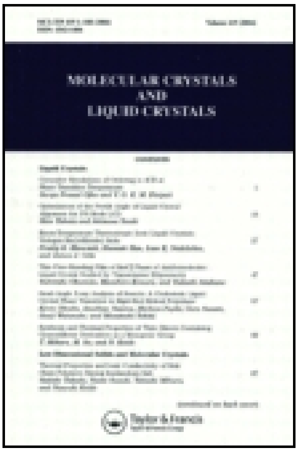

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# Photoluminescence and Electronic Structures of Gold Interactions $TL_2PT(CN)_4$ and $TL[AU(CN)_2]$: Evidence for Direct Thalliumgold Interactions

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# PHOTOLUMINESCENCE AND ELECTRONIC STRUCTURES OF $TL_2PT(CN)_4$ AND $TL[AU(CN)_2]$: EVIDENCE FOR DIRECT THALLIUM-GOLD INTERACTIONS

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Abstract Low temperature photoluminescence lifetime and spectroscopic studies coupled with relativistic extended Hückel calculations are used to reveal the role played by Tl-Pt and Tl-Au interactions in $Tl_2Pt(CN)_4$ and $Tl[Au(CN)_2]$, respectively.

## INTRODUCTION

For many years there has been interest in the electronic and spectroscopic properties of low dimensional compounds. In particular well known examples are found among compounds containing $Pt(CN)_4^{2-}$ in one-dimensional arrays of directly interacting platinum atoms.[1]

However, a recent crystal structure determination of $Tl_2Pt(CN)_4$[2] revealed, in contrast to the situation for over twenty other compounds of $Pt(CN)_4^{2-}$, that no columnar stacking occurs, but that $Tl^+$ cations (and not adjacent $Pt(CN)_4^{2-}$ anions) occupy the axial sites of the square $Pt(CN)_4^{2-}$ anions. Thus $Tl_2Pt(CN)_4$ can be considered to provide a molecular model for one-dimensional compounds of $Pt(CN)_4^{2-}$.

Certain compounds of $Au(CN)_2^-$ also exhibit metal-metal interactions and have structures with two-dimensional arrays (layers) of gold atoms. For example, $Tl[Au(CN)_2]$ and $Cs[Au(CN)_2]$ contain intersecting rows of Au atoms with Au-Au separations from 3.04 to 3.56 Å and 3.11 to 3.72 Å, respectively.[3]

As for the case of $Pt(CN)_4^{2-}$,[1] low energy absorption and luminescence are observed for compounds of $Au(CN)_2^-$ which are not present in the isolated ions.[4-6] Recent spectroscopic[4-6] and theoretical[6] investigations of these compounds have led to the suggestion that Au-Au and Tl-Au interactions are responsible for these effects in $Tl[Au(CN)_2]$.[6]

Here we report some of our recent spectroscopic and theoretical work on $Tl[Au(CN)_2]$[6] and $Tl_2Pt(CN)_4$[2,6,7] to provide additional information on the nature of the metal-metal interactions present. It is found that the valence orbitals of $Tl^+$, $Pt(CN)_4^{2-}$, and $Au(CN)_2^-$ are isolobal. This helps to account for the fact that Tl-Pt, Pt-Pt, Tl-Au, and Au-Au interactions in these compounds result in similar spectroscopic and photophysical properties.

## EXPERIMENTAL

$Tl[Au(CN)_2]$ was prepared by slow addition of $TlNO_3$ to aqueous solutions of $K[Au(CN)_2]\cdot 2H_2O$ (Spex). The bright canary-yellow precipitate was filtered and washed with several portions of cold water and dried and stored in a vacuum dessicator. $Tl_2Pt(CN)_4$ was prepared as described previously.[2]

Photoluminescence spectra and lifetime data were obtained using equipment and procedures described previously.[5] A Laser Science Inc. nitrogen-pumped BBQ dye for $Tl[Au(CN)_2]$ with a maximum output at 398 nm and a PPO dye (365 nm) for $Tl_2Pt(CN)_4$ were used for the lifetime measurements. Oriel 5755 or 5753 bandpass filters were used to select the luminescence for $Tl[Au(CN)_2]$ and $Tl_2Pt(CN)_4$, respectively. Measurements of emission spectra were obtained by filtering the output from a mercury lamp through an Oriel 5181 (365 nm maximum throughput) bandpass filter.

