Synthesis, Crystal Structure and Non-linear Optical Properties of $[WSe_4\{Cu(dppm)\}_4][ClO_4]_2 \cdot MeCN$

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The reaction of $Cu(MeCN)_4[ClO_4]$, dppm (bis(diphenylphosphino)methane) and $[Et_4N]_2[WSe_4]$ in DMF-CH_2Cl_2, affords the cationic cluster $[WSe_4\{Cu(dppm)\}_4]^{2+}$ whose structure was shown by X-ray analysis that four edges of the tetrahedral WSe_4 core are bridged by a square arrangement of four Cu(I) atoms with the dppm ligands bridging the edges. The cluster compound exhibits a strong optical limiting effect with threshold of 0.3 $J \cdot cm^{-2}$

Although the reactivities of the $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ anions have been extensively investigated,[1,2] the reactivities of the corresponding selenide have not.[3] After the search for new non-linear optical (NLO) inorganic clusters has been undertaken in Mo(W)-Cu(Ag, Au)-S clusters for five years,[4,5] our interests in this field have recently been directed towards the exploration of the third NLO properties of hetroselenometallic clusters having inorganic selenium atoms which are more important in non-linear optics and electronics.[6] Thus, an important goal in our researches is to design and synthesize new materials whose structures and optical properties can be predicted and controlled.

In the view of remarkable non-linear optical effects of various structural types of Mo(W)-Cu(Ag, Au)-S clusters, they include linear, cubane-like, incomplete cubane, butterfly, planar, prism, and cage etc.,[7-13] of which the pentanuclear planar cluster shows large optical limiting properties.[13] Herein, we describe a new W-Cu-Se cationic cluster $[WSe_4\{Cu(dppm)\}_4]^{2+}$ with WCu_4 core planar structural mode and its non-linear optical results.

The title cluster compound was synthesized by the reaction of $Cu(MeCN)_4[ClO_4]$ and $[Et_4N]_2[WSe_4]$ in the presence of excess dppm ligands. A $[Et_4N]_2[WSe_4]$ (0.22 g, 0.25 mmol) of 5 ml DMF solution was added to a solution of $Cu(MeCN)_4[ClO_4]$ (0.25 g, 1.0 mmol) and dppm (0.54 g, 1.4 mmol) in CH_2Cl_2 (15 ml), dark-red solution formed immediately. After stirring for *ca.* 30 min, little participates were filtered over. Vapor diffusion of diethyl ether into a dark-red filtrate gave the title cluster as big black flock crystals in a high yield (87%).[14] This preparation seems specific for dppm ligand, as similar clusters were not obtained with PPh_3 (triphenyphosphine) or dppe (1,2-bis(diphenylphosphino)ethane).

The structure of the cluster cation $[WSe_4\{Cu(dppm)\}_4]^{2+}$ is shown in Figure 1 together with the selected bond distances and angles.[15] It has an imposed crystallographic C_2 symmetry with the two-fold axis passing through the center W(1) atom (1/2, y, 1/4). The core structure is different from that of $[WS_4\{Cu(dppm)\}_3]^{+}$[16] as sulfuric analogue, but similar structures have been found previously in $[MoSe_4(CuS_2CNMe_2)_4]^{2-}$ anion[17] and $[MoS_4(CuSCN)_4]^{2-}$ anion clusters.[18] The tungsten atom is at the center of an essentially tetrahedral WSe_4 unit, in which the

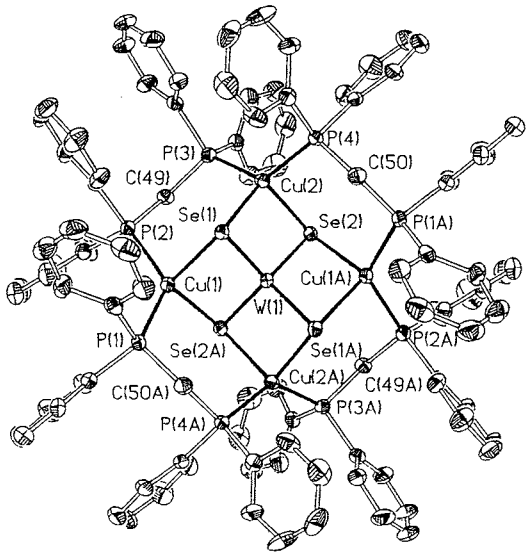

Figure 1. A perspective view of $[WSe_4\{Cu(dppm)\}_4]^{2+}$ cation with the ellipsoids drawn at 30% probability level. Important bond distances (Å) and angles (°): W(1)-Se(1), 2.3206(7); W(1)-Cu(1), 2.8172(8); Se(1)-Cu(1), 2.4513(11); Se(1)-Cu(2), 2.4202(11); Se(2)-Cu(2), 2.260(2); Se(1)-W(1)-Se(2), 111.40(2); Cu(2)-W(1)-Cu(1), 90.50(2); W(1)-Se(1)-Cu(1), 72.31(3); W(1)-Se(2)-Cu(2), 71.80; Cu(2)-Se(1)-Cu(1), 110.33(4).

