Chemistry of α-Diketone–Bis(thiosemicarbazone)copper(II) Complexes

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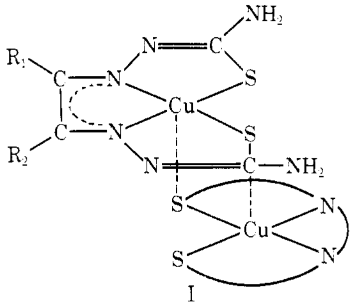
Abstract: α-Diketone–bis(thiosemicarbazone)copper(II) complexes have been characterized by magnetic, spectral, and electrochemical methods. The magnetic and spectral results are consistent with the results of empirical molecular orbital theory, which also provides a basis for the description of the electrochemical experiments. The diacetyl- and 2,3-octanedione–bis(thiosemicarbazone) complexes exhibit magnetic behavior which is dramatically altered by the alkyl substituent and which may reflect a consociation of neighboring planar units into distinct dimers.

Several α-diketone–bis(thiosemicarbazone)copper(II) complexes have validated biological activity. Kethoxal–bis(thiosemicarbazone)copper(II) (Cu–KTS), for example, has demonstrated carcinolytic and carcinostatic behavior against several established rat tumors.[2] The structural results for Cu–KTS (I) reveal that two planar molecules in the selected unit cell are related by an inversion center with the axial copper–sulfur internuclear distance within the unit cell being 3.102 Å, while the sixth coordination position of the copper ion is filled by a sulfur atom from a molecule in an adjacent unit cell. This latter Cu–S distance is 3.135 Å.[3] Therefore, the crystal structure may be described as containing chains of copper ions with alternating Cu–Cu internuclear distances of 3.833 and 3.896 Å.



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The biological function of these compounds is not clear, but presumably additional chemical insight into the nature of the compounds will contribute to the solution of the problem. Complexes where the donor atoms are nitrogen and sulfur may be expected to possess unusual electronic structures, since complexes with sulfur donor atoms have exhibited a variety of oxidation states,[4] and four-coordinated planar nitrogen complexes such as copper porphyrins and phthalocyanines are known to have highly delocalized electronic structures.[5] Except for the dithiosemicarbazones, there are only a very few other examples of coordination to copper where the donor atoms are sulfur and nitrogen. Two of these are the bis(*o*-aminobenzenethiol) complex[6] and the diacetylbis(2-mercaptoanil) complex.[7] In this article, the results of our studies on a series of α-diketone–bis(thiosemicarbazone)copper(II) complexes are described. This work has been directed toward an understanding of the chemistry and electronic structures of these compounds.

Experimental Section

The compounds were prepared following closely the methods described by Gingras, *et al.*[8] The magnetic susceptibilities of diacetylbis(thiosemicarbazone)copper(II) (hereafter referred to as Cu(ddts)) and 2,3-octanedione–(thiosemicarbazone)copper(II) [Cu(odts)] were determined in the range 77–300°K using a Faraday balance equipped with a variable temperature cryostat and in the temperature range 4.2–28°K with a Foner-type vibrating sample magnetometer.[9] Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard, and the susceptibilities were corrected with Pascal's constants[10] for the inherent diamagnetism of 105×10^{-6} and 152×10^{-6} cgs units, respectively. The analytical data were obtained by Galbraith Laboratories, Inc., Knoxville, Tenn., for the two compounds.

Anal. Calcd for $CuC_6H_{10}N_6S_2$: C, 24.52; H, 3.43; N, 28.60; S, 21.82. Found: C, 24.38; H, 3.24; N, 28.46; S, 21.57.

Anal. Calcd for $CuC_{10}H_{18}N_6S_2$: C, 34.4; H, 5.18; N, 24.0; S, 18.3. Found: C, 34.2; H, 5.37; N, 23.8; S, 18.1.

Visible absorption spectra of solutions in dimethylformamide were obtained using a Cary Model 17I spectrophotometer. Electron paramagnetic resonance spectra of solutions, frozen glasses, powdered samples of pure materials, and powdered samples of the diacetyl complex contained in the lattice of the corresponding diamagnetic nickel host were recorded at 9.2 GHz on a Varian E-3 spectrometer. Liquid nitrogen temperature measurements were made by inserting the sample tube into a small dewar flask which fitted into the cavity.

