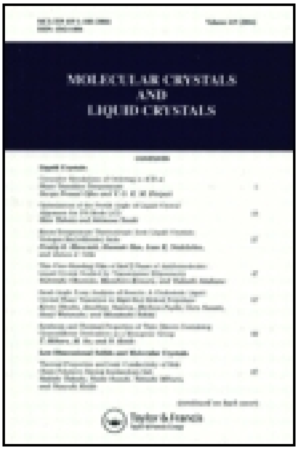

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Photoluminescence and Electronic Structure Studies to Probe Metal-Metal Interactions in Thallium Dicyanoargentate(I): A New Low Dimensional Solid State Class

Mohammad A. Omary [a], Howard H. Patterson [a] & George Shankle [b]

[a] Department of Chemistry, University of Maine, Orono, Maine, USA

[b] Department of Chemistry, Angelo State University, San Angelo, Texas, USA

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PHOTOLUMINESCENCE AND ELECTRONIC STRUCTURE STUDIES TO PROBE METAL-METAL INTERACTIONS IN THALLIUM DICYANOARGENATE (I): A NEW LOW DIMENSIONAL SOLID STATE CLASS

MOHAMMAD A. OMARY, HOWARD H. PATTERSON*
Department of Chemistry, University of Maine, Orono, Maine, USA
AND GEORGE SHANKLE[b]
Department of Chemistry, Angelo State University, San Angelo, Texas, USA

Abstract An experimental-theoretical investigation using low temperature photoluminescence studies and relativistically- parameterized extended Hückel calculations have revealed the importance of metal-metal interactions in the low-dimensional complex $Tl[Ag(CN)_2]$.

INTRODUCTION

Low dimensional compounds of the d^{10} metal ions such as Au(I), Ag(I), and Cu(I) are still the subject of increasing interest of many spectroscopic and electronic investigations. It is believed that the mixing between (n+1)s and (n+1)p orbitals with nd orbitals facilitates metal-metal covalent interaction.[1-3] For example, it has been demonstrated that certain 5d elements such as Pt and Au interact with 6p elements such as Tl and Pb.[4]

In our laboratory, we have been interested in $M[Au(CN)_2]$ and $M[Ag(CN)_2]$ compounds (e.g., with M= K^+, Cs^+, Tl^+, 1/3 Eu^{+3}, 1/3 Dy^{+3}) due to their unusual two-dimensional layered structures. The crystal structure of these compounds consists of layers of $Au(CN)_2^-$ or $Ag(CN)_2^-$ linear ions alternating with layers of M^+ ions. The photoluminescence properties of these compounds have been found to be directly related to the extent of metal-metal covalent interaction. For example, we recently reported that the presence of significant Tl-Au and Au-Au interactions in $Tl[Au(CN)_2]$

shifts both the absorption and luminescence bands to lower energies when compared to those of the isostructural compound $Cs[Au(CN)_2]$.[5]

In this paper, we present the results of an experimental-theoretical investigation of $Tl[Ag(CN)_2]$ to correlate metal-metal interactions with optical properties. While the literature of the d^{10} "coinage" metal ions is rich with investigations of Cu(I) and Au(I) compounds, most of the Ag(I) investigations are still limited to studies on the luminescence of Ag^+ in alkali halides. Unlike gold dicyanides, only a few complexes of $Ag(CN)_2^-$ are characterized structurally. It has been established, however, that silver atoms in the dicyanoargenate (I) groups have a layered arrangement in the Na^+, K^+, Ca^{2+}, and Sr^{2+} salts.[6] Recently, we have studied the photoluminescence of lanthanide ion complexes of dicyanoargenate (I) and dicyanoaurate (I).[7,8] However, the bands corresponding to f-f transitions of lanthanide ion origin totally quench any $Ag(CN)_2^-$ bands as a result of the strong energy transfer in these compounds.

In this paper we report for the first time the photoluminescence spectra as well as molecular orbital calculations for $Tl[Ag(CN)_2]$. To our knowledge, this is the first investigation that shows an example of $Ag(CN)_2^-$ luminescence.

EXPERIMENTAL

$Tl[Ag(CN)_2]$ crystals were grown by mixing a 1:1 mole ratio of TlCN and AgCN followed by slow evaporation of the aqueous solution. TlCN was prepared by passing HCN gas into an ether solution of thallium ethoxide (Aldrich) while AgCN was prepared by adding aqueous $AgNO_3$ to an ammonical solution of KCN (Sigma).

