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Syntheses and luminescence behaviour of dinuclear copper(I) selenolate and tellurolate complexes. X-Ray crystal structures of $[Cu_2(\mu\text{-dppm})_2(\mu\text{-SePh})]BF_4$ and $[Cu_2(\mu\text{-dppm})_2(\mu\text{-TePh})]BF_4$

Vivian Wing-Wah Yam,* Chi-Ho Lam and Kung-Kai Cheung

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China
E-mail: wwyam@hku.hk

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A series of novel dinuclear copper(I) μ-chalcogenolate complexes is synthesized and their photophysics studied; the X-ray crystal structures of $[Cu_2(\mu\text{-dppm})_2(\mu\text{-SePh})]BF_4$ and $[Cu_2(\mu\text{-dppm})_2(\mu\text{-TePh})]BF_4$ are reported.

Increasing interest in the investigation of copper(I) complexes with chalcogenide ligands has emerged.[1,2] The closely related class of ligands, the chalcogenolates, has also attracted enormous attention owing to their importance in biological systems and their propensity to form metal complexes and clusters of various bonding modes and structural motifs.[3] In view of this and the ready functionalization of the chalcogenolate ligands *via* a change in the substituent on the heteroatom to effect steric and electronic control of the ligating ability, it would be of interest to synthesize and study the related copper(I) chalcogenolate complexes. Compared with copper(I) thiolates, reports on selenolate and tellurolate complexes are relatively rare.[4] Moreover, the luminescence properties of copper(I) chalcogenolate complexes are almost unexplored[5] and represent a challenging area of research. Here we report the syntheses and photophysics of a new class of dinuclear copper(I) chalcogenolates and the X-ray crystal structures of $[Cu_2(\mu\text{-dppm})_2(\mu\text{-SePh})]BF_4$ and $[Cu_2(\mu\text{-dppm})_2(\mu\text{-TePh})]BF_4$.

Reaction of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$ with the corresponding sodium chalcogenolate (prepared *in situ* from the diaryldiselenide or diarylditelluride and $NaBH_4$) in a molar ratio of 1:1 in THF and under anaerobic and anhydrous conditions afforded dinuclear copper(I) μ-chalcogenolate complexes, $[Cu_2(\mu\text{-dppm})_2(\mu\text{-EAr})]BF_4$ (EAr = SePh **1**, SeC_6H_4Cl-*p* **2**, TePh **3**, TeC_6H_4Me-*p* **4**) in *ca.* 19–62% yield. Single crystals of **1** and **3** suitable for diffraction studies were grown by layering of diethyl ether on concentrated solutions of the complexes in acetone. All of the newly synthesized dinuclear copper(I) complexes gave satisfactory elemental analyses, and have been characterized by ^1H and ^{31}P NMR spectroscopy, and positive FAB mass spectrometry.† The X-ray crystal structures of complexes **1** and **3** have also been determined.‡

Fig. 1 shows the perspective drawing of the complex cation of **3**. The two copper atoms of the dinuclear complexes are held in close proximity by three bridging ligands, two dppm ligands acting through the P atoms and one chalcogenolate ligand acting through the Se/Te atom. The Se/Te atom asymmetrically bridges the two copper atoms, with the Cu(2)–Se/Te distances [**1**, Cu(2)–Se(1) 2.485 Å; **3**, Cu(2)–Te(1) 2.608 Å] longer than those of Cu(1)–Se/Te [**1**, Cu(1)–Se(1) 2.371 Å; **3**, Cu(2)–Te(1) 2.532 Å]. In addition, a short non-bonded contact of *ca.* 2.4 Å is observed between the Cu(2) atom of the complex cation and an oxygen atom of the acetone solvent molecule, with a tendency to afford a distorted trigonal bipyramidal arrangement about Cu(2) [**1**, Cu(1)···Cu(2)···O(1) 150.5(3)° with Cu(2) deviated 0.43 Å towards O(1); **2**, Cu(1)···Cu(2)···O(1) 153.7(3)° with Cu(2) deviated 0.39 Å towards O(1)], while Cu(1) assumes a distorted tetrahedral arrangement. It is noted that the phenyl ring of the chalcogenolate is bent towards one side of the Cu_2E triangle (E = Se, Te) due to the sp^3 hybridization of the Se/Te atom. The Cu···Cu distances in **1** and **3** are in the range 2.723–2.739 Å. They are shorter than the sum of van der Waals radii for copper (2.8 Å)[6] and this may indicate weak metal–metal interactions in the complexes.