Standard cyclic voltammetry equipment employing a platinum bead electrode was utilized for the electrochemical experiments carried out with 0.001 *M* acetonitrile (Eastman, spectrograde) solutions of diacetyl- and 2,3-octanedione–bis(thiosemicarbazone)copper(II), the latter complex being more suitable because of its greater solubility in acetonitrile. The solutions used were also 0.1 *M* in tetraethylammonium perchlorate supporting electrolyte (Eastman reagent grade, dried over P_2O_5 under vacuum).

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(1) NDEA Title IV Fellow, 1969–1970.

(2) H. G. Petering and G. J. Van Giessen in "The Biochemistry of Copper," J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N. Y., 1966, p 197.

(3) M. R. Taylor, E. J. Gabe, P. Glusker, J. A. Miukin, and A. L. Patterson, *J. Amer. Chem. Soc.*, **88**, 1845 (1966); J. Glusker, private communication.

(4) See, for example, S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 4594 (1964).

(5) I. Chen, M. Abkowitz, and J. H. Sharp, *J. Chem. Phys.*, **50**, 2237 (1969).

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(8) B. A. Gingras, T. Suprunchuk, and C. H. Bayley, *Can. J. Chem.*, **40**, 1053 (1962).

(9) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

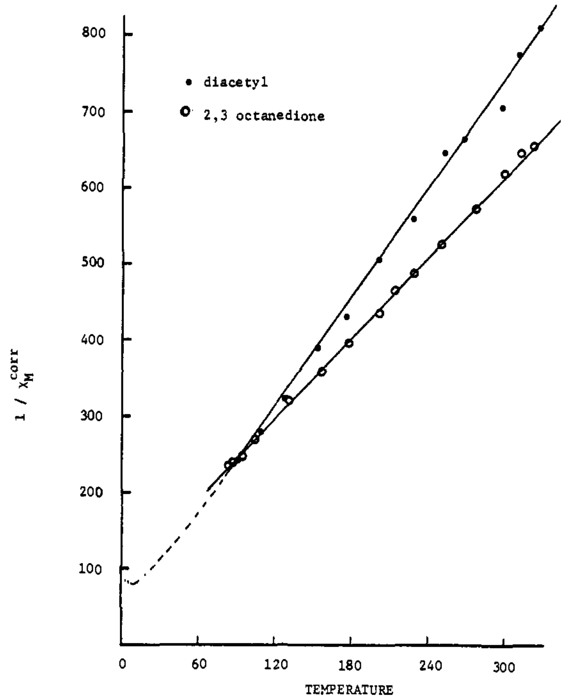

Figure 1. Inverse susceptibility *vs.* temperature from Faraday measurements for diacetylbis(thiosemicarbazone)Cu(II) and 2,3-octanedione–bis(thiosemicarbazone)Cu(II). Vsm data for diacetylbis(thiosemicarbazone)Cu(II) below 25°K, also shown, illustrates the compatibility of data from the two methods.

Results and Discussion

Magnetic Susceptibility Measurements. The inverse susceptibility *vs.* temperature plots for diacetyl– and 2,3-octanedione–bis(thiosemicarbazone)copper(II) are given in Figure 1. There are three important features of the data. At high temperatures the data for both compounds obey the Curie–Weiss law, $\chi = C/(T + \theta)$, with the best least-squares fit yielding

	θ, °K	μ_{eff}, BM
Cu(ddts)	6.1	1.78
Cu(odts)	48.0	1.90

The magnetic moments were calculated from $\mu_{eff} = 2.828C^{1/2}$. At low temperatures there is a minimum in the plot near 9°K for Cu(ddts). By rapidly cooling the sample in the magnetometer, a higher susceptibility below 9° was observed than obtained when the temperature was lowered slowly, and consequently the minimum must be associated with a phase transition. It is perhaps surprising that the exocyclic chelate substituent could have such a dramatic effect on the magnetic properties of these compounds.