Photoluminescence measurements were performed using a PTI spectrofluorometer equipped with two excitation monochromators and a 75W xenon lamp. Lifetime measurements were done as described elsewhere.[9] For low temperature measurements, liquid helium was used in a Model Lt -3-110 Heli-Tran cryogenic liquid transfer system equipped with a temperature controller. In all spectra, single crystals of high optical quality were selected using a microscope.

The computational method was of the extended Hückel type as described elsewhere.[5] Relativistic parameters were used for the energies and exponents of the atomic orbitals as reported by Pyykkö.[10]

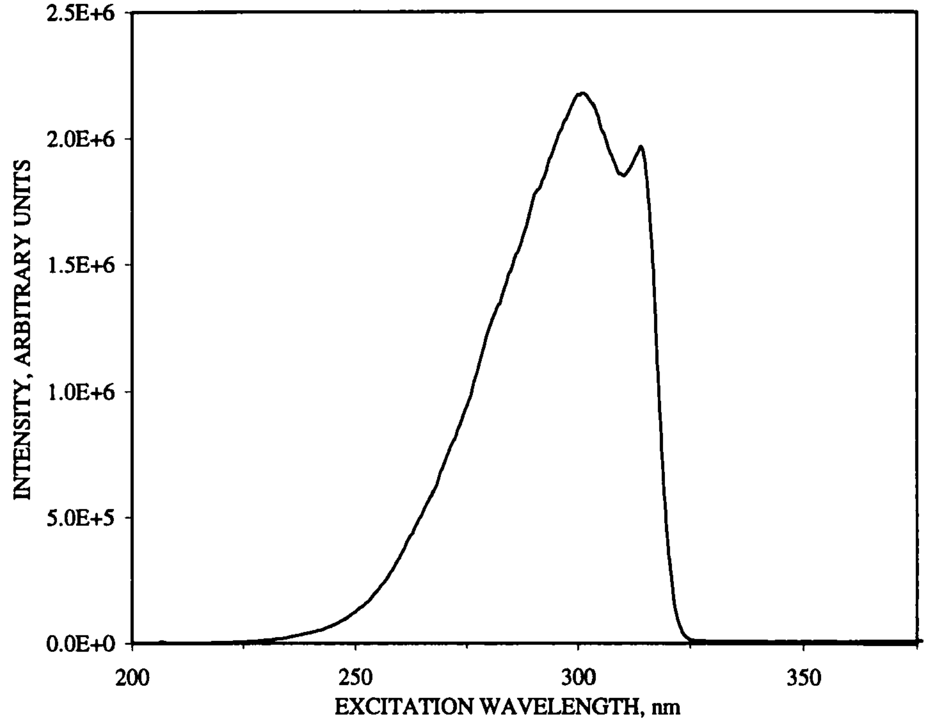

FIGURE 1 Excitation spectrum of $Tl[Ag(CN)_2]$ at 11K. Emission was monitored at 418nm.

RESULTS AND DISCUSSION

Photoluminescence Spectra

Figure 1 shows the excitation spectrum of $Tl[Ag(CN)_2]$ at 11K. The emission was monitored at 418 nm. The spectrum shows two maxima at 301 and 314 nm. Emission spectra using these excitations were scanned. Both these excitations yielded the same emission band at 419 nm. Figure 2 shows the 11K emission spectrum using

301nm excitation.

