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Electron Spin Resonance and Electrochemical Study of Thiohydroxamate and 1-Phenyl-3-imino-2(1*H*)-pyridinethione Complexes of Copper(II)

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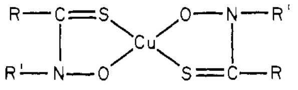
Syntheses, electronic spectra, ESR spectra, and electrochemical properties are described for a range of {S,O} chelates of copper(II)-containing bidentate thiohydroxamic acids, viz., $Cu(RC(=S)N(R')O)_2$, and for two tetradentate {S,N} 1-phenyl-3-imino-2(1*H*)-pyridinethione complexes. Both classes of compounds have square-planar geometries; the thiohydroxamates have a *trans*-$\{S_2,O_2\}$ chromophore while the pyridinethione derivatives have a *cis*-$\{S_2,N_2\}$ chromophore. S → Cu(II) charge-transfer bands are observed in the UV-visible spectra. Unusual solvent-dependent changes in the visible spectra are displayed by the R′ = H thiohydroxamates. The ESR spectra of the thiohydroxamate complexes give well-resolved lines with narrow line widths. Some unusual splittings of the parallel lines in the frozen solution spectra and in the four-line fluid solution spectra are observed. The ESR spectra of the $Cu\{S_2,N_2\}$ complex show broader and less well-resolved line shapes. Polarographic and cyclic voltammetric measurements on DMF solutions of the compounds are discussed in detail. The Cu(II)/Cu(I) reduction potentials are compared with those of related thio complexes and with those of copper redox proteins. A brief discussion of the likely binding groups in the active sites of copper proteins is given.

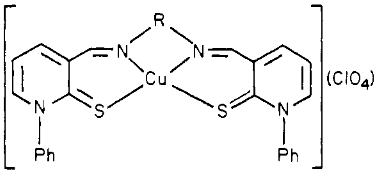
Introduction

As part of our current studies of mono-[2] and binuclear[3,4] complexes of copper(II) we have investigated the spectroscopic, magnetic, and redox properties of some mononuclear complexes that contain sulfur donor ligands. The complexes contain bidentate thiohydroxamate {S,O} ligands (I) and tetradentate {S,N} N,N′-substituted imines of 1-phenyl-3-formyl-2(1*H*)-pyridinethione (II). The thiohydroxamate derivatives form part of a wider study of the coordination of such ligands to transition metals.[5-7] The copper(II) thiohydroxamates are also important as antibiotics,[8,9] and one member, with R = H, R′ = Me (labeled Fluopsin C), can be isolated from cultures of *Pseudomonas fluorescens*. The Schiff base chelates are formed from 3-formyl-2(1*H*)-pyridinethione, whose preparation and conversion to dithiocins in the presence of primary amines have recently been described.[10,11] Spectroscopic and electrochemical studies of I and II allow a comparison of the effect of changing the donor atoms from {S,O} to {S,N}. These kinds of ligand variation may well be important in determining the likely protein binding sites to Cu in various copper enzymes. Cysteine and methionine S-donor sites are now known to bind to Cu in plastocyanin and azurin in conjunction with histidine N-donor atoms.[12,13] The stereochemistry in the active sites of these proteins is distorted tetrahedral, which contrasts with the essentially square-planar environments in I and II. The stereochemistry of the present compounds is more relevant to the types 2 and 3 copper found in multicopper enzymes. In the present study we have used ESR spectroscopy as the chief electronic probe since it is known[14] that the g_z and A_z parameters are sensitive to variations in donor group and stereochemistry.



I

R = H, aryl; R′ = H, Me, Ph



II

R = $-CH_2-CH_2-$

Experimental Section

Physical Measurements. UV-visible spectra and room-temperature magnetic susceptibilities were measured on instruments previously described.[5] The variable-temperature susceptibility study was determined with use of an Oxford Instruments Faraday balance. Diffuse-reflectance spectra were measured on a Unicam SP 700 instrument with a Unicam SP 735 diffuse-reflectance accessory. Magnesium oxide was used as the reflectance reflector. X-Band ESR spectra were measured on a Varian E-12 instrument. Computer simulations of line shapes were made with a program kindly supplied by Dr. J. R. Pilbrow. Mass spectra were measured on a V.G. Micromass 7070F mass spectrometer. dc polarography and cyclic voltammetry were performed with a Princeton Applied Research 170 Electrochemical System. All measurements were made in May and Baker Pronalys dimethylformamide (DMF) purified in the following manner. The solvent was stored over freshly dried 4-Å molecular sieves (200 °C in vacuo) for several days before being decanted onto barium oxide and left for several days with intermittent shaking. It was then decanted and a fractional distillation performed at approximately 35 °C under a vacuum of 2-3 torr. Only 150 cm^3 was collected at a time and stored under nitrogen at −30 °C in the dark. Samples were removed under nitrogen as required, and the solvent was never stored for more than 3 weeks before the process was repeated. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP) (Eastman Chemicals). The reference electrode was a saturated calomel electrode,

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and the solvent, in the presence of 0.1 M TBAP, gave an accessible range of +0.5 to −2.8 V on Hg and +1.2 to −2.5 V on Pt. All solutions were degassed thoroughly with high-purity nitrogen. The temperature of the cell was maintained at 25 ± 1 °C.

Preparations. The thiohydroxamic acids were prepared as described earlier.[5,6,15] *N*-hydroxypyridine-2-thione was purchased from Ega Chemie.

3,3′-[Ethylenebis(nitrilomethylidene)]bis(1-phenyl-2(1*H*)-pyridinethione). 1-Phenyl-3-formyl-2(1*H*)-pyridinethione (4.73 g, 0.022 mol) and ethylenediamine (0.6 g, 0.01 mol) were refluxed in a mixture of benzene (100 mL) and chloroform (30 mL) for 2 h. Cooling yielded 3.80 g of orange crystals, and washing with hydrazine hydrate (50%) and recrystallizing from 2-methoxyethanol afforded 3.0 g (66%) of the bis(imine), mp 232–233 °C. Anal. Calcd for $C_{26}H_{22}N_4S_2$: C, 68.69; H, 4.88; N, 12.32. Found: C, 68.10; H, 4.90; N, 12.26. ^1H NMR in $CDCl_3$, with δ referenced to Me_4Si and J in Hz: 4.05 (s, 4 H, CH_2), 6.71 (t, J = 7, 2 H, H-5), 7.15–7.55 (m, aryl H, 10 H), 7.70 (dd, J = 7 and 2, 2 H, H-4), 8.10 (dd, J = 7 and 2, 2 H, H-6), 9.12 (s, 2 H, CH=N). IR in KBr: 1636 cm^{-1} (C=N).

