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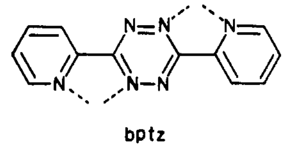
Paramagnetic Copper(I) Dimers

Sir:

The vast number of paramagnetic copper(II) dimers[1] have no parallel in copper(I) chemistry since Cu(I) exists in a closed-d-shell configuration, d^{10}.[2] We report here the preparation and characterization of the first paramagnetic Cu(I) dimers that must be described as anion radical complexes of binucleating α-diimines or α-iminoketones. Interest in the former species stems from the assertion that the emitting state of the electron-transfer-active (α-diimine) copper(I) complexes may be described as resulting from a metal-to-ligand charge transfer (MLCT),[3] i.e., involving the anion radical of the ligand:

$$\mathrm{LCu^{I}(\alpha\text{-diimine})} \xrightarrow[\text{MLCT}]{h\nu} {}^{*}[\mathrm{LCu^{II}(\alpha\text{-diimine}^{\bullet -})}] \qquad (1)$$

A highly electron-deficient, binucleating α-diimine with remarkable electron structure is 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, bptz.[4] Reaction of this ligand with 2 equiv of $\mathrm{Cu(PPh_3)_4{}^+BF_4{}^-}$,[3d] $\mathrm{Cu(BF_4)_2/Cu/1,2}$-bis(diphenylphosphino)ethane (diphos),[5] or $\mathrm{Cu(BF_4)_2/Cu/1,5}$-cyclooctadiene (cod) yields binuclear Cu(I) dications with intense ($\epsilon > 10\,000$) long-wavelength MLCT absorption bands at 13 890, 12 580, and 19 050 $\mathrm{cm^{-1}}$, respectively. These diamagnetic complexes[6] owe their long-wavelength absorption to a low-lying bptz ligand π^* orbital; in fact, electrochemical reduction occurs at positive potentials relative to a saturated calomel electrode, SCE (Table I).



bptz

Table I. ESR and Electrochemical Data of Paramagnetic Copper(I) Dimers[a,b]

compd	g	a_{Cu}	a_{P}	$a_{\mathrm{N}}{}^{c}$	$E^{2+/+}$
$\mathrm{bptz^{\bullet -}}$	2.0040			0.495	−0.72($E^{0/-}$)
$[(\mu\text{-bptz})\{\mathrm{Cu(PPh_3)_2}\}_2]^{\bullet +}$	2.0055	0.758	0.910	0.605 0.463	+0.13
$[(\mu\text{-bptz})\{\mathrm{Cu(diphos)}\}_2]^{\bullet +}$	2.0058	0.936	0.780	0.624 0.442	+0.08
$[(\mu\text{-bptz})\{\mathrm{Cu(cod)}\}_2]^{\bullet +}$	2.0053	0.960		0.646 0.427	+0.22
$[(\mu\text{-phdo})\{\mathrm{Cu(PPh_3)_2}\}_2]^{\bullet +}$	2.0058	0.643	0.835	*e*	+0.55[d]

[a] ESR coupling constants a in mT from computer simulations of 300 K spectra in dichloromethane solution; nuclear spins $I(^{14}\mathrm{N}) = 1$, $I(^{31}\mathrm{P}) = {}^1/_2$, and $I(^{63,65}\mathrm{Cu}) = {}^3/_2$. [b] Potentials E in V vs. SCE from cyclic voltammetry in dichloromethane/0.1 M $\mathrm{Bu_4N^+ClO_4^-}$. [c] The larger ^{14}N splitting is assigned to the coordinating tetrazine nitrogen center.[4c] Equivalent tetrazine N coupling constants for the free ligand anion may be due to free rotation and/or negligible spin density in the 2-pyridyl rings.[4c] [d] Irreversible step, anodic peak potential at 100 mV/s scan rate. [e] No phdo ligand hyperfine coupling observed.

Electrochemical as well as chemical one-electron reduction (e.g. with Zn metal) leads to the formation of paramagnetic copper(I) dimers[7] with the anion radical ligand,[8] $\mathrm{bptz^{\bullet -}}$. Evidence for this assignment comes from the analysis[9] of high-resolution spectra (Figure 1, Table I) and from comparison with reported data.[4b,c]

The series of coligands in Table I illustrates variable spin transfer from the radical ligand $\mathrm{bptz^{\bullet -}}$ to the metal fragments as evident from increasing ^{63,65}Cu hyperfine splitting and from increasing inequivalency of the ^{14}N coupling of the tetrazine nitrogen centers.[4] While the hyperfine coupling of the copper nuclei α to the spin-bearing π system originates mainly from σ/π spin po-

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(7) UV/vis/near-IR (in dichloromethane): $[(\mu\text{-bptz})\{\mathrm{Cu(PPh_3)_2}\}_2]^{\bullet +}$, $\nu_{\max} = 6200$, 19 400, and 24 040 $\mathrm{cm^{-1}}$; $[(\mu\text{-bptz})\{\mathrm{Cu(cod)}\}_2]^{\bullet +}$, $\nu_{\max} = 20\,100$, 25 300, and <7000 $\mathrm{cm^{-1}}$. Elemental analyses could not be obtained due to dissociative lability (loss of $\mathrm{PR_3}$ or cod).