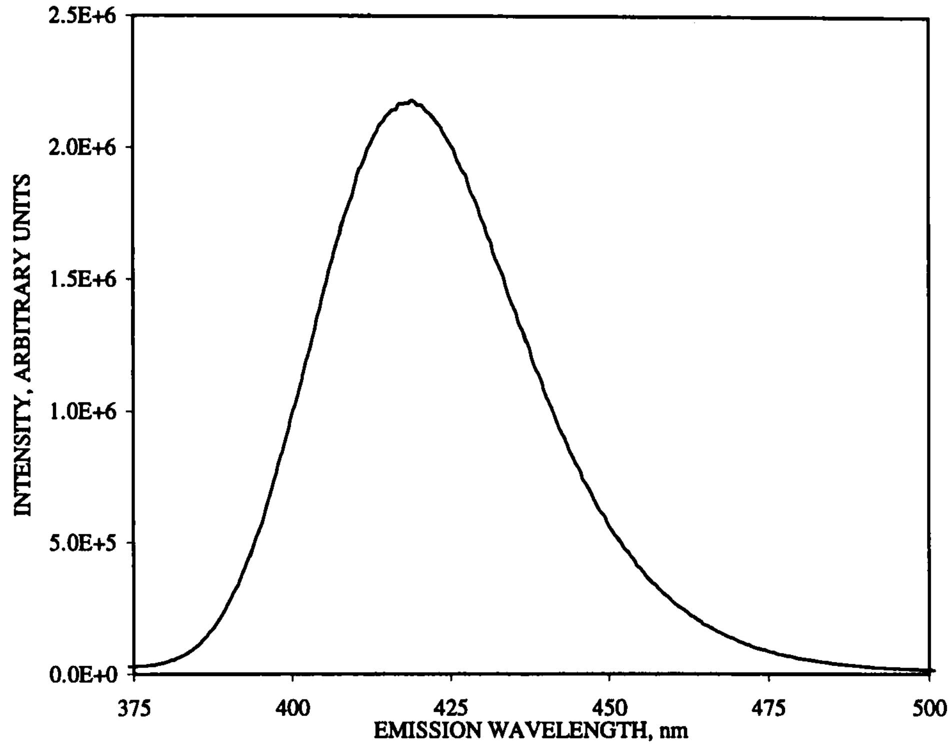

FIGURE 2 Emission spectrum of Tl[Ag(CN)$_2$] at 11K. The excitation wavelength used was 301nm.

Figures 3 shows the emission spectra as a function of temperature using 301nm excitation. The position of the peak slightly shifted to higher energies as the temperature increased. The peak was observed at 419, 418, 416, 414, 411, and 410 nm when the temperature was 11, 28, 48, 76, 127, and 195K, respectively. The total blue shift was, therefore, about 500 cm^{-1}. The spectrum at 195K is not shown in figure 3 due to its very low intensity.

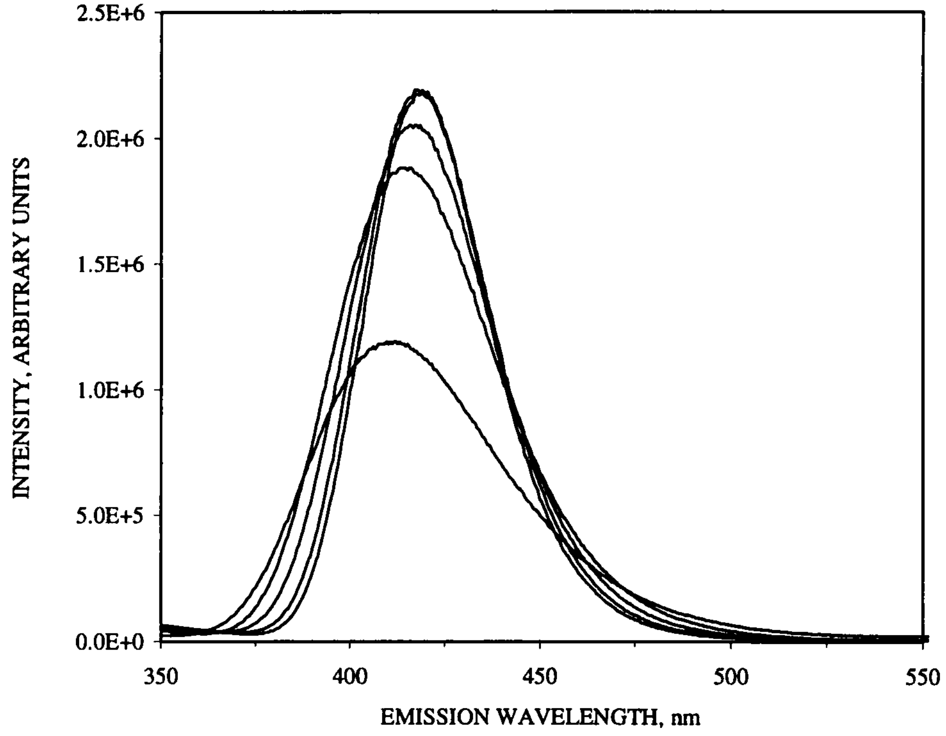

FIGURE 3 Emission spectra of Tl[Ag(CN)$_2$] as a function of temperature using 301nm excitation. The spectra from top to bottom were recorded at 11, 28, 48, 76, and 127K, respectively.