Data fitting of the temperature dependence of the luminescence lifetimes according to equations 1 and 2 was accomplished using the CET NLLSQ 1.3 nonlinear least squares program for an Apple II computer. Proper weighting of the data was included. All uncertainties reported in the parameters represent the standard deviations derived from such an analysis.

### Computational details

The calculations reported were of the extended Hückel type. Relativistic energy- and orbital-exponent parameters were taken from the literature.[8] Linear geometry was assumed for $Au(CN)_2^-$, and bond distances were taken to be the crystallographic values reported in the literature for $Tl[Au(CN)_2]$[3] and $Tl_2Pt(CN)_4$.[2]

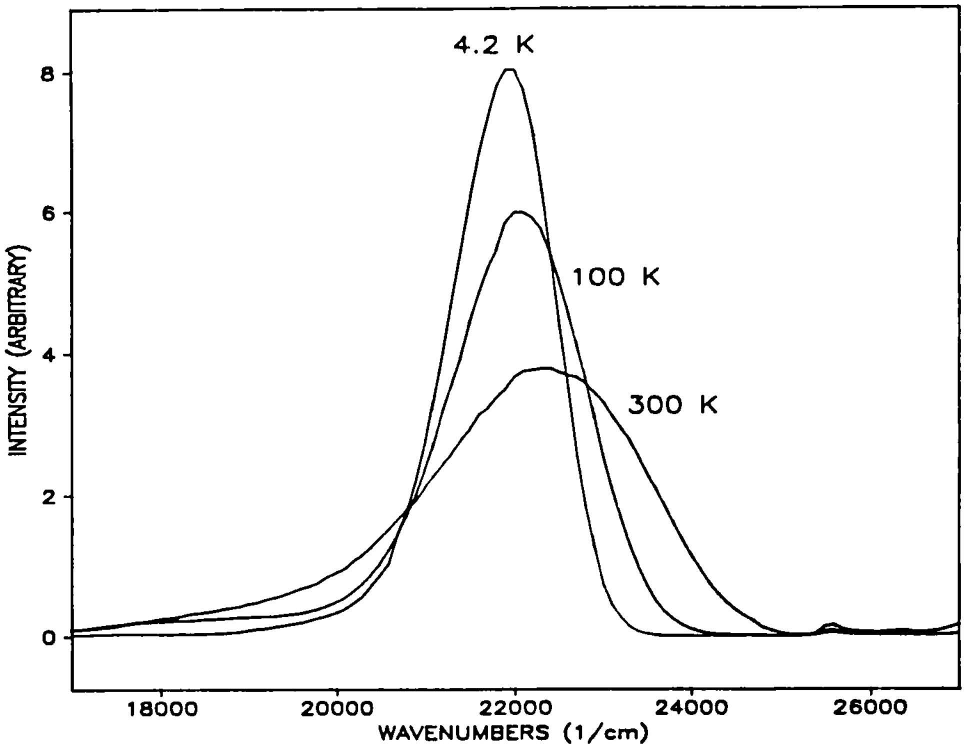

FIGURE 1. Luminescence spectra of microcrystalline $Tl_2Pt(CN)_4$ from 4.2 to 300 K. The integrated intensities were arbitrarily equalized.

## RESULTS AND DISCUSSION

### Luminescence Spectra

Figure 1 shows the luminescence spectra of a microcrystalline sample of $Tl_2Pt(CN)_4$. The intense 4.2 K peak at 21,930 $cm^{-1}$ broadens and shifts to 22,060 $cm^{-1}$ at 100 K and 22,400 $cm^{-1}$ at 300 K. At all three temperatures a very weak peak is just evident at 25,600 $cm^{-1}$. A weak, broad peak at around 18,000 $cm^{-1}$ is observable at 100 and 300 K and is of unknown origin.