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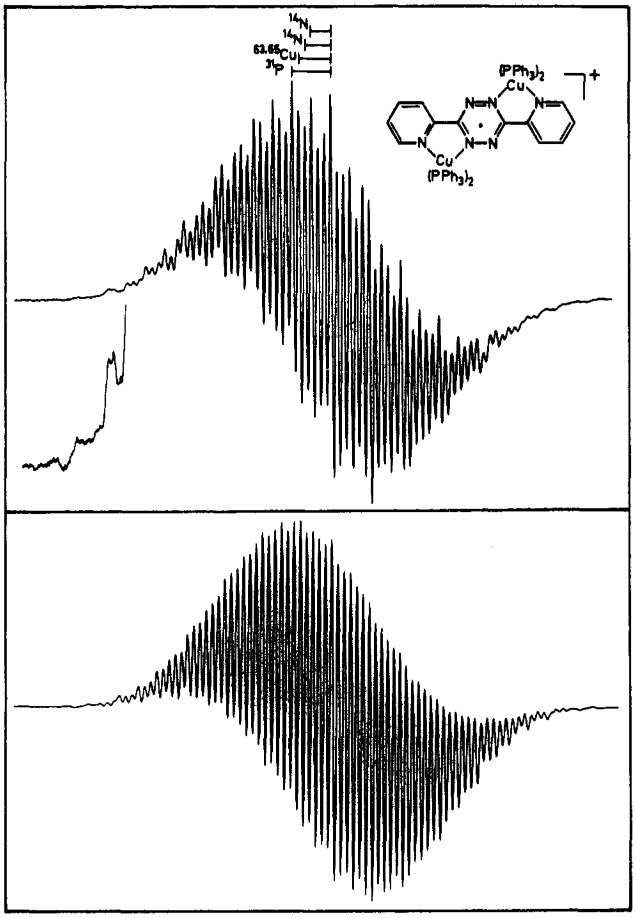
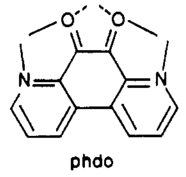
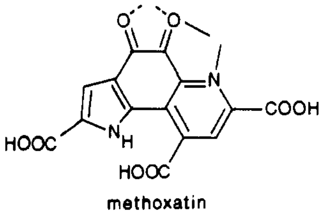


Figure 1. ESR spectrum of $[(\mu\text{-bptz})\{Cu(PPh_3)_2\}_2]^{\bullet+}$ at 300 K in dichloromethane solution with amplified low-field wing section (top) and computer simulation (bottom, 875 theoretical lines). Intensity differences at the periphery are due to selective line broadening of components with $M_N \neq 0$.[4b,c]

larization,[4c] the large ^{31}P coupling in the PPh_3 complex results from good hyperconjugative[8] overlap between Cu/P σ bonds and the π system; a smaller PCuP angle of only ~90° in the diphos complex[10] diminishes that kind of hyperconjugative interaction.[8]

In the reaction between excess[5] $Cu(PPh_3)_4{}^+BF_4{}^-$ and 4,7-phenanthroline-5,6-dione (phdo), the binuclear radical complex is the only stable product and can thus be conveniently isolated and identified (Table I).[11]


phdo



methoxatin

The phdo ligand is of particular interest because it may serve as a model[12a] for the dehydrogenase[12b] and copper-containing amine oxidase[12c] cofactor methoxatin, a potentially new vitamin,[12c] and because it can act as O,O′-chelate mononucleating ligand[12d] or as double N,O-chelating system,[12d,13,14] as in the present situation. *o*-Quinones are known to form mononuclear O,O′-coordinated copper(I) semiquinone complexes,[15] which have, however, not been isolated; the biochemical formation and conversion of *o*-quinones/catecholes is frequently catalyzed by copper-containing enzymes.[1c] Facile formation and stability of the paramagnetic complexes presented here suggest that cationic copper(I) fragments are particularly suitable in stabilizing anion radical intermediates, either through the charge effect alone or via additional contributions from σ/π hyperconjugation.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Stiftung Volkswagenwerk, and Flughafen Frankfurt/Main AG. 4,7-Phenanthroline-5,6-dione was a gift of Ciba-Geigy AG.

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Synthesis and Structure of the "Linear" Tetranuclear Cluster $[(MoO_2S_2)_2Fe_2S_2]^{4-}$: Implications for Aqueous Mo–Fe–S Chemistry

Sir:

Recent interest in and explorations of the chemistry of Mo, Fe, and S have been stimulated by inter alia the MoFe cofactor of nitrogenase.[1] Although the structure of this cofactor remains unsolved, the aforementioned explorations have led to several novel polynuclear Mo–Fe–S clusters of the so-called "linear" and "cubane" types.[2,3] During our explorations of aqueous and enzyme-mediated assembly of Fe–S and Mo–Fe–S clusters,[4] we noted the development of a novel absorption spectrum in aqueous mixtures containing salts of Fe(II) and $MoO_{4-x}S_x{}^{2-}$ (x = 2–4) at basic pHs. Subsequent isolation and characterization of this absorbing species showed it to be $[(MoO_2S_2)_2Fe_2S_2]^{4-}$. This cluster represents (i) the first example of a "linear" tetranuclear Mo–Fe–S

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