Noting the near equivalence of the copper–copper separations, the magnetic susceptibility data in the range 11.8–24.6°K for Cu(ddts) can be fitted to the Ising equation (refer to ref 11). This procedure yields $J = -14$ cm^{-1} when using the $\langle g \rangle = 2.04$ as determined from the solution epr measurements (see below). As expected, the Ising equation fails in the region of the phase transition, and the low-temperature boundary imposed by equipment limitations does not permit us to determine which magnetic model holds below the transition point. The broad maximum in the molar susceptibility *vs.* temperature plot may be an artifact arising from surface area properties of the sample. Since the epr absorption disappears at 1.5°K,[12] the phase transition likely involves a consociation of planar moieties into distinct dimers. This postulation is consistent with the alternating long and short Cu–Cu separations in the crystal structure.

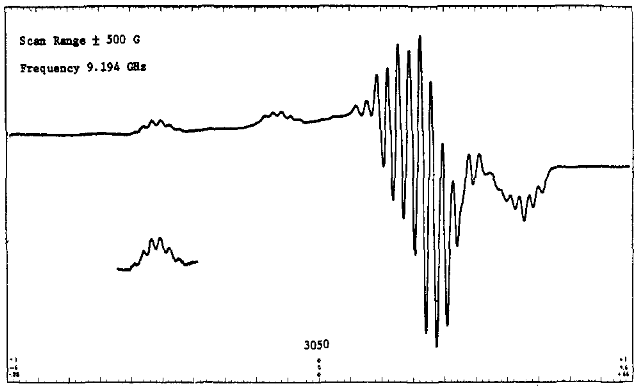

Figure 2. Epr spectrum of diacetylbis(thiosemicarbazone)Cu(II) prepared from copper-63 in DMF glass at 77°K. The $M_I = 3/2$ line is shown at increased gain.

A more correct interpretation of the magnetic data would be in terms of a Hamiltonian which recognized the alternating metal–metal separations and the differences in the axial copper–sulfur bond lengths, but the data presented here do not warrant such a treatment.

Electron Paramagnetic Resonance. In view of the effect of exocyclic chelate substituents on the magnetic susceptibilities of Cu(ddts) and Cu(odts), it became of interest to determine the effect of a variety of substituents on the features of the epr spectra. A series including Cu(ddts), Cu(odts), and complexes with glyoxal–, pyruvic aldehyde–, benzil–, and substituted benzil–dithiosemicarbazones were prepared. The spectra of all these complexes were essentially identical, and since the complexes were exceptionally difficult to purify owing to their lack of solubility even in DMF and DMSO, further experimentation other than solution epr was not pursued. The solution spectra exhibited copper hyperfine splittings of 89 G, nitrogen superhyperfine splittings of 15 G, and $\langle g \rangle = 2.04$. Thus, it becomes apparent that the effect of substituents on the static susceptibilities derives from the stereochemical characteristics of the substituent and not from electronic perturbations.

A closer examination of the superhyperfine structure was undertaken. A sample of Cu(ddts) was prepared from ^{63}CuO and the spectrum of a solution of the complex in DMF recorded. On the high-field hyperfine line there appears five well-resolved nitrogen superhyperfine lines with $\langle A_N \rangle = 15$ G. This structure arises, as expected, from the two nitrogen atoms bonded to the copper ion. The extra high-field structure arises from the ^{65}Cu nucleus. The latter has a slightly larger nuclear moment than ^{63}Cu. This extra structure led to an incorrect interpretation by Blumberg and Peisach[12] that all four nitrogen atoms in the chelate cycle were equivalent.

The spectrum of Cu(ddts) in DMF glass at 77°K is shown in Figure 2. The general features of the spectrum are the absorptions centered at 2790 and 2985 G,

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(11) M. E. Fisher, *J. Math. Phys.*, **4**, 124 (1963).

(12) W. E. Blumberg and J. Peisach, *J. Chem. Phys.*, **49**, 1793 (1968).

