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INFLUENCE OF *d–p* π-CONJUGATE INTERACTION UPON ELECTRONIC SPECTRA IN SOME CLUSTER COMPOUNDS

CHENG WEN-DAN,* GUO GUO-CONG, HUANG JIN-SHUN
and LU JIA-XI

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,
State key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China

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Abstract—The UV–vis electronic absorption spectra of the clusters $Mo_2S_4(dtp)_2$ and $Mo_3S_4(dtp)_4{\cdot}Py$ have been observed, and the electronic excitation energies have been calculated using the INDO/S-CI method. Comparing the calculated values with the observed results, the absorption bands have been assigned. The influence of *d–p* π-conjugate interaction strength upon the electronic absorption spectrum is discussed in the clusters $Mo_2S_4(dtp)_2$ (**1**), $Mo_3S_4(dtp)_4{\cdot}Py$ (**2**), $Mo_3O_4(H_2O)_9{}^{4+}$ (**3**) and $Mo_3S_4(H_2O)_9{}^{4+}$ (**4**) [dtp = $S_2P(OC_2H_5)_2$, Py = pyridine]. It has been found that the absorption bands of clusters **2** and **4**, with larger *d–p* π-conjugate interaction over rings, causes a red-shift compared with those of clusters **1** and **3**, with a smaller *d–p* π-conjugate interaction.

The inorganic and organometallic chemistry of transition metal cluster compounds, with oxygen- and sulphur-containing ligands, has experienced an exciting and expansive development in recent years, with a clear tendency of further significant growth. In particular, a number of cluster compounds of early transition metals with π-donor ligands such as O^{2-} and S^{2-} have been prepared and characterized.[1–3] These cluster compounds do not contain the maximum number of ligand atoms commensurate with the valence orbitals of metal atoms, except the orbitals forming M—M bonds, and they are called unsaturated cluster compounds. Although the electronic structures and bonding properties have been considered,[4–7] less attention has been paid to a detailed investigation of spectroscopic properties in the cluster compounds. In this study, the spectroscopic properties on low-lying states of the clusters $Mo_2S_4(dtp)_2$ (**1**), $Mo_3S_4(dtp)_4{\cdot}Py$ (**2**), $Mo_3O_4(H_2O)_9{}^{4+}$ (**3**) and $Mo_3S_4(H_2O)_9{}^{4+}$ (**4**) [dtp = $S_2P(OC_2H_5)_2$, Py = pyridine] are discussed and the observed UV–vis electronic spectra are interpreted with the calculated results of the intermediate neglect of differential overlap model including configuration interaction (INDO/S-CI). Moreover, an influence of *d–p* π-conjugate interaction strength upon the electronic absorption spectra is emphasized, and a red-shift in the absorption is explained according to both the theoretical and experimental results.

The INDO model has proved to be a useful tool in calculating ground state properties of various molecules, such as organic compounds[8] and transition metal compounds[9] in particular, and its spectroscopic modification INDO/S has been applied successfully to the spectroscopy of a variety of transition metal compounds.[10,11] A rather satisfactory representation of electronic spectra in a larger molecular system, requiring only a moderate computational effort,[12] has been obtained using the INDO/S-CI model, based on a self-consistent field molecular orbital calculation followed by a single excited configuration interaction (CIS) treatment. Therefore, the INDO/S-CI method provides a procedure for investigating the electronic spectra of

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* Author to whom correspondence should be addressed.

cluster compounds, and its results of calculation indeed reproduce the known spectra of these clusters.

EXPERIMENTAL AND CALCULATION PROCEDURES

The measurement of UV–vis spectra

The UV–vis electronic absorption spectra of clusters **1** and **2** at the concentration 1.38×10^{-4} M in $CH_3CO_2C_2H_5$ solutions have been obtained using a UV-300 Shimadzu recording spectrophotometer, and are shown in Fig. 1. The electronic spectral parameters are listed in Table 1.