The electronic absorption spectra for complexes **1**–**4** in dichloromethane are characterized by absorption shoulders at *ca.* 250 and 260–295 nm (Table 1). Since the electronic absorption spectra were rather featureless, no further attempts were made to unambiguously assign the absorption bands. The emission spectra of the dinuclear complexes **1**–**4** in degassed acetone showed a low energy emission at *ca.* 600–630 nm, with emission energies in the order $\mathbf{4} \geqslant \mathbf{3} > \mathbf{2} \geqslant \mathbf{1}$ (Table 1). Complexes **3** and **4** with tellurolate ligands show slightly higher emission energies than those with selenolate ligands **1** and **2**. Such an energy trend appears to depend upon the π-accepting ability of the chalcogenolate ligand, in which the areneselenolate is a better π-acceptor ligand than the arenetellurolate. This suggests that the low energy emission involves an excited state

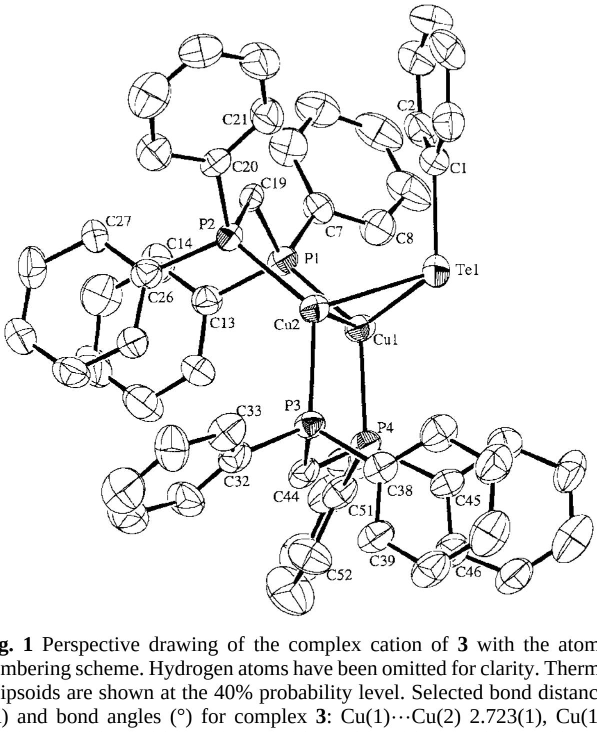

Fig. 1 Perspective drawing of the complex cation of **3** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and bond angles (°) for complex **3**: Cu(1)···Cu(2) 2.723(1), Cu(1)–Te(1) 2.532(1), Cu(2)–Te(1) 2.608(1), Cu(1)–P(1) 2.243(3), Cu(2)–P(2) 2.283(3), Cu(2)–O(1) 2.36(1); Te(1)–Cu(1)–P(1) 116.80(8), Te(1)–Cu(2)–P(2) 112.40(8), Te(1)–Cu(1)–P(4) 112.44(9), Te(1)–Cu(2)–P(3) 111.01(8), P(1)–Cu(1)–P(4) 129.3(1), P(2)–Cu(2)–P(3) 128.46(10), Cu(1)–Te(1)–C(1) 110.7(3), Cu(2)–Te(1)–C(1) 107.1(3). Selected bond distances (Å) and bond angles (°) for complex **1**: Cu(1)···Cu(2) 2.739(2), Cu(1)–Se(1) 2.371(2), Cu(2)–Se(1) 2.485(2), Cu(1)–P(1) 2.241(4), Cu(2)–P(2) 2.296(3), Cu(2)–O(1) 2.39(1); Se(1)–Cu(1)–P(1) 118.3(1), Se(1)–Cu(2)–P(2) 112.91(10), Se(1)–Cu(1)–P(4) 111.1(1), Se(1)–Cu(2)–P(3) 108.9(1), P(1)–Cu(1)–P(4) 129.0(1), P(2)–Cu(2)–P(3) 128.0(1), Cu(1)–Se(1)–C(1) 113.5(3), Cu(2)–Se(1)–C(1) 106.4(3).