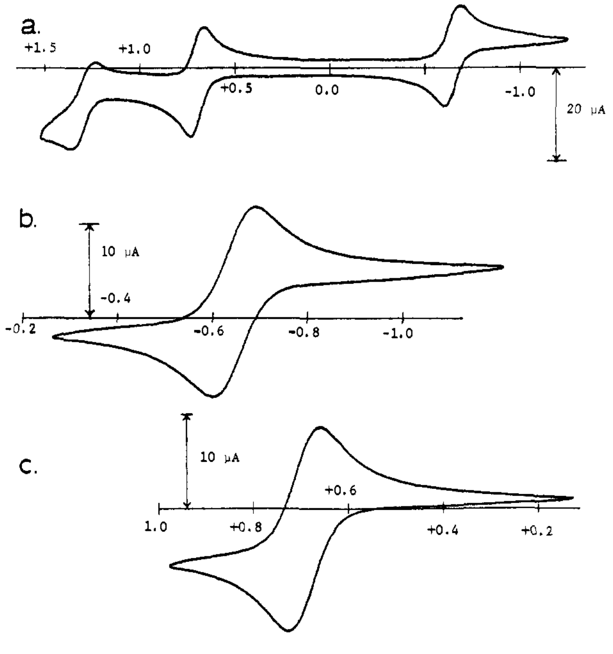

Figure 3. Steady-state cyclic voltammograms of 1 mM 2,3-octanedione–bis(thiosemicarbazone)Cu(II), 0.1 M TEAP, in acetonitrile: (a) voltammogram throughout useful range of solvent; (b) expanded reduction wave; (c) expanded first-oxidation wave.

which are interpreted as the $M_I = {}^3/_2, {}^1/_2$ components[13] with nitrogen superhyperfine structure. The more intense absorptions at 3200 G are likely the superimposition of the perpendicular spectrum and the $M_I = -{}^1/_2$ component of the parallel spectrum with the $M_I = -{}^3/_2$ component of the parallel copper hyperfine at 3380 G.

The spectrum of a powdered sample of a 1% solid–solution of Cu(ddts) in the diamagnetic nickel host of the same ligand has been reported by Getz and Silver.[14] The spectrum shows essentially the same features as the glass spectrum from which $g_{\parallel} = 2.12$ and $A_{\parallel} = 192.5$ G. Employing the room temperature solution epr data together with the relationships $\langle g \rangle = (g_{\parallel} + 2g_{\perp})/3$, and $\langle A \rangle = (A_{\parallel} + 2A_{\perp})/3$, we calculate $g_{\perp} = 2.00$ and $A_{\perp} = 37.2$ G. Nirogen superhyperfine is virtually isotropic and remains 15 G.

The spectrum of the 5% solid–solution shows a loss of resolution resulting from dipole–dipole interactions between paramagnetic sites. The spectrum of this sample had, however, an important feature in the 1500-G region at 77°K. This half-field line is the $\Delta M_S = \pm 2$ transition[15] of a spin system with $S = 1$ which arises from copper ions occupying adjacent sites.

From the relationship[16]

$$H_{\min} = [\omega_0^2 - 4D^2/3]^{1/2}/2g\beta$$

we calculate the zero-field splitting of the triplet state to be 0.014 cm^{-1}.

Since the major contributions to the zero-field splitting probably arise from the dipole–dipole (magnetic) and exchange (electronic) interactions, an approximation of the exchange energy may be derived from the experimental **D**.[16] From the point charge model

$$\mathbf{D}(\text{dipole–dipole}) \simeq 0.325 g_{\parallel}^2/r^3 |1 - 3\cos^2\theta|$$

where r is the known Cu–Cu separation and θ is the angle between the z components of the copper–copper vector (assumed **D** tensor) and the normal to the plane of the molecule (assumed $g_{\parallel}$), $\mathbf{D}_{\mathrm{dd}}$ is estimated to be 0.024 cm^{-1}. Further application of the Bleaney–Bowers[17] expression

$$\mathbf{D}_{\text{exchange}} \simeq -J\{[(g_{\parallel} - 2)^2/4] - (g_{\perp} - 2)^2\}/8$$

yields $J \simeq 22$ cm^{-1}, a value in qualitative agreement with that obtained from the analysis of the magnetic data above the transition point using the Ising model.

Electrochemistry. Planar metal complexes of unsaturated chelating ligands whose donor atoms are sulfur have been shown to undergo facile electron-transfer reactions.[18] In view of the unusual oxidation states produced electrochemically with the dithiolates, the electrochemistry of the dithiosemicarbazone system was thought to be especially relevant to the discussion of the electronic structure of these complexes.

