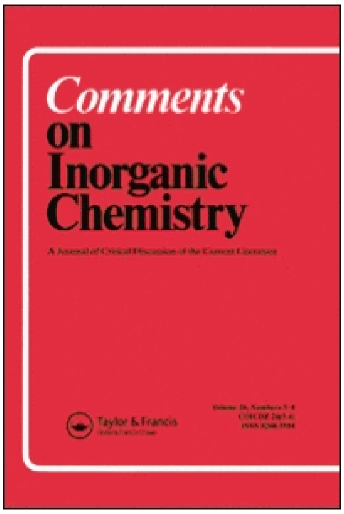

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Luminescent Tetranuclear Copper(I) and Silver(I) Chalcogenides

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A series of luminescent tetranuclear copper(I) and silver(I) chalcogenide complexes have been synthesized and characterized. The photophysical and photochemical properties of these complexes have also been investigated. The long-lived excited state of these luminescent clusters is believed to bear a high parentage of ligand-to-metal charge-transfer LMCT ($E^{2-} \rightarrow M_4$) character. The assignment has also been supported by molecular orbital calculations.

Key Words: *back-electron-transfer, chalcogenides, copper(I), intervalence-transfer transition, ligand-to-metal charge-transfer transition, luminescence, mixed-valence, oxidative quenching, silver(I), tetranuclear*

A. INTRODUCTION

Photochemistry of d^{10} metal complexes has been the subject of numerous studies for more than twenty years.[1] The photoluminescence properties of a series of phosphine complexes of d^{10} metals were first reported

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by Dori and co-workers in 1970.[2a] Besides, Caspar and Gray showed that dinuclear platinum(0) and palladium(0) complexes such as [$Pt_2(dppm)_3$] possess rich photophysical and photochemical properties.[2b–d] The excited state of the complexes has been assigned to be metal-centered in nature, modified by the interaction between the metal centers.

Another extensively studied system was the tetranuclear copper(I) iodide clusters with pyridines as ligands such as $Cu_4I_4(py)_4$ (py = pyridine).[3] Ford and co-workers reported that this series of clusters exhibited dual luminescence.[3c] An explicit picture of the nature of the lowest lying excited state of these clusters was brought about by detailed spectroscopic studies and *ab initio* calculations.[3d] The calculation results showed that the high-energy emissive state is of XLCT ($I^- \rightarrow$ py) character while the low energy one XMCT ($I^- \rightarrow Cu_4$) and metal-centered (3d → 4s) character delocalized over the Cu_4I_4 core. The photo-reactivities of this type of clusters towards a variety of both inorganic and organic quenchers have also been investigated in detail.[3e–h]

The photophysical and photochemical studies of a number of polynuclear copper(I) acetylides have also been reported by Yam and co-workers.[4] The excited state of these complexes has been assigned to an admixture of ligand-to-metal charge-transfer and metal-centered character.

On the other hand, the metal-to-ligand charge-transfer excited-state chemistry of a number of cuprous diimine complexes has also been studied extensively by McMillin and co-workers.[5] Recently, the interactions of these complexes with DNA have also been reported.[5d,e] In addition, halocuprates such as $[CuCl_n]^{(1-n)}$ (n = 2, 3) have also been shown to exhibit rich photophysical and photochemical properties.[6a,b] Furthermore, a copper(I) metallothionein has also been reported to show interesting luminescence properties.[6c]

The photochemistry of silver(I) complexes is generally less well documented compared with related copper(I) and gold(I) systems. One important reason is the light-sensitive nature of many silver-containing compounds. In the late 1970's, silver(I) was first shown to be luminescent in a matrix of alkali metal halides.[7a] In 1978, Marks and co-workers reported that silver(I) ion can cause the polymerization of THF upon irradiation of ultraviolet light.[7b] In 1988, Vogler and co-workers reported that irradiation of the azido complex [$Ag(PPh_3)_2N_3$] in CH_3CN led to the evolution of nitrogen, the release of PPh_3 and the deposition of metallic silver.[7c] An important study on luminescent polynuclear silver(I) was carried out in 1989 by the same research group on the system $Ag_4Cl_4L_4$ [L = $P(OMe)_3$ or PPh_3].[7d] The excited state was suggested to bear a metal-centered (d-s) state modified by silver–silver interaction within the tetramer. The photoluminescence study on the chair and cube isomeric forms of a related iodo-silver(I) cluster $Ag_4I_4(PPh_3)_4$ was later reported by Zink and co-workers.[7e]

Moreover, the photophysical studies on hexanuclear thiolato silver(I) complexes, $Ag_6(mtc)_6$ and $Ag_6(dtc)_6$ [mtc^- = di-*n*-propylmonothiocarbamate, dtc^- = di-(*n*-propyl)dithiocarbamate], together with a related copper(I) hexamer, $Cu_6(mtc)_6$, have also been investigated.[7f] The excited state of these copper(I) and silver(I) thiolates has been suggested to be of cluster-centered triplet state with mixed (d-s)/LMCT character. In addition, the unusual luminescence properties of β''-alumina doped with copper(I)[7g,h] and silver(I)[7h] ions have recently been reported by Zink and co-workers. The origin of the luminescence was interpreted in terms of formation of excimer or exciplex between the mobile ions in the conduction plane.