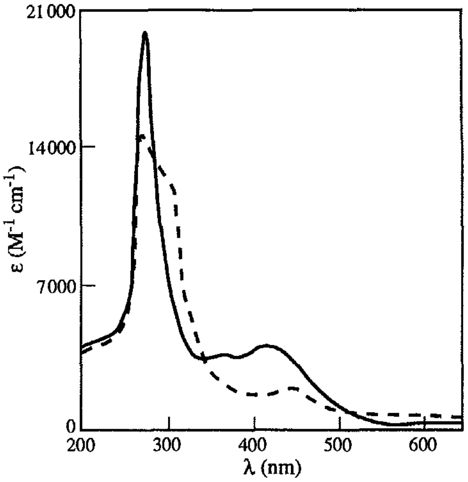

Fig. 1.

Computational procedures

The calculations are based on the INDO/S-CI model developed by Zerner *et al.*[9,13,14] The molybdenum atomic parameters β and ionization energies which are used to calculate the core integral $U_{\mu\mu}$ are taken from account,[14] and the other atomic parameters come from the ZINDO program in the calculations. The one-centre two-electron integrals $\gamma_{\mu\mu}$ are chosen from the Pariser approximation,[15] $\gamma_{\mu\mu} = F^0(\mu\mu) = \mathrm{IP}_\mu - \mathrm{EA}_\mu$, and the two-centre two-electron integrals are calculated using the Mataga–Nishimoto formula,[16] $\gamma_{\mu\nu} = 1.2/[R_{AB}+2.4/(\gamma_{\mu\mu}+\gamma_{\nu\nu})]$, in the spectroscopic version of series due to the fact that the ionization potential of the neutral atom with the two configurations, $d^{n-1}s(d^{n-1}p)$ and $d^{n-2}s^2(d^{n-2}sp)$, are related to the one-centre two-electron integrals γ.[13] The derived values are 5.57, 6.38 and 9.25 eV for $\gamma_{5s5s} = \gamma_{5p5p}$, $\gamma_{5s4d} = \gamma_{5s4p}$ and γ_{4d4d}, respectively. The other atomic parameters $\gamma_{\mu\mu}$ and the atomic orbital exponents ζ are taken from the ZINDO program in the calculations.

The molecular orbital calculations are performed by the restricted Hartree–Fock INDO method. The ground state, which is obtained from the calculated results of a self-consistent field (SCF), is taken as the reference state in the CI. Only single substituted determinants relative to the ground state configurations are considered and the determinant wavefunctions can be expressed in

$$\Phi_{CIS} = a_0\Phi + \Sigma\Sigma a_{i->b}\Phi_{i->b}.$$

Here, the summation indicator, i, b, take values of

Table 1. Electronic spectral data for $Mo_2S_4(dtp)_2$ and $Mo_3S_4(dtp)_4$

Model	Wavelength (nm)	Intensity (M^{-1} cm^{-1})	Contributions (%)	Assignment
$Mo_2S_4(dtp)_2$	λ_1 calc. 243		56 [80(4S) → 76(Mo_2)]	(4S) → (Mo_2)
	obs. 258	14,891		
	λ_2 calc. 323		91 [66(Mo_2) → (64(Mo_2) + 36(4S)]	$(d) \to (d\text{–}p)^*$
	obs. 285(sh)	12,609		
	λ_3 calc. 397		66 [66(Mo_2) → 70(Mo_2)]	$(d) \to (d)^*$
	obs. 440	1957		
$Mo_3S_4(dtp)_4$	λ_1 calc. 253		72 [75(4S) → 98(Mo_3)]	(4S) → (Mo_3)
	obs. 261	20,652		
	λ_2 calc. 342		68 [66(Mo_3) → 75(Mo_3) + 25(4S))]	$(d) \to (d\text{–}p)^*$
	obs. 350	3376		
	λ_3 calc. 436		49 [66(Mo_3) → (60(Mo_3) + 40(4S))]	$(d) \to (d\text{–}p)^*$
	obs. 416	4130		
	λ_4 calc. 591		68 [66(Mo_3) → 88(Mo_3)]	$(d) \to (d)^*$
	obs. 602[a]	351		

[a] Data from ref. 24.

