# Nonplanar Electron Transfer Complexes. II.[1] The Chemistry of Four Cu—N₂S₂^z Complexes Derived from Copper-bis-N,N-diethylphenylazothioformamide

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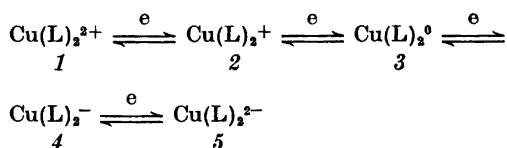Dedicated to Professor K. A. Jensen on his 70th birthday

The existence of a series of five electron transfer complexes derived from nonplanar copper-bis-N,N-diethylphenylazothioformamide, has been demonstrated by cyclic voltammetry and coulometric techniques. The obtained magnetic, spectral and structural data suggest that four of the $Cu-N_2S_2^z$ complexes can be described as simple Cu(II) or Cu(I) compounds coordinated by neutral or radical anion ligands.
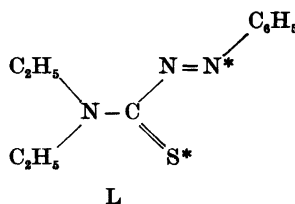
Relatively few investigations of copper-containing electron transfer complexes have been published. Apart from copper bis-dithiolenes, in which only the $Cu-S_4^-$ and $Cu-S_4^{2-}$ species are stable,[2,3] two series of the general type $Cu-N_2S_2^z$ have been described. In both systems a tetradentate ligand was used. Holm et al.[4] investigated copper-diacetyl-bis-thiobenzhydrazonate and demonstrated the existence of two discrete species, while Warren et al.[5] demonstrated the existence of a four-membered series in a similar system. In both cases only the neutral species, $Cu-N_2S_2^0$, was isolated and investigated, and was described as being planar with a $^2B_2(d^9)$ ground state.

Phenylazothioformamides, which have proven useful ligands in the preparation of new electron transfer series,[1,6,7] form stable copper compounds.[6] The present paper describes results obtained for copper complexes derived from N,N-diethylphenylazothioformamide (L).

L

The first of these copper compounds to be obtained[6] was the neutral bis complex, $Cu(L)_2^0$(3), which proved to be one of a series of five electron transfer species (1)−(5):

$$Cu(L)_2^{2+} \underset{1}{\overset{e}{\rightleftharpoons}} Cu(L)_2^+ \underset{2}{\overset{e}{\rightleftharpoons}} Cu(L)_2^0 \underset{3}{\overset{e}{\rightleftharpoons}}$$

$$Cu(L)_2^- \underset{4}{\overset{e}{\rightleftharpoons}} Cu(L)_2^{2-}$$
$$\phantom{Cu(L)_2^- \overset{e}{\rightleftharpoons}} 5$$

Two members of this series have been isolated, two were generated in solution, while the dinegative couple (5) could only be demonstrated by cyclic voltammetry. Additionally, results obtained for double salts of 2 are presented.

It is the purpose of the present work to document the existence of the series in question, to present results obtained for individual species, and to discuss the structural and electronic characteristics of this new electron transfer series.
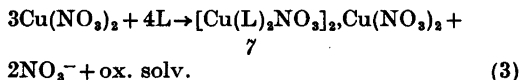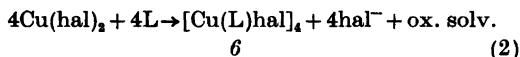
RESULTS

Preparation. The neutral member (*3*) of the series was prepared by quinone oxidation of the corresponding bis-thiosemicarbazidate. This preparation has been reported in detail elsewhere.[6] The monocationic complex (*2*) was prepared by treatment of 1 mol of $Cu(BF_4)_2$ in water with 2 mol of L dissolved in ethanol. The product first formed is *1*, which is reduced rapidly by the solvent to give *2*. Eqn. 1 summarizes the reactions:

$$Cu^{2+} + 2L \rightarrow Cu(L)_2^{2+} \rightarrow Cu(L)_2^+ + ox. \; solv. \qquad (1)$$
$$\qquad\qquad\qquad 1 \qquad\qquad 2$$
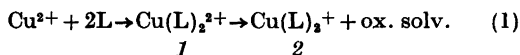
$Cu(L)_2^+$ was isolated as the tetrafluoroborate, which crystallizes from acetone – ether (1:1) with precisely 1 mol of acetone per copper atom. It was shown by thermogravimetry that the "crystal acetone" is given off at temperatures higher than 80 °C.