Furthermore, trinuclear silver(I) phosphine complexes with linear $\{[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+\}$[7i] and triangular $\{[Ag_3\{HC(PPh_2)_3\}_2]^{3+}\}$[7j] arrays of silver(I) centers have also been found to possess interesting photophysical properties. Recently, photoluminescence studies on polynuclear silver(I) complexes with bridging acetylide ligands have also been reported.[7k–m]

There have been a number of reports on the luminescence studies of polynuclear gold(I) systems. The lowest energy absorption and emission bands of tetranuclear gold(I) complexes $[Au(dta)]_4$ (dta = dithioacetate) and $[Au(pip)Cl]_4$ (pip = piperidine) were assigned to a metal-centered 5d-6s transition modified by the metal–metal interaction in the square-planar $Au(I)_4$ moiety.[8a] A series of dinuclear gold(I) complexes with sulfur-, carbon-, and phosphorus-coordinated bridging ligands has also been shown to exhibit interesting photophysical properties.[8b]

The complex $[Au_2(dppm)_2]^{2+}$ was found to exhibit a long-lived photoluminescence in fluid solutions, and the phosphorescent excited state of this complex undergoes oxidative and reductive quenching with methyl viologen and organic halides, and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, respectively.[8c] Photo-induced energy-transfer reactions of this complex with *trans*- and *cis*-stilbene, hept-1-ene and cyclohexene have also been reported.[8d] The photophysical and photochemical studies on $[Au_3(dmmp)_2]^{3+}$ [8e] and $[Au_3(dmmp)_3]^{3+}$ [8f] allowed direct comparison of these trimeric gold(I) to their dinuclear counterparts, $[Au_2(dmpm)_2]^{2+}$ and $[Au_2(dmpm)_3]^{2+}$, and further confirmed a metal-centered excited state modified by Au(I)-Au(I) interactions within the complexes.

Extension of Werner-type gold(I) phosphine complexes to organogold(I) systems represents a new class of luminescent materials. There have been reports on the photophysical and photochemical studies of organogold(I) phosphines such as $[Au_2(dmpm)R_2]$ and $[Au_3(dmmp)R_3]$,[9a] and gold(I) acetylide complexes.[9b–f] Recently, the photoluminescence behavior of dinuclear gold(I) thiolate complexes received considerable attention. A ligand-to-metal charge-transfer LMCT ($RS^- \rightarrow Au_2$) excited state has been proposed independently by Fackler,[10a] Zink,[10b] Bruce[10c,d] and Yam.[10e]

In addition to the copper triad, there have also been reports on other polynuclear d^{10} luminescent systems. For example, a luminescent tetranuclear zinc complex $[Zn_4O(OOCCH_3)_6]$ which serves as models for zinc oxides has been reported by Vogler and co-workers.[11a] A related complex with 7-azaindolate as the bridging ligand, $[Zn_4O(C_7H_5N_2)_6]$, has also been studied by Che and co-workers.[11b] Zinc(II), cadmium(II) and mercury(II) thiolate complexes have also been found to be emissive.[11c–e] The electron-transfer reaction from $[Zn_4(SPh)_{10}]^{2-}$ to methyl viologen has been reported.[11f]

On the other hand, transition metal chalcogen complexes represent a very important division of structural chemistry owing to the unusual stereochemistry and highly flexible bonding modes of the chalcogens.[12] The identities of the chalcogen-containing ligands can vary from unsubstituted monochalcogenide,[12a–e] polychalcogenide[12d–f] to chalcogenolate.[12g,h] Mixed-polychalcogenides have also been found to be versatile ligands towards different transition metals.[12i] Although structural information on numerous transition metal chalcogen clusters such as those of palladium, iridium, nickel and cobalt are known,[13a] the photophysical and photochemical studies on related complexes remain unexplored. Moreover, studies on these transition metal chalcogen clusters offer opportunities for model studies of redox-active proteins[13b] and insoluble metal chalcogenides,[13c] in particular those with a d^{10} electronic configuration. These species are usually important semi-conducting and photocatalytic materials, and some of them also exhibit intriguing optical properties related to their particle size.[13d]

While the structures and chemical reactivities of a number of transition metal chalcogenides are known, photophysical and photochemical properties of these species, especially soluble ones, have received little attention. In 1993, the first luminescent copper sulfide complex $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ (**1**) was isolated and characterized by our group.[14a] The copper(I) tetramer has been found to possess rich photophysical and photochemical properties. It is believed that an exploration to related chalcogenide clusters and further into the silver(I) counterparts would establish a new class of luminescent materials. It is also anticipated that through a systematic variation on the identities of the metal center and the chalcogenide ligand, more information on the nature of the lowest energy excited state would be obtained. In view of this, a series of copper(I) and silver(I) chalcogenide clusters $[M_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ [M = Cu, E = Se (**2**)[14b]; M = Ag,[14c] E = S (**3**); Se (**4**); Te (**5**)] have been synthesized and structurally characterized. All the complexes show rich photoluminescence properties. The photo-redox behavior of these novel luminescent clusters have also been investigated.[14d] The electronic structures of these clusters have also been studied by Fenske–Hall[14e] and *ab initio* molecular orbital calculations.[14f]

B. SYNTHESES AND CHARACTERIZATION

There have been a variety of synthetic approaches towards transition metal chalcogenide complexes. For example, the orange copper(I) sulfide cage anion $[Cu_{12}S_8]^{4-}$ was formed in the reaction of $CuCl_2{\cdot}2H_2O$ with EtS^- in the presence of Li_2S.[15a] Besides, dark red solid of $M_2Ag_6S_4$ (M = Na, K) was obtained from the reaction of M_2S, elemental sulfur and silver powder in supercritical ethylenediamine.[15b] Moreover, gold chalcogenide complexes have also been prepared by different methods.[15c] For example, the colorless tetranuclear gold(I) sulfido complex $[(Ph_3PAu)_4S](CF_3SO_3)_2$ was prepared from the reaction of $(Ph_3PAu)_2S$ with $[AuPPh_3(CF_3SO_3)]$ in CH_2Cl_2.[15d] In addition, Fenske and co-workers demonstrated that $(Me_3Si)_2E$ and its alkyl analogues are very useful starting materials for the preparation of chalcogenido clusters. For example, a series of high-nuclearity deep brown copper–selenium clusters can be synthesized from the reactions of CuCl, $(Me_3Si)_2Se$ and monodentate phosphines.[13a] Recently, several polynuclear silver(I) telluride/tellurolate complexes such as $[Ag_{48}Te_{12}(\mu_3\text{-Te}^nBu)_{24}(PEt_3)_{14}]$ were isolated from the reaction between $^nBuTeSiMe_3$ and silver(I) chloride in the presence of PEt_3.[15e]