Bis(benzothiohydroxamato)copper(II). The preparative method was based on reports of earlier work.[8,16–18] A solution of 0.28 g (1.63 mmol) of copper(II) chloride dihydrate in ethanol (20 mL) was added slowly with stirring to 0.5 g (3.26 mmol) of freshly prepared benzothiohydroxamic acid in ethanol (20 mL). The green solid that precipitated almost quantitatively was filtered, washed with three 20-mL portions of ethanol, and air-dried. Recrystallization from dimethylformamide/methanol gave dark microcrystals of the complex (0.49 g, 80%). Anal. Calcd for $C_{14}H_{12}N_2O_2S_2Cu$: C, 45.7; H, 3.3; N, 7.6; S, 17.4. Found: C, 45.3; H, 3.4; N, 7.4; S, 17.1.

The following were prepared by the same method.

Bis[(*p*-methoxyphenyl)thiohydroxamato]copper(II) was produced as green crystals from dimethylformamide/methanol. Anal. Calcd for $C_{16}H_{16}N_2O_4S_2Cu$: C, 44.9; H, 3.8; N, 6.5. Found: C, 44.8; H, 3.7; N, 6.6.

Bis(2-furanthiohydroxamato)copper(II) was produced as green crystals from dimethylformamide/methanol. Anal. Calcd for $C_{10}H_8N_2O_4S_2Cu$: C, 34.6; H, 2.3; N, 8.1. Found: C, 34.2; H, 2.4; N, 7.9.

Bis(*N*-methylbenzothiohydroxamato)copper(II) was produced as brown crystals from dimethylformamide/methanol. Anal. Calcd for $C_{16}H_{16}N_2O_2S_2Cu$: C, 48.5; H, 4.1; N, 7.1. Found: C, 48.5; H, 4.2; N, 6.9.

Bis(*N*-phenylbenzothiohydroxamato)copper(II) was produced as red-brown crystals from dimethylformamide/methanol. Anal. Calcd for $C_{26}H_{20}N_2O_2S_2Cu$: C, 60.1; H, 3.9; N, 5.4. Found: C, 59.8; H, 3.9; N, 5.1.

Bis(*N*-methylformothiohydroxamato)copper(II) was produced as brown prisms from chloroform. Anal. Calcd for $C_4H_8N_2O_2S_2Cu$: C, 19.7; H, 3.3; N, 11.5; S, 26.3. Found: C, 19.9; H, 3.3; N, 11.7; S, 25.9.

Bis(*N*-phenylformothiohydroxamato)copper(II) Hemichloroformate was produced as brown crystals from chloroform. Anal. Calcd for $C_{14}H_{12}N_2O_2S_2Cu\cdot{}^1/_2CHCl_3$: C, 40.7; H, 2.9; N, 6.6. Found: C, 41.2; H, 2.9; N, 6.9.

Bis(pyridine-2-thione 1-oxide)copper(II). This was prepared by the method of Robinson[19] as a light green solid, mp 230 °C (lit. 238 °C).

3,3′-[Ethylenebis(nitrilomethylidene)]bis(1-phenyl-2(1*H*)-pyridinethione-*S*,*N*)copper(II) Perchlorate (II). The free ligand (0.9 g) was suspended in 25 mL of warm absolute ethanol, and copper acetate monohydrate (0.4 g) was added. The mixture was kept at 50 °C for a few minutes, and then a saturated aqueous solution of $NaClO_4$ (5 mL) was added. When the mixture cooled to room temperature, maroon-brown crystals of the complex were deposited; yield 1.2 g (84%). The product was recrystallized from a 1:10 dimethylformamide/ethanol solution. λ_{max} (nm) in DMF: 527 (ϵ 750), 364 (ϵ 19500), 319 (ϵ 15100), 273 (ϵ 9130). Anal. Calcd for $C_{26}H_{22}N_4S_2Cl_2O_8Cu$: C, 43.01; H, 3.05; N, 7.72. Found: C, 43.14; H, 3.27; N, 7.61.

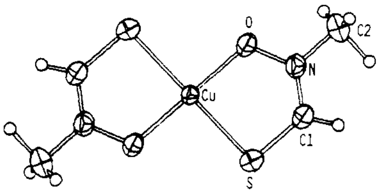

Figure 1. ORTEP drawing of bis(*N*-methylformothiohydroxamato)copper(II).

Results and Discussion

Synthesis and Structure. All the thiohydroxamate complexes are prepared by treating copper(II) chloride with the free thiohydroxamic acid in ethanol. The complexes were crystallized from either dimethylformamide/methanol mixtures or chloroform. Bis(*N*-phenylformothiohydroxamato)copper(II) crystallized as a chloroformate and lost the solvate molecule on standing.

Complexes of the type $(RC(=S)NHO)_2Cu$ are green whereas complexes substituted at the nitrogen, i.e., $(RC(=S)N(R')O)_2Cu$, are brown. The green non-N-substituted thiohydroxamic acid complexes are insoluble in all common solvents except donor solvents such as dimethylformamide, dimethyl sulfoxide, and pyridine. The brown N-substituted thiohydroxamic acid complexes, however, are appreciably soluble in solvents such as chloroform and acetone. The limited solubility of the green copper(II) complexes is probably indicative of an associated structure in the solid state. It is thought that the brown copper(II) complexes are monomeric as shown by the X-ray crystal structure of one example, bis(*N*-methylformothiohydroxamato)copper(II), the chemical analogue of the natural product, Fluopsin C (see below). Green and brown forms of other copper(II) chelates are known (e.g., β-ketoimines[20]), and it appears likely that polymorphs are involved.

The crystal structure of $Cu(HC(S)N(Me)O)_2$ shows a square-planar stereochemistry with the ligands adopting a trans configuration (Figure 1). The bond distances are Cu–S = 2.27 Å and Cu–O = 1.91 Å. The copper atom is 0.13 Å out of the plane of the ligand, and there are no intermolecular associations via copper atoms. Full details of the structure have been published elsewhere.[21]

Recently Leong and Bell have successfully separated the cis and trans isomers of the substitution-inert platinum(II) and palladium(II) complexes of *N*-methylformothiohydroxamic acid.[22] They also suggested that the nickel(II) and copper(II) complexes were in dynamic cis–trans equilibrium in solution, since thin-layer chromatography indicated only one band with similar R_f values. It is therefore not known for certain if bis(*N*-methylformothiohydroxamato)copper(II) crystallizes exclusively as the trans isomer or crystallizes as a mixture of cis and trans isomers, although we feel that the trans isomer is the predominant if not exclusive isomer.