The cyclic voltammogram of the complex through the useful potential range of the solvent is shown in Figure 3. There are three one-electron ($n = 1$) chemically reversible waves, two oxidations at $E_p^a = +0.73$ and $+1.35$ V, and one reduction at $E_p^c = -0.69$ V, all *vs.* sce. The reduction and first oxidation are clearly reversible as is shown by the equivalence of the forward and reverse peak heights in the expanded voltammograms. On the other hand, the second oxidation exhibits a current ratio less than one, indicating that the product of this second oxidation step is less stable.

Exhaustive electrolyses were carried out at the potentials of the reduction and first oxidation. Upon reduction, the solution turned deep red. The red color gradually returned to the characteristic orange of the complex after a few minutes, indicating reoxidation. The compound apparently decomposes when electrolyzed at the first oxidation potential, and thus no further studies could be made of the oxidation products.

Attempts were made to see an epr spectrum of the reduced species by electrolyzing a solution of the complex in the spectrometer cavity. If the complex were to reduce to a simple Cu(I) species, one might have been able to watch the characteristic solution spectrum disappear gradually upon electrolysis. On the other hand, if a radical anion of the ligand were produced, the characteristics of a triplet spectrum or of two doublets might appear. In actuality, after electrolysis the characteristic solution spectrum broadened and showed no structure at all, probably indicating that the compound had been reduced to a diamagnetic complex, but that exchange between diamagnetic and paramagnetic species remaining in solution caused line broadening and loss of structure. Such behavior is typical of organic radical-anions. No half-field line or other triplet characteristics could be discerned, but these experiments are not conclusive.

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(13) We do not know the sign of the coupling constant and have provided these arbitrary but consistent labels.

(14) D. Getz and B. L. Silver, *J. Chem. Phys.*, **52**, 6449 (1970); see also L. E. Warren, J. M. Flowers, and W. E. Hatfield, *ibid.*, **51**, 1270 (1969).

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Mass Spectral Studies. As we have reported earlier[19] mass spectrometry provided a very convenient and useful tool for characterizing the dithiosemicarbazone complexes. It was also of interest to determine whether the mass spectra gave indication of gaseous dimers, since we had observed pairwise interactions from magnetic data, and dimeric species had been observed in the mass spectra of other systems.[20]

The mass spectra of several types of complexes of copper(II) have been reported, *e.g.*, the 2,4-pentanedione complex and its trifluoro and hexafluoro derivatives,[21,22] the dibenzoylmethane complex,[23] the *N*-phenylcarbamoyldimelone complex,[24] and the heptafluorodimethyloctanedione complex.[25] However, study of the fragmentation of ligands is complicated by the competing loss of an entire ligand. Only one study of a complex from a single tetradentate ligand, bis(benzoylacetone)ethylenediamine, has been reported.[26] These present examples formed another study of a series of tetradentate ligands; in them cleavage of the ligand through single bonds is restricted to the expulsion of small molecules or radicals, not including halving the ligand as noted before. They comprise an analysis of species giving, for the most part, stable molecular ions and only small amounts of fragments and therefore differ from previously reported cases in this respect.

A prominent feature of the spectrum of the bis(*p*-bromophenyl) derivative was a triplet at *m*/*e* 334, 336, and 338, possibly the $BrC_6H_4C{\equiv}CC_6H_4Br^+$ ion, formed by a process which was almost undetected in the spectra of the aliphatic compounds. The aryl-substituted species did not lose neutrals of mass 42, 59, 69, and 88 as the aliphatic compounds did. This provided a basis for suggesting that the introduction of aromatic substituents alters the decomposition, since stability is provided to ions substituted by aromatic groups. Thus the more intense ions are no longer formed by processes giving one or two small nitrogen- and sulfur-containing neutrals, as in the aliphatic compounds, but instead a large stable organic ion is formed with the expulsion of the metal as a neutral compound. It is interesting that replacement of alkyl by aryl groups so alters the ability of different fragments to bear charge that the *m*/*e* 334 peak overwhelms the others in the spectrum of the bis(*p*-bromophenyl) compound (rel intensity = 1400) even though the metal is lost as a neutral.

