Synthesis, Structure and Nonlinear Optical Properties of a Novel Cluster Compound Containing 1,1′-Bis(diphenylphosphino)ferrocene(dppf)

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A novel cluster $WCu_2S_4(dppf)_2{\cdot}4DMF$ was synthesized by the reaction of $(NH_4)_2WS_4$ with CuCl and 1,1′-bis(diphenylphosphino)ferrocene (dppf) in the solid state, and its crystal structure has been characterized by X-ray diffraction. The cluster has a novel new skeletal structure with five metal atoms nearly in a line. Investigation of third-order optical nonlinear z-scan shows that it exhibits good nonlinear optical properties in a 1.2×10^{-4} mol·dm^{-3} DMF solution.

Mo(W)-Cu(Ag)-S clusters are important part in heterothiometallic clusters, we have studied them for several years and found that many of these clusters have good nonlinear optical (NLO) properties.[1–3] In the view of remarkable non-linear optical effects of various structural types of Mo(W)-Cu(Ag)-S clusters, they include linear, cube-like, incomplete cube, butterfly, planar, prism and cage etc..[4–6] In searching for new clusters with interesting structure and good non-linear properties, we firstly use dppf as ligand to synthesize Mo(W)-Cu(Ag)-S clusters. In this article, a novel cluster $WCu_2S_4(dppf)_2{\cdot}4DMF$ is reported on the synthesis, crystal structure and nonlinear optical studies. The cluster is firstly found to have a novel new skeletal structure with Fe-Cu-W-Cu-Fe nearly in a line. Investigation of third-order optical nonlinear z-scan shows that it exhibits strong self-focusing and good nonlinear refractive properties with α_2 value of 4.2×10^{-11} m·w^{-1} and n_2 value of 6.1×10^{-18} m^2·w^{-1}.

The cluster was synthesized by reaction of CuCl (0.198 g, 2 mmol), $(NH_4)_2WS_4$ (0.348 g, 1 mmol) and dppf (1.108 g, 2 mmol) in a reaction tube. A dark red solid was generated by heating the mixture at 100 °C for 10 h under pure nitrogen. The red solution obtained by extracting the product with DMF (25 ml) was allowed to evaporate in air. After several days, 0.45 g (24.5%) of red prismatic crystals suitable for X-ray crystallographic analysis was collected after washing with ethyl ether. Found: C, 52.04; H, 4.68; N, 3.06%. Calcd for $C_{80}H_{84}Cu_2Fe_2N_4O_4P_4S_4W$: C, 52.21; H, 4.60; N, 3.04%. In IR spectra (KBr), the ν(W-S) stretching vibration appears at 455.6 cm^{-1}. The elemental analysis and IR spectrum confirmed the formula of the cluster.

The crystal structure of the cluster consists of four discrete DMF solvent molecules and one $WCu_2S_4(dppf)_2$ molecule as shown in Figure 1, which contains a pentanuclear molecule that is symmetric with W as the center. W atom is coordinated by four μ_2-S atoms and two Cu atoms. As expected, the Fe atom is sandwiched by two staggered cyclopentadienes. The interesting aspect of the structure is that Fe_1-C_1-P_1-Cu_1-P_2-C_6- constitutes a distorted hexagon, and the bite angles are distorted by steric bulkiness of dppf. The Cu-S bond length [2.3094(12) Å] is longer than those observed in compounds $[PPh_4]_2[(CuNCS)_2WS_4]$,[7]

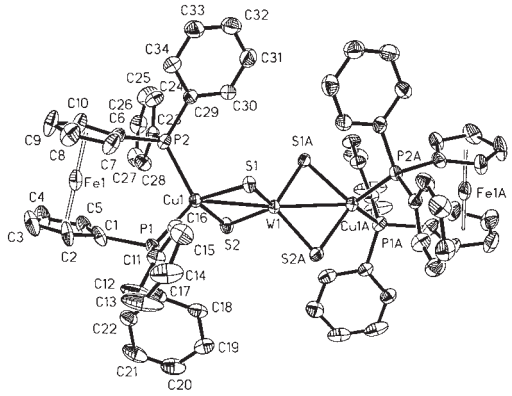

Figure 1. Diagram of the titled crystal structure. Selected bond length (Å) and angles (°): W1-Cu1 2.7649(6), W1-S1 2.1918(11), W1-S2 2.2010(11), Cu1-P1 2.2824(12), Cu1-P2 2.3055(12), Cu1-S1 2.3094(12), Cu1-S2 2.3139(12); S1-W1-S1A 108.52(6), S1-W1-S2 108.03(4), S1-W1-Cu1 54.05(3), S1-Cu1-S2 100.50(4), P1-Cu1-P2 112.48(5), Cu1-W1-Cu1A 172.92(2).

