Bonding Preferences of C_2X_4-Bridged Bimetallic Transition Metal Complexes of Ti, Cu, and Ag

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The bonding preference of transition metal species of general formula $[(PH_3)_2M]_2(\mu\text{-}C_2X_4)$, where M = Cu or Ag and X = O, S, Se, or Te, and $(Cp_2Ti)_2(\mu\text{-}C_2X_4)$, where X = S or Se, are explored using density functional theory. The relative energies of metal binding to the bridging ligand in a dithiolene-like vs dithiocarbamate-like manner are evaluated. In all cases, the most stable structure corresponds to dithiolene-like (or side−side) bonding, consistent with the vast majority of these compounds which have been experimentally characterized. However, for M = Ag and X = S, Se, or Te, the two isomers are nearly degenerate.

Introduction

Both natural and synthetic oxalates and their sulfur analogues have been well-known for quite some time. As a result, there is a rich body of literature regarding their syntheses, structures, and ligand properties.[1] The discovery of the first superconductor based solely on sulfur-containing units, bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), has led to a renewed interest in the C_2X_4 bridge because of its importance in this new class of "organic metals".[1]

Also of considerable interest are transition metal complexes containing the C_2X_4 moiety, especially those in which the C_2X_4 bridges two metals in a bimetallic complex or polymer.[2,3] Bimetallic complexes bridged by C_2X_4 can, in principle, exist in two different metal−bridge isomeric forms. The metal fragments can bind to the C_2X_4 ligand on the "sides", in a dithiolene-like (side−side) manner, yielding two five-membered rings, or they can bind to the C_2X_4 ligand on the "ends", in a dithiocarbamate-like (end−end) manner, as shown in Figure 1. Until recently, all known thio-oxalate compounds have exhibited exclusively dithiolene-like binding. In 1995, Strauch[2] and co-workers reported the first authentic case of a compound with both dithiocarbamate-like and dithiolene-like metal complexation in the same molecule.

Efforts to understand the factors affecting the isomeric preferences and electronic nature of C_2X_4 complexes bound to different transition metals have been spurred by their potential for electrical conductivity in two- and three-dimensional polymeric networks.[3] Theoretical studies concerning the electronic properties of C_2X_4 ligands bound to titanium metal fragments have been published by Harris et al.[4] at the Fenske−Hall level and Marynick and co-workers[5] at the PRDDO level. In addition, earlier studies by Hoffmann and co-workers[3] probed the relative stabilities of dithiolene-like and dithiocarbamate-like $(ML_2)_2(\mu\text{-}C_2X_4)$ systems at the extended Hückel level. They concluded that the dithiolene-like isomer was more stable due to better metal−bridge overlap for some of the molecular orbitals in this conformation. These findings, along with the unique Strauch structure,[2] have prompted this investigation using modern density functional techniques of the isomeric preferences of C_2X_4-bridged transition metal complexes. In this paper we examine the relative energetics of dithiolene-like and dithiocarbamate-like isomers of $(Cp_2Ti)_2(\mu\text{-}C_2X_4)$ where X = S and Se (Figure 2), and $[(PH_3)_2M]_2(\mu\text{-}C_2X_4)$ where M = Cu and Ag and X = O, S, Se, and Te (Figure 3). We show that, while dithiolene-like bonding is always preferred, some metal/chalcogen combinations are nearly as stable in the dithiocarbamate-like isomer.

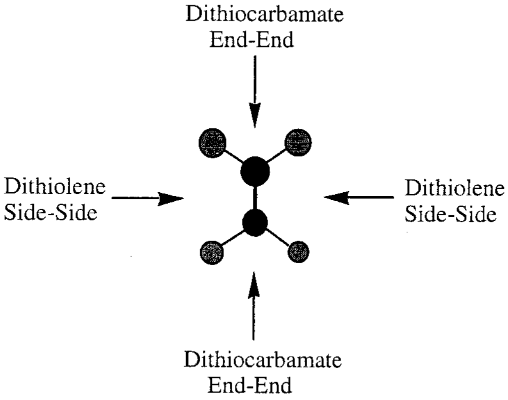

Figure 1. Two possible modes for a metal fragment to bind to the C_2X_4 bridge.

Computational Details

We employed density functional theory (DFT) calculations within the Gaussian 92[6] and Gaussian 94[7] suites of programs. All geometries were optimized, using the Becke3-P86[8] functional and a split-valence polarized[9] basis set for selenium, tellurium, and the transition metals. The 6-31G* basis set was used for all other atoms.