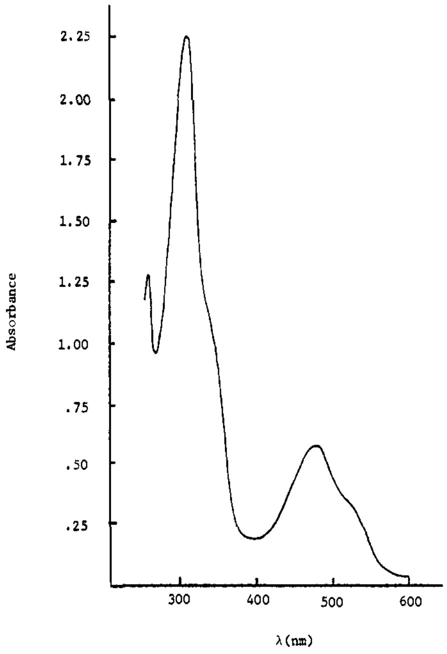

Figure 4. Visible–ultraviolet absorption spectrum of diacetylbis(thiosemicarbazone)Cu(II), 10^{-4} in DMF. Recorded on a Cary 171 spectrophotometer.

Table I. Uv Absorption Maxima and Extinction Coefficients

λ, Å	cm⁻¹	ε	Assignment
5300	18,900	3,000	$a_1 \rightarrow b_2$
4800	20,800	5,800	$b_1 \rightarrow b_2$
3400	29,400	11,500	$a_1 \rightarrow b_2$
3000	33,400	22,500	$a_2 \rightarrow b_2$
2650	37,800	12,500	

Electronic Spectra. The spectrum of Cu(ddts) dissolved in DMF is displayed in Figure 4, and the extinction coefficients are listed in Table I along with band assignments taken from the results of a semiempirical molecular orbital treatment using the Wolfsberg–Helmholz approximation. For the calculation the plane of the molecule was taken to be the *yz* plane. The $^2B_2$ ground state is a σ antibonding level consisting mainly of copper d_{yz}. The high extinction coefficients for the formally Laporte-forbidden transitions can be rationalized by noting that there are very large ligand orbital contributions to the antibonding molecular orbitals.

Calculations in which sulfur π orbitals were included were carried out using several sets of input assumptions, including sp^3 hybridization on the S, 5% s–95% p hybridization with coulomb integrals H_{ii} = 123,000 cm⁻¹, and 5% s–95% p hybridization with H_{ii} = 98,000 cm⁻¹. In all such calculations, there were several dominating characteristics which should be noted. First, in order to arrive at self-consistency, the sulfur energy was always returned higher than that of copper 3d. Second, the sulfur π orbitals were returned essentially nonbonded; that is to say wherever the input energy for sulfur is fixed, the sulfur π orbitals appear at about that same energy in the MO diagram. Furthermore, the order of d orbitals remains essentially the same in any self-consistent result, as does the d_{yz} spacing from the next highest d orbital. Therefore any error in placement of the sulfur energy probably has little effect on the prediction of the visible spectrum, although the positions of the essentially nonbonded sulfur π orbitals in the MO diagram probably are not correct. Sulfur π orbitals are most likely tied up in the extended π system of the ligand and appear at energies significantly different from those predicted from simple ionization potential data. These orbitals almost surely do not appear in the midst of the

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(24) E. P. Dudek and M. Barber, *Inorg. Chem.*, **5**, 375 (1966).

(25) B. R. Kowalski, T. L. Isenhour, and R. E. Sievers, *Anal. Chem.*, **41**, 998 (1969).

(26) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, and J. S. Shannon, *Aust. J. Chem.*, **18**, 1539 (1965).

copper d orbitals as is predicted by the MO calculation.

The same argument holds for nitrogen π bonding. Although the nitrogen π level is probably not at the same energy of $-139{,}000\ \mathrm{cm}^{-1}$ as the nitrogen sp^2 level, it is also unlikely that it is at an energy corresponding to "pure p" character ($-106{,}000\ \mathrm{cm}^{-1}$). Since we are unsure of the exact energy to use as input, it is reasonable to leave N_π at the same energy as Nsp^2, because like S_π, it too is not likely to be in the midst of the d molecular orbitals.