$[PPh_4]_2[(CuCl)_2WS_4]$.[8] It seems that the two Cu atoms are pulled outward in order to release the strain of the Cu-P-C-Fe-C-P- ring. To our best knowledge, the structure of $WCu_2S_4(dppf)_2$ is the first one with Fe-Cu-W-Cu-Fe nearly in a line.

The UV spectrum shows its two big absorption peaks at 262 nm and 414 nm and relatively low linear absorption in the visible and near IR region. The NLO properties of $WCu_2S_4(dppf)_2{\cdot}4DMF$ was determined by using a z-scan technique.[9] A z-scan measurement of the cluster is shown in Figure 2. This clearly illustrates that the absorption increases as the incident light irradiance rises since light transmittance (T) is a function of the sample's z position. Equations (1) and (2) describe the typical and pure absorptive behavior of a hypothetical third order NLO process, where α_0 is the linear absorptive coefficients index, τ is the time and L is the optical path length. The effective nonlinear absorptive index α_2 is 4.2×10^{-11} m·w^{-1}.

$$T(Z)=\frac{1}{\sqrt{\pi}q(Z)}\int_{-\infty}^{+\infty}\ln[1+q(Z)]e^{-\tau^2}d\tau \qquad (1)$$

$$q(Z)=\alpha_2\frac{I_0}{1+(Z/Z_0)^2}\frac{1-e^{-\alpha_0 L}}{\alpha_0} \qquad (2)$$

An effective nonlinear refractive index n_2 can be derived from the difference between normalized transmittance values at valley and peak positions(ΔT_{V-P}) by using equation (3), where I is the peak irradiation intensity at focus and λ is the wavelength of the laser.[10]

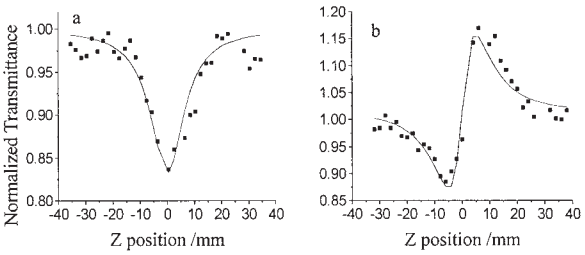

Figure 2. Z-scan measurement of the title compound in a 1.2×10^{-4} mol·dm^{-3} DMF solution in a 2 mm-thick cuvette. The linear absorption spectrum of the solution is UV spectrum. The optical pass lengths are 2 mm for Z-scan. The repetitive rate is 1 Hz. (a) The data were collected with an open aperture configuration. (b) The data were obtained by dividing the normalized z-scan measured with a closed aperture configuration.

$$n_2 = \frac{\lambda\alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})}\,\Delta T_{V-P} \tag{3}$$

The data show that the cluster has a positive refractive nonlinearity and self-focusing. The nonlinear refractive index n_2 was calculated to be 6.1×10^{-18} m^2·w^{-1}. A good fit was found between theory and experiment. The n_2 value of the titled cluster is comparable with those of many best known third-order NLO materials in neat solid form, such as SiO_2 (2×10^{-20} m^2·w^{-1}) and CdS (2.5×10^{-18} m^2·w^{-1}),[11] and also comparable to that of the known cluster $WCu_2OS_3(PPh_3)_4$ (8×10^{-18} m^2·w^{-1}).[4] A much larger n_2 value may be expected with more concentrated solutions.

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References and Notes

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10 $$\Delta\Phi_0 = \frac{2\pi}{\lambda}\,\Delta n_0(t)\,\frac{1 - e^{-\alpha_0 L}}{\alpha_0} \qquad \Delta T_{p-v} = 0.406|\Delta\Phi_0|$$
$$\Delta n_0 = n_2 I$$
From above equations, we can obtain the formula:
$$|n_2| = \frac{\lambda\alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})}\,\Delta T_{p-v}$$
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12 Crystal data for the cluster $C_{80}H_{84}Cu_2Fe_2N_4O_4P_4S_4W$, $M_r = 1840.26$, prismatic, space group $P4_32_12$, $a = 15.598(2)$ Å, $b = 15.598(2)$ Å, $c = 33.294(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 8100.1(23)$ Å, $Z = 4$, $F(000) = 3720$, $D_c = 1.507$ gcm^{-1}, Mo Kα radiation $\lambda = 0.71073$ Å, $R = 0.0467$, unique reflection number 5871. Atomic coordinates, bond length and angles, and thermal parameters have been sent to the Cambridge Crystallographic Data Center (CCDC176591).