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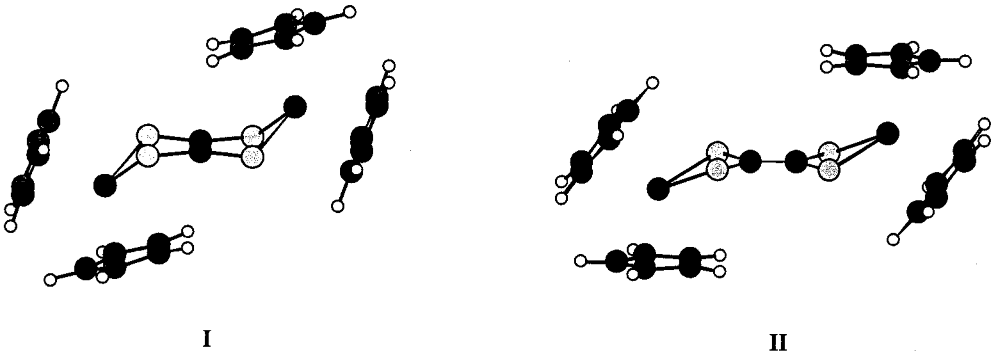

Figure 2. Dithiolene-like (I) and dithiocarbamate-like (II) isomers of $(Cp_2Ti)_2(\mu\text{-}C_2X_4)$.

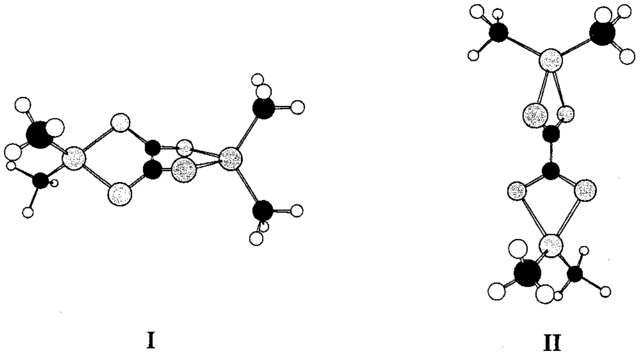

Figure 3. Dithiolene-like (I) and dithiocarbamate-like (II) isomers of $[(PH_3)_2M]_2(\mu\text{-}C_2X_4)$.

Table 1. Relative Energetics[a] of the $[(PH_3)_2M]_2(\mu\text{-}C_2X_4)$ and $(Cp_2Ti)_2(\mu\text{-}C_2X_4)$ Systems[b]

	relative energetics		
	M = Ti	M = Cu	M = Ag
	X = O		
$E_{ssp} - E_{sst}$			
$E_{eep} - E_{ssp}$		20.1	26.7
$E_{eet} - E_{eep}$		−0.1	−15.0
overall Δ*E*		**20.0**	**11.7**
	X = S		
$E_{ssp} - E_{sst}$			1.7
$E_{eep} - E_{ssp}$		11.8	4.1
$E_{eet} - E_{eep}$		−1.7	−5.0
overall Δ*E*	**22.5**	**10.1**	**0.8**
	X = Se		
$E_{ssp} - E_{sst}$		−0.4	2.4
$E_{eep} - E_{ssp}$		10.7	2.8
$E_{eet} - E_{eep}$		−1.5	−4.3
overall Δ*E*	**21.9**	**9.0**	**0.9**
	X = Te		
$E_{ssp} - E_{sst}$		0.7	5.3
$E_{eep} - E_{ssp}$		8.9	1.1
$E_{eet} - E_{eep}$		−2.7	−4.0
overall Δ*E*		**6.9**	**2.6**

[a] In kcal/mol. [b] ssp = side−side (dithiolene-like) bonding, planar geometry; sst = side−side bonding, twisted (minimum energy) conformation; eep = end−end (dithiocarbamate-like) bonding, planar geometry; eet = end−end bonding, twisted conformation.