The excitation bands occurred at significantly lower energies than the absorption maximum of 50,700 cm^{-1} (197 nm) for aqueous Ag(CN)$_2^-$ reported by Mason.[11] Our preliminary lifetime measurements at 77K yielded a 1.2 μs value for the emission band of Tl[Ag(CN)$_2$]. Laser excitation at 337 nm was used in the lifetime measurement. Therefore, we assign the luminescence bands of Tl[Ag(CN)$_2$] to originate from a triplet state. This phosphorescence is due to the large spin-orbit coupling expected in heavy metals such as Ag and Tl. This leads to the relaxation of the spin-forbidden transition from the triplet state. It is worthwhile in this context to compare the band energies of Tl[Ag(CN)$_2$] with those of the analogous Tl[Au(CN)$_2$] compound. The gold complex has a lower luminescence energy.[5] This result is consistent with the theoretical prediction that metal-metal interactions in $Tl[Au(CN)_2]$ are more significant than those in $Tl[Ag(CN)_2]$ which results in a smaller gap between the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO (*vide infra*).

The shift to higher luminescence intensity and lower band energy at lower temperatures for $Tl[Ag(CN)_2]$ is a typical trend for layered compounds that exhibit metal-metal interaction. In such compounds, thermal contraction of in-chain or in-plane M-M distances at lower temperatures leads to increased in-chain or in-plane interaction between the molecular units resulting in a smaller frontier energy gap.[12]

Molecular Orbital Calculations

Extended Hückel calculations were used in which parameters corrected for the relativistic effects were employed.[10] Table 1 lists the orbital energies as well as the orbital exponents for the atoms in $Tl[Ag(CN)_2]$. Bond distances were taken as 2.13Å for the Ag-C bond and 1.15Å for the C-N bond as described in the literature for $K[Ag(CN)_2]$.[6e]

A. The $Ag(CN)_2^-$ anion

Calculations on the dicyanoargenate (I) anion have been carried out to establish a reference for the Tl-Ag bonding in $Tl[Ag(CN)_2]$ as well as the Ag-Ag interaction in the $[Ag(CN)_2^-]_2$ dimer.

A linear arrangement was assumed for $Ag(CN)_2^-$ ($D_{\infty h}$ symmetry). The calculation results revealed a HOMO-LUMO gap of 4.82 eV. This value is 0.40 eV higher than that for $Au(CN)_2^-$.[5] The HOMO was a σ orbital that had a 32.7% Ag character (15.5% 5s and 17.2% $4d_{z^2}$). The LUMO, on the other hand, was a π orbital that had mostly (88.5%) a cyanide character. Finally, the calculations yielded an overlap population of 0.264 for the Ag-C bond.

TABLE 1 Relativistic parameters used in the Extended Hückel calculations.[10]

Atom	Orbital	H_{ii} (eV)	Slater Exponent
Ag	5s	-6.453	1.594
	5p	-3.289	1.170
	4d	-13.91	3.248
Tl	6s	-12.22	2.520
	6p	-5.120	1.696
	5d	-22.90	4.010
C	2s	-19.39	1.577
	2p	-11.07	1.434
N	2s	-26.25	1.886
	2p	-13.83	1.728

B. Tl[Ag(CN)$_2$]

Different orientations of Tl$^+$ bonded to Ag(CN)$_2^-$ were studied. The perpendicular arrangement of Tl$^+$ to the C_∞ axis of Ag(CN)$_2^-$ yielded the lowest energy. A C_{2v} symmetry is, therefore, assumed. The Tl-Ag distance was varied and plotted versus the resulting potential energy. Figure 4 shows that a minimum energy was obtained corresponding to a Tl-Ag separation of 3.13 Å. This clearly demonstrates the importance of the Tl-Ag covalent bonding in Tl[Ag(CN)$_2$]. Several other results support this argument. Analysis of the calculation results was carried out for Tl[Ag(CN)$_2$] at 3.13 Å Tl-Ag separation. First, a binding energy of -0.26 eV has resulted. This means that the Tl[Ag(CN)$_2$] species is more stable than the two separate Tl^+ and $Ag(CN)_2^-$ species by 0.26 eV owing to the resulting Tl-Ag covalent interaction.

