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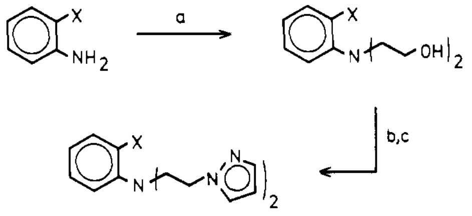
Synthesis of New Tripod Ligands Providing a Phenolate Donor. Structure of a Stable Monomeric Copper(I) Phenolate Complex

Sir:

The possibility that a tyrosine phenolate may bridge the copper(II) ions in the oxy form of hemocyanin[1] led us to consider whether a phenolate ion might also be bound to the copper(I) centers in the reduced forms of that protein. In order to address this question, we realized that we first needed to understand the properties of copper(I)–phenolate complexes having nitrogen donors as the only ancillary ligands in the coordination sphere. Already, we[2] and others[3] have reported *binuclear* complexes of that type in which two copper(I) ions are bridged by a phenolate ion. However, to our knowledge, there is only one structurally characterized *mononuclear* complex of Cu(I) having only O- and N-donor ligands, and in that case, neither of the nitrogen ligands is a heterocycle.[4] We report here the synthesis of a new series of pyrazole-containing tripod ligands and their copper(I) derivatives, the crystal structure of a stable, mononuclear Cu(I)–phenolate complex having only nitrogen donors as ancillary ligands, and the luminescence properties of the Cu(I)–CO adducts.

The ligands are prepared by a route similar to that utilized for the synthesis of the related binucleating ligand Hbpeac (Scheme I).[5] The appropriate aniline is treated with ethylene oxide in aqueous acetic acid, and the resulting diol is converted to the pyrazolyl derivative via the chloride. Deprotection of the phenol and thiophenol is readily accomplished with sodium methyl mercaptide in refluxing DMF. The potassium salt of phenolate ligand **1** reacts with $Cu(CH_3CN)_4BF_4$ in methanol to give the off-white Cu(I) complex **6** after crystallization from hot/cold acetonitrile. The other tripodal ligands react to form the corresponding cationic Cu(I) complexes and are crystallized from methanol–THF.[6] That these tripod ligands should be useful chelating agents for other metals has been demonstrated as well, and those results will be reported in separate publications.[7]

Scheme I



1, X = OH: Hbpeap
2, X = OCH_3: bpeaa
3, X = SH: Hbpeatp
4, X = SCH_3: bpeata
5, X = CH_3: bpeat

[a] Ethylene oxide, $HOAc–H_2O$. [b] $SOCl_2$, CH_2Cl_2. [c] $NaC_3H_3N_2$, DMF, 60 °C.

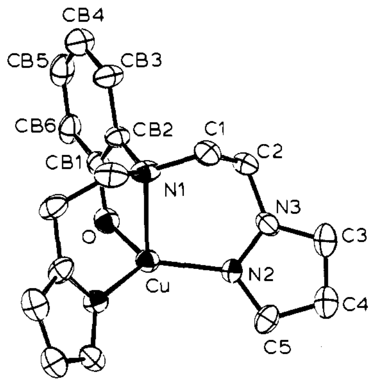


Figure 1. Structure of Cu(bpeap) showing 40% probability thermal ellipsoids. Bond lengths (Å) and angles (deg): Cu–O = 2.032 (3), Cu–N1 = 2.195 (3), Cu–N2 = 1.952 (2); O–Cu–N1 = 82.4 (1), O–Cu–N2 = 115.4 (1), N1–Cu–N2 = 100.6 (1), N2–Cu–N2′ = 126.7 (1), Cu–O–CB1 = 112.4 (3). The molecule sits on a mirror plane passing through the copper atom and containing the phenyl ring.

