Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 353–355
DOI: 10.1021/ic901143h

Indium Chalcogenido Clusters Coordinated by 1,10-Phenanthroline, [InQ(phen)Cl]$_4$ (Q = Se, S), a Simplified Model of Inorganic−Organic Hybrid Material with Cluster-to-Ligand Charge Transfer

Zhi-Xin Lei,[†] Qin-Yu Zhu,[*,†,‡] Ming-Hui Zhang,[†] Jian-Bing Jiang,[†] Ya-Ping Zhang,[†] and Jie Dai[*,†,‡]

[†]*Department of Chemistry and Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, People's Republic of China and* [‡]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China*

Received June 13, 2009

Most metal−1,10-phenanthroline-complex-sensitized inorganic semiconductors are multicomponent materials. This fundamental study was devoted to the single-phase materials fused with moieties of the phen complex and inorganic chalcogenide. Compounds **1** and **2** are new types of cubic clusters with cluster-to-ligand charge transfer.

Metal chalcogenido clusters are playing an important role in several scientific areas of current interest such as material science, biochemistry, and catalysis. A well-known class of such compounds is the cubane-type metal chalcogenido clusters, in which the metal and chalcogen atoms occupy adjacent vertices in a cube. These cubane-type clusters have found important applications as typical and simplified models in the study of metal chalcogenido clusters, especially in the electronic state of the clusters.[1] For this reason, M_4Q_4 (Q = S, Se) clusters have been extensively studied, and up to now, about a thousand homo- or heterometallic cubane-type compounds have been synthesized and characterized crystallographically. Most of them are transition-metal compounds, especially those of Mo, W, Fe, and Cu elements.[1,2] In contrast, the reported cubane-type main-group metal chalcogenido clusters are limited. The reported homometallic clusters among them are Na_4Q_4,[3] Mg_4Q_4,[4] Al_4Q_4,[5] Ga_4Q_4,[6] and In_4Q_4,[7] in which the ligands are usually Cp*, M(CO)$_n$, Me_3Si−, alkyl substituents, or tetrahydrofuran belonging to organometallic compounds. Herein we report a new type of main-group metal chalcogenido cluster of cubic In_4Q_4 (Q = S, Se) coordinated with 1,10-phenanthroline (phen), [InSe(phen)Cl]$_4$ (**1**), and [InS(phen)Cl]$_4\cdot 1.5C_2H_6O_2\cdot 0.5H_2O$ (**2**; $C_2H_6O_2$ = ethylene glycol).

After publication of the first synthetic procedure in 1898,[8] phen is now still of major interest to diverse scientific communities because it is an excellent chelating agent and the presence of 14 electrons delocalized over the aromatic ring confers peculiar spectroscopic, photochemical, and

---

*To whom correspondence should be addressed. E-mail: zhuqinyu@suda.edu.cn (Q.-Y.Z.), daijie@suda.edu.cn (J.D.).

(1) (a) Wang, X.-B.; Niu, S.; Yang, X.; Ibrahim, S. K.; Pickett, C. J.; Ichiye, T.; Wang, L.-S. *J. Am. Chem. Soc.* **2003**, *125*, 14072–14081. (b) Feliz, M.; Llusar, R.; Uriel, S.; Vicent, C.; Coronado, E.; Gómez-García, C. J. *Chem.—Eur. J.* **2004**, *10*, 4308–4314. (c) Andérs, J.; Feliz, M.; Fraxedas, J.; Hernández, V.; López-Navarrete, J. T.; Llusar, R.; Sauthier, G.; Sensato, F. R.; Silvi, B.; Bo, C.; Campanera, J. M. *Inorg. Chem.* **2007**, *46*, 2159–2166. (d) Fu, Y.-J.; Yang, X.; Wang, X.-B.; Wang, L.-S. *Inorg. Chem.* **2004**, *43*, 3647–3655. (e) Fu, Y.-J.; Niu, S.; Ichiye, T.; Wang, L.-S. *Inorg. Chem.* **2005**, *44*, 1202–1204.

(2) (a) Barron, A. R. *Chem. Soc. Rev.* **1993**, 93. (b) Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5431–5434. (c) Yamauchi, T.; Takagi, H.; Shibahara, T.; Akashi, H. *Inorg. Chem.* **2006**, *45*, 5429–5437. (d) Feliz, M.; Guillamón, E.; Llusar, R.; Vicent, C.; Stiriba, S.-E.; Pérez-Prieto, J.; Barberis, M. *Chem.—Eur. J.* **2006**, *12*, 1486–1492.