The chalcogenido complexes **1–5** were prepared from the reactions of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2]^{2+}$ or $[Ag_2(\mu\text{-dppm})_2]^{2+}$ and sodium sulfide, lithium selenide or sodium telluride in a mixture of acetone/methanol.[14a–c] For the preparations of the copper(I) and silver(I) sulfido complexes, addition of sodium sulfide immediately turned the color of the solution to yellow and finally orange. For the other chalcogenido clusters, in addition to similar color changes, precipitation of a black solid also occurred. The insoluble substance is most likely to be binary copper or silver chalcogenides.

All the chalcogenido copper(I) and silver(I) clusters gave satisfactory elemental analyses and were characterized by positive-ion FAB-MS or ESI-MS, and ^1H and ^{31}P NMR spectroscopy. The structures of all the copper(I) and silver(I) complexes have also been established by X-ray crystallography.

In general, all these tetranuclear chalcogenido copper(I) and silver(I) clusters adopt a similar molecular structure. Figure 1 depicts the per-

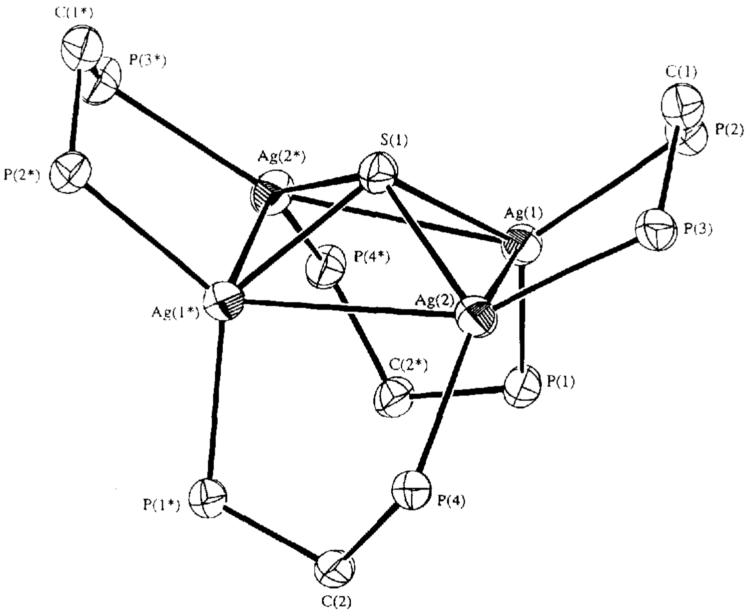


FIGURE 1 Perspective drawing of the complex cation $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ with the atomic numbering scheme (data taken from Ref. 14c).

spective drawing of the complex cation of **3**, $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ with the atomic numbering scheme. The four copper(I) or silver(I) centers arranged in a distorted rectangular array are bridged by an unsubstituted μ_4-chalcogenido ligand. The M · · · M distances (Table I) observed in the copper(I) [2.869(1)–3.271(4) Å] and silver(I) [3.038(2)–3.357(1) Å] tetramers are comparable to those reported in related systems such as $[Cu_3(dppm)_3(\mu_3\text{-Cl})_2]^+$ [3.175(4)–3.281(3) Å],[16a] $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-OH})]^{2+}$ [3.120(2)–3.322(2) Å],[16b] $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-Br})_2]^+$ [3.192(3)–3.362(3) Å][16c] and $[Ag_3\{HC(PPh_2)_3\}_2]^{3+}$ [3.1618(5)–3.2228(9) Å].[7j] Remarkably, the Ag · · · Ag distances in **3**–**5** are shorter than the sum of van der Waals' radii (3.40 Å).[16d]

The μ_4-capping mode of the chalcogenide ligand has been observed in different transition metal complexes.[13a,15d,17] However, the occurrence with silver(I) has been exceptionally scarce. The four dppm ligands are arranged in a manner such that two of them opposite to each other are located above the M_4 plane while the remaining two below it. This is the consequence of the steric crowding of the bulky phenyl rings.

C. PHOTOPHYSICAL PROPERTIES

Electronic Absorption Spectroscopy

All the tetranuclear copper(I) and silver(I) chalcogenide clusters are soluble in common organic solvents to give orange-yellow solutions. The electronic absorption spectral data for these complexes are listed in Table II. In general, the electronic absorption spectra of these clusters in

TABLE I

Metal–metal distances of complexes **1**–**5**.

Complexes	Cu···Cu or Ag···Ag/Å
1[a]	2.869(1), 3.128(1)
2[b]	2.908(4), 3.271(4)
3[c]	3.038(2), 3.160(2)
4[c]	3.055(2), 3.222(2)
5[c]	3.071(1), 3.357(1)

[a] Data taken from Ref. 14a.
[b] Data taken from Ref. 14b.
[c] Data taken from Ref. 14c.