Table I. Spectroscopic Properties of Cu(I)–Tripod Complexes

starting complex	ν_{CO}, cm^{-1} [a]	λ_{max}(emission), nm[b]	
		N_2	CO
Cu(bpeap)	2074	507	552
Cu(bpeat)(BF_4)	2098	425	497
Cu(bpeaa)(BF_4)	2102	390	520
Cu(bpeata)(BF_4)	*c*	435	485[d]

[a] CH_2Cl_2 solution, 298 K. [b] Methanol/ethanol glass, 77 K. [c] No reaction at 298 K. [d] An emission at 435 nm was also observed, corresponding to the complex without CO bound.

The crystal structure of Cu(bpeap) is shown in Figure 1.[8] The copper adopts a geometry that is distorted slightly from trigonal

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(1) Wilcox, D. E.; Long, J. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 2186–2194.
(2) Sorrell, T. N.; Borovik, A. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1489–1490.
(3) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 3372.
(4) Haitko, D. A.; Garbauskas, M. F., paper presented at the Conference on Inorganic and Biochemical Perspectives in Copper Coordination Chemistry, SUNY—Albany, Albany, NY, July 23–27, 1984.
(5) Sorrell, T. N.; O'Connor, C. J.; Anderson, O. P.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 4199–4206.
(6) Anal. Calcd for Cu(bpeaa)BF_4: C, 44.20; H, 4.59; N, 15.16. Found: C, 44.34; H, 4.74; N, 15.39. Calcd for Cu(bpeat)BF_4: C, 45.81; H, 4.76; N, 15.70. Found: C, 45.83; H, 4.81; N, 15.78. Calcd for Cu(bpeata)BF_4: C, 42.73; H, 4.44; N, 14.65. Found: C, 43.06; H, 4.60; N, 14.76. We have not yet been able to obtain Cu(bpeatp) in a pure form.

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pyramidal, and the copper ion sits 0.178 Å above the plane formed from O, N2, and N2′. The Cu–N distances are very similar to those observed for $Cu_2(bpeac)^+$,[6] but the shorter Cu–O bond (2.03 Å in **6** vs. 2.08 Å in the binuclear complex) may simply reflect the fact that, for **6**, the charge of the metal ion is balanced by that of the phenolate ion. Note that, for the binuclear analogue, there are *two* positively charged metal ions per phenolate group; therefore, the electrostatic attraction should be weaker, making the Cu–O bonds longer. Other distances and angles within the complex are unexceptional.[9]

Despite being coordinatively saturated, the tripod complexes with N_3O donor sets react with CO in solution at room temperature, apparently by dissociation of the amino nitrogen atom.[10] These carbonyl adducts have not been isolated; however, the solution infrared spectrum shows a strong band between 2070 and 2100 cm^{-1}, indicative of the terminal carbonyl group (Table I).[11] Only the complex with a thioether ligand fails to react with CO at room temperature. It apparently binds carbon monoxide at low temperature since the emission spectrum changes when CO is added.

At 77 K, all of the complexes (with and without CO) show a low-energy emission between 390 and 550 nm when excited with light having a wavelength between 280 and 310 nm (Table I).[12] We associate this emission with a Cu → pyrazole charge-transfer state on the basis of our results from investigating several different Cu(I) complexes including those having *no* aromatic residues other than pyrazole or imidazole and spanning the range of coordination numbers 2–4.[13] To our knowledge, this is the *first* demonstration of luminescence from synthetic copper carbonyl complexes, and we suggest that this property might eventually provide a convenient probe for comparing synthetic analogues with copper proteins once the luminescence properties of copper complexes with other donor sets (particularly those containing imidazole) have been established. The carbonyl derivative of hemocyanin, for instance, shows an emission at 550 nm.[14] Further work on the spectroscopic behavior and reactivity of these complexes is currently in progress.

Acknowledgment is made to the National Science Foundation and to the Research Corp. for support of this research. Assistance with the crystallography was generously provided by Prof. D. J. Hodgson.

