

Theoretical and Experimental Studies of the Electronic States of Cobalt (II) Stearate and Dimeric Copper (II) Stearate

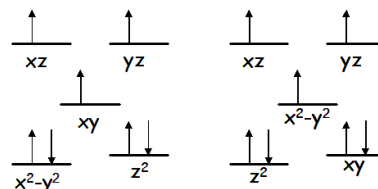
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The electronic states of two metallomesogens were studied by both experimental and computational means. The geometries of cobalt (II) stearate and copper (II) stearate were determined using Density Functional Theory with Gaussian98 software. All calculations utilized the B3LYP functional. To determine the optimal model, several basis sets were tested and the lengths of the carboxylate ligands were varied.

Initial geometry optimizations were performed on cobalt (II) formate using the sto-3g basis set. This calculation yielded a square pyramidal geometry about the cobalt center. However, both the 3-21G* and 6-311G(d,p) basis sets resulted in distorted tetrahedral geometries. Between the 3-21G* and 6-311G(d,p) geometries there were a few discrepancies in bond lengths and bond angles. To best model the complexes, the 6-311G(d,p) basis set was used for subsequent calculations.

Adding carbons to the carboxylate moiety also provided a test of the model's sensitivity to the length of the alkane chain. A geometry optimization for cobalt (II) acetate was successfully calculated using the 6-311G(d,p) basis set and a near-optimized geometry for cobalt (II) propionate was calculated with the 3-21G* basis set. The results suggest that the length of the alkane chain has little effect on the geometry about the metal center.

The best model for cobalt (II) stearate was cobalt (II) acetate, optimized with the 6-311G(d,p) basis set. Using the distorted tetrahedral geometry, excitation calculations were performed with TDDFT and a 6-311G(d,p) basis set. The calculations predict two possible "ground states" very close in energy (See Figure 1) and several electronic excitations that might occur from each "ground state."



The experimental test of these calculations was provided by polarized UV-VIS spectroscopy. The mesogenic properties of cobalt (II) stearate were determined using polarizing microscopy. By interrogating the mesogenic phase with polarized incident light, a UV-VIS spectrum of cobalt (II) stearate was obtained for both parallel (z)- and perpendicular (xy)-polarized excitations. In practice, inducing the mesogenic phase in cobalt (II) stearate proved exceedingly difficult. Enough alignment of the mesophase was observed at 384K, however, to reduce the spectra and identify peaks distinct to each polarization. A comparison of the calculated and observed excitation energies is shown in Table 1 below.

Table 1. Excitation energies for cobalt (II) stearate. Large intensity excitations are shown in bold.

Co(st) ₂ Excitation Energies (cm ⁻¹)		
Polarization	Calculated	Observed
z	9,600	17,000
xy	9,280	16,200
	9,440	17,300
	9,680	18,800
	15,810	(Some peaks
	16,130	near 21,000)

The calculated excitation energies for cobalt (II) stearate are consistently low compared to the observed excitations. This may be due to a recently-discovered limitation of TDDFT. Dreuw et al. have reported that TDDFT fails to accurately predict charge-transfer excitation energies and that conventional TDDFT calculations provide characteristically low excitation energies.¹ This may indicate that cobalt (II) stearate has charge-transfer states that have not been accounted for in this study.

Copper (II) stearate was modeled as dimeric copper (II) formate. Both the geometry optimization and excitation calculations were performed using the 6-311G(d,p) basis set. Calculations were performed for both the singlet and triplet states. The resulting ground state molecular orbital diagram for the complex is shown in Figure 2.

Polarized UV-VIS spectroscopy was also performed on the copper dimer, which was more easily aligned than the cobalt complex at the temperature of study, 411K. The polarizations of the observed peaks were readily assigned. The calculated and observed excitations are shown in Table 2 below.

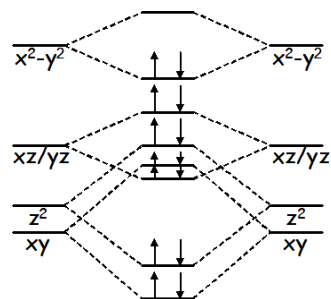


Figure 2. Ground state MO diagram for dimeric $\text{Cu}_2(\text{st})_4$.

Table 2. Excitation energies for dimeric copper (II) stearate. Large intensity excitations are shown in bold. Singlet and triplet excitations are denoted with (s) and (t) respectively.

$\text{Cu}_2(\text{st})_4$ Excitation Energies (cm^{-1})		
Polarization	Calculated	Observed
z	24,350(s)	12,810
		15,560
xy	17,890(t)	11,100
	18,140(t)	14,490
	18,270(s)	22,510
	18,680(s)	24,380
	28,820(t)	

Like the cobalt complex, the calculated excitation energies do not match observations. However, unlike the cobalt complex, the calculated values are consistently high for the copper complex. This cannot be attributed to charge-transfer states. The discrepancy likely indicates that either our model is not representative of the system or that there are additional limitations to TDDFT.

This study has identified several problems in using TDDFT to model two specific metallomesogens. Future work with these complexes may be directed towards improving the model and the computational methods. Dreuw et al. propose using a hybrid of TDDFT with configuration interaction singles (CIS) to obtain more accurate excitation energies.¹ This method could be applied to both complexes to improve the calculations. It would also be of interest to eventually perform geometry optimization calculations on stacked complexes to determine the stacking geometry in the mesogenic phases. Such calculations would better represent the systems as they are studied with polarized UV-VIS spectroscopy.

¹ Dreuw, A., Weisman, J. L., Head-Gordon M. *J. Chem. Phys.* **2003**, *119*, 2943-2346.