TABLE II

Electronic absorption spectral data for complexes **1–5** in CH_3CN at 298 K.

Complexes	Absorption λ/nm (ϵ/dm^{3}mol^{-1}cm^{-1})
1[a]	265 sh (41,490), 285 sh (34,650)
2[b]	262 sh (42,670)
3[c]	246 sh (91,745), 400 sh (970)
4[c]	256 sh (53,985), 402 sh (1,445)
5[c]	254 sh (67,075), 440 sh (1,475)

[a] Data taken from Ref. 14a.
[b] Data taken from Ref. 14b.
[c] Data taken from Ref. 14c.

acetonitrile at 298 K reveal a high energy absorption shoulder at *ca.* 240–260 nm with an extinction coefficient on the order of 10^4 dm^{3}mol^{-1}cm^{-1}, and a lower energy absorption tail in the 350–450 nm region. The high-energy absorption band is assigned as an intraligand IL (dppm) transition.

Steady-State Emission Spectroscopy

Excitation of these coinage metal chalcogenido clusters in the solid state and in fluid solutions with $\lambda > 350$ nm results in intense long-lived orange luminescence for the copper(I) complexes and green to orange emissions for the silver(I) analogues.[14a–c] The photophysical data for these complexes are summarized in Table III. The emission spectrum of **1** in acetone at 298 K is shown in Fig. 2. The decays of the emissions are single-exponential, and the lifetimes of the emissions of these clusters fall in the microsecond range. This suggests that the emissions are most probably associated with a spin-forbidden transition.

The emissions of these clusters do not appear to be associated with an excited state of pure d-s origin modified by metal–metal interactions because on going from sulfido to selenido tetranuclear copper(I), and from sulfido to selenido and to tellurido silver(I), the metal–metal distances increase gradually. An elongation of M· · ·M distance would predict a blue shift in the emission energies owing to the increasing separation of the d-s energy gap. However, such a trend is not observed and the assignment of a pure d-s metal-centered excited state resulting from metal–metal interactions is not substantiated.

TABLE III

Photophysical data for complexes **1–5**.

Complexes	Medium (T/K)	Emission λ/nm	$\tau_o/\mu s$	Quantum Yield Φ^a
1[b]	Solid (298)	579	3.6 ± 0.3	0.22
	Solid (77)	606		
	$(CH_3)_2CO$ (298)	622	8.1 ± 0.4	
	CH_3CN (298)	618	7.8 ± 0.4	
2[c]	Solid (298)	595	3.9 ± 0.3	0.19
	Solid (77)	619		
	$(CH_3)_2CO$ (298)	626	7.1 ± 0.4	
	CH_3CN (298)	622	6.9 ± 0.4	
3[d]	Solid (298)	516	1.0 ± 0.1	0.014
	Solid (77)	536		
	$(CH_3)_2CO$ (298)	628	1.2 ± 0.1	
	CH_3CN (298)	628	1.5 ± 0.2	
4[d]	Solid (298)	527	0.9 ± 0.1	<0.001
	Solid (77)	552		
	$(CH_3)_2CO$ (298)	570	1.3 ± 0.1	
	CH_3CN (298)	572	3.4 ± 0.3	
5[d]	Solid (298)	574	3.1 ± 0.2	<0.001
	Solid (77)	588		
	$(CH_3)_2CO$ (298)	615	1.4 ± 0.1	
	CH_3CN (298)	626	3.3 ± 0.3	

[a] In acetone at 298 K.
[b] Data taken from Ref. 14a.
[c] Data taken from Ref. 14b.
[d] Data taken from Ref. 14c.

The possibilities that the origin of the emission is derived from a metal-to-ligand charge-transfer MLCT [M_4 → dppm] or a ligand-to-ligand charge-transfer LLCT [E^{2-} → dppm] transition are also excluded, based on the fact that the emission energies of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ and its dtpm analogue $[Cu_4(\mu\text{-dtpm})_4(\mu_4\text{-S})](PF_6)_2$ {where dtpm = bis[bis(4-methylphenyl)phosphino]methane} are very similar.[14d] The presence of electron-donating methyl groups on the dtpm ligand would destabilize its π^* orbital, thereby increase the MLCT (Cu_4 → phosphine) or LLCT (E^{2-} → phosphine) transition energy. However, such an increase in emission energy is not observed, and the solid-state emission energy for $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ (579 and 606 nm at RT and 77 K, respectively) is even higher than that of the dtpm counterpart (604 and 658 nm at RT and 77 K, respectively), suggesting that the π^* of dppm is not likely to be the acceptor orbital. The assignment of a MLCT

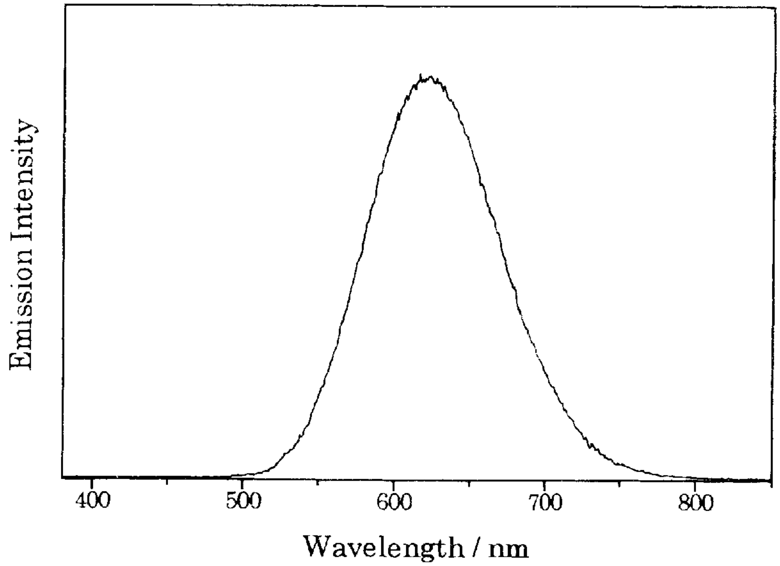


FIGURE 2 Emission spectrum of **1** in CH_3CN at 298 K (data taken from Ref. 14a).