Figure 2 shows the luminescence spectra of a microcrystalline sample of $Tl[Au(CN)_2]$. Again, a broadening and shift to higher energies of the intense 5 K peak at 19,290 $cm^{-1}$ is seen, the band maxima being 19,800 $cm^{-1}$ at 113 K and 20,500 $cm^{-1}$ at 300 K. A weak intensity peak is seen at 17,400 $cm^{-1}$ at 5 K and 17,800 $cm^{-1}$ at 113 K and is likely due to imperfections in the microcrystalline samples used.[6] The overall shift in energy of the intense

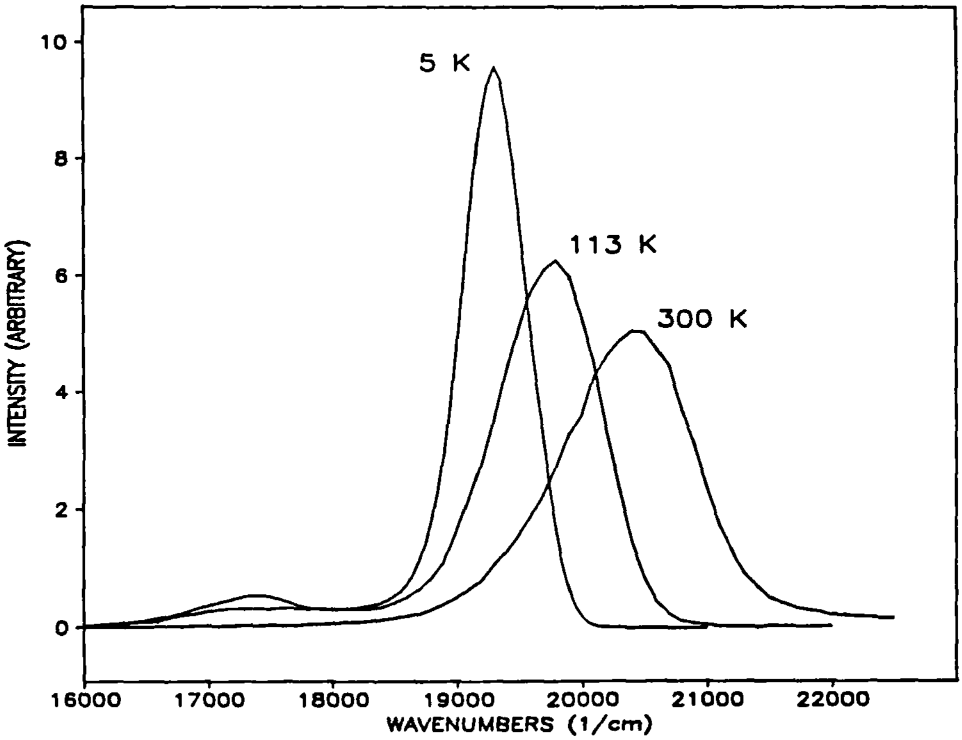

FIGURE 2. Luminescence spectra of microcrystalline $Tl[Au(CN)_2]$ from 5 to 300 K. The integrated intensities were arbitrarily equalized.

band is about twice at great as for $Tl_2Pt(CN)_4$, and its width is substantially smaller at all three temperatures.

Luminescence Lifetimes

Figure 3 shows the variation with temperature from 1.7 to 38.7 K of the lifetime of the intense luminescence band of $Tl_2Pt(CN)_4$. A plateau corresponding to a value of 77.4 μs is seen at temperatures below about 10 K. A sharp dropoff occurs between 10 and 30 K, the lifetime being 7.0 μs at 29.3 K. A gradual and regular decrease of the lifetime to 2.5 μs at 300 K occurs above 30 K.