one to 12 in the present studies. This means that the electron is promoted from the twelfth highest occupied orbitals to the twelfth lowest unoccupied orbitals in the reference state corresponding to the Hartree–Fock INDO solution. The orbitals which involve the electron transfer mostly have metal *d*- and ligand *p*-orbital character. The coefficients, *a*, are varied to minimize the expected value of the energy, leading to the equations

$$\Sigma(H_{ij}-E_k\delta_{ij})a_{ij} = 0, j = 0,1,2,\ldots.$$

Here, the H_{ij} are configurational matrix elements and E_k are energy elements. The excited states correspond to the configuration interaction wavefunctions Φ_{CIS} with higher energy roots E_k ($k > 0$), and the ground state and all excited states have the same spin symmetry (multiplicity for one). The energy difference between excited state and ground state is defined as the electron transition energy. The oscillator strength is evaluated with the dipole length operator, maintaining all one-centre charge and polarization terms in the CI calculations. Higher order correlations are neglected since their influence is taken into account through the choice of semi-empirical two-electron integrals *r* and empirical resonance *β*. The low-lying excited states with leading configuration containing most contributions from metal *d*- and bridging ligand *p*-orbital character are chosen to investigate the UV–vis electronic spectroscopic properties.

The calculations of clusters **1** and **2** are carried out in the core models $Mo_2S_4^{2+}$ and $Mo_3S_4^{4+}$, and the calculations in models are used with the same configurations as in clusters **1** and **2**,[17,18] respectively. All of the geometrical parameters are taken from the crystal structure data.[17–20] Simplified drawings of clusters **1**–**4** are shown in Fig. 2.

RESULTS AND DISCUSSION

These four cluster compounds will be divided into two groups in the following discussion. One consists of clusters **1** and **2**, in which the ligand dtp symbolizes $S_2P(OC_2H_5)_2$, and this group has different sized [Mo_2S_2] and [Mo_3S_3] rings; the other group contains clusters **3** and **4**, and has the same size but a different member X in the non-planar ring [Mo_3X_3].

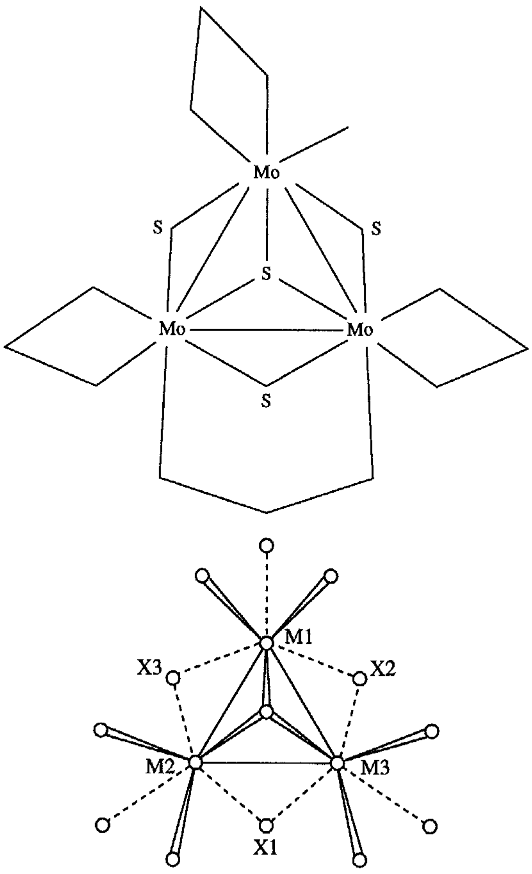

Fig. 2—*continued.*

Clusters $Mo_2S_4(dtp)_2$ (**1**) *and* $Mo_3S_4(dtp)_4 \cdot Py$ (**2**).

