Figure 1. ORTEP drawing of one of the two independent $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC_2C_6H_5)$ molecules with 36% probability ellipsoids. Selected averaged interatomic distances (Å) and angles (deg) are as follows: Co(1)–Co(2) = 2.451 (1), Co(1)–Co(4) = 2.722 (1), Co(2)–Co(3) = 2.697 (1), Co(3)–Co(4) = 2.449 (1), Co–S = 2.250 (1), Co–C(1) = 1.978 (6), Co–C(2) = 2.032 (6), C(1)–C(2) = 1.404 (11), C(2)–C(3) = 1.519 (9); C(1)–C(2)–C(3) = 120.4 (6).

A subsequent step could be coordination to the "activated" Co_3S system of a second $Co_3S(CO)_9$ molecule, which may act as a source of $Co(CO)_2$ fragments. The chemical form in which the residual dicobalt fragment might be partially recovered in the reaction mixture would be $Co_2(CO)_6HC_2C_6H_5$. The stability of complex I could be the "driving force" of the reaction, considering that it is a 64-electron cluster, electron precise according to the EAN rule. By a similar reaction $Fe_4(CO)_{10}(\mu_4\text{-}PC_6H_5)_2$ was obtained in good yield from $Fe_3(CO)_9(\mu_3\text{-}PC_6H_5)_2$.[25]

Registry No. I, 116263-38-8; $Co_3(\mu_3\text{-}S)(CO)_9$, 12261-15-3; $Co_4\text{-}(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$, 57034-21-6; $[Co_3(CO)_7S]_2S_2$, 15927-92-1; $Co_2\text{-}(CO)_6(HC_2C_6H_5)$, 12154-91-5; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables of fractional atomic coordinates, isotropic and anisotropic thermal parameters, and interatomic distances and angles of the two independent molecules (6 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Luminescence Studies of Copper Phenanthrolines in Aqueous Media: Colloids and DNA Complexes

Sir:

This work demonstrates that charge-transfer (CT) luminescence from copper phenanthrolines can be an extremely useful probe of intermolecular interactions that occur in aqueous media, including binding to DNA. As is well-known, CT absorption occurs in the visible spectra of $[Cu(NN)_2]^+$ complexes, where NN denotes a derivative of 1,10-phenanthroline (phen).[1–4] Although the lowest energy CT excited state is generally quite reactive,[5–8] it tends to be short-lived; for example, in acetonitrile the excited-state lifetime of $[Cu(dmp)_2]^+$, where dmp is 2,9-dimethyl-1,10-phenanthroline, is only 2 ns at room temperature.[9] In donor media the lifetime appears to be limited by an unusual quenching reaction involving nucleophilic attack at the metal center,[9–11] although so far we have been unable to detect the species (exciplex) with an expanded coordination number. Nevertheless, studies of steric effects[12,13] as well as studies of the temperature[9] and pressure[14] dependence of quenching strongly support the proposed quenching mechanism. As we will show below, intermolecular interactions also influence the quenching rate, and the model is readily extended to explain these effects.

Absorption and emission data pertaining to $MeOH/H_2O$ solutions of $[Cu(bcp)_2]^+$, where bcp denotes 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, are presented in Figure 1 and Table I. As the percentage of water increases, the charge-transfer absorption exhibits hypochromism and undergoes a bathochromic shift. A comparison of the emission yields in CH_2Cl_2 and MeOH reveals that the emission is almost completely quenched in the donor solvent, yet surprisingly intense emission is observed in 6% MeOH. As we shall see, however, the 6% MeOH solution is actually a colloidal suspension. The presence of colloidal particles is difficult to detect by absorbance measurements, although there is a small offset in the absorption spectrum above 650 nm, presumably due to a scattering phenomenon (Figure 1). A more telling observation is that $[Cu(bcp)_2]Cl$ fails to dissolve when directly combined with 6% MeOH. Rather, we obtain stable, emissive solutions by diluting a MeOH solution of the complex into water. (Even with this method, however, turbid solutions are obtained when the final solution is 20–25% MeOH. In 33% MeOH direct dissolution of $[Cu(bcp)_2]Cl$ is possible, but the emission intensity is essentially the same as it is in pure MeOH.) The formation of particulates/aggregates is also indicated by the relatively high degree of emission polarization in 6% MeOH, by the fact that the emission lifetime is anion-dependent (Table I), and by the effect of added polyelectrolyte in 33% MeOH. Polyelectrolytes are known to be capable of inducing aggregation/colloid formation,[15] and in line with this reasoning small