Registry No. **1**, 100113-67-5; **2**, 100113-68-6; **3**, 100113-69-7; **4**, 100113-70-0; **5**, 100113-71-1; **6**, 100113-73-3; $Cu(bpeat)(BF_4)$, 100113-75-5; $Cu(bpeaa)(BF_4)$, 100113-77-7; $Cu(bpeata)(BF_4)$, 100113-79-9; $Co(bpeap)(BF_4)$, 100113-81-3; $Mn(bpeap)(ClO_4)$, 100113-83-5; HOC_6H_4-*o*-NH_2, 95-55-6; $CH_3OC_6H_4$-*o*-NH_2, 90-04-0; HSC_6H_4-*o*-NH_2, 137-07-5; $CH_3SC_6H_4$-*o*-NH_2, 2987-53-3; $CH_3C_6H_4$-*o*-NH_2, 95-53-4; HOC_6H_4-*o*-$N(CH_2CH_2OH)_2$, 19966-11-1; $CH_3OC_6H_4$-*o*-$N(CH_2CH_2OH)_2$, 28005-76-7; HSC_6H_4-*o*-$N(CH_2CH_2OH)_2$, 100113-72-2; $CH_3SC_6H_4$-*o*-$N(CH_2CH_2OH)_2$, 100055-33-2; $CH_3C_6H_4$-*o*-$N(CH_2CH_2OH)_2$, 28005-74-5; $NaC_3H_3N_2$, 40958-82-5; ethylene oxide, 75-21-8.

Supplementary Material Available: Tables S1–S4, including final positional and thermal parameters, bond distances and angles, and values of F_o and F_c for **6** (10 pages). Ordering information is given on any current masthead page.

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(7) (a) Shaw, J., unpublished results. Anal. Calcd for $Co(bpeap)BF_4\cdot H_2O$: C, 41.76; H, 4.35; N, 15.23. Found: C, 42.16; H, 4.29; N, 15.18. (b) Schwartz, B. J., unpublished results. Anal. Calcd for $Mn(bpeap)ClO_4\cdot{}^1/_2THF$: C, 44.41; H, 4.56; N, 14.39. Found: C, 44.47; H, 4.70; N, 13.91.

(8) The crystal structure of **6** was determined by the same procedure and with the same system as described previously (cf. ref 11). Crystal data for **6**: orthorhombic; $a = 14.613$ (5) Å, $b = 13.023$ (5) Å, $c = 8.297$ (4) Å; $Z = 4$; space group *Pnma*; Mo Kα radiation; 908 independent nonzero $[I > 3\sigma(I)]$ reflections, with 2θ between 2 and 55°; $R = 3.8\%$; $R_w = 3.4\%$. The copper atom position was located by the Patterson function, and all non-hydrogen atoms were located on difference Fourier maps.

(9) At first glance, it might appear that the Cu–O–CB1 angle is unusually small; however, that angle is dictated by the five-membered chelate formed by the *o*-aminophenol unit and is in the same range as the corresponding angles observed for both the Cu(I) and the Cu(II) derivatives of bpeac. $Cu_2(bpeac)^+$:[2] Cu1–O–CB1 = 111.6 (8)°; Cu2–O–CB1 = 113.9 (8)°. $Cu_2(bpeac)(OAc)^{2+}$:[5] Cu1–O1–CB1 = 113.9 (12)°; Cu2–O1–CB1 = 112.6 (12)°. $Cu_2(bpeac)(N_3)^{2+}$: Cu1–O1–CB1 = 110.6 (5)°; Cu2–O1–CB1 = 110.8 (5)°.