The necessity of using BF_4^- as counter ion is illustrated by the formation of products such as (*6*) and (*7*), when other cupric salts are used (eqns. 2 and 3).

$$4Cu(hal)_2 + 4L \rightarrow [Cu(L)hal]_4 + 4hal^- + ox. \; solv.$$
$$\qquad\qquad\qquad\qquad 6$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2)$$

$$3Cu(NO_3)_2 + 4L \rightarrow [Cu(L)_2NO_3]_2, Cu(NO_3)_2 +$$
$$\qquad\qquad\qquad\qquad 7$$

$$2NO_3^- + ox. \; solv. \qquad\qquad\qquad\qquad (3)$$

These two examples demonstrate that the system Cu – L exhibits some tendency to cluster or double salt formation. Compound *6* has been prepared previously by a different procedure.[6]

The dicationic complex (*1*) was generated by electrolysis of *2* in methylene chloride at a fairly positive potential ($E_t = +1.3$ V *vs.* SCE). This is in accord with the observation that *1* is so easily reduced by labile solvents. However, methylene chloride solutions of *1* are stable when protected from moisture.

The monoanion (*4*) was generated by electrolytic reduction of *3* in either methylene chloride or acetonitrile. The solutions are stable when protected from oxygen and moisture. Attempts to prepare the dianion (*5*) either electrolytically or by Na – Hg reduction of *3* were, however, unsuccessful.

Electrochemical evidence for the existence of the electron transfer complexes (1) – (5). CH_2Cl_2. The solution equilibria established as a consequence of reduction or oxidation of (*2*) are illustrated by the cyclic voltammogram of Fig. 1. In the cathodic scan starting at A, *2* is reduced to *3* at R_2 in a reversible process. Coulometric reduction [8] uses precisely 1 F/mol and *3* can be reoxidized to *2* in nearly 100 % yield. The peak separation $R_2 - O_2$ is approximately 100 mV, slightly larger than the 60 mV required for a reversible one-electron transfer. This is due, however, to the use of a relatively low concentration of depolarizer (0.1 M); increasing the concentration of the latter or changing the solvent to acetonitrile improved
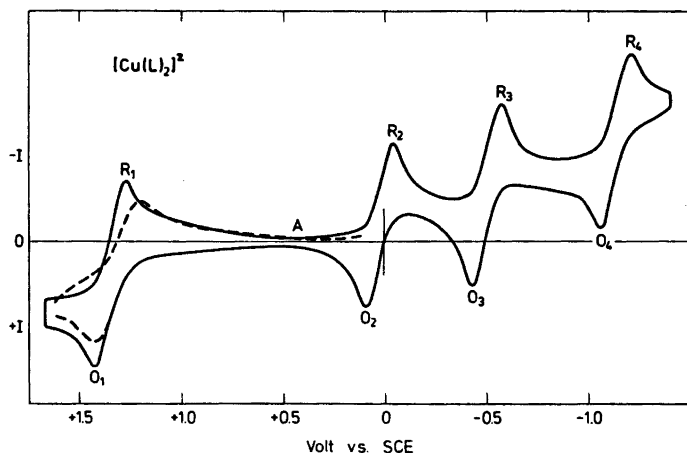

Fig. 1. Cyclic voltammogram of $Cu(L)_2^z$ in CH_2Cl_2 at 298 K (full line). At 248 K (broken line).