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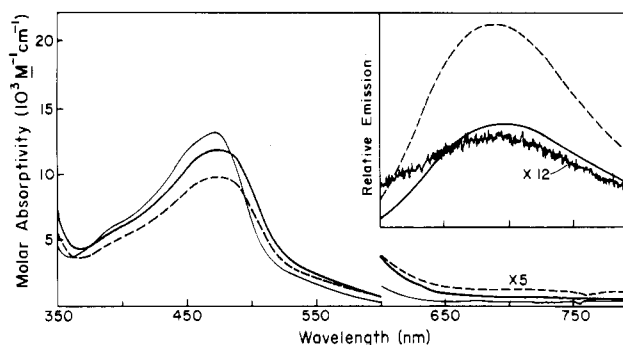
Figure 1. Absorption and uncorrected emission (inset) spectra of [Cu-(bcp)$_2$]BF$_4$ in MeOH (—, thin trace; ×12 for the emission spectrum), in 6% MeOH/H$_2$O (v/v) containing 50 equiv of DNA-P (—, thick trace), and in 6% MeOH/H$_2$O (v/v) (---). The temperature was 20 °C.

Table I. Absorption and Emission Spectral Properties of [Cu(bcp)$_2$]X in Various Solvents

solvent	X	λ_{max},[a] nm	$10^{-3}\epsilon$,[b] M^{-1} cm^{-1}	$10^4\phi_{em}$[c]	τ, ns	P[d]
CH$_2$Cl$_2$	BF$_4^-$	473.5	13.2	4.2	72	0.004
MeOH	BF$_4^-$[e]	473.5	13.2	~0.1		
33% MeOH	BF$_4^-$[e]	474.4	12.78	~0.1		
6% MeOH	BF$_4^-$	480	9.76	2.9	86	0.37
	Cl$^-$	476.5	9.14	1.0	62	
	HSO$_4^-$	478.2	9.16		70	
33% MeOH/DNA[f]	BF$_4^-$[e]	477.7	11.84	1.2	52	0.41
6% MeOH/DNA[f]	BF$_4^-$[e]	477.7	11.84	1.6	52	0.41
33% MeOH/PSS[g]	BF$_4^-$	478.7	11.40	1.5		0.39
33% MeOH/PSS[h]	BF$_4^-$	474.5	12.6			

[a] Absorption maximum. [b] Apparent molar absorptivity calculated from the ratio of the solution absorbance and the copper concentration. [c] Quantum yield of emission at 20 °C. [d] Polarization ratio of the emission. $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. See: Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983; Chapter 5. [e] Similar values obtained for the Cl$^-$ and HSO$_4^-$ derivatives. [f] DNA-P/Cu = 50. [g] PSS/Cu = 2. [h] PSS/Cu = 50.

amounts of poly(styrenesulfonate), or PSS, profoundly enhance the emission from [Cu(bcp)$_2$]$^+$ in 33% MeOH (Figure 2). At higher PSS concentrations, when the copper complex dissolves/disperses in the polymer solution,[16] the emission is quenched again. Qualitatively similar results are obtained with poly-L-glutamate, but the emission intensity persists to much higher L-glutamate-to-copper ratios. In contrast to the bcp system, [Cu(dmp)$_2$]BF$_4$ exhibits only weak emission regardless of the MeOH/H$_2$O ratio; however, the emission shows a PSS dependence in 6% MeOH.

When DNA is added as the polyelectrolyte in 33% MeOH, a solution of [Cu(bcp)$_2$]$^+$ exhibits a maximum in the emission intensity at a DNA phosphate-to-copper (DNA-P/Cu) ratio of about 2 (Figure 2). At high ratios the emission intensity decreases until DNA-P/Cu $\simeq$ 5 whereupon the emission intensity begins to increase again and then plateaus when DNA-P/Cu > 20. In contrast no effect is observed on the addition of up to a 300-fold excess of 2'-deoxyadenosine. This profile indicates (at least) two independent types of binding, a phenomenon that is well-known from DNA-binding studies involving relatively hydrophobic intercalating agents such as proflavin.[17,18] By analogy with the PSS results, at low DNA-P/Cu ratios the emission is attributed to an aggregate formed on the surface of DNA. In the case of the colloids and/or the aggregated states the "crystallite" lattice
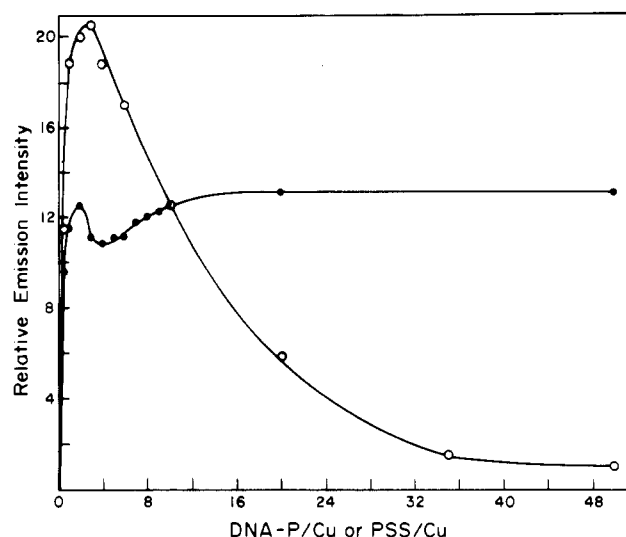

