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Mendeleev Commun., 2023, **33**, 484–486

Mendeleev Communications

Cu_4I_4-cubane cluster based on tris(*p*-anisyl)arsine: synthesis, crystal structure and photophysical properties

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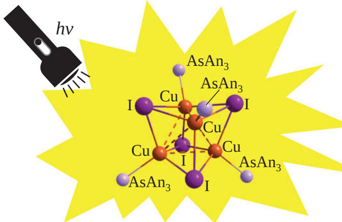
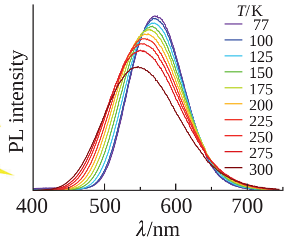
DOI: 10.1016/j.mencom.2023.06.014

A new cubane cluster $[Cu_4I_4(AsAn_3)_4]$ was synthesized in 82% yield by the reaction of tris(*p*-anisyl)arsine ($AsAn_3$) with CuI. At ambient temperature, this cluster exhibits bright yellow-green phosphorescence (λ_{max} = 546 nm) with the quantum yield of 35% and 4.1 μs decay time.



λ_{em} = 546 nm, PLQY 35%, τ_{em} = 4 μs



Keywords: copper(I) complexes, tris(*p*-anisyl)arsine, cubane-like clusters, photoluminescence, crystal structure.

Recently, an increased attention has been paid to luminescent copper(I) complexes due to their fascinating structural diversity[1–6] affecting to photophysical properties such as efficient thermally activated delayed fluorescence (TADF),[7,8] room temperature phosphorescence[9–13] and stimuli-responsive luminescence.[14] Compared to conventional luminescent materials, copper-based phosphors are low cost and easy to prepare and store, making them good candidates for electroluminescent devices, sensors and photosensitizers for solar cells.[15–17] One of the most intriguing subclasses of luminescent Cu^I complexes is represented by tetranuclear cubic Cu_4I_4 clusters. Cuprophilic interactions play an important role in the emission properties of these clusters. For example, a decrease in the Cu···Cu distances caused by thermal or mechanical impacts affects the LUMO energy of $[Cu_4I_4]$, which leads to a bathochromic shift of the emission maximum.[14] Generally, the largest number of such luminescent complexes are based on N- and P-donor ligands.[18–24] At the same time, there are much fewer examples of such complexes with 'heavier' pnictine ligands, such as arsines,[25–29] although arsine ligands show some advantages over their phosphine counterparts, *e.g.*, an increase in the rate of TADF at ambient temperature[30–32] due to the 'heavy atom' effect of pnictogen. Thus, the synthesis and photophysical study of new luminescent copper complexes based on heavy pnictine ligands is an urgent task of coordination chemistry. Herein, we report the synthesis of a Cu_4I_4-cubane cluster based on tris(*p*-anisyl)-arsine ($AsAn_3$) and investigation of its photophysical properties.

The interaction of CuI with an equimolar amounts of $AsAn_3$ in EtCN/CH_2Cl_2 at room temperature leads to the formation of a tetranuclear complex $[Cu_4I_4(AsAn_3)_4]$ isolated as a solvate **1**·CH_2Cl_2 in 82% yield. The obtained complex is moisture- and air-stable white powder, poorly soluble in EtCN, CH_2Cl_2 and $CHCl_3$. However, upon storage in air, it can lose the solvate CH_2Cl_2 molecule. The phase purity of **1**·CH_2Cl_2 has been verified by powder X-ray diffractometry and microanalysis data (Figure S1, see Online Supplementary Materials). The FTIR spectrum of the product displays characteristic bands of coordinated arsenic ligands and also contains a specific band at 750 cm^{-1} belonging to the $\nu_{C–Cl}$ stretching vibrations of the CH_2Cl_2 solvate molecule (Figures S2 and S3). According to thermogravimetric analysis, the solvate **1**·CH_2Cl_2 loses the solvate molecules in the range of 99–120 °C (Δm_{exp} = 4.1%, Δm_{calc} = 3.5%), after which it remains stable up to 210 °C (Figure S4).