In an effort to understand the factors influencing the isomeric preference of each system as the chalcogen and the metal were systematically varied, we analyzed the Hartree−Fock frontier molecular orbitals by performing Hartree−Fock single-point calculations at the DFT optimized geometries. We chose to examine the HF molecular orbitals because the Hartree−Fock energetics exhibit the same qualitative trends as the DFT energetics and the HF eigenvalues have a well-defined physical significance.[10]

All of the molecular orbital plots in this investigation were drawn using the program PltOrb found in the source code distribution of GAMESS 95.[11] The structures visible in the plots contain the C_2X_4 bridge and the two metal atoms. The bonds of the phosphine ligands in the copper and silver systems have been eliminated for clarity. The contour lines represented constant values of the wave function with the increment between successive contours set to 0.015 bohr$^{-3/2}$.

The MO analysis was somewhat complicated by the fact that most of the optimized structures contained nonplanar C_2X_4 bridges. Therefore, we simplified the procedure by dividing it into two parts. After geometry optimization, the C_2X_4 bridge was made planar by adjusting the X−C−C−X torsion angle and reoptimizing the structure. This allowed for a direct comparison of the planar dithiolene-like orbitals to planar dithiocarbamate-like orbitals. In this manner, we were able to treat the distortion from the planar to nonplanar structure(s) as a separate issue from the metal−bridge bonding preferences.

Results and Discussion

Energetics. The relative energetics of all systems in this study, along with the energy differences between the various planar and twisted forms, are presented in Table 1. Here, we consider only the overall energy differences between the nonplanar (twisted) side−side and end−end structures ($E_{sst} - E_{eet}$, listed in bold in Table 1). The energetic effects of the internal rotation about the C−C bond in the bridging ligand will be discussed later. As the table indicates, the dithiolene-like isomer is more stable in all of the systems investigated, although in some cases the energy difference is very small. Both titanium systems favor dithiolene-like complexation by over 20 kcal/mol, and the underlying reasons for this preference have been discussed previously.[3]

The results for the $[(PH_3)_2M]_2(\mu\text{-}C_2X_4)$ systems are quite different. The copper/oxygen system exhibits the largest difference in energy between the two isomers (20.0 kcal/mol), and

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Table 2. Mulliken Charges on the Dithiolene-like Bridging Ligands and Metals of Each B3-P86 Optimized Metal−Chalcogen System

bridging ligand	charge on bridge	charge on metal
Cu/O	−1.368	0.344
Cu/S	−0.665	0.005
Cu/Se	−0.752	0.003
Cu/Te	−0.768	0.016
Ag/O	−1.461	0.536
Ag/S	−1.034	0.310
Ag/Se	−1.003	0.284
Ag/Te	−0.916	0.247

Table 3. Mulliken Atomic Overlap Populations for Each Metal−Chalcogen Bond

	dithiolene-like conformation	dithiocarbamate-like conformation
Ti/S	0.706	0.642
Ti/Se	0.713	0.682
Cu/O	0.243	0.206
Cu/S	0.376	0.287
Cu/Se	0.431	0.336
Cu/Te	0.420	0.341
Ag/O	0.148	0.152
Ag/S	0.260 (0.252)[a]	0.229 (0.229)[a]
Ag/Se	0.338	0.273
Ag/Te	0.363	0.322

[a] Values in parentheses are overlap population with equal Ag−S distances for both isomers.

as the size of the chalcogen atoms increases, the energy difference decreases to 6.9 kcal/mol for the copper/tellurium system. The ΔE's for the silver series are much smaller, although the energetic trends are similar. The silver/oxygen species favor the dithiolene-like isomer by 11.7 kcal/mol, and the remaining chalcogen species exhibit much smaller energy differences, from 0.8 to 2.6 kcal/mol.

In order to explore which factors are important in determining the isomeric preferences, it is convenient to treat the $C_2O_4^{2-}$ bridged systems separately. These systems have a strong ionic component in the M−O bonding. This is clearly reflected in the group charges on each of the bridging ligands (Table 2). In addition, the Mulliken overlap populations found in Table 3 are much smaller for the oxygen-bridged systems than for any other chalcogen.

To model the effects of pure ionic bonding, we replaced the metal−phosphine fragments with alkali metals having similar Pauling crystal radii[12] (r_p). Each $Cu(PH_3)_2$ fragment was replaced with Na^+ (r_p (Na^+) = 95 pm and r_p (Cu^+) = 96 pm) and each $Ag(PH_3)_2$ moiety with K^+ (r_p (K^+) = 133 pm and r_p (Ag^+) = 126 pm). The geometries of these alkali metal bridge species were fully optimized using the Becke3-P86 functional. The relative energetics of the dithiolene-like versus the dithiocarbamate-like isomers for both the Na/O (17.6 kcal/mol) and the K/O (14.4 kcal/mol) species closely reproduced the corresponding energetics of the Cu/O (20.0 kcal/mol) and the Ag/O (11.7 kcal/mol) systems. These comparisons, along with the population analysis discussed above, suggest that the energetics of both the Cu/O and the Ag/O systems are dominated by ionic effects, while covalent interactions are clearly important for the other systems.