Table 1. Voltammetry of $Cu(L)_2^+$ in CH_2Cl_2 and CH_3CN.

| Compound | Solvent [b] | Peak potentials [a] | | | | | | | |
		O_1	R_1	O_2	R_2	O_3	R_3	O_4	R_4
$Cu(L)_2^+$	CH_2Cl_2	+1.34	+1.24	+0.05	−0.05	−0.48	−0.59	−1.14	−1.24
$Cu(L)_2^+$	CH_3CN	−	−	−0.06	−0.12	−0.53	−0.59	−1.18	−1.24

[a] Volts vs. SCE. Platinum button electrode, sweep rate 200 mV/s. [b] Depolarizer Bu_4NBF_4 (0.1 M).

the voltammograms. However, owing to the presence of trace amount of water in the depolarizer it was convenient to use low concentrations. The peak current ratio is 1:1. There thus seems to be no doubt that *3* is formed by reversible one-electron reduction of *2*. At the more negative potential R_3, *3* is reduced to *4*. Again the criteria of reversible electron transfer are fulfilled and *4* is stable under the conditions employed. At an even more negative potential R_4, *4* is reduced to *5* reversibly. *5* is stable within the time scale of cyclic voltammetry but decomposes on allowing the solution to stand.

In the anodic scan starting at A, *2* is oxidized to *1* at O_1 in a quasi-reversible process. Coulometric oxidation of *2* uses precisely 1 F/mol and *1* can be reduced back to *2* quantitatively. The peak current ratio is 1:1, but the peak separation $R_1 - O_1$ turns out to be temperature dependent, as illustrated in Fig. 1. Although the peak separation at 298 K is 100 mV, it is larger than 250 mV at 243 K. This behaviour is unique for the couple $R_1 - O_1$, and strongly suggests that although the redox reaction is chemically reversible, the electron transfer is followed by another process, probably a structural change (see below). The latter process must clearly proceed at rates compatible with the voltammetric technique, since the

voltammograms change so drastically on lowering the temperature.

CH_3CN. In acetonitrile the three reversible couples $R_2 - O_2$, $R_3 - O_3$ and $R_4 - O_4$ established in the investigation in CH_2Cl_2 are again apparent. However, it was not possible to achieve reversibility of the couple $R_1 - O_1$, since trace amounts of water or other nucleophiles immediately destroy *1*.

To summarize, the results obtained clearly demonstrate the existence of a five-membered series of electron transfer complexes but they also indicate that a reversible chemical change occurs on going from *2* to *1*.

Structure

$Cu(L)_2^0$, (3). It has been shown by X-ray powder diffraction that *3* is isostructural with the analogous nickel compound, $Ni(L)_2^0$. The metal atom in $Ni(L)_2^0$ was shown to be sited in a distorted tetrahedral N_2S_2 coordination sphere. Due to the isostructurality it is thus reasonable to conclude that $Cu(L)_2^0$ has a closely similar coordination geometry.

Thus, $Cu(L)_2^0$, like $Ni(L)_2^0$, is a member of a series of electron transfer complexes, in which at least one member is nonplanar.

ESR and magnetic susceptibility. Results are collected in Tables 2 and 3. The ESR spectrum

Table 2. ESR results

| Compound | Medium | $\langle g \rangle$ | Frozen solution | | | a_{Cu} gauss |
			g_1	g_2	g_3	
$Cu(L)_2^0$	2-Me-THF	−	⋯ 2.001 [a] ⋯			20
$Cu(L)_2^{2+}$	CH_2Cl_2	2.06 [b]	$g_\perp = 2.01$, $g_{||} = 2.16$			$a_{||} = 137$

[a] No resolvable anisotropy. [b] Calc. from $g_\perp$ and $g_{||}$.

Table 3. Magnetic susceptibility.

Compound	T K	χ^{a} cgs/mol	μ_{eff} BM
	80	458×10^{-5}	1.71
$Cu(L)_2^{0}$	203	181×10^{-5}	1.72
	300	122×10^{-5}	1.71

[a] Faraday method. Diam. correction -26×10^{-5} cgs/mol.

$[Cu(L)_2]^0$ H →

$\vdash\!\!\!-\!\!\!-\!\!\!-\!\!\!\dashv$ 100 gauss
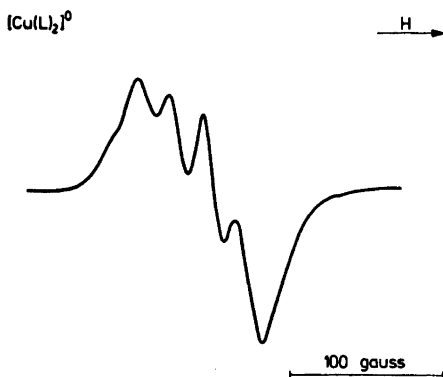
Fig. 2. X-Band ESR spectrum of $Cu(L)_2^{0}$ in 2-Me-THF at 77 K.