(3) Kückmann, T. I.; Hermsen, M.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Inorg. Chem.* **2005**, *44*, 3449–3458.

(4) Xia, A.; Heeg, M. J.; Winter, C. H. *J. Organomet. Chem.* **2003**, *669*, 37–43.

(5) (a) Schnitter, C.; Klemp, A.; Roesky, H. W.; Schmidt, H.-G.; Röpken, C.; Herbst-Irmer, R.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **1998**, 2033–2039. (b) Harlan, C. J.; Gillan, E. G.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5479–5488. (c) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed.* **1993**, *32*, 1728–1729.

(6) (a) Schulz, S.; Gillan, E. G.; Ross, J. L.; Rogers, L. M.; Rogers, R. D.; Barron, A. R. *Organometallics* **1996**, *15*, 4880–4883. (b) App, U.; Merzweiler, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 478–482. (c) Linti, G.; Bühler, M.; Urban, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 517–520. (d) Uhl, W.; Benter, M.; Saak, W. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1622–1628. (e) Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055–1063. (f) Cowley, A. H.; Jones, R. A.; Harris, P. R.; Atwood, D. A.; Contreras, L.; Burek, C. J. *Angew. Chem., Int. Ed.* **1991**, *30*, 1143–1145. (g) Gillan, E. G.; Bott, S. G.; Barron, A. R. *Chem. Mater.* **1997**, *9*, 796–806.

(7) (a) Merzweilier, K.; Rudolf, F.; Brands, L. *Z. Naturforsch., Teil B* **1992**, *47*, 470. (b) Uhl, W.; Graupner, R.; Pohlmann, M.; Pohl, S.; Saak, W. *Chem. Ber.* **1996**, *129*, 143. (c) Wiberg, N.; Blank, T.; Amelunxen, K.; Nöth, H.; Schnöckel, H.; Baum, E.; Purath, A.; Fenske, D. *Eur. J. Inorg. Chem.* **2002**, 341–350. (d) Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1–C5.

(8) Blau, F. *Monatsh. Chem.* **1898**, *19*, 647.

(9) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Zelewsky, A. V. *Coord. Chem. Rev.* **1988**, *84*, 85−277 and references cited therein.(b) Lainé, P. P.; Campagna, S.; Loiseau, F. *Coord. Chem. Rev.* **2008**, *252*, 2552–2571. (c) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Lagref, J.-J.; Liska, P.; Comte, P.; Barolo, C.; Viscardi, G.; Schenk, K.; Grätzel, M. *Coord. Chem. Rev.* **2004**, *248*, 1317–1328. (d) Polo, A. S.; Itokazu, M. K.; Iha, N. Y. M. *Coord. Chem. Rev.* **2004**, *248*, 1343–1361. (e) Grätzel, M. *Nature* **2001**, *414*, 338–344. (f) Liu, F.; Meyer, G. J. *Inorg. Chem.* **2005**, *44*, 9305–313. (g) Chen, C.-Y.; Lu, H.-C.; Wu, C.-G.; Chen, J.-G; Ho, K.-C. *Adv. Funct. Mater.* **2007**, *17*, 29–36.

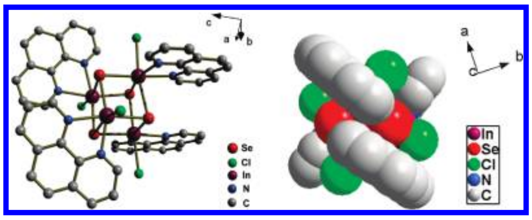

Figure 1. Structure of compound **1** (left) and the space-filling model showing S_4 symmetry (right).

electrochemical properties on phenanthroline-based transition-metal complexes.[9−11] In spite of the existence of numerous metal−phen complexes, the coordination of phen to the M site in metal cubane-type clusters has not been observed yet (CCDC database update to 2009.9). To our knowledge, compounds **1** and **2** are the first M_4Q_4 clusters coordinated with the phen ligand.

Compounds **1** and **2** are main-group metal coordination cubanes obtained from a solvothermal reaction system during our series studies of the inorganic−organic hybrid Ga/In chalcogenides.[12] The reagents $InCl_3 \cdot 4H_2O$ and phen reacted with element S or Se in an aqueous solution of ethylene glycol in a thick Pyrex tube [see the Supporting Information (SI)]. The compounds are stable under ambient conditions and are insoluble in any solvents. Herein the structures of **1** and **2** are presented in the views of topology and chirality. The electronic states of the clusters are also discussed and concentrated on the charge-transfer (CT) effect between the phen and the cluster. We found that introducing phen to chalcogenido clusters can improve the photoabsorption of the cubanes in the visible range and can induce a bathochromic shift of the photoemission.