The $Cu\{N_2,S_2\}$ complex contains a tetradentate ligand formed betwen ethylenediamine and 1-phenyl-3-formyl-2-(1*H*)-pyridinethione. It is maroon-brown and is a new compound that has a coordination sphere similar to those of Schiff base complexes of the mercaptobenzaldimine and mercapto-β-ketoimine types.[2,23–25] The yellow-orange free ligands can

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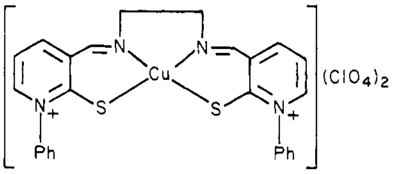
Table I. Optical Spectra and Magnetism of Copper(II) Thiohydroxamates, $Cu(RC(=S)N(R')O)_2$

R	R′	state	abs max, nm (ε)^a	μ_{eff}, μ_B^{b}
Ph	H	solid	580, 830	1.86
Ph	H	Me_2SO	324 (11 482), 555 (240), 820 (18)	
Ph	H	py	340 (12 735), 560 (166), 820 (23)	
Ph	H	DMF	349 (14 591), 488 (6200)	
p-$MeOC_6H_4$	H	solid	580, 820	1.88
p-$MeOC_6H_4$	H	Me_2SO	330 (11 821), 558 (192), 820 (22)	
p-$MeOC_6H_4$	H	DMF	348 (12381), 496 (8651)	
2-C_4H_3O	H	DMF	342 (10 173), 492 (7357)	1.89
Ph	Me	solid	550, 850	1.82
Ph	Me	$CHCl_3$	330 (11 252), 560 (371), 820 (82)	
Ph	Me	DMF	328 (11 890), 550 (227), 820 (67)	
Ph	Ph	solid	550, 840	1.85
Ph	Ph	$CHCl_3$	338 (12 289), 550 (298), 830 (35)	
Ph	Ph	DMF	330 (12 727), 550 (330), 828 (41)	
H	Me	solid	570, 835	
H	Me	$CHCl_3$	320 (5836), 350 sh (5029), 559 (227), 828 (20)	
H	Me	DMF	318 (6327), 350 sh (5283), 560 (130), 830 (14)	
H	Ph	DMF	320 (7283), 562 (298), 830 (61)	

^{a} Units are L mol^{-1} cm^{-1}. ^{b} Temperature 295 K.

be isolated in these reactions with primary amines, as the 1-phenyl substituent in 1-phenyl-3-formyl-2(1*H*)-pyridinethione prevents formation[11] of the bicyclononane (dithiocin) species. The formation of the bicyclononane species has also been encountered in mercaptobenzaldimine–copper chemistry.[2] Although we have drawn structure II in the thione form, there is evidence to suggest that II possesses thiolato character in the C–S bond and pyridinium character in the ring:



The stereochemistry is undoubtedly cis planar since the ESR spectrum of compound II (discussed below) is very similar to that of Cu(mben), whose structure is known to be of this type.[2]

Optical Spectra and Magnetism. The optical spectra of the copper(II) thiohydroxamate chelates were recorded both in solution and in the diffuse-reflectance mode. (Table I). All of the complexes show an intense band at ca. 350 nm, which is assigned to a Cu(II) ← S(σ) LMCT transition.[26-28] The complexes with ligands substituted at the nitrogen are pale yellow in dilute chloroform solution and show two weaker absorptions at 550 nm (ε ~300) and 830 nm (ε ~20), which are the d–d bands. The diffuse-reflectance spectra showed only small shifts in the position of these absorptions. There are no band shifts in donor solvents such as dimethylformamide or pyridine. The extinction coefficient for the band at 550 nm is somewhat higher than would be expected for a d–d transition, and it is probable that this band is borrowing intensity from the intense band at 350 nm. Similar effects have been noted in the optical spectra of other sulfur-liganded copper(II) complexes.[2,23-26] The weak band at 820 nm is probably due to the z^2 to $x^2 - y^2$ transition.

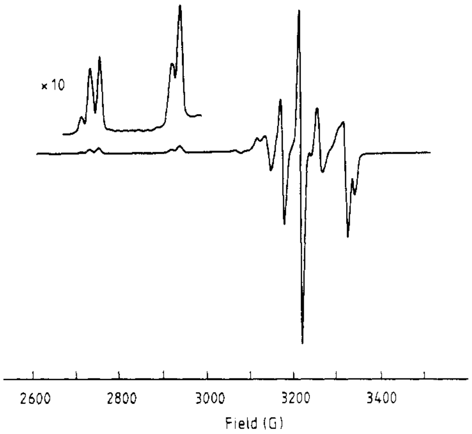


Figure 2. X-Band ESR spectrum of $Cu(HC(=S)N(Me)O)_2$ in frozen DMF with microwave frequency 9140 MHz.

The diffuse-reflectance spectra of the non-N-substituted copper(II) complexes, $Cu(RC(S)NH(O))_2$, showed bands at 580 and 820 nm, which are again assigned to d–d transitions. The visible spectra of these complexes show unusual solvent dependence. Freshly prepared solutions in dimethyl sulfoxide (Me_2SO) and pyridine (py) gave similar spectra to those recorded for the N-substituted complexes. However, in dimethylformamide (DMF), the solutions are cherry red and an intense band at 490 nm (ε ~7000) is observed. The very high extinction coefficient suggests that this band is partly or wholly charge transfer in origin. This immediately rules out cis–trans isomerization as the reason for the change in spectrum. There are a number of possible explanations for the intense 490-nm band; these include (i) charge transfer arising from a donor–acceptor interaction between the complex and DMF, (ii) rapid reaction of the complex with DMF, e.g., at the –NH group, and (iii) distortion of the copper–ligand chromophore induced by the solvent. Reason i seems unlikely when the solvent dependence of the spectra is considered. Since it is known[29] that metal thiohydroxamates react with strong base to deprotonate the NH and form thiohydroximate chelates, it is possible, in reason ii, that there would be more negative charge on S and a consequent shift of the band to the red. Against this proposal, however, is the fact that the original green thiohydroxamate complex can be crystallized from the red solutions. Further, it is unlikely that DMF would be basic enough to effect such a reaction. Distortion of the planar stereochemistry by solvation, as in reason iii, is possible, but it should be reflected in changes in the ESR spectra compared to those of the N-substituted complexes, which it is not. The origin of the 490-nm band therefore remains unsolved, yet it is more likely a Cu ← S charge-transfer transition by analogy with recent studies on tetragonal and pseudotetrahedral complexes.[26-28]