Table 4. Electronic spectral data for $Cu(L)_2^{z}$ in CH_2Cl_2.

Complex	$\lambda_{\max}$ nm	ε^{a}
$Cu(L)_2^{2+}$	530 sh	1 400
	490	4 100
	380	7 400
	332	25 700
$Cu(L)_2^{+}$	695	7 700
	359	29 400
	790	5 400
	531	6 500
$Cu(L)_2^{0}$	510 sh	6 370
	362	27 300
	330 sh	22 000
	505	7 200
$Cu(L)_2^{-}$	471	7 400
	380	32 100
	294	18 700

[a] Uncorrected for underlaying absorptions.

reported for *1* was recorded in a frozen methylene chloride solution containing Bu_4NBF_4 (0.1 M) at liquid nitrogen temperature; at the latter temperature a microcrystalline matrix is formed. Owing to the instability of *1* spectra of *1* at room temperature were not recorded. The ESR spectrum quoted for *3* is that recorded for 2-Me-THF solutions ($10^{-3} - 10^{-5}$ M). *3* exhibits no solution spectrum at room temperature, indicating that an effective relaxation mechanism is operating. However, at 77 K, at which 2-Me-THF forms a glass, the characteristic spectrum shown in Fig. 2 is observed. Compounds *2* and *4* appear to be diamagnetic, since no spectra were observed even at low temperature.

The magnetic susceptibility of powdered samples of *3* was determined in the temperature range 80 – 278 K.

Electronic spectra of *2* and *3* were recorded for solutions in dry methylene chloride, while the spectra of *1* and *4* were recorded for methylene chloride solutions containing Bu_4BF_4 (0.1 M). Spectral parameters are given in Table 4.

DISCUSSION

$Cu(L)_2^{2+}$ (1). The rather anodic potential (+ 1.3 V *vs.* SCE) at which *1* is formed probably excludes the possibility of isolating *1* as a pure salt. However, stable CH_2Cl_2 solutions can be prepared. The ESR spectrum of (*3*) in frozen CH_2Cl_2 exhibits an axial or near axial g-tensor, which is characteristic of Cu(II), d^9, in a planar or octahedral (BF_4^{-} or solvent) environment.[10-12] The spectrum cannot be rationalized in terms of tetrahedral coordination, which would lead to a rhombic g-tensor.[13,14] Likewise, the observed electrochemical irreversibility of the couple $R_1 - O_1$ at low temperature indicates that the oxidation of $Cu(L)_2^{+}$ to give $Cu(L)_2^{2+}$ is followed by another transformation which could very well be a flattening of the tetrahedron to give planar $Cu - N_2S_2$. It therefore seems reasonable to describe $Cu(L)_2^{2+}$ in simple terms as Cu(II), d^9, coordinated by two closed shell azothioformamide ligands in a planar arrangement. This situation, in which members of a series of electron transfer complexes have different geometries [$Cu(L)_2^{0}$ is tetrahedral], has to the present authors' knowledge not been described elsewhere.

$Cu(L)_2^+$ *(2)*. The one-electron relationship between *1* and *2* is obviously most simply explained as reduction of Cu(II) to Cu(I). A similar case, in which a Cu(II)-bis-thiosemicarbazonate is spontaneously reduced by the solvent, has been described previously.[15] $Cu(L)_2BF_4$ is diamagnetic and can be described as Cu(I), d^{10}, with azothioformamide ligands in a tetrahedral arrangement, since all known tetracoordinated Cu(I) compounds are tetrahedral.[16]

$Cu(L)_2^+$ is isoelectronic with the previously described $Ni(L)_2^0$, for which a simple model of the bonding was proposed. If this model is used in the description of $Cu(L)_2^+$ as Cu(I), d^{10}, the π^* orbitals of the ligands must be interchanged with d_{xy}. A similar interchange has been used to explain the observed differences in the properties of planar isoelectronic nickel and copper bis-dithiolenes.[4]

The two compounds *6* and *7* (eqns. 2 and 3) are variants of $Cu(L)_2^+$. *7* exhibits $\mu_{eff} = 1.8$ BM per 3 Cu atoms at 300 K in the solid state and both behave like $Cu(L)_2^+$ in solution (electronic spectra and cyclic voltammetry). It is therefore reasonable to describe both as double salts of $Cu(L)_2^+$, presumably formed because crystal packing of $Cu(L)_2^+$ and various counter ions leave open spaces in the structure.