Single crystal XRD analysis[†] revealed that the compound **1**·CH_2Cl_2 crystallizes in the space group $P\bar{1}$. The packing of **1**·CH_2Cl_2 contains the following van der Waals interactions: C_{Me}–H···C_{Ar} (2.877 Å), C_{Me}–H···π (2.905 Å), C_{Me}–H···I (3.139 Å), $C_{CH_2Cl_2}$–H···C_{Ar} (2.872 Å), $C_{CH_2Cl_2}$–H···π (2.737 Å), $C_{CH_2Cl_2}$–H···O (2.697 Å), C_{Ar}–H···O (2.679 Å), C_{Ar}–H···C_{Ar} (average 2.878 Å), C_{Me}···C_{Ar} (3.376 Å), C_{Me}···O (3.150 Å) and C_{Ar}···O (3.182 Å). Its molecular structure is shown in Figure 1 and selected interatomic distances are listed in Table 1. The compound **1**·CH_2Cl_2 consists of a $[Cu_4I_4]$ core supported by four An_3As ligands. Each copper atom adopts a tetrahedral environment $[Cu@I_3As]$, which is represented by three iodine atoms and one arsenic atom. In **1**·CH_2Cl_2

[†] *Crystal data for* **1**·CH_2Cl_2. $C_{84}H_{84}As_4Cu_4I_4O_{12}\cdot CH_2Cl_2$ (*M* = 2431.87), triclinic, space group $P\bar{1}$, *a* = 12.9602(8), *b* = 15.4260(9) and *c* = 24.2353(15) Å, *α* = 86.713(2)°, *β* = 81.975(3)°, *γ* = 89.061(2)°, *V* = 4789.7(5) $Å^3$, *Z* = 2, *T* = 200 K, *μ*(MoKα) = 3.645 mm^{-1}, d_{calc} = 1.686 g cm^{-3}. Total of 58510 reflections were measured, and 18813 independent reflections (R_{int} = 0.070) were used in the further refinement. The refinement converged to wR_2 = 0.1877 and GOF = 1.014 for all independent reflections [R_1 = 0.0668 was calculated against *F* for 13006 observed reflections with $I > 2\sigma(I)$]. Single crystals of **1**·CH_2Cl_2 were grown by diffusion of hexane vapor into an EtCN/CH_2Cl_2 solution overnight. The data were collected on a Bruker Kappa Apex II CCD diffractometer using *φ*,*ω*-scans of narrow (0.5°) frames with MoKα radiation (*λ* = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods (SHELXL97) and refined by the full-matrix least-squares anisotropic-isotropic (for H atoms) procedure using the SHELXL-2014/7 program.[33] Absorption corrections were applied by the empirical multiscan method using the SADABS program.[34] The positions of hydrogen atoms were calculated in the riding model.

CCDC 2222588 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 1 Selected interatomic distances in $\mathbf{1}\cdot CH_2Cl_2$.

Bond	Cu–Cu/Å	Bond	Cu–I/Å	Bond	Cu–I/Å	Bond	Cu–As/Å
Cu(1)–Cu(2)	2.7570(17)	Cu(2)–I(1)	2.6765(13)	Cu(1)–I(3)	2.6625(14)	Cu(1)–As(2)	2.3683(15)
Cu(1)–Cu(3)	2.8241(17)	Cu(4)–I(1)	2.7019(14)	Cu(3)–I(3)	2.6724(14)	Cu(2)–As(3)	2.3670(15)
Cu(1)–Cu(4)	2.8459(18)	Cu(1)–I(1)	2.7028(14)	Cu(2)–I(3)	2.6860(14)	Cu(3)–As(4)	2.3730(16)
Cu(2)–Cu(3)	2.7194(18)	Cu(3)–I(2)	2.6767(15)	Cu(1)–I(4)	2.6621(14)	Cu(4)–As(1)	2.3877(15)
Cu(2)–Cu(4)	2.7968(17)	Cu(4)–I(2)	2.6879(14)	Cu(3)–I(4)	2.6973(15)		
Cu(3)–Cu(4)	2.9899(18)	Cu(2)–I(2)	2.6942(15)	Cu(4)–I(4)	2.7013(15)		

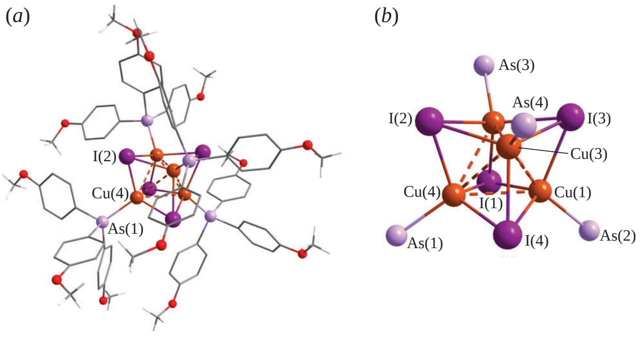


Figure 1 (*a*) Molecular structure of $\mathbf{1}\cdot CH_2Cl_2$. The H atoms of the arene rings and the CH_2Cl_2 solvate molecule are omitted for clarity. (*b*) Structure of the $[Cu_4I_4]$ core in $\mathbf{1}\cdot CH_2Cl_2$ with coordinated As atoms. *p*-Anisyl substituents in arsine ligands are not shown.