The magnetic moments of all the thiohydroxamate complexes are in the region 1.8–1.9 μ_B at room temperature, characteristic of square-planar copper(II) complexes. Complex II has a moment of 1.76 μ_B at 300 K that is independent of temperature down to 4.2 K. The visible–UV spectrum in DMF of this complex shows a medium-intensity d–d band at 527 nm (ε 750) and an intense Cu(II) ← RS(σ) LMCT band at 364 nm (ε 19 500), the latter being shifted a little from its position in other *cis*-Cu{S_2,N_2} thiolato and thioether chelates.[2,23-26,30-32]

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Table II. ESR Parameters for Cu(II) Thio Complexes[a, b]

complex	donor atoms	g_x	g_y	g_z	A_x	A_y	A_z
Cu(HC(=S)N(Me)O)$_2$ (I)	$\{S_2,O_2\}$	2.033	2.034	2.159	35	40	190
II	$\{S_2,N_2\}$[c]	2.020	2.020	2.140	31	31	184

[a] The z direction is at 90° to the Cu-chelate plane. The x and y directions bisect the Cu-ligand bond direction. [b] Complexes of type I measured in frozen $CHCl_3$/toluene or dimethylformamide; complex II measured in frozen dimethylformamide. A values are in $cm^{-1} \times 10^{-4}$. [c] $A^N = 13 \times 10^{-4}$ cm^{-1}.

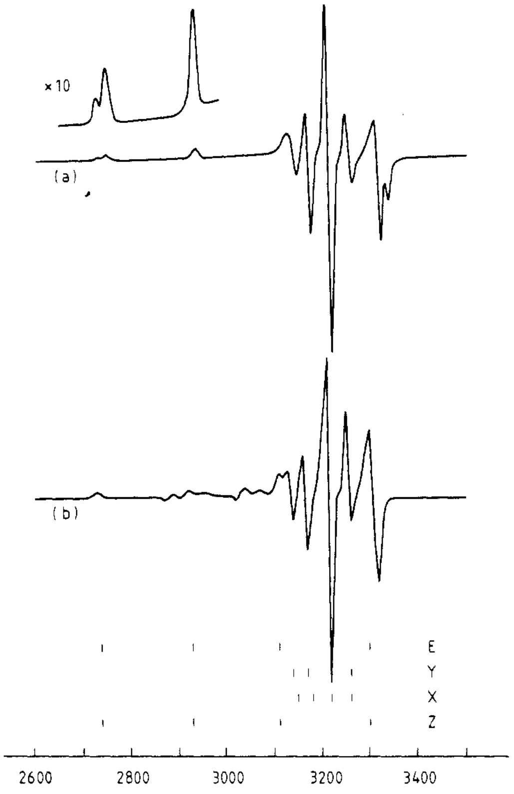

Figure 3. X-Band ESR spectrum of Cu(HC(=S)N(Me)O)$_2$ in frozen chloroform/toluene with microwave frequency 9140 MHz: (a) experimental spectrum; (b) computer-simulated spectrum using parameters of Table II. Only one isotope of Cu was included.

Electron Spin Resonance Spectra. Cu$\{S_2,O_2\}$ Species (I). All the Cu(II) thiohydroxamate complexes gave the same spectral line shape when measured as frozen glasses in dimethylformamide. The spectrum of one example, Cu(HC(=S)N(Me)O)$_2$, is shown in Figure 2. It has narrow and extremely well-resolved lines of a similar nature to those observed in the well-studied copper dithiocarbamate systems.[33,34] Only two of the z lines are visible while the other two are masked by the x,y lines, which in turn are almost, but not exactly, axial. One unusual feature of the z lines, at high gain, is the splitting of the $M_I = {}^3/_2$ and ${}^1/_2$ lines into three and two parts, respectively. This splitting is solvent dependent as we can see in a chloroform/toluene glass (Figure 3), where only the characteristic splitting of the $M_I = {}^3/_2$ z line due to ^{63}Cu and ^{65}Cu isotopes is evident. For a further probe into this feature the fluid solution spectrum of a more soluble derivative, Cu(PhC(=S)N(Me)O)$_2$, was determined. The X-band spectrum is the same in DMF or acetonitrile and is shown in Figure 4. It has a most unusual line shape compared to the normal four-line solution spectra of Cu(II) compounds and seems to consist of two superimposed sets of lines, each with slightly different line widths. (There is the usual decrease in line width in going to higher field due to the dependence of the width on the M_I value.) The total spin concentration under *all* the component lines is exactly 1. $\bar{g}$ is 2.078, and $\bar{A}$ is 87 G. The structure is lost when the fluid solution spectrum is measured at the Q-band frequency (Figure 5), although there are some indications of extra lines. The best interpretation that we can offer is that dimethylformamide (or acetonitrile) solvates *some* of the Cu chelate molecules such that the tumbling molecules can be differentiated even at room temperature. The glass spectrum shows that the solvation is preferentially in the axial position. Other alternative explanations such as (i) hyperfine splitting of the lines, (ii) cis–trans isomerism, and (iii) partial dissociation of the thiohydroxamate ligand are less likely.

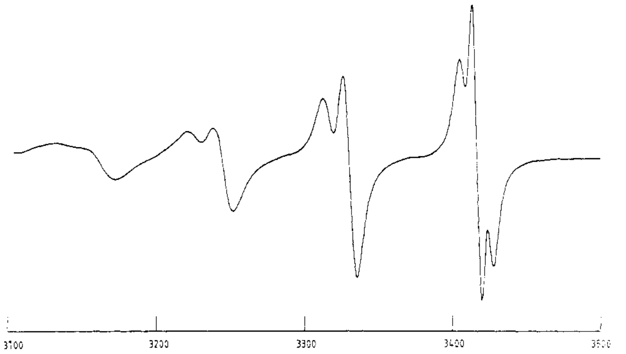

Figure 4. X-Band ESR spectrum of a fluid solution of Cu(PhC(=S)N(Me)O)$_2$ in acetonitrile at 300 K with microwave frequency 9511 MHz.