Figure 2. Dependence of CT emission intensity from [Cu(bcp)$_2$]BF$_4$ on the DNA-P/Cu (●) and the PSS/Cu (O) ratios. The solvent was 33% MeOH/H$_2$O (v/v), and the concentration of [Cu(bcp)$_2$]BF$_4$ was 2.6 × 10^{-5} M. The temperature was 20 °C.

structure is expected to inhibit solvent attack; hence, relatively intense emission can be observed.

At higher DNA-P/Cu ratios, [Cu(bcp)$_2$]$^+$ presumably binds in a monomeric form. Whatever the details of binding, the emission data require that the five-coordinate form (or the associated transition state) be destabilized relative to the original four-coordinate excited state. In this event the rate of solvent-induced quenching may be determined by the rate of dissociation of the DNA adduct, a scenario that would also explain the fact that the emission of the DNA adduct is strongly polarized, too. It is possible that the bcp complex binds by intercalation; Barton and co-workers have previously proposed that 4,7-diphenyl substitution disposes phenanthroline complexes to intercalative binding via the major groove of DNA,[19] despite the problems associated with achieving a planar conformation of the ligand. This type of adduct formation would also be consistent with the observation that a pressure of 1 atm of O$_2$ has no significant effect on the emission.[20] In contrast, [Cu(dmp)$_2$]$^+$ must bind in a "looser" fashion since for this system solvent-induced quenching is unimpeded in the presence of excess DNA. Sigman's group[21-23] and others[24] have previously shown that the related [Cu(phen)$_2$]$^+$ complex binds at the minor groove of DNA, especially where there are adenine–thymine-rich runs in the sequence. In view of the close relationship between the structures of the dmp and the phen systems, similar groove binding may be expected to occur with [Cu(dmp)$_2$]$^+$.[25,26] Further studies of the photophysics and photochemistry of [Cu(NN)$_2$]$^+$ systems bound to DNA are under way.

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Synthesis and Characterization of $Mo_4Te_{16}(en)_4{}^{2-}$: A Molybdenum Telluride with Linked $Mo\equiv Mo^{6+}$ Subunits

Sir:

In contrast to the large number of discrete, metal-containing polysulfide complexes known,[1] there are few characterized transition-metal polytelluride complexes.[2-5] We have recently found that the ethylenediamine (en) extraction of certain ternary melts of composition $(M^1)_x(M^2)_yTe_z$ [M^1 = alkali metal, M^2 = Hg, Au, As] provides a convenient preparative route to a variety of structurally diverse polytelluride clusters and polymers such as $Hg_4Te_{12}{}^{4-}$,[6] $\frac{1}{\infty}[Hg_2Te_5{}^{2-}]$,[6] $\frac{1}{\infty}[K_2Au_4Te_4{}^{2-}\cdot 4solvent]$,[7] $KAu_9Te_7{}^{4-}$,[7] $Au_2Te_4{}^{2-}$,[8] and $As_{10}Te_3{}^{2-}$.[9] These compounds have no analogues in sulfur or selenium chemistry, suggesting that the transition-metal polytelluride systems may also be quite different from those of the other chalcogens. The solubility of polytelluride ions[10-12] such as $Te_5{}^{2-}$, $Te_4{}^{2-}$, and $Te_3{}^{2-}$ in en and DMF presents an attractive entry into transition-metal tellurium solution chemistry. The potential of this method is best illustrated by Kolis and co-workers' recent report[4] of $NbTe_{10}{}^{3-}$, formed in the reaction between $NbCl_5$ and polytelluride anions in DMF, in which the Nb atom is encapsulated in a "birdcage-like" Te sheath. We report here the synthesis and structural characterization of the unusual $Mo_4Te_{16}(en)_4{}^{2-}$ ion comprising two d^3–d^3 $Mo_2{}^{6+}$ subunits linked by a central $Te_2{}^{2-}$ ligand and two $Te_3{}^{2-}$ chains. These compounds, together with $[RbNbAs_8{}^{2-}]$[13] and $Sn_9Cr(CO)_3{}^{4-}$,[14] represent a new class of main-group cluster anions, namely those containing transition metals.