From the observed and calculated results, the three types of electronic transfer excitation of clusters **1** and **2** have been assigned and are listed in Table 1. The observed absorption bands at the shor-

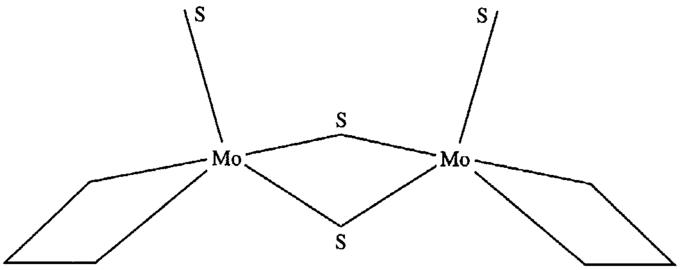

Fig. 2.

test wavelength with the strongest intensity (14,891 and 20,652 $M^{-1}cm^{-1}$) result from transition of a *p*-electron of the sulphur atom to an unoccupied *d*-orbital of the molybdenum atom, i.e. ligand-to-metal electronic transfer excitation (LMCT). As shown in Table 1, the leading configuration contains 80% sulphur and 76% molybdenum atomic orbital character and 75% sulphur and 98% molybdenum atomic orbital character (contributions for 56% and 72%) at wavelength λ_1 for clusters **1** and **2**, respectively. The observed absorption band at the longest wavelength with the weakest intensity is a *d–d* electronic transfer excitation within the molybdenum atomic skeleton [(M—M)CT)]; there are mostly contributions of molybdenum atomic orbital character in the leading configuration of cluster **1** at λ_3 and cluster **2** at λ_4, respectively. The observed absorption between the two bands of shortest and longest wavelength results from the transition of a *d*-electron to an unoccupied *d–p* π-orbital constructed by molybdenum and sulphur atoms [M(M+L)CT]; there is some mixing of molybdenum and sulphur atomic orbitals in the leading configuration. These three assignments are only a general trend, and there is some mixing among the three types of charge transfer due to electron delocalization in clusters **1** and **2**. Generally, charge transfer excitation from a terminal ligand to a metal atom has greater energy, and the influence of the dtp ligand on the spectrum is not considered in low-lying excited states. Hence, it is reasonable to discuss the spectroscopic properties of low-lying excited states in terms of the calculated results for the models $Mo_2S_4^{2+}$ and $Mo_3S_4^{4+}$.

It is found from Fig. 1 that the wavelengths ($\lambda_1 = 258$ nm for cluster **1** and $\lambda_1 = 261$ nm for cluster **2**) of the absorption bands originating from the LMCT excitations do not differ substantially, but the wavelengths ($\lambda_2 = 285$ nm for **1** and $\lambda_2 = 350$ nm for **2**) of the absorption bands for the M(M+L)CT excitations show a sharp difference between clusters **2** and **1**, i.e. the red-shift for λ_2 of cluster **2**. This can be explained as follows. In view of the calculated energy levels using the INDO-MO method, as shown in Fig. 3, the direct Mo—Mo interactions, compared with the interactions between sulphur and molybdenum atoms, are neglected or considered as non-bonding interactions within the puckered rings [Mo_2S_2] and [Mo_3S_3], as shown in Fig. 4. It is found that the energy of the first *d–p* $\pi \rightarrow \pi^*$ typical transition is smaller for cluster **2** than cluster **1** and the number of conjugated double bonds is larger in cluster **2** than cluster **1**. This means that the increasing conjugation in an unsaturated cluster compound shifts the first $\pi \rightarrow \pi^*$ absorption maximum towards longer wavelengths (red shift). This trend is the same as that of aromatic hydrocarbons, i.e. the energy of the first spin-allowed transition maximum decreases as the number of conjugated double bonds increases.

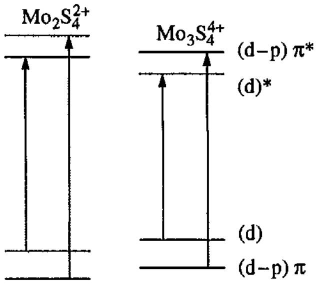

Fig. 3.