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Table 1 Photophysical and electrochemical data of complexes **1–4**

Complex	Absorption,[a] λ/nm (ε_{max}/ dm^3 mol^{-1} cm^{-1})	Emission[b] Medium (T/K)	λ_{em}/nm (τ_o/µs)	Oxidation,[d,e] $E_{1/2}$ (V *vs.* SCE)
1	286sh (21 850)	Acetone (298)	630 (6.0)[c]	+0.68
		Solid (298)	431, 452 (< 0.1)	
2	266sh (34 290),	Acetone (298)	626 (< 0.1)[c]	+0.70
	296sh (31480)	Solid (298)	440, 468sh (< 0.1)	
3	256sh (42 380)	Acetone (298)	607 (< 0.1)[c]	+0.79
		Solid (298)	439, 464sh (< 0.1)	
4	256sh (40 530)	Acetone (298)	601 (< 0.1)[c]	+0.80
		Solid (298)	438, 463sh (< 0.1)	

[a] In CH_2Cl_2. [b] Excitation wavelength at 350 nm. [c] Excitation wavelength at 370 nm. [d] In MeCN (0.1 M $^nBu_4NPF_6$), glassy carbon electrode, scan rate 100 mV s^{-1}, 298 K. [e] $E_{1/2}$ is taken to be the average of E_{pa} and E_{pc}, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials of the quasi-reversible couple, respectively.

of metal-to-ligand charge transfer (MLCT) [$Cu_2 \rightarrow ER^-$] origin. A related dinuclear copper(I) complex, [Cu_2(µ-dppm)$_2$(µ-O_2CMe)]$^+$,[7] in which the lowest lying excited state was suggested to be MLCT [copper → phosphine/acetate] in character, as supported by molecular orbital calculations, shows a relatively high energy emission at *ca.* 470 nm. However, low energy emissions at *ca.* 600–630 nm are observed for complexes **1–4** and the emission energy difference between the dinuclear copper(I) selenolate and tellurolate complexes is relatively small. This, together with the fairly short Cu···Cu contacts (*ca.* 2.7 Å) found in these dinuclear complexes, may be more suggestive of an assignment of the emission as having a metal-centered ds/dp origin. Thus, the low energy emission in the dinuclear copper(I) chalcogenolate complexes is tentatively assigned as derived from an excited state that is predominantly metal-centered ds/dp in origin, mixed with some MLCT [copper → chalcogenolate/phosphine] character.

The cyclic voltammograms of complexes **1–4** show quasi-reversible oxidation couples in the range 0.68 to 0.80 V *vs.* SCE (Table 1). A relatively small shift in the potential of the oxidation couples is observed. The oxidation couple is tentatively assigned as a copper(I/II) metal-centered oxidation. No reduction wave was observed even when the potential was scanned to −2.4 V *vs.* SCE. Further oxidation and reduction of the complexes resulted in decomposition, as suggested by the irreversibility of the couples at higher anodic and cathodic potentials.

