

SYNTHESIS, CHARACTERIZATION AND THEORETICAL INVESTIGATION ON THE OPTICAL NONLINEARITY OF $WS_4Co(dppe)(DMF)$ HETEROMETALLIC CLUSTER COMPOUND

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A novel hetero-metallic binuclear cluster $WS_4Co(dppe)(DMF)$ has been synthesized and characterized. The crystal has a structure of monoclinic space group $P2_1$. *Ab initio* CPHF calculations are performed on the static first hyperpolarizabilities of the molecular building blocks of the cluster. The microscopic structural origin of nonlinear optical properties are discussed in-depth. The charge-transfer between tungsten ion and cobalt ion in a molecular building block critically contributes to the optical nonlinearity, while the joint effect of the ligands makes sufficient enhancements. The study is helpful to search for novel IR nonlinear optical materials among the transition metal cluster compounds.

Keywords: Nonlinear optical properties; Metal cluster compound; Crystal structure characterization; Quantum chemical studies; Structure-property relationship; IR nonlinear optical material

1. INTRODUCTION

The first synthesis of transition metal cluster compounds can trace to the beginning of the last century. The initial motivation came from the biological activity of these compounds in some important proteins and

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protease. Recent developments have extended the field to new catalysts [1] and new functional materials [2]. Some positive optical measurements have already shown that transition metal cluster compounds are the potential candidates of nonlinear optical (NLO) materials. The large third-order NLO responses of several Mo(W)—Cu(Ag)—S metal cluster compounds have been reported [3–5].

However, there are some basic questions that have not been answered. Does the metal–metal interaction contribute to NLO responses, and in what way? Which kinds of metal core configurations contribute more efficiently to the specified NLO effect? The first question is crucial in searching novel NLO metal cluster compounds. Answering the other question requires the in-depth understanding of the relationship between the microscopic metal core structure and NLO effects.

Most synthesized metal cluster compounds are central symmetric. The experiments thus, limit to report the third-order NLO properties [3–5]. The metal cluster compounds of acentric space symmetries are potential second-order NLO materials. Recently, we have synthesized several novel transition metal sulfido compounds which have non-central symmetries, such as $\{[WAg_2S_3C_5H_5NS] (PPh_3)_2(X)] \cdot CH_2Cl_2$ ($X = S, O$) [6], $[M_2Cu_2S_4(PPh_3)_2(SCH_2CH_2S)_2]$ ($M = Mo, W$) [7], $(Et_4N) [M_2CuS_4(PPh_3)(SCH_2CH_2S)_2]$ ($M = Mo, W$) [8] and $[WS_4Co(dppe)(DMF)]$ to name a few. Among these compounds, the binuclear heterometallic $[WS_4Co(dppe)(DMF)]$ compounds ($dppe = \text{bis}(\text{diphenylphosphino})\text{ethane}$; $DMF = \text{dimethyl formamide}$) have relatively simple core structure and thus are a suitable example for theoretical treatment.

Quantum chemical calculation is now widely used to explore NLO hyperpolarizabilities [9–12]. But there are few reports on those of transition metal cluster compounds. This paper attempts to theoretically elucidate the structural NLO origin of transition metal cluster compounds. The result will be beneficial to the design of novel NLO materials among transition metal cluster compounds.

2. EXPERIMENTS

2.1. Chemical Synthesis

All operations were carried out in air. $(NH_4)_2WS_4$ was prepared following Ref. [13]. $Co(dppe)Cl_2$ was obtained from the CH_2Cl_2

solution of dppe and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (molar ratio 1:1). $(\text{NH}_4)_2\text{WS}_4$ (0.348 g) was dissolved in 15 ml of DMF, a solution of 0.528 g $\text{Co}(\text{dppe})\text{Cl}_2$ in 30 ml CH_2Cl_2 was then added. Being stirred for a while, the solution was filtered. The dark red filtrate was stood at room temperature in the air for 3 days and 0.20 g dark red crystals were obtained.