($M_4 \rightarrow$ phosphine) or LLCT ($E^{2-} \rightarrow$ phosphine) excited state is therefore not appropriate. Furthermore, copper(I) is much more easily oxidized than silver(I), given the higher energy of the Cu(I) 3d orbitals relative to those of the Ag(I) 4d orbitals. The ionization energy of $Ag^+(g)$ (173.30×10^3 cm^{-1})[18a] is almost 10^4 cm^{-1} larger than that for $Cu^+(g)$ (163.67×10^3 cm^{-1}).[18b] The observation that the tetranuclear copper(I) and silver(I) complexes with the same chalcogenido ligand emit at fairly similar energies with a blue shift of only *ca.* 0.27 eV does not appear to be compatible with a metal-to-ligand charge-transfer excited state assignment.

In view of the σ-donating capability of chalcogenides, the transitions associated with the emissions of these copper(I) and silver(I) clusters are assigned to originate predominantly from a ligand-to-metal charge-transfer LMCT ($E^{2-} \rightarrow M_4$) triplet excited state, and probably with mixing of a metal-centered MC(d-s or d-p) state of Cu(I) or Ag(I). Similar assignments have also been suggested in other luminescent polynuclear d^{10} thiolato-,[3a,7f,10,11d,19] halo-[3a,c–h] and alkynyl-[4,7l,m] systems. The solid-state emission energies of the clusters at 298 K follow the orders:

1(579 nm) > **2**(595 nm); and **3**(516 nm) > **4**(527 nm) > **5**(574 nm)

This is in line with the changes in the ionization potentials of the chalcogens,[20a] and implies that the donor orbital would bear a high parentage of chalcogenide character. It is also interesting to note that the ionization energies of atomic copper and silver are similar (6.232×10^4 and 6.111×10^4 cm^{-1}, respectively),[20b] with copper(I) being slightly easier to reduce than silver(I). This can account for the observation that the emission of the silver(I) tetramer occurs at higher energy than the corresponding copper(I) analogue with the same chalcogenido ligand.

Although similar trends were not observed for the complexes in fluid solutions, it is unlikely that decomposition or structural changes have occurred, as evidenced by positive-ion ESI-MS and NMR spectroscopic data.

Triplet-State Absorption Spectroscopy

The triplet-state absorption behavior for the copper(I) chalcogenide complexes **1** and **2** have been studied with nanosecond transient absorption spectroscopy.[14d] Figure 3 presents the transient absorption difference spectra of **1** in degassed acetone following pulse excitation at 355 nm. The assignment of the transient absorption due to the emissive triplet state has been confirmed by matching the decay of the transient absorption with that of the phosphorescence. A plot of ln(ΔA) of the

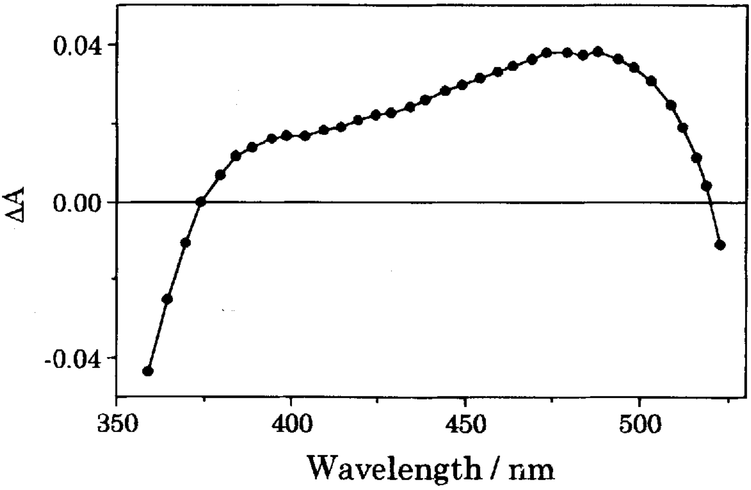


FIGURE 3 Transient absorption difference spectrum recorded 5 μs after laser flash for a degassed acetone solution of **1** (data taken from Ref. 14d).

triplet-state absorption *vs.* time gives a straight line (data not shown), indicating that the decay follows first-order kinetics. Generally, there is an absorption shoulder at *ca.* 380 nm in all these spectra and the structureless absorption extend to a lower energy region (*ca.* 500 nm). The 480-nm absorption band is probably an artifact due to the tailing effect of the intense phosphorescence of the complexes at *ca.* 630 nm. For the same reason, the absorption beyond 520 nm is impossible to record. The origin of the triplet-state absorption bands cannot be assigned with certainty. Similar excited state absorption has also been observed in related tetranuclear copper(I) iodide clusters and the origin has been assigned as a transition from the metal cluster centered (^{3}CC) state to a higher energy triplet halide-to-ligand charge transfer (^{3}XLCT) state.[3i]

