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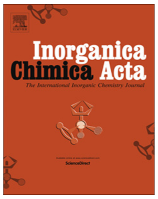

# Synthesis, characterization and optical properties of a series of binuclear copper chalcogenolato complexes

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ABSTRACT

A series of isolated binuclear copper(I) thiolate and selenolate complexes $[Cu_2(ER)_2(dpppt)_2]$ (**1**, E = S, R = $C_4H_3S$; **2**, E = S, R = *p*-$C_6H_4OMe$; **3**, E = Se, R = $C_6H_5$; **4**, E = Se, R = *p*-$C_6H_4SMe$; **5**, E = Se, R = *p*-$C_6H_4NMe_2$) was synthesized. It was found that the luminescence of these complexes could be modulated by the chalcogenolate ligands. The five complexes show optical transitions with HOMO–LUMO gaps of ca. 2.95 eV (**1**), 2.82 eV (**2**), 2.99 eV (**3**), 2.95 eV (**4**) and 2.64 eV (**5**), respectively. Two of them (**2** and **5**) show a significant luminescence at room temperature at 465 or 480 nm, respectively. This might most probably result from the influence of the electron donating nature of the substituents –OMe and $-NMe_2$.

## 1. Introduction

Polynuclear metal chalcogenide or metal chalcogenolate complexes attract much attention due to their rich structural, chemical and physical properties [1–4]. The perfect size homogeneity and long range order of these compounds make them serve as excellent model systems for investigations of quantum confinement effects at the lower size limit of “quantum dots” [5]. The properties of such crystalline complexes depend on the nature of the individual clusters, their spatial arrangement, and the properties of shell ligands [6,7].

As luminescent materials, copper(I) complexes are considered as remarkably attractive candidates for organic light-emitting diodes (OLEDs), due to their rich structural and photophysical properties [8–10]. But reports on well-defined and structurally characterized luminescent copper(I) thiolate or selenolate clusters are relatively rare. Selective functionalization of the organic shell in such compounds results in different properties and unusual core geometries [11–17].

Recently we have reported a series of highly luminescent polynuclear copper thiolate compounds all containing the same thiolate unit: $S-C_6H_4-NMe_2$ [18]. One of them is the binuclear $[Cu_2(p\text{-}S-C_6H_4-NMe_2)_2(dpppt)_2]$ (**A**, dpppt = 1,5-bis(diphenylphosphino)pentane) showing a bright blue emission at 480 nm. In this paper we present a series of five analogous binuclear complexes using the same phosphane, dpppt, but varying the bridging chalcogen (sulfur or selenium) and the organic group of the bridging unit. Their structures are determined via single crystal X-ray diffraction and the influence of the bridging units on the optical properties is investigated.

## 2. Experimental

### 2.1. General

Because of the high oxygen and moisture sensitivity of the compounds used, all reactions were performed under dry, oxygen free nitrogen by using standard Schlenk techniques. Toluene were heated to reflux over sodium/benzophenone and distilled under a nitrogen atmosphere. Copper(I) acetate (CuOAc) [19] and chalcogenide compounds [11,12,34] were synthesized according to literature procedures; dpppt was obtained from commercial sources.

IR spectra of all compounds were recorded with samples as KBr pellets with a Perkin–Elmer Spectrum GX FTIR system. The

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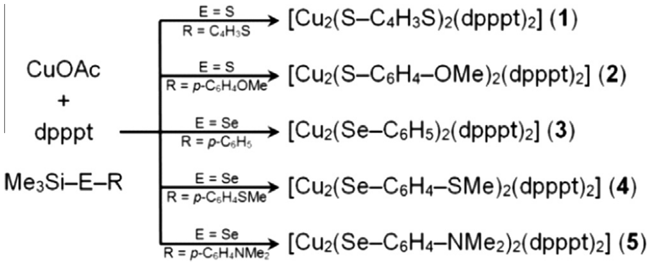

**Scheme 1.** Reactions leading to compounds **1**–**5**.

following abbreviations are used for the IR data: very strong (vs), strong (s), medium (m), weak (w), very weak (vw) and broad (br). Elemental analyses were performed with an Elementar VarioEL V2.10 instrument. NMR spectroscopic data were recorded with a Bruker AC 500 spectrometer in $CDCl_3$ at room temperature. Solid-state absorption spectra were measured as micron-sized crystalline powders between quartz plates with a Labsphere integration sphere attached to a Varian Cary 500 spectrophotometer; luminescence was measured using the same powder samples between quartz plates on a Varian Cary Eclipse spectrometer.