The populations of the ground state and coefficients of eigenvectors correlate well with parameters obtained from electron paramagnetic resonance. McGarvey[27] suggests the equations for $g_\perp$ and $g_{\parallel}$ become

$$g_{\parallel} = 2.0023 - [8\lambda/\Delta E]P_{\mathrm{d}}^*$$

and

$$g_\perp = 2.0023 = [2\lambda/\Delta E]P_{\mathrm{d}}^*$$

where P_{d}^* is the one-electron population of the d orbital in the ground state. Using the more accurate $g_{\parallel}$ value from the 1% dilute solid solution spectrum, a value for $P_{\mathrm{d}}^* = 0.362$ is calculated, in excellent agreement with the d populations of the ground-state B_2 orbital returned by the MO calculations of 0.4029 (sulfur sp^3), 0.4447 (sulfur 5% s, 95% p, H_{ii} (σs,πs) $= -123{,}000\ \mathrm{cm}^{-1}$), 0.3085 (sulfur 5% s, 95% p, H_{ii} (σs,πs) $= -98{,}000\ \mathrm{cm}^{-1}$), 0.2872 (no sulfur π orbitals, H_{ii} (σs) $= -98{,}000\ \mathrm{cm}^{-1}$).

The extent of delocalization on nitrogen can be calculated by the relation[28]

$$|W| = (4\pi/9)\gamma_0\beta_{\mathrm{N}}(\alpha'')^2\delta(r)$$

where $|W|$ is the ligand superhyperfine splitting, γ is the gyromagnetic ratio of the ligand nucleus, β_0 and β_{N} are the Bohr and nuclear magnetons, $\delta(r)$ is the electron "s" density at the nucleus of the ligand, calculated by McGarvey for nitrogen $= 33.4 \times 10^{24}\ \mathrm{cm}^{-3}$, and α'' is the coefficient of nitrogen in the ground-state MO

$$\psi_{\mathrm{B^2}} = \alpha\psi_{\mathrm{d}} + \beta\psi_{\mathrm{p}} + \frac{\alpha'}{\sqrt{2}}(\sigma_1 - \sigma_2)_{\mathrm{S}} + \frac{\alpha''}{\sqrt{2}}(\sigma_3 + \sigma_4)_{\mathrm{N}} + \frac{\alpha'''}{\sqrt{2}}(\pi_1 + \pi_2)_{\mathrm{S}}$$

From the observed splitting of 15 G, the calculation gives $\alpha'' = 0.565$. Remembering that the coefficients for $\phi\sigma_{\mathrm{N}}$ in the eigenvectors must be multiplied by $\sqrt{2}$ to give α'', we have as calculated by the empirical method $\alpha'' = 0.465$, 0.548, 0.334, and 0.357, a reasonable qualitative correlation.

More detailed treatment of the epr parameters, using g values and metal nuclear hyperfine constants to calculate MO coefficients have been described; however, these calculations have nearly always involved axial symmetry and identical ligands, conditions which do not apply here. Furthermore, the inclusion of spin–orbit coupling from sulfur would probably be necessary. The details of such a calculation have not been worked out.

Conclusion

α-Diketone–bis(thiosemicarbazone)copper(II) complexes have been characterized by theoretical, physical, and chemical methods. An empirical molecular-orbital treatment resulted in a qualitatively correct prediction of the electronic spectra and provided a theoretical model for the interpretation of electron paramagnetic resonance parameters. The nature of magnetic interactions in the solid material was determined by low-temperature susceptibility measurements. The molecules exist as extended chains through Cu–S linkages, except in very dilute solids or liquid solutions. These results were confirmed by the presence of a half-field line in the epr spectrum. Future studies might be directed at comparing the static magnetic properties of complexes derived from different diketones; preliminary indications are that small structural differences markedly affect the magnetism.

Electrochemically, the one-electron reduction and two one-electron oxidations shown by the dithiosemicarbazone–Cu(II) complexes are analogous to the facility of electron transfer observed for other complexes with sulfur donor ligands. The reduction and first oxidation likely involve the B_2 ground state predicted in the MO treatment, but the second oxidation may come from an unaccounted-for orbital which is mainly ligand since the complex apparently decomposes at this step.

Mass spectra of these compounds presented one of the first examples of fragmentations from the ligand of a tetradentate metal complex without loss of the metal atom.

Unfortunately a sample of the anticarcinogenic kethoxal-bis(thiosemicarbazone)copper(II) was not available; it would be well to compare its magnetism and electrochemistry, for example, with the compounds studied here.

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