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TDDFT Studies of Electronic Structure and First Hyperpolarizability of Tetra-nuclear Cubane-like Transition Metal Clusters

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Abstract: The TDDFT method is first applied in a series of tetra-nuclear transition metal clusters studies for nonlinear optical properties. The results indicate that the charge transfer inside the metal core [MCu_3X_4] (M=W, Mo; X=S, O, Cl, Se, Br) makes contribution to the optical nonlinearity. It is possible to enhance the hyperpolarizability by substituting the ligands of the clusters.

Keywords: Nonlinear optical properties, transition metal clusters, TD- DFT method.

A series of tri-nuclear transition metal clusters with incomplete cubane-like configurations have been studied by TDDFT method. The calculations show that they have enormously large second-order polarizabilities (β) and are potential nonlinear optical materials for infrared double frequency conversion[1]. In this paper some tetra-nuclear transition metal clusters with cubane-like configurations, $MCu_3X_4(PPh_3)_3$ (M=W, Mo; X= S, O, Cl, Se, Br), were studied by TDDFT method for a reference. The structure-NLO property relationship was discussed for future NLO material design.

The structures of model clusters of the study were shown in **Figure 1**. All the structural parameters were taken from the X-ray structural data[2]. The PPh_3 ligands were simplified by simpler (PH_3) ligands to enhance the computational efficiency. The first-order hyperpolarizabilities, β, of these molecular clusters were calculated by TDDFT method at GGA/LB94 level[3]. The electronic structures were calculated at GGA/BLYP level[4]. The basis sets for transition metal atoms and nonmetals were triple-ζ STO basis sets and double-ζ STO basis sets, respectively. The cores (N, O, C: 1s; S, Cl, P: 2p; W: 4d; Cu: 3p; Mo, Se, Br: 3d) were kept frozen. The Foster-Boys[5] scheme has been applied to form the localized molecular orbital (LMOs). All calculations were performed by the ADF 2000 package[6].

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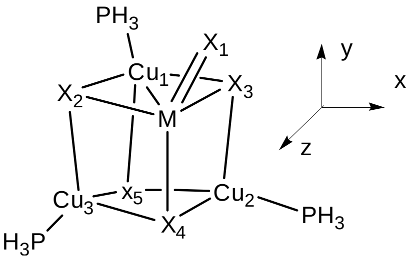
Figure 1 Molecule structures and orientation of cluster **1–4**



1: M=W, X1=X2=X3=X4=S, X5=Cl **2**: M=Mo, X1=O, X2=X3=X4=S, X5=Cl
3: M=Mo, X1=X2=X3=X4=X5=Se **4**: M=Mo, X1=O, X2=X3=X4=S, X5=Br

The Mulliken charge density distribution of cluster **1**, $WCu_3S_4Cl(PH_3)_3$, is shown in **Figure 2**. The charge transfer (CT) occurs in two ways: (i) inside the metal core from Cu, S, Cl atoms to W atom; (ii) from metal core to the ligands $(PH_3)_3$ (MLCT). Considering the μ–bond effect, the first way of CT is dominate, which means the metal-to-metal CT (MMCT) in this type of transition metal cluster contributes to the optical nonlinearity.

Figure 2 The Mulliken charge distribution of cluster **1**

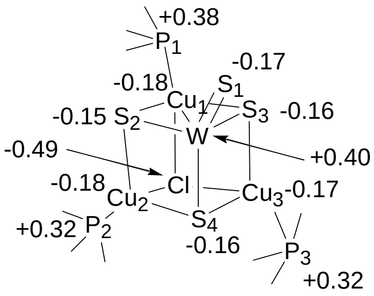


Table 1 listed the composition percentages of the frontier orbitals of cluster **1**. We found that the HOMO and HOMO-1 are mainly consisted of the orbitals of Cu, S and Cl atoms, while those of P atoms only contribute a little (2.04% of HOMO). The orbitals of W and μ-S atoms dominated the LUMO and LUMO+1 orbitals. Thus we found again that the dominant CT inside the metal core from the bottom of Cu, S_4 and Cl to the top containing W.

Table 1 Calculated percent population of frontier molecular orbitals of cluster **1**

HOMO-1			HOMO			LUMO			LUMO+1		
ε (eV.)	-4.674		ε (eV.)	-4.645		ε (eV.)	-2.168		ε (eV.)	-2.150	
Cu1	3d	25.40	Cu1	3d	23.10	W	5d	47.13	W	5d	47.70
Cu2	3d	5.40		4p	1.20	S2	3p	17.40	S2	3p	11.90
Cu3	3d	4.25	Cu3	3d	9.24	S3	3p	11.90	S4	3p	7.60
S3	3p	20.30	Cu2	3d	2.30	S8	3p	11.21	S3	3p	7.20
S1	3p	8.20	Cl	3p	16.60	S1	3p	9.50	S1	3p	6.14
S2	3p	5.90	S2	3p	13.80	Cu	3d	5.03	Cu2	3d	3.75
S4	3p	3.91	S3	3p	7.80				Cu1	3d	1.38
Cl	3p	15.00	S4	3p	7.40						
			S1	3p	7.30						
			P3	3p	2.04						

Table 2 shows the calculated β values and dipole moment of cluster **1–4**. Due to the symmetry of the cubane-like core structure, the cluster models have small β values comparing to those of the clusters with incomplete cubane-like structures. The largest β component is in z direction, $\beta_{av,z}$, because of the relatively poor structural symmetry of the metal core in this direction. The order of dipole moment is opposite to the order of β value. Compare cluster **1** to cluster **2**, the dipole increasing from 7.3 to 8.9 Debye while the β value is decreased from 4.1 to 1.2×10^{-30}esu. With the atom radius increases, the electronegativity decreases and the capability to form conjugation increases in the increase of the corresponding β values. This trend is different from the organic system, in which the β values depend on the ability of “push-pull” electrons.

Table 2 The calculated β (unit: 10^{-30} esu) and dipole moment μ (unit: Debye)of cluster **1-4**.

	1	**2**	**3**	**4**
$\beta_{av,x}$	0.2	0.4	0.2	0.7
$\beta_{av,y}$	2.4	0.8	0.3	1.3
$\beta_{av,z}$	3.4	0.8	2.1	3.2
β_{tot}	4.1	1.2	2.1	3.5
μ	7.3	8.6	6.5	6.2

In summary, the theoretical studies revealed that the CT inside the metal core of these series of cubane-like tetra-nuclear metal clusters contributes to the NLO property. The small first-order hyperpolarizabilities are due to their symmetric structures. The enhanced NLO property of this type of clusters could be obtained by substituting the ligands to result in the asymmetric cubane-like configurations.

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