As for other compounds of $Pt(CN)_4^{2-}$,[1] these observations can be accounted for using a simple model based on $D_{4h}$ symmetry which postulates luminescence from spin-orbit split $A'_{1u}$ and $E'_u$ excited states in thermal equilibrium with each other. A fit of the data to equation 1 yields the

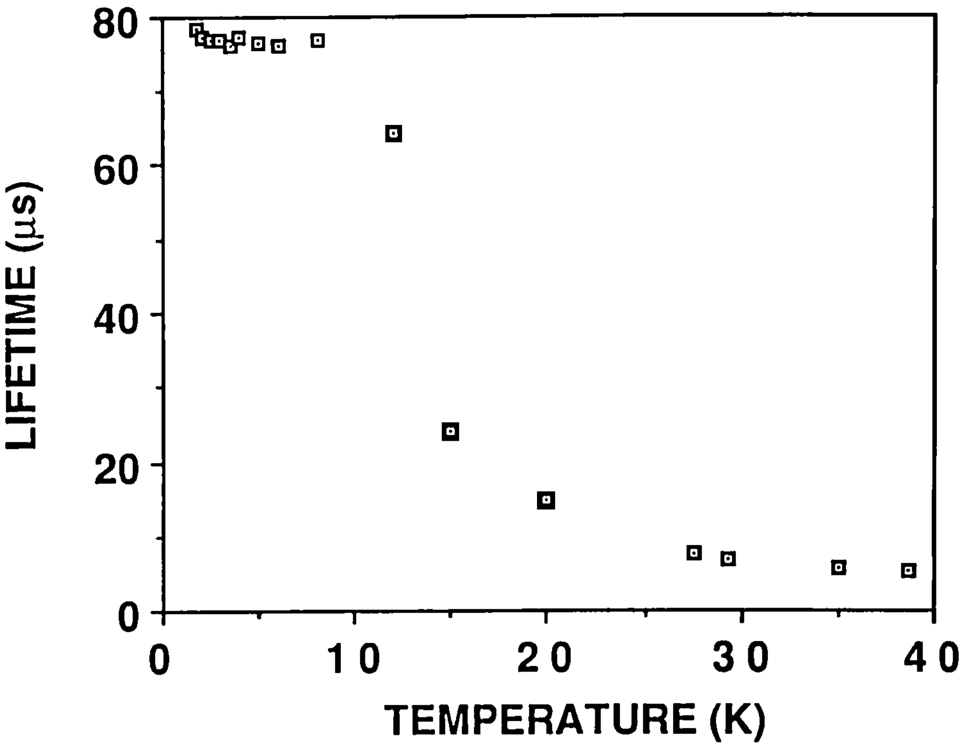

FIGURE 3. Luminescence lifetimes of microcrystalline $Tl_2Pt(CN)_4$ from 1.7 to 38.7 K.

$$k_{obs} = (k_1 + 2k_2e^{-\Delta E/kT}/(1 + 2e^{-\Delta E/kT}) \qquad (1)$$

parameters $\Delta E = 45 \pm 2$ cm$^{-1}$, $k_1 = 1.29 \pm 0.02 \times 10^4$ s$^{-1}$, and $k_2 = 7.0 \pm 0.7 \times 10^5$ s$^{-1}$ where $\Delta E$ is the energy difference between the $A'_{1u}$ and $E'_u$ levels and $k_1$ and $k_2$ represent the respective decay rates from the two levels. $k_{obs}$ represents the observed luminescence decay rate (reciprocal of the lifetime).

Figure 4 shows the variation with temperature from 1.7 to 15 K of the intense luminescence band of $Tl[Au(CN)_2]$. The same general pattern as for $Tl_2Pt(CN)_4$ is seen, with a plateau of 168 μs below 5 K which drops steeply to 0.94 μs at 20 K, followed by a smooth and more gradual decrease to 0.21 μs at 250 K. The sharp decrease in lifetime from 5 to 20 K is about 15 times greater than the analogous 10 to 30 K decrease observed for $Tl_2Pt(CN)_4$.