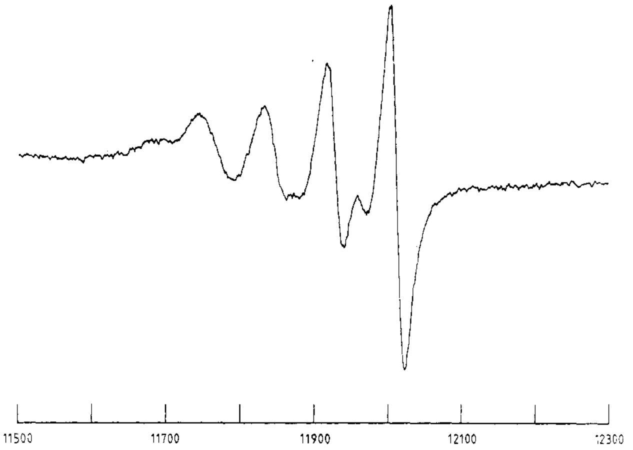

Figure 5. Q-Band ESR spectrum of a fluid solution of Cu(PhC(=S)N(Me)O)$_2$ in acetonitrile at 300 K with microwave frequency 34 540 MHz.

The chloroform/toluene glass spectrum of Cu(HC(=S)N(Me)O)$_2$ was simulated by computer methods;[35] the best-fit spectrum is shown in Figure 3, and the parameters are given in Table II. The parameters are similar to those reported for the only two available Cu$\{S_2,O_2\}$ complexes that contain monothio-β-diketonate ligands.[34] If we construct the Blum-

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Table III. Parameters for Redox Processes for $Cu(RC(=S)N(R')O)_2$ Complexes[a]

		redn						oxidn	
		dc polarography			cyclic voltammetry			cyclic voltammetry[f]	
R	R′	$E_{1/2}$, V	slope, mV[b]	i_d/c, mA mol^{-1}	E_{pc}, V	i_{pc}/i_{pa}[c]	ΔE_p, mV	E_{pa}, V[d]	i_{pa}/i_{pc}
Ph	H	*e*			-0.56^f	...	...	+0.97	...
Ph	Me	-0.69_8	61	1.01	$-0.72_9{}^g$	1.0	61	+0.93	...
Ph	Ph	-0.57_2	63	0.98	$-0.60_1{}^g$	1.0	60	+1.04	...
H	Me	-0.60_3	62	1.15	$-0.63_2{}^g$	1.0	60	+1.01	...
NPT[h]		-0.49_5	61	1.12	$-0.52_2{}^g$	1.0	61	+0.89	...

[a] Potentials vs. SCE at 25 °C. The solvent is DMF. [b] Determined from slope of E vs. $\log [i/(i_d - i)]$. [c] Scan rate 5 V s^{-1}. [d] Scan rate 200 mV s^{-1}. [e] Ill-defined. [f] Platinum working electrode. [g] Mercury working electrode. [h] Anion of *N*-hydroxypyridine-2-thione.

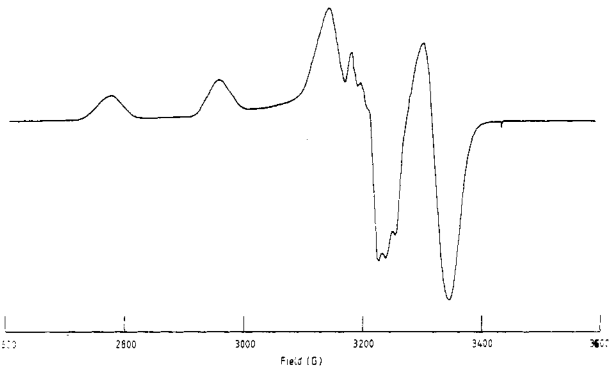

Figure 6. X-Band ESR spectrum of complex II in frozen DMF with microwave frequency 9144 MHz.

berg–Peisach plots[14] of g_z vs. A_z, then we find that these $Cu\{S_2,O_2\}$ values lie in a confined area between the areas observed for $Cu\{S_4\}$ and $Cu\{O_4\}$ species.

$Cu\{S_2,N_2\}$ Species (II). The ESR spectrum of complex II in frozen dimethylformamide is shown in Figure 6. The line shape is quite different from that of the thiohydroxamate complexes, and the line widths are much broader. The spectrum is very similar to those displayed by other *cis*-$Cu\{S_2,N_2\}$ compounds of the mercaptobenzaldimine and thioacetylacetone imine types.[2,23] Three of the z lines are observed at the low-field end while the strong line at 3345 G is a combination of the fourth z line and extrema lines. The strong lines at ca. 3240 G are the x and y lines, which are virtually superimposed. Superhyperfine coupling due to the cis-nitrogen nuclei is evident. The g and A parameters are given in Table II, with those in the z direction again falling in the tetragonal $\{S_2,N_2\}$ region of the Blumberg–Peisach maps.[14] The g_z and A_z values for the $Cu\{S_2,N_2\}$ chromophore are lower than those for the $Cu\{S_2,O_2\}$ chromophore.

Electrochemistry. $Cu\{S_2,O_2\}$ Species (I). The electrochemistry of several copper(II) thiohydroxamates was studied in order to investigate the electron-transfer characteristics of these compounds. All measurements were made in DMF with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. All potentials were measured relative to a saturated calomel electrode (SCE) separated from the test solution by two salt bridges filled with 0.1 M TBAP in DMF.

Results obtained from dc polarography are presented in Table III. All of the complexes except $Cu(PhC(=S)NHO)_2$ exhibited one extremely well-defined polarographic wave at ca. −0.6 V vs. SCE. Graphical plots of the diffusion current vs. the square root of the column height of mercury were linear, indicating diffusion control. Plots of E vs. $\log [i/(i_d - i)]$ were also linear with a slope of 60 ± 3 mV (Table III), indicating that the electrode process was a reversible one-electron process. This was further substantiated by examining the cyclic voltammograms of these compounds on a single mercury drop at the DME. The peak separation was 60 mV over all scan ranges used, and the ratio of currents was equal to 1 at a fast scan rate. These results indicate that the complexes behave in a similar fashion to the analogous iron(III) tris complexes,[7] i.e., the electrode process may be written

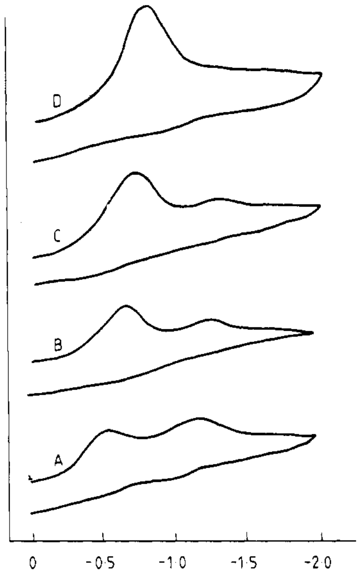

Figure 7. Cyclic voltammograms of $Cu(PhC(=S)NHO)_2$ in a DMF solution on a Pt electrode. Scan rates: A, 1 V s^{-1}; B, 5 V s^{-1}; C, 10 V s^{-1}; D, 20 V s^{-1}.