D. PHOTO-INDUCED ELECTRON-TRANSFER REACTIONS

The phosphorescent state of the copper(I) clusters has been found to be quenched in the presence of pyridinium acceptors.[14a,b] In order to gain more insight into the photo-redox behavior of these complexes, a study of electron-transfer quenching of the phosphorescent states of **1** and **2** by a series of pyridinium acceptors of variable reduction potentials has been carried out. The bimolecular quenching rate constants for the photoreactions between **2*** and the quenchers are listed in Table IV. Excited-state reduction potentials $E^{\circ}[\mathrm{Cu}_4^{3+/2+*}]$ of −1.71 (10) and −1.55(10) V for **1** and **2**, respectively, *vs.* saturated sodium chloride calomel electrode (S.S.C.E.) have been estimated by three-parameter, non-linear least-squares fits to Eq. (1),

$$(RT/F)\ln k_q' = (RT/F)\ln K\kappa\nu - (\lambda/4)[1 + (\Delta G/\lambda)]^2 \qquad (1)$$

where k_q' is the rate constant corrected for diffusional effects, $K = k_d/k_{-d}$ which is approximately 1–2 dm^{3}mol^{-1}, k_d is the diffusion-limited rate constant which is taken to be 1.0×10^{10} dm^{3}mol^{-1}s^{-1}, κ is the transmission coefficient, ν is the nuclear frequency, and λ is the reorganization energy for electron transfer and ΔG is the standard free energy change of the reaction.

A plot of $\ln k_q'$ *vs.* $E(\mathrm{A}^{+/0})$ for the oxidative quenching of $[\mathrm{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+*}$ is shown in Fig. 4. The close agreement between the theoretical curve with the experimental data suggests that the mechanism of the photo-reactions are outer-sphere electron-transfer in nature. It is envisaged that both **1** and **2** are strongly reducing in the excited state in view of their highly negative excited-state reduction potentials.

TABLE IV

Bimolecular rate constants for the oxidative quenching of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+*}$ by pyridinium acceptors in degassed acetone (0.1 moldm^{-3} $^nBu_4NPF_6$)[a].

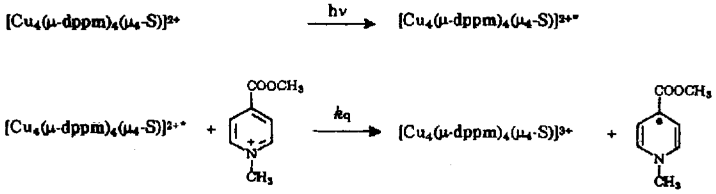
Quencher[b]	$E(A^{+/0})$/V (*vs.* S.S.C.E.)	k_q/ dm^{3}mol^{-1}s^{-1}	k_q'/ dm^{3}mol^{-1}s^{-1} [c]	ln k_q'
4-cyano-*N*-methylpyridinium	−0.67	5.35×10^9	1.15×10^{10}	23.17
4-methoxycarbonyl-*N*-methylpyridinium	−0.78	3.39×10^9	5.13×10^9	22.36
4-aminoformyl-*N*-ethylpyridinium	−0.93	1.76×10^9	2.14×10^9	21.48
3-aminoformyl-*N*-methylpyridinium	−1.14	2.12×10^8	2.17×10^8	19.20
N-ethylpyridinium	−1.36	1.02×10^7	1.02×10^7	16.14
4-methyl-*N*-methylpyridinium	−1.49	9.80×10^5	9.80×10^5	13.80

[a] Data taken from Ref. 14b.

[b] All the compounds are hexafluorophosphate salts.

[c] $(1/k_q') = (1/k_q) - (1/k_d)$, where k_d is the diffusion-limited rate constant, taken to be 1.0×10^{10} dm^{3}mol^{-1}s^{-1}.

In order to gain more direct spectroscopic evidence into the mechanism of the photo-reactions between these luminescent clusters and pyridinium acceptors, a nanosecond transient absorption spectroscopic study has been carried out.[14d] The transient absorption difference spectrum of the laser flash photolysis of a degassed acetone solution of **1** (0.27 mM) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (7.93 mM) is shown in Fig. 5. A sharp absorption band is observed at approximately 390 nm, concomitant with the growth of a lower intensity band at *ca.* 484 nm and a broad absorption band at *ca.* 693 nm with a larger extinction coefficient. The high-energy absorption band at *ca.* 390 nm is characteristic of the pyridinyl radical and matches very well with the reported spectrum of the reduced radical of 4-(methxoycarbonyl)-*N*-methylpyridinium.[21a] The reaction mechanism is likely to be:



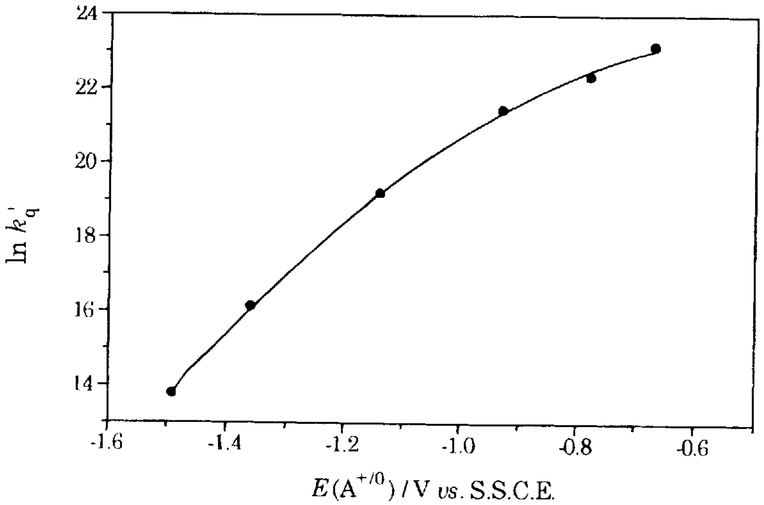


FIGURE 4 Plot of lnk'_q, *vs.* $E(A^{+/0})$ for the oxidative electron-transfer quenching of **2*** by pyridinium acceptors in degassed acetone: (•) experimental data taken from Table IV; (—) calculated (data taken from Ref. 14b).