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Notes and references

† *Selected spectroscopic data* for **1**. ^1H NMR (300 MHz, acetone-d_6, 298 K): δ 3.6 (m, 4H, CH_2), 6.6–7.6 (m, 45H, Ph); $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 298 K): δ −6.3. Positive FAB-MS: *m/z* 1052 [M − BF_4]$^+$. Calc. for $Cu_2C_{56}H_{49}P_4SeBF_4$: C, 59.21; H, 4.63; Found: C, 59.13; H, 4.75%. For **2**. ^1H NMR (300 MHz, acetone-d_6, 298 K): δ 3.6 (m, 4H, CH_2), 6.7–7.6 (m, 44H, Ph); $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 298 K): δ −5.9. Positive FAB-MS: *m/z* 1088 [M − BF_4]$^+$. Calc. for $Cu_2C_{56}H_{48}P_4SeClBF_4{\cdot}CH_2Cl_2$: C, 54.42; H, 4.01; Found: C, 54.67; H, 3.96%. For **3**: ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 3.5 (m, 4H, CH_2), 6.5–7.7 (m, 45H, Ph); $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 298 K): δ −6.9. Positive FAB-MS: *m/z* 1102 [M − BF_4]$^+$. Calc. for $Cu_2C_{56}H_{49}P_4TeBF_4{\cdot}CH_2Cl_2$: C, 53.81; H, 4.04; Found: C, 53.81; H, 3.97%. For **4**. ^1H NMR (300 MHz, acetone-d_6, 298 K): δ 2.1 (s, 3H, CH_3), 3.5 (m, 4H, CH_2), 6.5–7.7 (m, 44H, Ph); $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 298 K): δ −6.8. Positive FAB-MS: *m/z* 1116 [M − BF_4]$^+$. Calc. for $Cu_2C_{57}H_{51}P_4TeBF_4{\cdot}CH_2Cl_2$: C, 54.16; H, 4.15. Found: C, 54.36; H, 4.05%.

‡ *Crystal data* for [Cu_2(µ-dppm)$_2$(µ-SePh)]BF_4 **1**: [($C_{56}H_{49}P_4SeCu_2$)$^+$ $BF_4^-{\cdot}(CH_3)_2CO{\cdot}(C_2H_5)_2O$], M_r = 1270.96, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 13.539(3), b = 21.137(4), c = 21.223(4) Å, V = 6073(2) Å^3, Z = 4, D_c = 1.390 g cm^{-3}, μ(Mo-Kα) = 14.59 cm^{-1}, F(000) = 2608, T = 301 K, using Mo-Kα radiation (λ = 0.71073 Å). 5305 unique reflections were measured, of which 3923 reflections with $I > 3\sigma(I)$ were used in the structural analysis. Convergence for 430 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.024F_o^2)^2]$ for 3923 reflections with $I > 3\sigma(I)$ was reached at R = 0.054 and wR = 0.071 with a goodness-of-fit of 2.98. For [Cu_2(µ-dppm)$_2$(µ-TePh)]BF_4 **3**: [($C_{56}H_{49}P_4TeCu_2$)$^+BF_4^-{\cdot}(CH_3)_2CO{\cdot}(CH_3CH_2)_2O$], M = 1319.60, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 13.546(2), b = 21.094(3), c = 21.274(3) Å, V = 6078(1) Å^3, Z = 4, D_c = 1.442 g cm^{-3}, μ(Mo-Kα) = 13.29 cm^{-1}, F(000) = 2680, T = 301 K, using Mo-Kα radiation (λ = 0.71073 Å). 6114 unique reflections were obtained from a total of 32593 measured reflections (R_{int} = 0.056). 4642 reflections with $I > 3\sigma(I)$ were used in the structural analysis. Convergence for 624 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.034F_o^2)^2]$ for 4742 reflections with $I > 3\sigma(I)$ was reached at R = 0.055 and wR = 0.072 with a goodness-of-fit of 2.09. CCDC 155745 and 155746. See http://www.rsc.org/suppdata/cc/b0/b009676h/ for crystallographic files in .cif or other electronic format.

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