The asymmetric unit of **1** is shown in Figure 1. The central framework In_4Se_4 is a distorted cube and similar to the structures of $[InSeCpFe(CO)_2]_4$, $[InSeSiMe_3]_4$, and $[InSeC(SiMe_3)_3]_4$.[7] The corners of the cluster are alternatively occupied by In and Se atoms, with the In−Se−In angles varying from 81.40(2) to 91.80(2)° and the Se−In−Se angles ranging from 90.00(2) to 99.46(2)°. As a consequence, the Se atoms are somewhat drawn away from the corners of the regular cube.

The In−Se bond lengths range from 2.598(1) to 2.937(1) Å, showing larger retractability than that found in the organometallic compounds, for example, 2.653(2)−2.699(2) Å for $[InSeCpFe(CO)_2]_4$, 2.674(1)−2.681(1) Å for $[InSeSiMe_3]_4$, and 2.664(2)−2.681(2) Å for $[InSeSi(CMe_3)_3]_4$.[7] Each of the In^{III} centers takes an octahedral coordination mode, coordinated by three μ_3-bridged Se atoms, one chelating phen, and one chloride ion to balance the positive charge of the cubane. The symmetry of the cluster belongs to the unusual S_4 group, in which there is a S_4 axis (also an appurtenant C_2 axis). Thereby, it is a good example for teaching the point group. For this symmetry, the cluster is a nonchiral molecule. The cluster $[InS(phen)Cl]_4$ of **2** is analogously structured to **1**, while the asymmetric unit of **2** contains two symmetrically independent In_4S_4 clusters (SI-Fig 1 in the SI) with In−S bond distances from 2.504(2) to 2.695(2) Å.

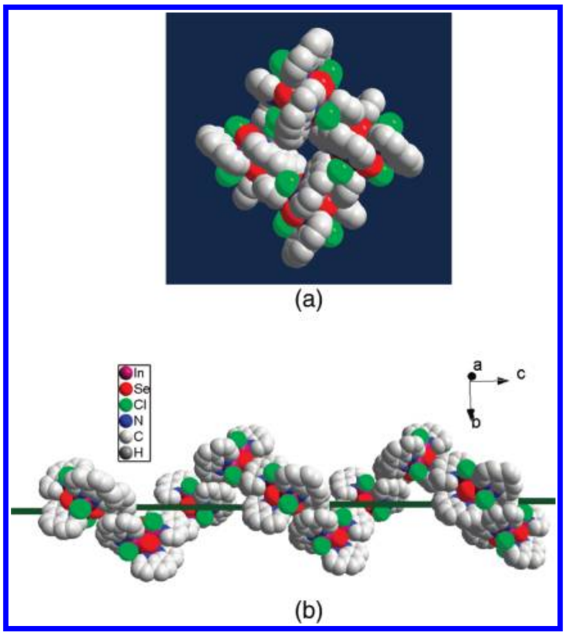

Figure 2. Helical chain structure of **1** assembled by strong $\pi-\pi$ stacking around a 4_1 axis: (a) view along the *c* axis; (b) view along the *a* direction.

The crystal structure of **1** shows a chiral space group $P4_1$, while the structure of **2** has an inversion center belonging to space group $P\bar{1}$ (see the SI). In compound **1**, the clusters interact with strong $\pi \cdots \pi$ stackings of the phenanthroline molecules (the reason for the insolubility of the samples). By the strongest double $\pi \cdots \pi$ stacking, 3.33(1) Å for C(27)$\cdots$C(48) and 3.32(1) Å for C(28)$\cdots$C(47), the clusters assemble to a helical chain around a 4_1 axis that parallels the *c* axis (Figure 2 and SI-Fig 2 in theSI). Figure 2a presents the view along the 4_1 axis (*c* axis) and Figure 2b that along the *a* direction. The crystal structure of compound **1** is chiral, in which all of the helical chains take a clockwise mode and parallel each other with interchain $\pi \cdots \pi$ stacking (SI-Table 1 in the SI). The $\pi \cdots \pi$ stacking in compound **2** is also listed in SI-Table 1 in the SI and shown in SI-Fig 3 in the SI. The shortest one is 3.25(1) Å for C(35)$\cdots$C(69) within the same symmetric operation (SI-Fig 1 in the SI).