The preference for dithiolene-like bonding in ionic systems is easy to understand. The dithiolene-like bonding arrangement, in which the chalcogens are rather far apart, allows for shorter metal−chalcogen distances and therefore more favorable electrostatic interactions (see Tables 4 and 5).

Table 4. DFT Optimized Geometries of the $[(PH_3)_2Cu]_2(\mu\text{-}C_2X_4)$ Systems

	optimized parameters[a]			
	X = O	X = S	X = Se	X = Te
Dithiolene-like				
C−C	1.57	1.52	1.48	1.43
C−X	1.26	1.70	1.85	2.09
Cu−X	2.06	2.29	2.41	2.59
Cu−P	2.23	2.26	2.26	2.25
P−H	1.41	1.41	1.41	1.41
C−C−X	117.4	121.3	122.3	122.7
X−C−X	125.3	117.4	115.3	114.6
X−Cu−X	82.8	91.9	93.0	94.3
P−Cu−P	122.4	117.0	114.1	114.9
X−C−C−X	0.2	0.4	17.9	30.5
Dithiocarbamate-like				
C−C	1.52	1.49	1.46	1.42
C−X	1.26	1.69	1.84	2.08
Cu−X	2.14	2.41	2.51	2.67
Cu−P	2.22	2.24	2.24	2.25
P−H	1.41	1.41	1.41	1.41
C−C−X	118.5	119.2	120.1	121.9
X−C−X	123.1	121.6	119.7	116.1
X−Cu−X	62.4	75.6	78.9	82.9
P−Cu−P	136.0	127.1	125.2	124.2
X−C−C−X	77.6	58.0	44.2	34.4

[a] The bond lengths are in angstroms, and the bond angles are in degrees.

Table 5. DFT Optimized Geometries of the $[(PH_3)_2Ag]_2(\mu\text{-}C_2X_4)$ Systems

	optimized parameters[a]			
	X = O	X = S	X = Se	X = Te
Dithiolene-like Conformation				
C−C	1.58	1.52	1.48	1.44
C−X	1.26	1.70	1.84	2.09
Ag−X	2.29	2.58	2.68	2.83
Ag−P	2.54	2.57	2.57	2.58
P−H	1.41	1.41	1.41	1.41
C−C−X	118.0	120.2	121.1	122.7
X−C−X	123.9	119.5	117.7	114.7
X−Ag−X	74.5	84.2	86.6	88.9
P−Ag−P	125.3	115.8	115.5	118.5
X−C−C−X	1.6	51.5	54.0	48.1
Dithiocarbamate-like Conformation				
C−C	1.53	1.49	1.47	1.43
C−X	1.26	1.69	1.84	2.08
Ag−X	2.36	2.67	2.76	2.89
Ag−P	2.54	2.56	2.56	2.56
P−H	1.41	1.41	1.41	1.41
C−C−X	117.5	117.3	117.8	120.2
X−C−X	124.9	125.4	124.3	119.7
X−Ag−X	56.5	68.7	72.2	77.2
P−Ag−P	133.2	128.4	128.7	123.9
X−C−C−X	89.9	89.3	89.7	40.9

[a] The bond lengths are in angstroms, and the bond angles are in degrees.

For the remaining systems, we examined the Mulliken overlap populations[13] between the metals and the chalcogens of the planar bridges. In all cases, the overlap populations for the metal−chalcogen bond in the dithiolene-like isomers are greater than the corresponding values for the dithiocarbamate-like isomer. In order to determine if this trend is simply an artifact of the longer metal−ligand bond distances in the dithiocarbamate-like isomer, we examined both isomers of the Ag/S system