### 2.2. X-ray structure determination

Data were collected with a STOE IPDS II diffractometer by using Mo Kα radiation ($\lambda = 0.71073$ Å). Structure solution and refinement against $F^2$ were carried out with SHELXS and SHELXL [20]; molecular drawings were performed with Diamond 3.2i [21]. The purity of the compounds **1**–**5** was proved by X-ray powder diffraction. Measured and calculated diffraction patterns can be found in the Supporting Information in Figs. S11–S15.

### 2.3. Syntheses

#### 2.3.1. [$Cu_2(SC_4H_3S)_2(dpppt)_2$] (**1**)

CuOAc (0.042 g, 0.343 mmol) and dpppt (0.151 g, 0.343 mmol) were dissolved in toluene (30 mL), and the solution was stirred at room temperature for three hours. Then, $SC_4H_3SSiMe_3$ (0.065 g, 0.343 mmol) was added to give a green-yellow solution. Light yellow crystals were isolated from the reaction mixture after one day, yield 0.040 g (0.105 mmol, 61%). $C_{80}H_{82}Cu_2P_4S_4$ (1422.7): C, 67.53; H, 5.81; S, 9.01. Found: C, 67.51; H, 5.71; S, 9.12%. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 7.17–7.40 (m, 50H: 8 $C_6H_5$ from dpppt + 2 $C_6H_5$ from toluene), 6.83 (br, 2H: from $C_4H_3S$), 6.78 (br, 2H from $C_4H_3S$), 6.61 (br, 2H from $C_4H_3S$), 2.39 (s, sharp, 6H from $CH_3$ of toluene), 2.08 (br, 8H: 4 $CH_2$ from dpppt), 1.40–1.57 (br, 12 H: 6 $CH_2$ from dpppt); $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): $\delta$ 12.8 (br). IR (KBr): 3052 (m), 2929 (m), 2854 (m), 2345 (vw), 2173 (vw), 1957 (vw, br), 1901 (vw, br), 1823 (vw, br), 1745 (vw, br), 1628 (w, br), 1587 (w), 1546 (vw), 1482 (m), 1452 (w), 1433 (m), 1338 (w), 1309 (w), 1265 (vw), 1225 (vw), 1188 (w), 1157 (w), 1136 (vw), 1094 (m), 1071 (w), 1024 (w), 887 (w), 841 (w), 811 (vw), 795 (vw), 753 (m), 728 (s), 697 (s), 670 (w), 629 (w), 606 (w), 584 (vw), 558 (vw), 540 (vw), 506 (m), 485 (vw).