Most reported Ga_4Q_4 and In_4Q_4 cubanes are organometallic compounds; those are usually synthesized by the reaction of organometallic starting materials with chalcogens or $S(Me_3Si)_2$ and so on.[6,7] Most of these compounds are used as the single-source precursors for metal−organic chemical vapor deposition growth of gallium/indium sulfides because they have very low volatility temperatures of around 200 °C. Compounds **1** and **2** are not volatile main-group metal coordination cubanes. Thermal analysis results showed that their decomposition temperature is about 350 °C (SI-Fig 4 in the SI). The potential application of these types of compounds might be as inorganic−organic hybrid functional materials.

---

(10) (a) Armaroli, N. *Chem. Soc. Rev.* **2001**, 113–124. (b) Scaltrito, D. V.; Thompson, D. W.; O'Callaghan, J. A.; Meyer, G. J. *Coord. Chem. Rev.* **2000**, *208*, 243–266. (c) Lavie-Cambot, A.; Cantuel, M.; Leydet, Y.; Jonusauskas, G.; Bassani, D. M.; McClenaghan, N. D. *Coord. Chem. Rev.* **2008**, *252*, 2572–2584.

(11) (a) König, E. *Coord. Chem. Rev.* **1968**, *3*, 471–495. (b) Pomeranc, D.; Heitz, V.; Chambron, J.-C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2001**, *123*, 12215–12221.

(12) (a) Zhou, J.; Bian, G.-Q.; Zhang, Y.; Zhu, Q.-Y.; Li, C.-Y.; Dai, J. *Inorg. Chem.* **2007**, *46*, 6347–6352. (b) Zhou, J.; Zhang, Y.; Bian, G.-Q.; Zhu, Q.-Y.; Li, C.-Y.; Dai, J. *Cryst. Growth Des.* **2007**, *9*, 1889–1892. (c) Zhou, J.; Zhang, Y.; Bian, G.-Q.; Li, C.-Y.; Chen, X.-X.; Dai, J. *Cryst. Growth Des.* **2008**, *8*, 2235–2240. (d) Li, C.-Y.; Chen, X.-X.; Zhou, J.; Zhu, Q.-Y.; Lei, Z.-X.; Zhang, Y.; Dai, J. *Inorg. Chem.* **2008**, *47*, 8586–8588. (e) Zhou, J.; Li, C.-Y.; Zhang, Y.; Dai, J. *J. Coord. Chem.* **2009**, *253*, 1221–1247.

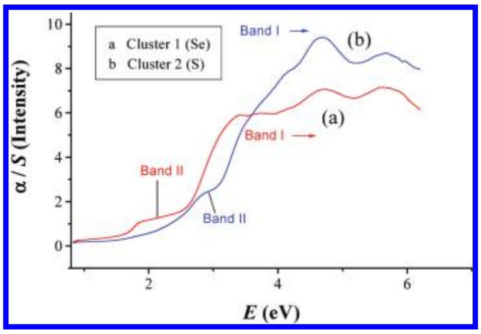

Figure 3. Optical diffuse-reflection spectra of **1** (curve a, red) and **2** (curve b, blue), showing band I (LC and CC bands overlapped) and band II (CLCT).

The metal-to-ligand CT (MLCT) absorption and luminescence features of the phen−metal complexes have been interesting until now for their potential application in photoelectronic materials. The Ru^{II}phen system offers new possibilities in solar light harvesting and energy conversion.[9] Besides the Ru^{II}phen complexes, Cu^{I}phen,[10] Fe^{II}phen,[11] and so on are also candidates for photochemical sensitizers. On the other hand, chalcogenido Ga/In metal compounds are important inorganic semiconductive materials for photoelectronic devices.[13] Most metal−phen-complex-sensitized inorganic semiconductors are surface-modified or embedded materials, belonging to multicomponent materials.[9d] This fundamental study is devoted to the single-phase compounds fused with structural moieties of phen complexes and inorganic semiconductors. Introducing metal-phen into chalcogenido structures can decrease the energy gap of the highest occupied orbital to the lowest unoccupied orbital of the materials and can also avoid the interphase electron transition between organometallic dye and inorganic semiconductor. Chalcogenido clusters of **1** and **2** are typical and simplified models of these types of compounds. For these reasons, spectroscopic studies of the phen−Ga/In metal clusters are attractive for us.