$Cu(L)_2^0$ *(3)*. X-Ray diffraction data indicate strongly that this species is tetrahedral. μ_{eff} of the solid is 1.72 BM at temperatures between $80-300$ K, indicating that spin-orbit coupling effects are small. This is fully supported by the ESR results. The observed isotropic g-tensor is in accordance with a simple description which places the unpaired spin in a ligand π^* orbital of minimal metal character. Similar observations have been described for planar Cu-phthalocyanine compounds.[17] The Cu hyperfine splitting ($a_{Cu} = 20$ gauss) for $Cu(L)_2^0$ is as far as is known the smallest observed for any copper compound. This further supports the proposal that the odd-electron orbital is of predominantly π^* character and that the observed splitting is of a similar origin to alkalimetal induced splittings observed for aromatic anion radicals.[18]

The weak inflection in the $m_I = -\frac{3}{2}$ component of the ESR spectrum (Fig. 2) is tentatively assigned to the presence of different copper isotopes, in accordance with what is usually seen when isotopically impure copper is used.

$Cu(L)_2^0$ is isoelectronic with $Ni(L)_2^+$, for which weak but resolvable g-tensor anisotropy was observed.[1] By analogy with $Cu(L)_2^+$ and $Ni(L)_2^0$ the simple bonding model proposed for the nickel compounds[1] is again useful for the copper compound if π^* and d_{xy} are interchanged.

$Cu(L)_2^0$ exhibits no ESR signal in solution at room temperature, indicating that an effective relaxation mechanism is operating. Degeneracy or near degeneracy of π^* (a) and π^* (b) could provide such a mechanism.[19]

On a simple basis $Cu(L)_2^0$ is reasonably described as Cu(I), d^{10}, with one neutral and one radical anion ligand. The low energy transition of $Cu(L)_2^+$ at 695 nm is probably an M→L transition; in $Cu(L)_2^0$ it moves to lower energy as more anion character is transferred to the ligand.

$Cu(L)_2^-$ *(4)*. If the π^* orbitals of $Cu(L)_2^0$ are degenerate or near degenerate the one-electron reduction might lead to ^3B or ^1A ground states of equal energy. The isoelectronic $Zn(L)_2^0$ is an example of such a system.[6]

$Cu(L)_2^-$ solutions are unfortunately rather unstable and the experimental results therefore few. For $Cu(L)_2^-$ in frozen CH_2Cl_2 at 77 K ^1A rather than ^3B is indicated since no ESR spectrum is observed. However, since ^3B $Cu(L)_2^-$ might possess effective relaxation mechanisms line broadening could occur. Attempts to isolate solid $Cu(L)_2^-$ as the sodium salt were unsuccessful and no magnetic susceptibility results were obtained.

$Cu(L)_2^{2-}$ *(5)*. The only experimental evidence for the existence of this species is provided by the cyclic voltammetry results. No further data were obtained.

EXPERIMENTAL

Equipment and experimental techniques are described in Ref. 1.

$Cu(L)_2(BF_4)$. 10 ml of a 0.5 M aqueous solution of $Cu(BF_4)_2$ were added to a solution of 2.2 g of *N,N*-diethylphenylazothioformamide (0.01 mol) in 40 ml abs. ethanol. The solution was heated under reflux for 10 min. The solution was filtered and cooled in ice, and the precipitate was collected and dried. Soxhlet extraction with 100 ml ether–acetone (2:1) yielded $Cu(L)_2BF_4 \cdot (CH_3)_2CO$. After drying for 6 h at 80 °C dark green crystals were obtained in yields of $60-80$ %. M.p. not well defined. Aanl. $C_{23}H_{30}N_6BCuF_4S_2$: C, H, N.

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