**Table 1**
Crystallographic data and structure refinement details of **1**–**5**.

| | **1**·2$C_6H_5CH_3$ | **2**·0.5$C_6H_5CH_3$ | **3**·2$C_6H_5CH_3$ | **4**·2$C_6H_5CH_3$ | **5**·$C_6H_5CH_3$ |
|---|---|---|---|---|---|
| Empirical formula | $C_{80}H_{82}Cu_2P_4S_4$ | $C_{75.50}H_{78}Cu_2O_2P_4S_2$ | $C_{84}H_{86}Cu_2P_4Se_2$ | $C_{86}H_{90}Cu_2P_4S_2Se_2$ | $C_{95}H_{104}Cu_2N_2P_4Se_2$ |
| Formula weight | 1422.65 | 1332.45 | 1504.40 | 1596.57 | 1682.68 |
| Temperature (K) | 180(2) | 180(2) | 180(2) | 180(2) | 180(2) |
| Crystal system | monoclinic | triclinic | monoclinic | triclinic | triclinic |
| Space group | $C2/c$ | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (pm) | 2335.00(8) | 1181.81(7) | 2364.6(2) | 1034.72(5) | 1014.67(5) |
| $b$ (pm) | 1488.01(6) | 1467.11(10) | 1498.39(9) | 1454.22(6) | 1466.93(7) |
| $c$ (pm) | 2085.18(7) | 2101.67(12) | 2086.27(14) | 1471.36(6) | 1495.02(7) |
| $\alpha$ (°) | 90 | 92.139(5) | 90 | 113.129(3) | 85.793(4) |
| $\beta$ (°) | 98.810(3) | 96.641(5) | 98.319(6) | 98.723(4) | 76.294(4) |
| $\gamma$ (°) | 90 | 112.137(5) | 90 | 104.813(3) | 75.396(4) |
| $V$ ($10^6$ pm$^3$) | 7159.5(5) | 3339.7(4) | 7314.0(9) | 1887.57(15) | 2091.83(18) |
| $Z$ | 4 | 2 | 4 | 1 | 1 |
| $D_{calc}$ (g cm$^{-3}$) | 1.320 | 1.325 | 1.366 | 1.405 | 1.336 |
| $\mu$ (mm$^{-1}$) | 0.844 | 0.841 | 1.708 | 1.713 | 1.502 |
| $F(000)$ | 2976 | 1394 | 3104 | 824 | 874 |
| Reflections collected | 21256 | 27162 | 12008 | 14819 | 15411 |
| Independent reflections | 6725 ($R_{int} = 0.063$) | 11119 ($R_{int} = 0.133$) | 6061 ($R_{int} = 0.109$) | 7072 ($R_{int} = 0.044$) | 7754 ($R_{int} = 0.022$) |
| Reflections with $I > 2\sigma(I)$ | 4577 | 4801 | 2551 | 5986 | 6773 |
| Parameters/restrains | 403/0 | 769/6 | 410/14 | 436/0 | 473/0 |
| Goodness-of-fit (GoF) | 0.902 | 0.814 | 0.802 | 0.980 | 1.018 |
| 2$\theta$ range (°) | 4.9–51 | 4.4–50 | 4.9–50 | 4.4–51 | 4.5–51 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.038/0.086 | 0.059/0.122 | 0.048/0.071 | 0.029/0.071 | 0.027/0.067 |
| $R_1/wR_2$ [all data] | 0.064/0.095 | 0.155/0.150 | 0.153/0.091 | 0.036/0.074 | 0.033/0.069 |
| Maximum/minimum res. el. den. (e Å$^{-3}$) | 0.706/−0.414 | 0.760/−0.819 | 0.729/−0.482 | 0.743/−0.663 | 0.521/−0.439 |
| CCDC number | 971045 | 971046 | 971047 | 971048 | 971049 |

**Table 2**
Selected distances and bonding and torsion angles in **1**–**5** and **A**.

| | **1** (E = S) | **2** (E = S) | **3** (E = Se) | **4** (E = Se) | **5** (E = Se) | **A** (E = S) |
|---|---|---|---|---|---|---|
| Cu···Cu (pm) | 356.1 | 361.9 | 370.8 | 373.5 | 370.3 | 359.3 |
| Cu–E (pm) | 238.9/239.8 | 235.6–247.2 | 250.1–250.3 | 249.4–253.3 | 248.7–252.1 | 237.5–243.4 |
| Cu–P (pm) | 228.4/229.0 | 226.9–229.4 | 226.7–228.0 | 226.7–227.3 | 226.3–226.9 | 227.7–229.3 |
| E–Cu–E (°) | 83.7/84.1 | 81.3/82.6 | 84.4/84.5 | 84.1 | 84.6 | 82.1/83.2 |
| P–Cu–P (°) | 112.0/116.3 | 115.2/117.2 | 114.9/118.3 | 120.1 | 120.4 | 115.3/118.1 |
| Cu–E–Cu (°) | 96.1 | 96.1/99.8 | 95.6 | 95.9 | 95.4 | 96.5/98.3 |
| Cu–E–E–Cu (°) | 180 | 177.3 | 180 | 180 | 180 | 178.9 |