2.2. X-ray Structure Determination

A piece of the dark red crystal of $0.3 \times 0.3 \times 0.5$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer for data collection with $\text{Mo } K\alpha$ radiation at room temperature. The structure was solved by direct methods and Fourier techniques, and was refined by the full-matrix least-squares calculation. The final R is 0.053 and $R_w = 0.058$, $w = [\sigma(\text{Fo})^2]^{-1}$, $\Delta/\sigma = 0.07$, $S = 1.41$. The W, Co, S, P, O atoms and the C atoms of dppe were refined with anisotropic temperature factors except the C atoms of phenyl (for detail structural information consult CCDC 134716).

3. COMPUTATIONAL DETAILS

The discrete molecular clusters, $[\text{WS}_4\text{Co}(\text{dppe})(\text{DMF})]$ (see Fig. 1), are the building blocks of the title compound. However, the molecular polyhedron of $[\text{WS}_4\text{Co}(\text{dppe})(\text{DMF})]$ which consists of $[\text{WS}_4\text{Co}]$ core structure, DMF and dppe ligands is still too large for *ab initio* calculation. In order to reduce the molecular size, four simplified models are proposed and shown in Figure 2. The four phenyl groups connected to the phosphorus atoms are cut off in model I due to their small effect on the metal–metal interaction. A further simplification leads to the model II, in which the organic ligand dppe' (dppe ligand without four phenyl groups) is omitted. Contrasting with model I, the function of dppe' ligand to hyperpolarizabilities is retained. The model III cuts off DMF ligands and is the core structure, $[\text{WS}_4\text{Co}]$, containing metal–metal bonds. In order to elucidate the effect of DMF ligand, model IV is set up.

Ab initio coupled perturbed Hartree-Fock (CPHF) equations are solved at 6-31G(d,p) /lanl2dz level, at which the basis sets used for O,

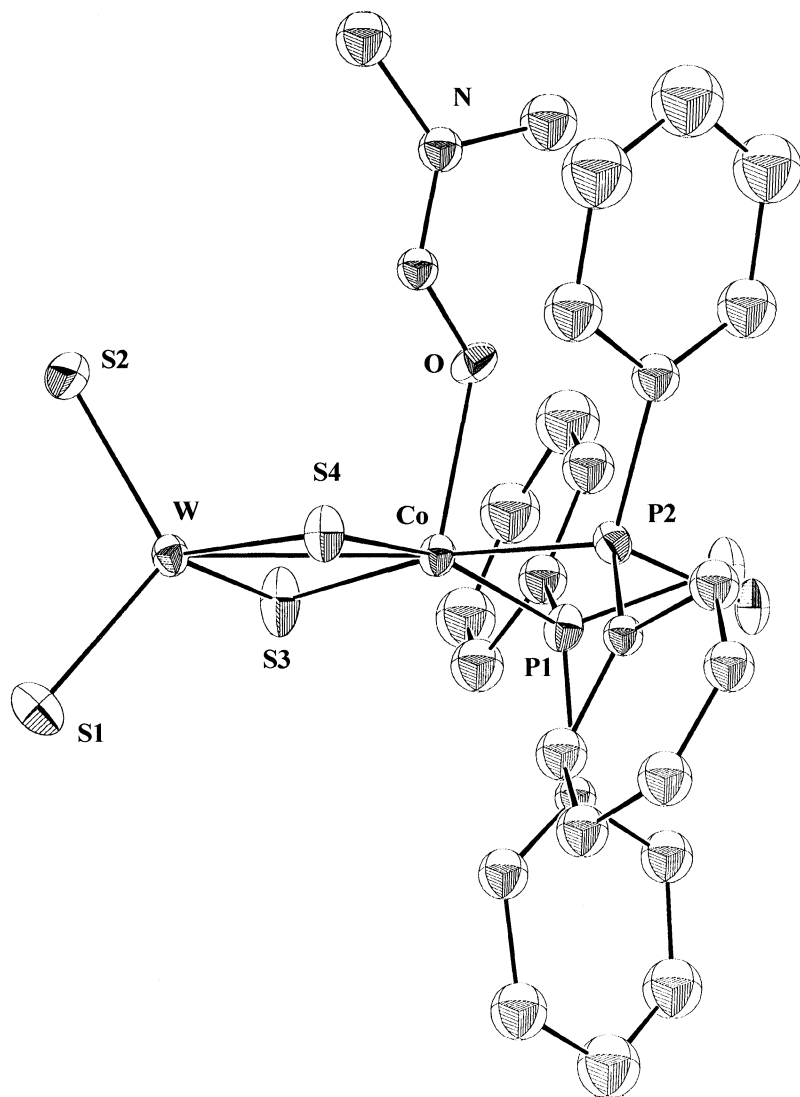
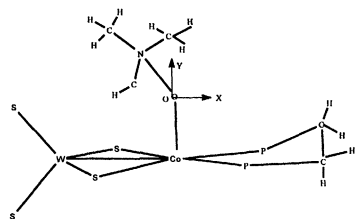
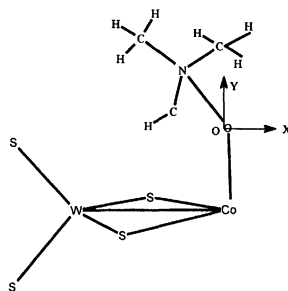