$$[Cu^{II}L_2] + e^- \rightleftharpoons [Cu^{I}L_2]^-$$

$L = RC(=S)N(R')O$; $R = Ph$, $R' = CH_3$; $R = Ph$, $R' = Ph$; $R = H$, $R' = CH_3$ (L = *N*-hydroxypyridine-2-thione)

In the case of bis(benzothiohydroxamato)copper(II), $Cu(PhC(=S)NHO)_2$, it was apparent that the complex reacted with the mercury electrode, giving an ill-defined wave. All measured results were made on clean Pt-wire electrodes. Cyclic voltammetry at a slow scan rate (0.500 V s^{-1}) showed two irreversible peaks, the first at −0.56 V corresponding to the Cu(II)/Cu(I) reduction couple and the second peak at −0.142 V apparently due either to a Cu(I)/Cu(0) couple or to the reduction of another species arising from rapid decomposition of the reduced copper chelate. There are no ligand reduction waves in this region. Evidence suggests that the second scheme is more likely, since as the scan rate was gradually increased, the height of the second wave decreased until at 20 V s^{-1} the peak was no longer evident (Figure 7). Thus the suggested redox processes for $Cu(PhC(=S)NHO)_2$ may be represented by an ECE mechanism:

$$Cu(PhC(=S)NHO)_2 + e^- \rightarrow Cu(PhC(=S)HNO)_2{}^- \quad E_1$$

$$Cu(PhC(=S)NHO)_2{}^- \xrightarrow{k_d} \text{product} \quad C$$

$$\text{product} + e^- \rightarrow \text{product}^- \quad E_2$$

Table IV. Electrochemical Processes for the Cu $\{N_2,S_2\}$ Complex II in DMF Solution

	$E_{1/2}$,[a] V	i_d/c, mA mol^{-1}	slope,[d] mV	cyclic voltammetric characteristics
redn wave				
1	−0.218	1.15	56	rev
2	−0.478	1.04	79	irrev on Pt, quasi-rev on Hg
3	−1.620[b]	1.00	99	quasi-rev rapidly becoming irrev as scan rate increases
4	−2.56	ca. 1.4	irrev	
oxidn wave	+0.22[c]			apparently irrev on Pt; product plated onto electrode; probably ligand-based process

[a] Relative to SCE. [b] Small prewave, possibly due to adsorption of reduced species. [c] E_{pa} from cyclic voltammetry on a Pt electrode. [d] Slope = slope of E vs. log $[i/(i_d - i)]$ from dc polarography.

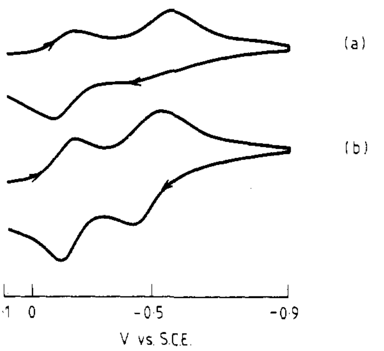

Figure 8. Cyclic voltammograms of a DMF solution of II on a mercury-drop electrode. Scan rates: (a) 10 V s^{-1}; (b) 2 V s^{-1} (amplified 2.5 times as much as (a)).

At fast scan rates, the second reduction, E_2, is not observed.

All of the complexes showed an irreversible ligand-based oxidation at ca. +1.0 V (Table III). There was no evidence for stabilization of the copper(III) state, which has been obtained in copper(III) dithiocarbamates and copper(III) complexes with deprotonated amides.[36,37]

Cu$\{S_2,N_2\}$ Species (II). The electrochemistry of complex II was investigated with use of the same solvent (DMF), supporting electrolyte, and electrodes as used for the thiohydroxamate compounds. The results are summarized in Table IV. There are four reduction processes and one oxidation. Plots of limiting current (i_l) against the square root of the height of the head of mercury ($h_{Hg}^{1/2}$) showed the first two reductions to be diffusion controlled. Only the first reduction was found to be a one-electron electrochemically reversible process. All other reductions are quasi-reversible or irreversible one-electron processes.

Wave 1, with $E_{1/2} = -0.218$ V, is considered to be due to the couple Cu(II)/Cu(I) while wave 2 is due to Cu(I)/Cu(0). Waves 3 and 4 are ligand-based reductions, and an apparently irreversible ligand-based oxidation is at $E_{pa} = +0.22$ V on Pt.

The first reduction couple [Cu(II)/Cu(I)] is found to be electrochemically reversible on both Pt and Hg electrodes with use of the criteria of Nicholson and Shain.[38] On Pt the potential separation (ΔE_p) between the cathodic peak (E_{pc}) and the anodic peak (E_{pa}) is 60 ± 4 mV at all scan rates up to at least 1 V s^{-1} while on Hg a similar ΔE_p is obtained up to at least 10 V s^{-1}. The heterogeneous electron-transfer process is considerably slower for the second couple and is different on the two electrode materials. Figure 8 shows the first two reduction couples on a Hg electrode at 2 and 10 V s^{-1}. An anodic peak for the second couple is clearly seen at a scan rate of 2 V s^{-1} (ΔE_p = ca. 90 mV—quasi-reversible). However, at the faster scan rate of 10 V s^{-1} no distinct anodic peak is observed. Furthermore, the cathodic peak for the second reduction process is shifted to more negative potentials as the scan rate increases. Both these observations are consistent with a slower electron-transfer process for the second couple compared to that for the first. The absence of an anodic peak for the second couple at 10 V s^{-1} is not indicative of an EC mechanism in this case. If the reduced species $[Cu^0L]^0$ were to react and was thus partially (or fully) removed from solution around the electrode before it could be reoxidized, increasing the voltage scan rate would result in a larger peak for the oxidation process rather than the opposite effect that is observed (at 2 V s^{-1}).

