{eff}}$ is an effective one-electron Hamiltonian. By solving these secular equations, the orbital energies E_k and LCAO coefficients C_{jk} are obtained. After occupying the lowest MO's in agreement with the spin multiplicity of the ground state, the Mulliken charges[5] for all atoms are calculated. The Hamiltonian matrix, which is chosen to be charge dependent, is recalculated with these charges. This procedure is repeated until self-consistency is reached, *i.e.*, until the differences between the atomic charges in two successive cycles are less than 0.001 charge unit.

1. **Structure.**—Because the epr results have been obtained from single-crystal studies of Cu(dtc)$_2$ doped into single crystals of the diamagnetic Ni$^{\text{II}}$(dtc)$_2$ complex,[2,6] we used for our calculations the crystal struc-

---

* Address correspondence to this author, Department of Theoretical Chemistry, University of Nijmegen, Nijmegen, The Netherlands.

(1) H. van Willigen and J. G. M. van Rens, *Chem. Phys. Lett.*, **2**, 283 (1968); H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, **88**, 633 (1969); J. G. M. van Rens, C. P. Keijzers, and H. van Willigen, *J. Chem. Phys.*, **52**, 2858 (1970); J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **10**, 81 (1971).

(2) M. J. Weeks and J. P. Fackler, *ibid.*, **7**, 2548 (1968).

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(4) The authors wish to thank Professor P. Ros and Dr. W. Th. A. M. van der Lugt for making the computer program available to them.

(5) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(6) J. G. M. van Rens, unpublished results.