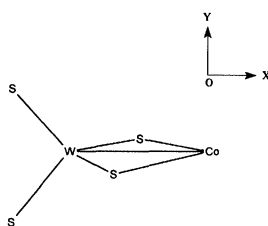
FIGURE 1 The ORTEP drawing of $WS_4Co(dppe)(DMF)$. Selected distances (\AA) and angles ($^\circ$): W—Co 2.817(2), W—S1 2.136(7), W—S2 2.162(5), W—S3 2.226(4), W—S4 2.225(5), Co—O 2.15(1), Co—P1 2.212(3), Co—P2 2.236(5); S1—W—S2 109.79(2), S1—W—S3 112.0(2), S1—W—S4 110.8(2), S2—W—S3 111.0(3), S2—W—S4 110.2(2), S3—W—S4 103.0(2), S3—Co—S4 100.7(2), P1—Co—P2 85.8(2).



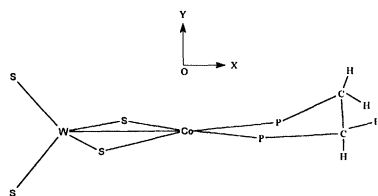
(a)



(b)



(c)



(d)

FIGURE 2 Molecular configurations of model I to model IV: (a) Model I, $[WS_4Co(dppe')(DMF)]$; (b) Model II, $[WS_4Co(DMF)]$; (c) Model III, $[WS_4Co]$; (d) Model IV, $[WS_4Co(dppe')]$.

N, C, P, H atoms in the modeling clusters are 6-31G(d,p) while the basis sets used for W and Co atoms are ECP lanl2dz [14]. The structural data come from crystal structure measurements. There are 305, 221, 116 and 200 basis functions for model I to model IV, respectively. All calculations are performed with Gaussian 98 package [15].

4. RESULTS AND DISCUSSION

The crystal data for [WS₄Co(dppe)(DMF)] are as follows: space group monoclinic P2₁, $a = 10.424(3) \text{ \AA}$, $b = 16.931(3) \text{ \AA}$, $c = 10.592(4) \text{ \AA}$, $\gamma = 119.43(3)^\circ$, $V = 1628.2 \text{ \AA}^3$, $Z = 2$, $f_w = 842.5$, $\rho = 1.72 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 44.8 \text{ cm}^{-1}$ and $T = 296 \text{ K}$. Figure 1 shows the ORTEP drawing of the molecular cluster structure. The tungsten atom is coordinated by two μ_2 -S atoms and two terminal S atoms with slightly distorted tetrahedral geometry. The Co atom is located at the centre of a pyramid coordination geometry with the O atom of DMF, two P atoms of dppe ligand and two μ_2 -S atoms as the vertexes of the pyramid. The Co—O bond length is $2.15(1) \text{ \AA}$, and those of Co—P1 and Co—P2 are $2.212(3) \text{ \AA}$ and $2.236(5) \text{ \AA}$, respectively. W—Co metal–metal bond length is $2.817(2) \text{ \AA}$. As expected, μ_2 -S atoms form longer bonds to W [W-S3 $2.226(4) \text{ \AA}$, W-S4 $2.225(5) \text{ \AA}$] than the terminal sulfur atoms do [W-S1 $2.136(7) \text{ \AA}$, W-S2 $2.162(5) \text{ \AA}$].