(10) We base this conclusion on the results of variable-temperature NMR studies. For both of the copper complexes with N_3O donor sets, we observe only a single set of sharp resonances for the pyrazole protons that show no line broadening between 20 and −60 °C. If one of the pyrazolyl ligands dissociates upon CO binding, we would expect to see two sets of signals for the inequivalent pyrazolyl groups or some type of temperature-dependent coalescence or line broadening of the signals caused by a ligand-exchange process. This behavior is different from that observed by Karlin for a related binuclear complex in which the ligand contains two pyridylethyl side arms bound to each copper(I) ion. A crystal structure of an adduct with triphenylphosphine shows one of the pyridyl groups has dissociated upon phosphine binding: Karlin, K. D.; Gultneh, Y.; Cruse, R. W.; Hayes, J. C.; Zubieta, J. *Rev. Port. Quim.* **1985**, *27*, 20–21. The difference between the two systems probably results from the fact that in the complexes reported here, the amino group is attached directly to an aromatic ring and is therefore much less basic than the benzylic amino donors in Karlin's ligand.

(11) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013–6018 and references therein.

(12) Corrected emission spectra were recorded on an SLM Smart 8000 spectrofluorimeter at 77 K. A frozen glass of each complex in methanol/ethanol was used for these studies. For the carbonyl adducts, the solution was first saturated with CO and then frozen in liquid nitrogen.

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(15) Fellow of the Alfred P. Sloan Foundation, 1985–1987.

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Relationship of Adduct Formation to Bimolecular Reductive Elimination from Rhodium Polyhydrides

Sir:

Nucleophilic attack by a transition-metal hydride on a coordinatively unsaturated complex is implicated in certain bimolecular reductive eliminations,[1,2] in inner-sphere electron transfer[3] and in the "condensation route" to produce hydride dimers and clusters.[4] We report here several results that support the idea that μ-hydrides provide a pathway for bimolecular reductive elimination to yield heterobimetallic species.

Zinc was attractive to us as a participant in bimolecular reductive elimination since this metal is a component of the catalyst that transforms CO/H_2 mixtures to methanol.[5] The need for a *soluble* zinc bis(alkoxide) was satisfied by the synthesis[6] of $Zn(OAr)_2(THF)_2$ (Figure 1), Ar = 2,4,6-tri-*tert*-butylphenyl. The reaction of equimolar $H_3Rh[(Ph_2PCH_2)_3CMe]$[7] (**1**) with $Zn(OAr)_2(THF)_2$ proceeds in benzene at 25 °C with the formation of bimetallic compound **2** (eq 1).

$$H_3Rh[(Ph_2PCH_2)_3CMe] + Zn(OAr)_2(THF)_2 \rightarrow \mathbf{2} \quad (1)$$

The ^1H and selectively hydride-coupled ^{31}P NMR spectra of **2** both show AA′A″MXX′X″ patterns[8] analogous to that of **1**,

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(4) Venanzi, L. M. *Coord. Chem. Rev.* **1983**, *43*, 251.

(5) Kung, H. L. *Catal. Rev.* **1980**, *22*, 235.

(6) From $Zn[N(SiMe_3)_2]_2$ and HOAr in THF. Crystallographic data: space group $P2_1/c$ with (−161 °C) $a = 17.604$ (9) Å, $b = 15.607$ (8) Å, $c = 17.679$ (8) Å, $\beta = 114.19$ (2)°, and $Z = 4$. $R(F) = 0.062$ and $R_w(F) = 0.061$ for 2961 reflections with $F > 2.33\sigma(F)$. Positional and thermal parameters are available as supplementary material.

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(8) ^1H NMR (360 MHz, 22 °C, C_6D_6): δ 7.52 s (*m*-H, 4 H), 7.03 m (PPh, 12 H), 6.85 m (PPh, 18 H), 2.00 s (*t*-Bu, 36 H), 1.91 d ($J(PH) = 6.5$ Hz, PCH_2, 6 H), 1.46 s (*t*-Bu, 18 H), 1.1 m (CCH_3, 3 H), −8.7 m (RhH_3). $^{31}P\{^1H\}$ NMR (40.5 MHz, 30 °C, C_6D_6): δ 18.7 d ($J(RhP) = 93$ Hz); unchanged at −80 °C in toluene. IR (Nujol): 1920 (m), 1810 (m) cm^{-1}, $\nu(RhH_3Zn)$.

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