Optical diffuse-reflection spectra of **1** and **2** were measured at room temperature using $BaSO_4$ as a standard reference (Figure 3). The absorption (α/S) data were calculated from the reflectance. The optical bands were estimated by extrapolation of the linear portion of the absorption edges. There are two sets of light absorption bands observed for both compounds. The first set of bands (band I) is in the area larger than 2.60 eV for **1** (Se) and 3.20 eV for **2** (S). These intense bands are assigned to cluster-centered (CC) bands with overlapped ligand-centered (LC) bands, typically the $\pi-\pi^*$ transitions of the phen ligands. The second set of bands (band II; 1.70−2.60 eV for **1** and 2.20−3.20 eV for **2**) in the visible area is assigned to the MLCT absorption,[10a] more exactly cluster-to-phen ligand CT (CLCT). Though In^{III} is an electron-poor center, unlike Ru^{II}, Cu^{I}, and Fe^{II},[9−11] the In_4Q_4 (Q = S, Se) cluster is an electron-rich donor owing to the S or Se atoms and the electron-delocalized system within the cluster. The inorganic In_xQ_y clusters are usually colorless or pale-yellow (corresponding to band I). The reddish-brown color of crystal **1** and the yellow-brown color of crystal **2** are ascribed to the absorption of band II (CLCT).

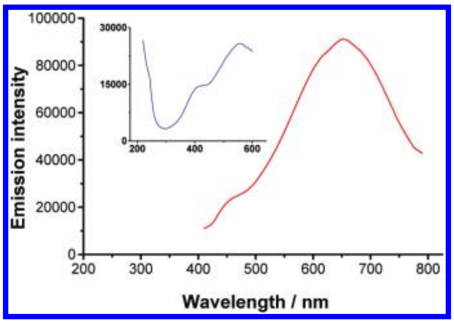

Figure 4. Fluorescence emission spectrum of **2** in the solid state at room temperature (inset: excitation spectrum).

The fluorescence emission spectrum of **2** in the solid state was measured at room temperature (Figure 4; the inset shows the excitation spectrum), showing a broad and strong emission at 650 nm. While the emission spectrum of the free phen shows a main peak at 381 nm (SI-Fig 5 in the SI; LC emission of phen). This significant bathochromic shift is undoubtedly ascribed to the CT effect of the cluster on the ligand because of the direct coordination of phen to the In_4S_4 cluster. This spectral character has been well discussed for Ru^{II}phen compounds, which are considered viable photochemical sensitizers.[9b] The emission spectrum of **1** is similar to that of **2** and shows a broad band at 550−700 nm (SI-Fig 6 in the SI).

In summary, new types of cubic clusters In_4Q_4 (Q = S, Se) with the ligand of phen are first reported. The symmetry of the cluster belongs to the unusual S_4 group. By strong $\pi\cdots\pi$ stacking, the clusters in crystal **1** assemble into parallel helical chains with a 4_1 axis, forming a chiral structure with space group $P4_1$. A spectroscopic study indicates that introducing phen to chalcogenido clusters significantly decreases the energy gap of the frontier orbitals due to CLCT. The similarity of **1** and **2** to Ru^{II}phen compounds in spectra is notably in terms of MLCT absorption bands and fluorescence emission, which are important properties being added to the inorganic InQ moiety. These results prompt us to explore a new type of inorganic−organic hybrid semiconductor for photophysical applications.

Acknowledgment. This work was supported by the National Natural Science Foundation (Grant 20971092) and by the Program of Innovative Research Team of Soochow University.

Supporting Information Available: Experimental preparation, CIF files, molecular packings, fluorescence spectra, thermal analysis, and table of $\pi-\pi$ stacking. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(13) (a) Avivi, S.; Palchik, O.; Palchik, V.; Slifkin, M. A.; Weiss, A. M.; Gedanken, A. *Chem. Mater.* **2001**, *13*, 2195–2200. (b) Tang, J.; Hinds, S.; Kelley, S. O.; Sargent, E. H. *Chem. Mater.* **2008**, *20*, 6906–6910. (c) Lai, K.; Peng, H.; Kundhikanjana, W.; Schoen, D. T.; Xie, C.; Meister, S.; Cui, Y.; Kelly, M. A.; Shen, Z.-X. *Nano Lett.* **2009**, *9*, 1265–1269. (d) Panthani, M. G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. *J. Am. Chem. Soc.* **2008**, *130*, 16770–16777. (e) Lin, L.-H.; Wu, C.-C.; Lee, T.-C. *Cryst. Growth Des.* **2007**, *7*, 2725–2732.