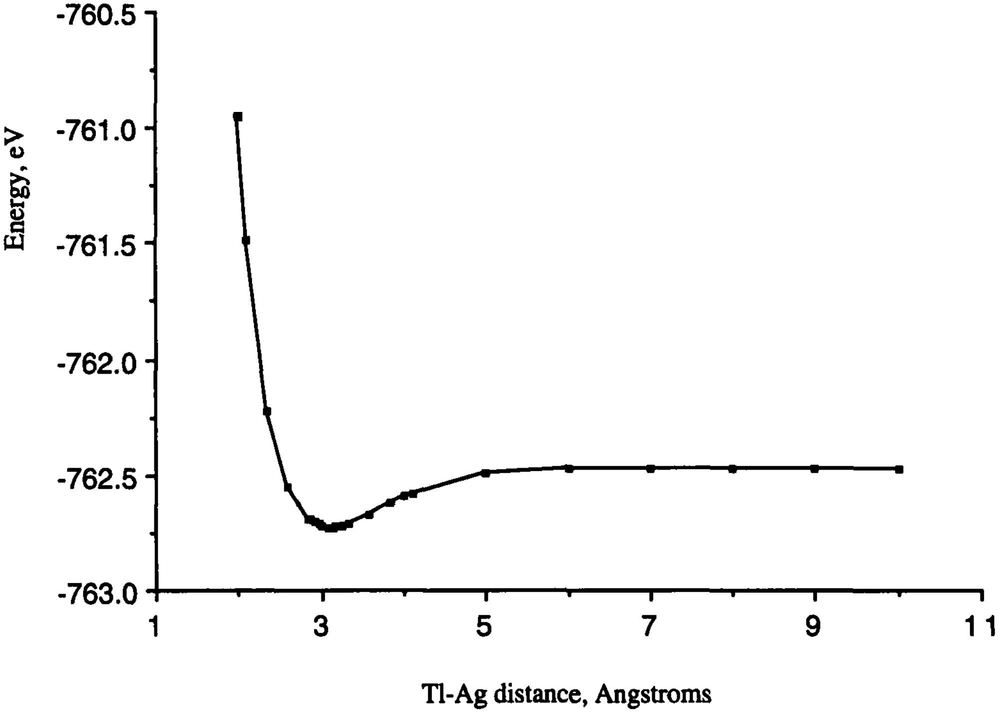

FIGURE 4 Potential energy diagram for $Tl[Ag(CN)_2]$. The total one-electron energy is plotted versus the Tl-Ag distance. C_{2v} symmetry is assumed.

Second, the HOMO-LUMO gap in $Tl[Ag(CN)_2]$ was calculated as 4.41 eV, some 0.41 eV smaller than the value obtained for the dicyanoargenate (I) anion. This is an important result in the sense that it predicts lower band energies for $Tl[Ag(CN)_2]$ relative to similar $M[Ag(CN)_2]$ complexes that lack M-Ag interaction. Finally, the results show an overlap population of 0.257 for the Tl-Ag bond formed concomitant with a decrease of the overlap population of the Ag-C bond to 0.223, a 16% decrease from the value in $Ag(CN)_2^-$.

Analysis of the composition of the HOMO for Tl[Ag(CN)$_2$], a_1 symmetry, reveals a 27.8% Ag contribution (10.6% 5s; 11.8% $4d_{x2-y2}$, 4.6% $4d_{z2}$; and 0.8% $5p_z$). The thallium atom contributed 11.7% (9.8% 6s; 1.9% $6p_z$). The LUMO, on the other hand, had a b_1 symmetry and a 17.9% Tl character (all $6p_y$). The Ag contribution was only 11.2% (all $5p_y$). The Tl contribution seems to destabilize the HOMO and stabilize the LUMO compared to the Ag(CN)$_2^-$ anion, therefore resulting in a smaller HOMO-LUMO gap.