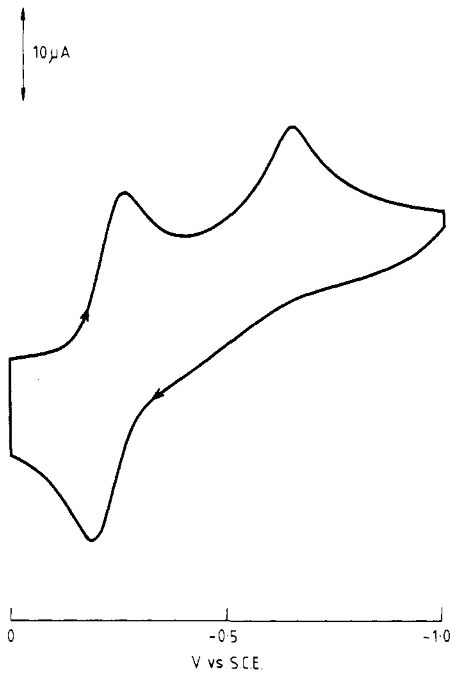

Figure 9. Cyclic voltammogram of a DMF solution of II on a platinum-wire electrode with scan rate 0.1 V s^{-1}.

No anodic peak is observed for the second couple on a Pt electrode even at the much slower scan rate of 0.1 V s^{-1} (Figure 9). This is not considered to be due to a contaminated Pt surface since it was cleaned and reduced by a method similar to that of Adams.[39] The more facile electron transfer on Hg may infer some bonding to the electrode surface, possibly through the sulfur of the ligand.[40]

The electrochemical properties of the oxidation process are not entirely clear. The size and shape of the anodic peak infers a multielectron reversible or quasi-reversible process with some evidence that adsorption may be occurring prior to oxidation. It is thought that an EC type mechanism is occurring where the product of the oxidation is undergoing a chemical reaction. Further evidence for this is the observation that the electrode surface becomes fouled.

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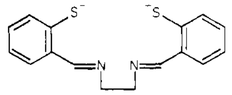
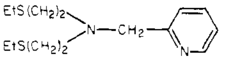
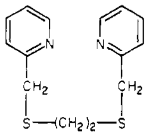
Table V. Reduction Potentials for Cu $\{S_2,N_2\}$ Species

complex	types of donor atoms[a]	$E°(Cu^{2+}/Cu^{+})$, V (vs. NHE)	ref
II	2 N_I, 2 S_T	+0.03	this work
Cu(mben)	2 N_I, 2 S^-	−0.58[b]	30
Cu(pma)$SO_4 \cdot 3H_2O$	N_H, N_S, 2 S	+0.40[c]	41
		+0.54[d]	42, 43
Cu(pdto)$^{2+}$	2 N_H, 2 S	+0.59[c]	41
		+0.71[e]	32, 42
plastocyanin (pH 7)	2 N_H, S, S^-	+0.37	44

[a] Donor atoms bonded to Cu in both oxidation states, excluding the solvent molecules: N_I = imine nitrogen, N_H = heterocyclic nitrogen, S_T = thione sulfur, S^- = thiolate sulfur, S = thioether sulfur. [b] In DMF with polarography and voltammetry. [c] Measured in H_2O with potentiometric titrations. [d] In 80% MeOH/H_2O with use of voltammetry. [e] In MeCN with use of voltammetry. [f] The abbreviations mben, pma, and pdto stand for the structures


mben


pma


pdto

The Cu(II)/Cu(I) reduction potential for II is compared to other reported Cu$\{N_2,S_2\}$ values in Table V. To facilitate comparison, we have converted the $E_{1/2}$ values to the NHE scale by adding 0.245 V to the SCE value. This is, of course, a procedure fraught with difficulties due to factors such as (i) the derivation of nonstandard potentials in some cases from irreversible polarography, (ii) use of nonaqueous solvents and the solvent dependence of $E_{1/2}$, and (iii) no correction for liquid-junction potentials. The values determined in water by Yandell et al.[41] using potentiometric titrations are the most reliable. Despite these reservations the comparisons are illustrative.

The more positive $E°$ value of II, compared to that of the related planar complex Cu(mben),[30] must in part reflect the negative charge on the S-donor atoms in Cu(mben), which will stabilize the Cu(II) state. If we assume that an additive relationship of the following type applies to the observed potentials[41]

$$E° = E°(Cu^{2+}(aq)/Cu^{+}(aq)) + n_L[E°(L)]$$

then the aryl-thiolato sulfur in Cu(mben) gives a more negative $E°$(L) contribution than the C⋯S group in II. Comparison of these two complexes to the pyridyl thioether derivatives Cu(pma)$^{2+}$ and Cu(pdto)$^{2+}$ is complicated by the change in N-donor as well as S-donor atoms, but it would appear that thioether sulfur atoms give more positive $E°$ values. The latter models give $E°$ values equal to or greater than those of "blue" copper proteins such as plastocyanin. However, as noted elsewhere,[41] the geometrical constraints imposed on the Cu(II) and Cu(I) states by the protein are more important in determining the magnitude of $E°$ than is the nature of the donor atoms. The trend toward more positive $E°$ values in the pma and pdto complexes compared to those for II and Cu(mben) is compatible with the pma and pdto ligands being more flexible and allowing pseudotetrahedral geometry around Cu(I).[43] Finally we note that the $\{O_2,S_2\}$ donor set in the thiohydroxamates is more difficult to reduce than is the $\{N_2,S_2\}$ set, the former giving $E°$ values comparable to those of $\{O_2,N_2\}$ donor groups.

Relationship to Copper Proteins. As indicated in the Introduction, studies of the present kind are useful for comparing the electronic and redox properties of suitably chosen copper(II) compounds with these properties in copper proteins. Prior to the crystal structure determinations of type 1 copper in plastocyanin and azurin,[12,13] it became possible to predict the donor atoms and stereochemistry at the copper site with some degree of accuracy by means of model studies. Of course, such studies can only at best complement investigations of the biomolecules. Although complex II has the same donor atoms as are found in plastocyanin, the stereochemistry around Cu and spectroscopic properties are quite dissimilar. In contrast to the case for type 1 copper, the detailed stereochemistries and binding groups attached to types 2 and 3 copper in multicopper oxidases and in proteins such as hemocyanin are less well-defined. Blumberg and Peisach concluded in 1974[14] that type 2 or "normal" copper was not bonded to $\{N_2,S_2\}$ or $\{S_4\}$ amino acid residues. Comparison of the ESR parameters in Table II with those of various type 2 centers in laccases, ceruloplasmin, ascorbate oxidase, and galactose oxidase[45] shows that the g_z values in *trans*-$\{S_2,O_2\}$ and *cis*-$\{S_2,N_2\}$ chromophores (2.14–2.16) are lower than those in the enzymes (2.23–2.27), while the A_z values are very similar. Thus, despite the limitations inherent in the Blumberg–Peisach correlations,[45] our results would support their prediction that Cu–S bonds are not involved and the binding groups are more likely nitrogen and oxygen arranged in a tetragonal disposition.