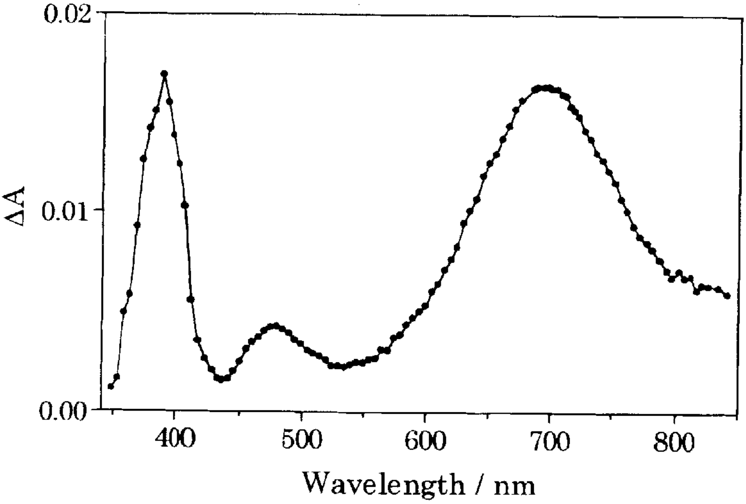


FIGURE 5 Transient absorption difference spectrum recorded 10 μs after laser flash for the reaction of **1*** and 4-methoxycarbonyl-*N*-methylpyridinium in degassed acetone (data taken from Ref. 14d).

The 484-nm absorption band and the much lower-energy broad band at *ca.* 693 nm are not the consequence of the pyridinyl radical, but should be characteristic of the oxidized form of the copper(I) cluster, $[Cu^ICu^ICu^ICu^{II}(\mu\text{-dppm})_4(\mu_4\text{-S})]^{3+}$. The ligand-field (d-d) transitions for copper(II) metal center in an unsymmetric environment can occur in a low energy region.[21b] However, such an assignment for both the 484- and 693-nm absorption bands in the transient absorption difference spectrum is not substantiated, given that the extinction coefficients for the bands are estimated to be 1,200 and 6,700 $dm^3mol^{-1}cm^{-1}$, respectively, assuming that both $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ and $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{3+}$ do not have significant absorption at *ca.* 390 nm. Another possible assignment is the ligand-to-metal charge-transfer LMCT $[S^{2-} \rightarrow Cu(II)]$ absorption which is commonly suggested in many mixed-valence copper(I,II) thiolate complexes. For example, the absorption band at *ca.* 518 nm observed in $Cu^I_8Cu^{II}_6[SC(CH_3)_2CH_2NH_2]_{12}Cl$ and related thiolate clusters[22a–d] has been assigned to be a LMCT $[S^{2-} \rightarrow Cu(II)]$ transition. The extinction coefficient of this band [3400 $dm^3mol^{-1}cm^{-1}$ per Cu(II)] is similar to that of the 484-nm band observed in the transient absorption difference spectrum. A similar assignment has also been suggested for the absorption bands at 400–500 nm of a series of copper(II) complexes with thioethers as ligands.[22e–f] However, such an assignment for the broad absorption band at 693 nm is not tenable in view of its occurrence at such a low energy region.

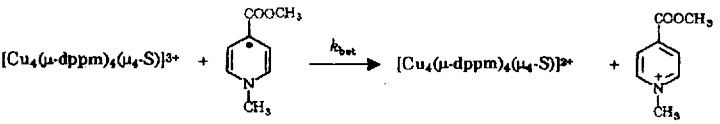
A more probable assignment for the absorption is the intervalence-transfer (IT) transition:

$$Cu^ICu^ICu^ICu^{II} + h\nu \rightarrow Cu^ICu^ICu^{II}Cu^{I*}$$

There have been a number of intervalence-transfer transitions reported in a variety of mixed-valence copper(I,II) systems. For example, the 756-nm absorption band ($\epsilon = 5000\ dm^3mol^{-1}cm^{-1}$) of a dinuclear complex $[Cu^ICu^{II}L]^{3+}$ with a macrocyclic ligand L = $N(CH_2CH_2N{=}C{-}C{=}NCH_2CH_2)_3N$ has been assigned as an intervalence-transfer transition.[23a] A similar assignment has also been suggested in other mixed-valence Cu(I)Cu(II) systems with thiolato-,[23b] halo-[23c] and N,O-containing macrocyclic ligands.[23d–e]

Similar low-energy transient absorption bands for the mixed-valence copper species have also been observed in the photo-induced electron-transfer reactions between a series of alkynylcopper(I) trimers and various pyridinium acceptors.[4b,d] Intervalence-transfer transitions have also been suggested for the near-infrared absorptions observed in these systems with nanosecond transient absorption spectroscopy.

Besides, the transient absorption spectroscopic studies can also provide important information on the back-electron-transfer reaction:



A plot of (1/ΔA) *vs.* time gives a straight line (data not shown), indicating that the decays follow second-order kinetics.

A back-electron-transfer rate constant k_{bet} of 9.7×10^9 $\mathrm{dm^3 mol^{-1} s^{-1}}$ is determined based on the decay of the intervalence-transfer absorption. This value agrees well with that obtained from the pyridinyl radical decay trace.