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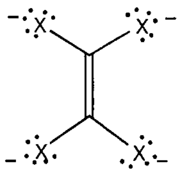
Table 6. DFT Optimized Geometries of the $(Cp_2Ti)_2(\mu\text{-}C_2X_4)$ Systems

	optimized parameters[a]	
	X = S	X = Se
Dithiolene-like Conformation		
C−C	1.40 (1.41)[a]	1.38
C−X	1.75 (1.74)	1.90
Ti−X	2.41 (2.41)	2.53
C−C−X	120.6 (120)	121.3
X−C−X	118.7 (119)	117.5
X−Ti−X	82.9 (82)	82.8
X−C−C−X	0.0 (0)	0.0
α	49.3 (45)	49.4
Dithiocarbamate-like Conformation		
C−C	1.39	1.37
C−X	1.76	1.90
Ti−X	2.42	2.57
C−C−X	122.1	122.8
X−C−X	115.8	114.4
X−Ti−X	76.0	77.1
X−C−C−X	4.4	2.1
α	43.7	38.3

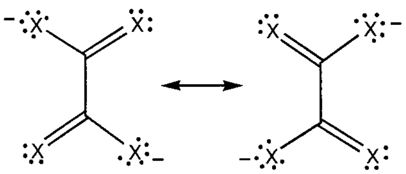
[a] The bond lengths are in angstroms, and the bond angles are in degrees. Experimental values are in parentheses (Harris, H. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1987**, *109*, 4739).

with fixed Ag−S bond lengths of 2.625 Å (an average of the Ag−S bond lengths of the two isomers). Even when the Ag−S bond lengths were equal for the two isomers, the overlap population for the dithiolene-like conformation was still greater than that for the dithiocarbamate-like isomer (Table 3). This suggests, in agreement with earlier theoretical studies,[3] that there is better intrinsic overlap between the metal and the chalcogens in this conformation.

Geometries. There is a fundamental difference between the electronic structures of the Ti systems and the Cu/Ag complexes. The former complexes, with Ti in a +4 oxidation state, lead to a formal +2 charge on each Cp_2Ti fragment and a −4 charge on the bridging ligand. This tetraanionic bridge should have the resonance structure



and the carbon−carbon double bond results in a rigid bridge, with no free rotation about the C−C bond. Conversely, the copper and silver atoms, formally in the +1 oxidation state, result in a $(PH_3)_2M$ fragment with a formal charge of +1 and a −2 charge on the bridging ligand. The appropriate resonance structure



implies a C−C a single bond, and thus free rotation about this bond.

The structures for the titanium systems are shown in Figure 2, and the optimized parameters are found in Table 6. For both the Ti/S and Ti/Se dithiolene-like isomers, the $C_2X_4^{4-}$ bridges were constrained to planarity, based on earlier theoretical and experimental studies[4,5] and the resonance argument discussed above. The corresponding dithiocarbamate-like isomers were not similarly constrained, and the $C_2X_4^{4-}$ bridges were found to be only very slightly nonplanar (4° for $C_2S_4^{4-}$ and 2° for $C_2Se_4^{4-}$). In each of the four isomers, the Cp_2Ti^{2+} metal fragment was located well outside the plane of the bridging ligand, forming a chairlike structure. Both of the dithiolene-like isomers exhibited fold angles, α, of 49° while the dithiocarbamate-like isomers yielded fold angles of 44° ($C_2S_4^{4-}$) and 38° ($C_2Se_4^{4-}$). Detailed theoretical analyses of the chairlike structures found for these systems have been published previously[3−5] and will not be further discussed here.

The structures for the copper and silver systems are shown in Figure 3, and the optimized geometries are found in Tables 4 and 5. The copper and silver systems all have planar MX_2C moieties. In addition, the bridges are generally twisted about the C−C bond, consistent with the resonance structures discussed above.

The carbon−carbon twist angles (X−C−C−X) for the dithiolene-like copper isomers (Table 4) reveals that for the smallest two chalcogens, oxygen and sulfur, the bridges are essentially planar, whereas the selenium and tellurium bridges exhibit rotation about the C−C bond by 18° and 31°, respectively.[14] In the silver systems (Table 5), only the oxygen bridge is planar, while all three remaining bridges rotate by approximately 50°. The dithiocarbamate-like isomers of copper all have rotated bridges, with the copper/oxygen bridge revealing the largest rotation (78°). As the size of the chalcogen increases, the magnitude of the rotation decreases from 58° (sulfur) to 44° (selenium) to 34° (tellurium). This trend is not seen in the silver systems, which all have a twist angle of approximately 90°, except for silver/tellurium, which has a twist angle of 41°.