The reaction of 2–3 equiv of K_2Te_4 with $Mo_2(O_2CMe)_4$ in en results in the formation of black, crystalline [K-(crypt)]$_2$Mo$_4$Te$_{16}$(en)$_4$ (**1**) in which all the acetate groups are replaced and the Mo_2 units are retained, albeit with changes of oxidation state and internuclear distance.[15] The best yield (ca. 40%) and product purity are obtained when 2.2 equiv of K_2Te_4 is used, although a balanced equation cannot be written under

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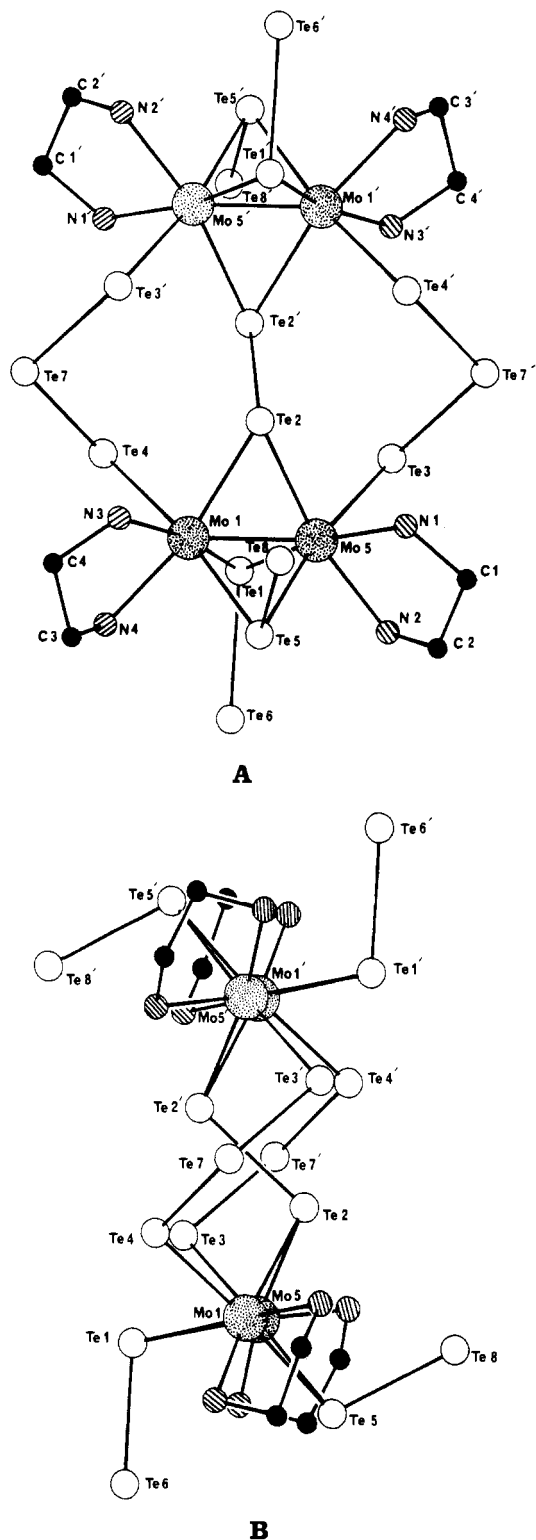

A

B

Figure 1. Two ball-and-stick representations of the $Mo_4Te_{16}(en)_4{}^{2-}$ ion: (A) front view showing the central Mo_4Te_2 core and the connectivity of the $Te_3{}^{2-}$ chains; (B) side view down the Mo–Mo bonds showing the conformation of the $Te_2{}^{2-}$ fragments relative to the M–M vectors.

these conditions. The crystalline product will not redissolve in en or MeOH.

The structure[16] of the anion in **1** (Figure 1) consists of two confacial bioctahedral d^3–d^3 $Mo_2{}^{6+}$ units with Mo–Mo bond distances of 2.469 (3) Å. Each Mo_2 dimer possesses two μ_2,η^1-$Te_2{}^{2-}$ ligands and two chelating en ligands. The two Mo_2

(16) Crystal data for **1**: space group $P2_1/c$, with $a = 15.720$ (4) Å, $b = 23.400$ (4) Å, $c = 12.955$ (4) Å, $\beta = 97.29$ (2)°, $V = 4726$ (1) Å^3, and $Z = 4$. Final R values are $R = 0.0397$ and $R_w = 0.0455$.