Similar transient absorption difference spectra have also been observed for the photo-induced electron-transfer reactions between **1** and 4-(aminoformyl)-*N*-methylpyridinium hexafluorophosphate, and methyl viologen hexafluorophosphate, respectively. For the case with methyl viologen, a sharp band at *ca.* 390 nm and a broad band at around 605 nm are observed, both of them attributable to the reduced methyl viologen radical.[24] The absorption bands of the mixed-valence $\mathrm{Cu^{I}Cu^{I}Cu^{I}Cu^{II}}$ species are most likely to be embedded into the intense absorption of the bipyridinyl radical.

Similar transient absorption difference spectra have also been observed for the electron-transfer reactions between **2*** and 4-(methoxycarbonyl)-*N*-methylpyridinium, 4-(aminoformyl)-*N*-methylpyridinium, and methyl viologen hexafluorophosphates, respectively. There are no significant differences between the spectra of the sulfido- and selenidocopper(I) complexes except that the 480-nm band is less intense for the latter. There is also a broad and intense absorption at 685 nm in the difference spectrum for the reaction between **2*** and 4-(methoxycarbonyl)-*N*-methylpyridinium, and it is also assigned as the absorption of the mixed-valence $\mathrm{Cu^{I}Cu^{I}Cu^{I}Cu^{II}}$ species. The occurrence of this absorption band at similar energy compared with that of the sulfido analogue (693 nm) reveals that these absorption bands are not due to LMCT transitions, as a much lower energy absorption would be expected for the selenido analogue. Therefore, an assignment of intervalence-transfer transition appears to be more possible for these low energy absorption bands.

In conclusion, characteristic pyridinyl radical absorptions have been observed in all transient absorption difference spectra, and therefore the electron-transfer nature of the photo-reactions between the phosphorescent states of these tetranuclear copper(I) chalcogenido clusters and the pyridinium acceptors can be established. The highly reducing capabilities of the excited states of these copper(I) clusters have also been demonstrated.

E. MOLECULAR ORBITAL CALCULATIONS

Considerable attention has been focused on the electronic structures of many polynuclear d^{10} systems.[3d,25] In order to gain more insight into the nature of the excited states of these coinage metal chalcogenido clusters, Fenske–Hall[14e] and *ab initio*[14f] molecular orbital calculations have been employed, in particular on the silver(I) series.

The geometry of the model complexes $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$ (E = S, Se, Te) is taken directly from that crystallographically determined for $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-}E)]^{2+}$ with hydrogen atoms replacing the phenyl groups on the dppm ligand (P–H bond distance taken to be 1.41 Å) and idealized to the C_{2v} point group. The relative positions of four silver atoms are adjusted to form a rectangle.

The compositions of the frontier molecular orbitals for the three model complexes from the Fenske–Hall molecular orbital calculations are summarized in Table V. The calculation results reveal that the three

TABLE V

Energies and percent compositions for the frontier orbitals of $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$[a].

Complex	Molecular Orbital	Energy/ eV	E	4Ag (%)	$4H_2PCH_2PH_2$
E = S	LUMO 65(a2)	−4.135	0.00	96.54	3.46
	HOMO 64(b1)	−11.080	46.12	42.00	11.88
E = Se	LUMO 65(a2)	−4.521	0.00	96.52	3.48
	HOMO 64(b1)	−10.754	50.16	39.26	10.58
E = Te	LUMO 65(a2)	−5.157	0.00	96.30	3.70
	HOMO 64(b1)	−10.545	51.64	38.40	9.96

[a] Data taken from Ref. 14e.

highest occupied molecular orbitals are mainly of Ag–E bonding character (between the 4d orbitals of the four silver(I) centers and the 3p orbitals of E), while the LUMOs of all these clusters are almost metal-localized. The calculated HOMO-LUMO energy gaps of $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$ decrease in the order:

$$E_{gap,\,E=S}(6.94\,eV) > E_{gap,\,E=Se}(6.23\,eV) > E_{gap,\,E=Te}(5.39\,eV)$$

which is in line with the trend observed in the solid-state luminescent energies of the tetranuclear silver(I) clusters. Similar results have also been obtained from the *ab initio* studies.

These results suggest that the transitions associated with the emissions of the silver(I) clusters originate essentially from a ligand-to-metal charge-transfer LMCT ($E^{2-} \rightarrow Ag_4$) excited state, with mixing of a metal-centered MC (d-s/d-p) silver(I) state. Similar assignments have also been suggested for other related polynuclear d^{10} thiolato-,[3a,7f,10,11d,19] halo-[3a,c–h] and alkynyl-[4,7l,m] systems.

F. CONCLUSION

A new series of tetranuclear copper(I) and silver(I) complexes containing a μ_4–chalcogenide ligand has been synthesized and structurally characterized. All the complexes are strongly emissive under ambient conditions. The phosphorescent state of these clusters is assigned to originate predominantly from a ligand-to-metal charge-transfer LMCT ($E^{2-} \rightarrow M_4$) triplet excited state, with mixing of a metal-centered MC(d-s or d-p) state of Cu(I) or Ag(I), which has also been supported by both spectroscopic studies and molecular orbital calculations. The photo-induced electron-transfer reactions between the excited copper chalcogenide complexes have been studied by Stern–Volmer quenching experiments, and the electron-transfer mechanism has also been confirmed by nanosecond transient absorption spectroscopy. In addition to the characteristic absorption of the reduced pyridinyl radical, the transient species $[Cu^{I,I,I,II}]^{3+}$ has been found to absorb at *ca.* 484 and 693 nm, which are tentatively assigned to be ligand-to-metal charge-transfer LMCT [$E^{2-} \rightarrow$ Cu(II)] and intervalence-transfer IT transitions, respectively.

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