To understand the origin of the nonplanarity of these systems it is only necessary to examine the HOMOs. In all of the copper/chalcogen and silver/chalcogen systems, the DFT level calculations predict that the b_{2g} molecular orbitals (Figure 4) are the HOMOs.[15] These orbitals consist largely of a linear combination of in-plane p orbitals on the chalcogens, with little contribution from the carbon atoms. There is an out-of-phase interaction among all of the chalcogen atoms on the bridge. Rotation about the C−C bond relieves this unfavorable interaction between the adjacent chalcogens which are bonded to different carbon atoms. On the other hand, a large carbon−carbon twist angle will not allow for the metal to bond to both chalcogens in a dithiolene-like manner, and therefore the calculated twist angles for the dithiolene-like species are in general significantly smaller than those of the dithiocarbamate species. Most of the internal rotation barriers (Table 1) are small (<5 kcal/mol); however, for M = Ag and X = S, Se, or Te, the distortion from nonplanarity is actually more important energetically than the intrinsic energy difference between the two planar forms ($E_{\text{eep}} - E_{\text{ssp}}$).

In all of the systems examined, we also noted a trend in the carbon−carbon bond lengths of the C_2X_4 bridge. For all three metal systems in both the dithiolene-like and the dithiocarbamate-like isomers, as the size of the chalcogen atom increased,

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(14) Note that the optimized geometry for the dithiolene-like Cu/Se system has a twist angle of 18° (Table 2), but the energy of the planar structure is −0.4 kcal/mol *lower* than the optimized twisted structure. This is most likely a numerical artifact, and the true minimum probably lies somewhere between the planar structure and the structure with the 18° twist.

(15) This is also true at the HF level, except for the dithiolene-like Cu/O system, for which the b_{2g} orbital is the second HOMO.

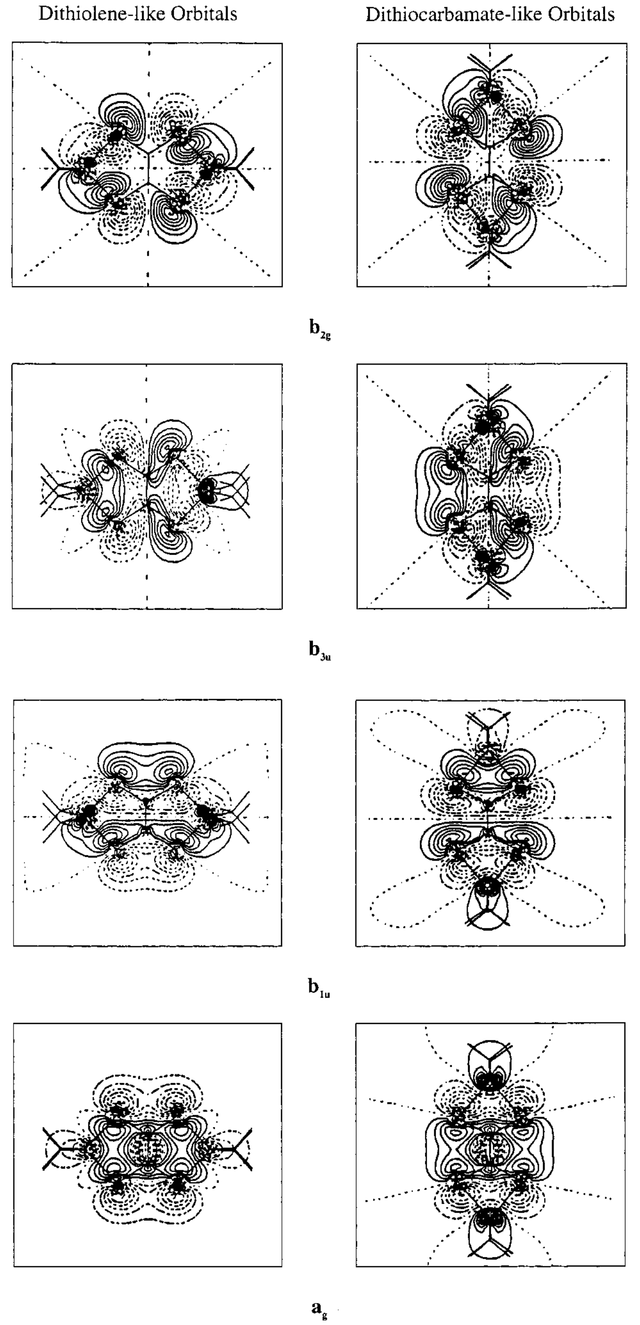

Figure 4. The four highest occupied molecular orbitals for the Cu/S system.

the C—C bond length decreased. For the $(Cp_2Ti)_2(\mu\text{-}C_2X_4)$ systems (Table 6), the C—C bond lengths range from 1.40 to 1.37 Å. These distances are just slightly longer than the typical sp^2—sp^2 C—C double bond length of 1.34 Å,[16] which would be expected in the case of C_2X_4 tetraanion bridges.