Clusters $Mo_3O_4(H_2O)_9^{4+}$ (3) *and* $Mo_3S_4(H_2O)_9^{4+}$ (4)

Clusters **3** and **4** have the same geometrical structure, and both are treated as having C_{3v} symmetry during our calculations. The calculated transition energies and the observed values coming from the literature[21,22] are listed in Table 2. The calculated electronic transition energy from the ground state (A_1) to the excited state ($^1A_2$) is 22,500 cm^{-1} for cluster **3**. The two molecular orbitals, involving electron transfer in the leading configuration of this excited state ($^1A_2$), have about 72% and 82% metal character, respectively. The calculated excited state ($^1A_2$) of cluster **4** is at 17,800 cm^{-1} and there are about 75% and 84% metal orbital character in the two molecular orbitals of the leading configuration, respectively. Comparing the calculated values with the observed ones,[21,22] as shown in Table 2, the lowest observed bands at 19,800 cm^{-1} (longest wavelength $\lambda = 505$ nm) for cluster **3** and 16,600 cm^{-1} ($\lambda = 602$ nm) for cluster **4** have been assigned as charge transfer between a delocalized metal-based bonding orbital to a delocalized metal-based

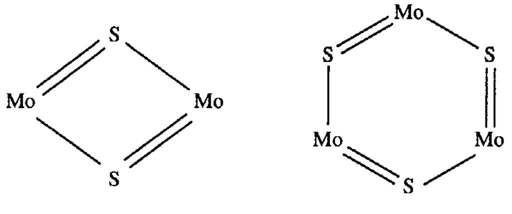

Fig. 4.

Table 2. Electronic spectral data (units of 1000 cm^{-1}) for $Mo_3X_4(H_2O)_9^{4+}$

	X = O		X = S		
	obs. (ε, M^{-1} cm^{-1})	calc.	obs. (ε, M^{-1} cm^{-1})	calc.	Assignment
I	19.8 (189)	22.5	16.6 (351)	17.8	$M(4d) \rightarrow M(4d)$
II			20.0 sh (290)	20.5	
III	33.0 (795)	32.8	27.2 (5190)	28.5	$M(4d) \rightarrow [M(4d),X(p)]$

antibonding orbital (M—M bonded charge transfer). The calculated transition energies from the ground state to the excited state $(^{2'}A_2)$ are 32,800 and 28,500 cm^{-1} for clusters **3** and **4**, respectively. The excited states $(^{2'}A_2)$ of these two clusters are formed mostly from transitions between metal-based orbitals, but also contain some metal-to-ligand (oxygen or sulphur atom) charge transfer (MLCT) in terms of analyses of the calculated results. Therefore, compared to the calculated transition energies of the excited states $(^{2'}A_2)$ of clusters **3** and **4**, separately, the absorption bands observed at 33,000 cm^{-1} ($\lambda = 303$ nm) for cluster **3** and 27,200 cm^{-1} ($\lambda = 368$ nm) for cluster **4** have been assigned as charge transfer between the metal-based orbitals, but involve a small amount of MLCT, especially in cluster **4**. This mixing of the two types of charge transfer can be used to explain a red-shift in the absorption, comparing cluster **4** with cluster **3**. It is not difficult to understand this red-shift from the relationship between the *d–p* π-conjugate interaction and atomic electronegatitvity. According to Pauling, electronegativity represents the ability of an atom to attract electrons in a molecule. In other words, the more electronegative an atom is, the less ability it will have to donate electrons to another atom in the molecule. Sulphur's electronegativity (2.58) is less than that of oxygen (3.44) and the ability to donate electrons is stronger for sulphur than oxygen, hence the electronic delocalization for the sulphur atom in Mo_3S_3 is larger than it is at the oxygen atom in Mo_3O_3. This evidence can also be proved by the calculated results of ref. 23. The orbitals are more mixed and the molecular orbital energies are less well separated for cluster **4**, i.e. the two types of charge transfer (M—M bonded and MLCT) are mixed more in cluster **4** than in cluster **3**. The reason for this is that the ability of the π-lone pair electron donation is larger in the sulphur atom than in the oxygen atom, and the *d–p* π-conjugate interaction is stronger over ring $[Mo_3X_3]$ in cluster **4** than in cluster **3**. As a result, the absorption band of cluster **4** causes a red-shift compared with that of cluster **3**. This red-shift in cluster compounds can naturally be interpreted by virtue of the variation of charge distribution from the population analyses of calculated results.

From the above discussions, we have found that the less electronegative a ligand atom, the stronger the *d–p* π-interaction and the more shift towards red of the absorption band, among cluster compounds with the same transition metal but with a different ligand atom.

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