For type 3 binuclear Cu–Cu centers in oxidase enzymes or the related centers in hemocyanin and tyrosinase,[44] the ESR parameters of these strongly coupled "ESR-silent" copper atoms are now available through the work of Solomon et al.[46] and Reinhammer et al.[47] Reductive experiments on two laccases and cytochrome oxidase (heme a_3–Cu_B), as well as preparations of Met-apo (Cu^{II}) and half-Met (Cu^{II}Cu^{I}) derivatives of various hemocyanins and tyrosinase (*Neurospara crassa*), have yielded paramagnetic species that are ESR active. The spectra of the uncoupled Cu(II) ions are all tetragonal or rhombic with parameter values occurring in confined ranges, viz., g_z = 2.23–2.30, g_x = 2.02–2.05, g_y = 2.10–2.15, and A_z = (110–170) × 10^{-4} cm^{-1} (except[47] tree laccase; A_z = 82 × 10^{-4} cm^{-1}). A comparison with the ESR parameters for the present compounds shows significant differences in the g_z and A_z values. This suggests that sulfur to copper coordination in these binuclear sites is most unlikely. We would favor nitrogen (histidine) and oxygen ligation in agreement with the predictions of other recent spectroscopic[46] and EXAFS studies.[48] One form of tyrosinase and hemocyanin that does appear to contain Cu–S binding is that obtained after treatment of the Met (resting) form with 2-mercaptoethanol. Though they are poorly resolved, the ESR spectral parameters (g_z = 2.17–2.19, $g_\perp$ = 2.05–2.10) are now much more like those reported here. The mercaptoethanol

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molecule presumably binds in the half-Met (in-plane) position of the resulting mixed-valence Cu(II)–Cu(I) moiety, in agreement with the proposal of Solomon et al.[46]

Acknowledgment. The authors wish to thank Mr. G. Hanson and Dr. A. Edgar for help with Q-band ESR measurements, Dr. J. R. Pilbrow for the use of computer simulation programs, and Dr. Y. K. Yandell for discussions.

Registry No. I, R = Ph, R′ = H, 80734-29-8; I, R = *p*-MeOC$_6$H$_4$, R′ = H, 80734-30-1; I, R = 2-C$_4$H$_3$O, R′ = H, 80662-60-8; I, R = Ph, R′ = Me, 80662-61-9; I, R = Ph, R′ = Ph, 40791-41-1; I, R = H, R′ = Me, 67069-47-0; I, R = H, R′ = Ph, 80662-62-0; II, 80662-64-2; bis(pyridine-2-thione 1-oxide)copper(II), 14915-37-8; 3,3′-[ethylenebis(nitrilomethylidene)]bis(1-phenyl-2(1*H*)pyridinethione), 80658-35-1; 1-phenyl-3-formyl-2(1*H*)-pyridinethione, 61856-49-3; ethylenediamine, 107-15-3; NPT, 45529-38-2.

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Cyclic and Noncyclic Electron Delocalization in Cyclic π-Conjugated Molecules. Relative Delocalizabilities of Donor–Acceptor Disposition Isomers

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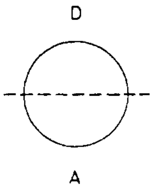
One-electron delocalization energy was defined, calculated, and analyzed to study the *relative* electron delocalizabilities of cyclic π-conjugated isomers where the donor (D)–acceptor (A) components are differently disposed. The present calculation showed that the number of the adjacent D–A pairs is an influential factor in addition to the continuity–discontinuity of both conjugation and orbital phase previously proposed. The continuity–discontinuity properties control *cyclic* delocalizability, and its significance in cyclic polyenes was confirmed. The number of the adjacent D–A pairs primarily determines *noncyclic* delocalizability, to which the delocalizability in both organic and inorganic heterocycles was found to be proportional. This may be the first study to predict the relative delocalizability of the inorganic D–A disposition isomers.

Introduction

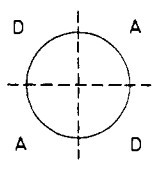
The mechanism of electron delocalization has been extensively studied to disclose chemical fundamentals such as the charge-transfer force,[1] the frontier orbital theory,[2] and so on. However, the theoretical study was limited almost exclusively to the two-system interaction until the three-system interaction theory was developed for the mechanism of catalytic action on the basis of the perturbation theory.[3] The theory was shown to reproduce the orbital-phase requirements,[4] which cover the $4n + 2$ π-electron rule for aromaticity[5] and the stereoselection rule for chemical reactions via cyclic transition states.[2c,6] More importantly, the theory gives a clue to studying the mechanism of the electron delocalization in more detail.

Organic chemists have developed the idea of functional group to understand chemical behaviors of innumerable molecules in a unified manner, to predict the property of the molecules in their hands, and to design their target molecules. Molecular orbital methods, widely used for the recent theoretical studies, are not always suitable to the view of functional group but to the gross property of whole molecules. This is a gap of basic terms that chemists have to bridge over in order to advance their own systematic theories. The many-system delocalization theory enables us to take the functional group property into consideration explicitly.

An interesting chemical consequence of the theory is the concept of the continuity–discontinuity of cyclic conjugation.[7] Cyclic conjugation is classified into continuous and discontinuous conjugations. In the continuously conjugated systems all electron-donating components (D's) are aligned on a part of a cyclic chain with electron-accepting ones (A's) all on the other part, as is illustrated by **1**. In the discontinuously conjugated systems the components are separated into at least four D–A groups as in **2**, **3**, and so on. We could say that the "frequency of D–A alternation" is 1 in the continuous conjugation and more in the discontinuous conjugation. The orbital-phase property is crucial for electron delocalization in the continuous conjugated molecules, but not in the discontinuously conjugated ones. The requirements for cyclic delocalization[3,4,7] are as follows: (1) the HOMO and LUMO in phase; (2) the HOMO's out of phase; (3) the LUMO's in phase. The continuous conjugation is subdivided into the electron-delocalizing and electron-localizing conjugations.[7] The delocalizing molecules satisfy the orbital-phase continuity requirements to be stable due to cyclic delocalization. The Hückel $4n + 2$ π-electron systems are among them. The localizing molecules do not satisfy the requirements and include unstable anti-Hückel $4n$ π-electron systems. The delocalization



1



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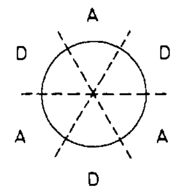

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