As all the four models have C₁ point group symmetries, the static first hyperpolarizabilities have 27 non-zero components. The spatially averaged $\beta_{av,i}$ values ($i = x, y, z$) are defined as [16],

$$\beta_{av,i} = \frac{1}{3} \sum_j (\beta_{ijj} + \beta_{jji} + \beta_{jjj})$$

Table I lists the calculated results as well as those of organic ligands DMF and dppe' which are calculated at the same theoretical level.

Model I has the largest second-order polarizabilities $\beta_{av,i}$ by about four orders of magnitude larger than those of typical organic NLO molecules (like a urea molecule, $\beta_{av} \sim 10^{-31} \text{ esu}$ [8]). The direction x is almost parallel to the metal–metal bond directing from W to Co atom

TABLE I Calculated second-order polarizabilities (10^{-29} esu) of Model I to Model IV as well as those of two organic ligands

	Model I	Model II	Model III	Model IV	dppe'	DMF
$\beta_{av,x}$	407.5	-0.02	9.5	0.8	-0.21	-0.04
$\beta_{av,y}$	40.5	2.9	1.8	-1.7	0.02	0.04
$\beta_{av,z}$	285.5	-3.9	2.8	-5.5	-0.1	0.05
β_{av}	244.5	-0.34	4.7	-2.1	-0.28	0.05

(see Fig. 2). The large value of $\beta_{av,x}(I)$ indicates the great charge transfer (CT) from W ion to Co ion. This metal-to-metal CT effect originally contributes to the NLO polarizabilities. The z direction is almost perpendicular to the W—Co bond and is almost parallel with the $[WS_2Co]$ four-member-ring plane. Unexpectedly, the first hyperpolarizability along this direction $\beta_{av,z}$ is quite large. Large CT usually does not occur in the vertical direction to the π conjugated plane in organic NLO molecules. The calculated results of model I show that it is also true for this system because $\beta_{av,y}$ is much smaller than $\beta_{av,x}$ and $\beta_{av,z}$ indicating similar π conjugated characteristics in this metal cluster molecular block.

Model III is the core structure of this binuclear cluster. It has a strong nonlinear-optically polarizability, especially in x direction (metal–metal binding direction). $\beta_{av,x}(III)$ is about 9×10^{-29} esu., which is nearly three orders of magnitude higher than that of a urea molecule. Model II has the smallest β_{av} among the four models. This indicates that DMF is not a “good” ligand for large NLO response. $\beta_{av}(IV)$ is also very small. However, the average hyperpolarization along z direction is relatively strong. This shows the ability of the dppe ligand to pull the electric charges along the z direction.

It is clear that neither of the two organic ligands (dppe' or DMF) is able to improve the hyperpolarizability of the core structure. Unexpectedly, the joint effects of DMF and dppe' ligands result in sufficiently enhanced NLO polarizabilities (model I). The fact indicate it is sure an effective means to improve the NLO effects by suitably choosing the organic (or inorganic) ligands, while their joint effects (if there are two or more ligands) should be seriously considered. As this crystalline compound is in non-central symmetry, the macroscopic NLO process will display second harmonic generation (SHG) effect. A rough estimation is made by using gas-oriented model approximation [17]. The largest NLO coefficient component of the crystal (d_{12})

obtained to be approximately 400 pm/V, which is close to that of semiconductor tellurium (Te) which has the largest NLO coefficients ever known (Te, $d_{11} = 570$ pm/V, 28 μm [18]).

In summary, a novel hetero-metallic binuclear cluster [WS₄Co(dp-pe)(DMF)] has been synthesized and characterized. The static first-order hyperpolarizabilities of the building blocks of this compound have been studied by means of *ab initio* CPHF calculations. The contributions of each building block to the NLO polarization are elucidated and the origin of the NLO response are discussed. The CT between tungsten ion and cobalt ion makes substantial contribution to the NLO polarization, while the joint effect of the organic ligands also greatly enhances the CT effect. It should be pointed out that our theoretical studies on these modeling clusters do not take the further theoretical treatments into consideration, such as electron correlation effect and relativistic effect. The calculated data thus might not be quantitatively accurate. However, as the four models are studied at the same theoretical level and are placed in the same coordinate system, the results are sure to reveal the relative contributions of each building block of the molecular cluster to NLO polarization. The result might help us to elucidate the origin of NLO effects in the metal cluster compounds. The further studies with more accurate theoretical methods are already in proceeding.

Acknowledgements

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