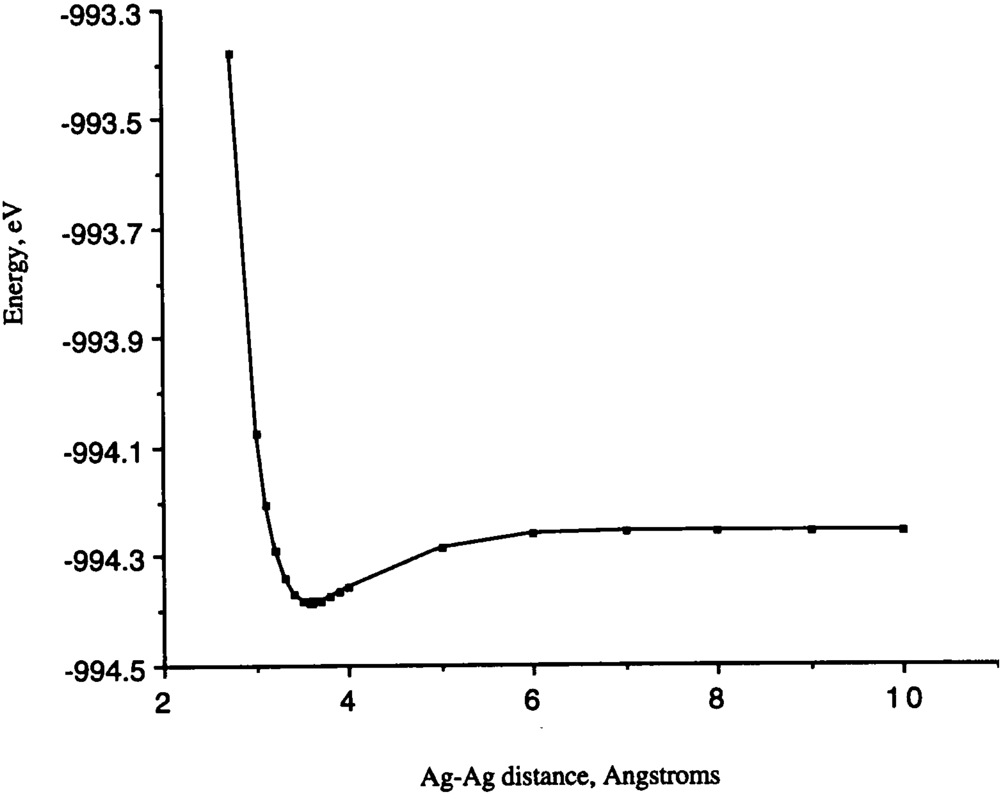

FIGURE 5 Potential energy diagram for the dimer [Ag(CN)$_2^-$]$_2$. The total one-electron energy is plotted versus the Ag-Ag distance. $D_{\infty h}$ symmetry is assumed.

$Tl[Ag(CN)_2]$ has a larger HOMO-LUMO gap by about 0.43eV in comparison to $Tl[Au(CN)_2]$.[5] However, the decrease in the HOMO-LUMO gap in $Tl[Ag(CN)_2]$ versus the $Ag(CN)_2^-$ value as well as the resulting binding energy were very comparable to the corresponding changes in $Tl[Au(CN)_2]$ versus $Au(CN)_2^-$.

C. The $[Ag(CN)_2^-]_2$ dimer

Theoretical calculations were also performed on the dimer $[Ag(CN)_2^-]_2$ to assess the Ag-Ag interaction in $Tl[Ag(CN)_2]$. The Ag-Ag distance was varied as a function of potential energy. A minimum energy was observed at a Ag-Ag separation of 3.59Å (Figure 5). A small binding energy of -0.13 eV relative to the monomer anion was obtained. Interestingly, despite the apparently long equilibrium distance and the small binding energy, the dimer formation has resulted in a relatively large decrease in the HOMO-LUMO gap by 0.56 eV. This is even more than the value resulting from the Tl bonding which yielded twice the binding energy and shorter equilibrium distance (*vide supra*). On the other hand, the analogous $[Au(CN)_2^-]_2$ had a smaller HOMO-LUMO gap than $[Ag(CN)_2^-]_2$ by about 0.48 eV.

CONCLUSIONS

The role of metal-metal interactions appears to be significant in $Tl[Ag(CN)_2]$ as revealed by our photoluminescence measurements and molecular orbital calculations in this study. $Tl[Ag(CN)_2]$ showed a photoluminescence behavior typical for low-dimensional layered complexes that exhibit metal-metal interactions, that is, a red shift of the luminescence band with decreasing temperature. The emitting state has a triplet character. Our molecular orbital calculations using the extended Hückel method have indicated significant Tl-Ag as well as Ag-Ag covalent interactions in $Tl[Ag(CN)_2]$. The emission band in $Tl[Ag(CN)_2]$ appears at a higher energy compared to the analogous $Tl[Au(CN)_2]$ compound. Interestingly, our calculations predicted 90% of this energy difference between $Tl[Ag(CN)_2]$ and $Tl[Au(CN)_2]$. Of this difference, only about 20 % was due to less metal-metal interactions in the silver complex relative to the gold complex.

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