such Cu···Cu distances as Cu(1)–Cu(2) [2.7570(17) Å], Cu(2)–Cu(3) [2.7194(18) Å] and Cu(2)–Cu(4) [2.7968(17) Å] are shorter than the sum of the van der Waals radii of Cu (2.80 Å). At the same time, some of them, Cu(1)–Cu(3) [2.8241(17) Å] and Cu(1)–Cu(4) [2.8459(18) Å], are close to this value, which indicates metallophilic interactions. The Cu–As (average 2.37 Å), Cu–I (average 2.69 Å) and Cu···Cu (average 2.82 Å) distances in $\mathbf{1}\cdot CH_2Cl_2$ are comparable with the literature values for related $[Cu_4I_4]$ arsine complexes.[25–27] It is noteworthy that the Cu···Cu distances in $\mathbf{1}\cdot CH_2Cl_2$ are significantly shorter than the corresponding values [$d_{Cu\cdots Cu}$ up to 3.317(1) Å] for the related complex $[Cu_4I_4(An_3P)_4]$,[18] whereas the Cu–I distances are very similar to those in $[Cu_4I_4(An_3P)_4]$ (average 2.69 Å).

Under UV irradiation at 298 K, the powder of $\mathbf{1}\cdot CH_2Cl_2$ exhibits bright photoluminescence (PL) with a quantum yield of 35% (λ_{ex} = 330 nm). The normalized emission and excitation spectra at 298 K and the temperature-dependent PL spectra are shown in Figure 2. According to these data, the PL spectrum of $\mathbf{1}\cdot CH_2Cl_2$ appears as a broad band with λ_{max} = 546 nm. Upon cooling from 298 to 77 K [Figure 2(*b*)], the emission maximum undergoes a bathochromic shift by ~26 nm, which can be explained by low-temperature compression of the $[Cu_4I_4]$ core, which causes a slight decrease of Cu···Cu distances. These changes are accompanied by a visual change in the PL color from green to yellow-green (λ_{max} = 572 nm). Interestingly, only one low-energy emission band is observed for $\mathbf{1}\cdot CH_2Cl_2$. On the contrary, cubic Cu_4I_4 clusters surrounded by N- or P-donor ligands, in particular $[Cu_4I_4(An_3P)_4]$, demonstrate dual-mode emission represented by high-energy and low-energy emission bands belonging to ^{3}(M+X)LCT and ^{3}CC (cluster-centered) states, respectively.[18] The absence of a high-energy band at low temperature suggests that the luminescence of $\mathbf{1}\cdot CH_2Cl_2$ probably belongs to the ^{3}CC type phosphorescence. The PL decay time at 298 K is 4.1 μs. At 77 K, the PL lifetime sharply increases to 167 μs, which is comparable with the lifetimes for known Cu^I arsine complexes at this temperature.[27]

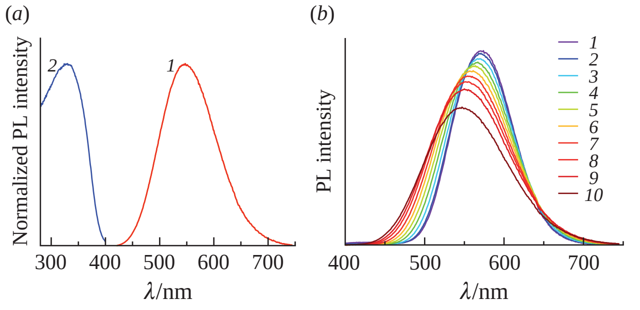


Figure 2 (*a*) Normalized (*1*) emission and (*2*) excitation spectra of solid $\mathbf{1}\cdot CH_2Cl_2$ at 298 K. (*b*) Temperature-dependent emission spectra (λ_{ex} = 320 nm) of solid $\mathbf{1}\cdot CH_2Cl_2$ recorded at (*1*) 77, (*2*) 100, (*3*) 125, (*4*) 150, (*5*) 175, (*6*) 200, (*7*) 225, (*8*) 250, (*9*) 275 and (*10*) 300 K.

In summary, a new Cu^I arsine complex $[Cu_4I_4(AsAn_3)_4]$ was synthesized and characterized. At ambient temperature, it exhibits a bright yellow-green luminescence, tentatively assigned to cluster-centered phosphorescence.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project nos. 121031700321-3, 121031700313-8 and 1021051503141-0-1.4.1).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.014.

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Received: 21st February 2023; Com. 23/7106