mean W-Se bond length is 2.3207(7) Å and Se-W-Se angles lie between 104.12(4) and 111.40(2)°. Four copper atoms are bound to the WSe_4 core in which each is symmetrically attached to one edge of the tetrahedral, and are in a square arrangement in which each edge is doubly bridged by a dppm ligand. It is interesting to note that the six-membered ring comprising each dppm ligand, chelated adjacent two Cu atoms and their bridging Se atom has a distorted chair formation. Such four related rings are around WSe_4^{2-} anion. The WSe_4Cu_4 aggregate approximates to D_{2d} symmetry. An average W-Cu distance of 2.815(8) Å is longer than those in $WSe_4(CuPPh_3)_3Cl$ (av. 2.753(3) Å)[19] and in $[(\mu_3\text{-}WSe_4)_3(\mu_3\text{-}Se)_2(Cu_3)_2]^{4-}$ (av. 2.738(3) Å),[20] but is slightly shorter than that of 2.873(2) Å in $WSe_4[Cu(PMe_2Ph)_2]_2$.[18] The 4:1 copper to tungsten stoicheiometry is the largest metal uptake so far obtained in a metal-chalcogenide cluster with dppm ligands.[21] This is probably due to the steric crowding of the phenyl groups of dppm and the strong σ donor of P atoms to result in specific coordination type.

Optical limiting properties of the title cluster have been examined in a 1 mm cell with 7 ns laser pulses of 532 nm. The

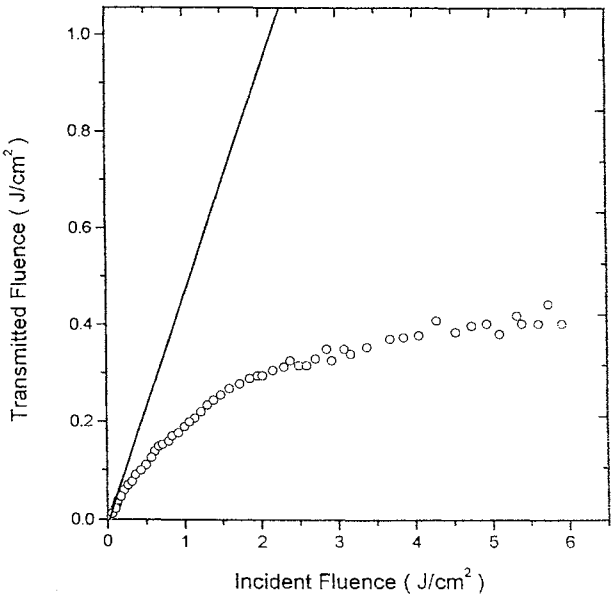

Figure 2. Optical limiting effect of the title cluster. Solution straight with 72% transmittance at 532 nm correspond to 4.8 × 10^{-3} M.

optical limiting ability of the title cluster is illustrated in Figure 2. At very low fluences it responds linearly to the incident light obeying Beer's law. Deviation from the linear response takes place when the incident fluence exceeds 0.1 J·cm^{-2}. The solution become increasingly less transparent as the light fluence rises, thus exhibiting a typical optical limiting effect. At 72% linear transmittance, the limiting threshold of the cluster in MeCN solution was measured to be *ca.* 0.3 J·cm^{-2}. This value of the present cluster is five times better than 1.6 J·cm^{-2} of C_{60} and three times higher than 0.1 J·cm^{-2} of phthalocyanine derivatives.[22,23] Further studies on NLO properties and similar systems are going on in our laboratory.

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14 Anal. Found: C, 48.15; H, 3.44; P, 9.19%. Calcd. for $C_{102}H_{101}N_1P_8O_8Cl_2Cu_4Se_4W$: C, 47.34; H, 3.51; P, 9.58%. UV-Vis (CH_2Cl_2, nm): 318(s), 375(sh), 428(b). IR (KBr, cm^{-1}): $\nu_{W\text{-}Se}$, 294; $\nu_{Cu\text{-}P}$, 405; $\nu_{Cl\text{-}O}$, 1095; ν_{CN}, 2091; ν_{dppm}, 1432, 1095, 742, 691, 521, 489. ^{31}P NMR (CH_2Cl_2, ppm): –2.1.
15 Crystal data: crystal dimensions 0.44 × 0.42 × 0.36 mm, $C_{102}H_{101}N_1P_8O_8Cl_2Cu_4Se_4W$, M = 2225.7, monoclinic, space group C2/c, a = 19.5880(2), b = 22.85200(10), c = 24.4305(2) Å, β = 91.4387(71)°, V = 10932.25(15) Å^3, Z = 4, D_c = 1.604 g·cm^{-3}. 42877 intensity data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation at room temperature, of which 13718 (R_{int} = 0.1360) are independent. $R(_wR)$ = 0.0630(0.1406) for 7009 reflections with $I \geq 2.0\sigma(I)$ and 567 refined parameters.
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