The same trend is evidenced in the copper and silver systems (Tables 4 and 5) where the C—C bond distances range from 1.58 to 1.42 Å. A typical sp^2—sp^2 C—C single bond length is 1.46 Å. Thus, all of these bond lengths are generally consistent with the distance of a C—C single bond, supporting the proposal that the C_2X_4 bridge is a dianion for the copper and silver systems; however, the nature of the chalcogen has a significant effect on the calculated C—C distance.

Table 7. Results of Natural Bond Orbital Analysis for the $C_2X_4{}^{2-}$ Bridges

chalcogen (X)	atomic electronegativity[11]	hybridization		C—C bond length (Å)
		C—X bond	C—C bond	
sulfur	2.5	$sp^{3.7}$	$sp^{2.0}$	1.51
selenium	2.4	$sp^{5.5}$	$sp^{1.8}$	1.48
tellurium	2.1	$sp^{7.4}$	$sp^{1.6}$	1.45

This trend can be explained qualitatively in a localized framework by invoking concepts first introduced by Bent. The lone pairs on the chalcogens reside in hybrid orbitals with increased s character. Bent[17] showed in 1961 that as the electronegativity of an atom decreases, the percent s character in the lone pair hybrid orbital(s) increases. This in turn implies that the percent p character in the remaining hybrid orbitals increases. Consequently, as the electronegativity of the chalcogen decreases (i.e., as the size increases), there is increased p character in the carbon—chalcogen bond. This increased p character induces a slight rehybridization in the carbon atom so as to shift s character from the carbon—chalcogen bond to the carbon—carbon bond, shortening the carbon—carbon bond. As a result, as the size of the chalcogen increases, the C—C bond length decreases.

A natural bond orbital[18] analysis was performed on the B3-P86 optimized geometries of the $C_2X_4{}^{2-}$ bridges, without the two metal—phosphine fragments present. From this analysis, we obtained the hybridization of the C—X and C—C bonds for each bridge. The results are found in Table 7. (The $C_2O_4{}^{2-}$ bridge will be omitted from this discussion concerning covalent bonding, since we demonstrated that the oxygen system is dominated by ionic effects.) Table 7 reveals that as the size of the chalcogen increases from sulfur through tellurium, the atomic electronegativites decrease from 2.5 to 2.1. This corresponds to an increase in the p character of the carbon—chalcogen bond from $sp^{3.7}$ for sulfur to $sp^{7.4}$ for tellurium. As is expected, the corresponding carbon—carbon bond experiences an increase in its s character from $sp^{2.0}$ in the sulfur bridge to $sp^{1.6}$ in the tellurium bridge. This increased s character is consistent with the carbon—carbon bond shortening from 1.51 Å in the sulfur system to 1.45 Å in the tellurium case.

Orbital Correlations

We examined in detail four HOMOs involved in metal—ligand bonding for each of the corresponding planar dithiolene-like and planar dithiocarbamate-like covalent metal/chalcogen systems (shown in Figure 4 for the Cu/S system), and we correlated the MOs between the two conformations based on the local symmetry (phase relationships) of the bridging ligand part of each orbital. In all cases, the dithiolene-like orbitals are more stable than their corresponding dithiocarbamate-like orbitals, mimicking the overall energetic trend between the two conformations. The same general trend holds for the other copper and silver systems as well.

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Conclusions

In conclusion, the conformations of the Cu/O and Ag/O systems were found to be dominated by ionic effects, with the dithiolene-like isomer energetically preferred in both cases because the metal can approach the chalcogens more closely. Covalent effects were found to be important for understanding the conformations of the other chalcogen systems. While the dithiolene-like isomer is energetically favored in all cases, as the size of the chalcogen increases and as the size of the metal increases, the energy difference between the two conformations becomes increasingly smaller. For M = Ag and X = S, Se, or Te, the energy differences are sufficiently small that dithiocarbamate-like bonding in these or related systems is a real possibility.

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