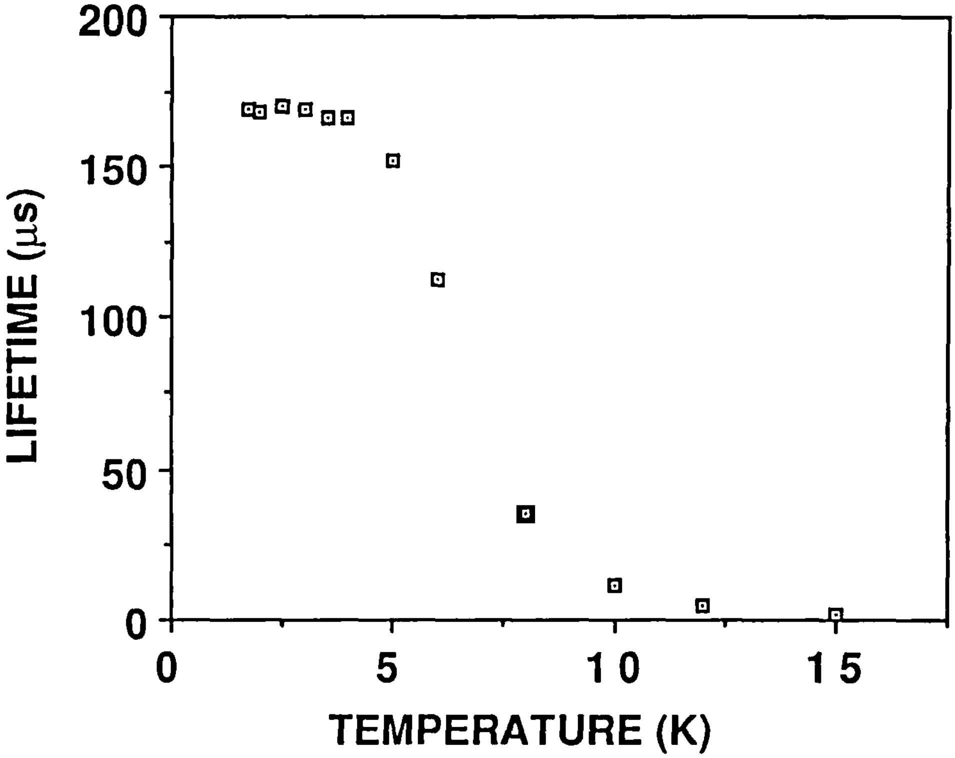

FIGURE 4. Luminescence lifetimes of microcrystallineTl[Au(CN)$_2$] from 1.7 to 15 K.

The luminescence lifetime results can be accounted for in a manner similar to that for $Tl_2Pt(CN)_4$. However, the change to $D_{2h}$ symmetry in $Tl[Au(CN)_2]^3$ lifts the degeneracy of the $E'_u$ state and splits it into $B'_{1u}$ and $B'_{2u}$ states, postulated to be nearly equal in energy.[6] A fit of the lifetime data to equation 1 yields the parameters $\Delta E = 36.0 \pm 0.4$ cm$^{-1}$, $k_1 = 5.94 \pm 0.03 \times 10^3$ s$^{-1}$, and $k_2 = 8.4 \pm 0.3 \times 10^6$ s$^{-1}$. The smaller uncertainties in these parameters compared to the analogous values for $Tl_2Pt(CN)_4$ reflects the better adherence of the data to equation 1.

The poorer fit for $Tl_2Pt(CN)_4$ may indicate the involvement of additional excited state levels as predicted theoretically.[7] In fact, a three level model (assuming no state degeneracies) according to equation 2 provides a better

$$k_{obs} = (k_1 + k_2 e^{-\Delta E_1/kT} + k_3 e^{-\Delta E_2/kT})/(1 + e^{-\Delta E_1/kT} + e^{-\Delta E_2/kT}) \qquad (2)$$

fit to the data and yields $\Delta E_1 = 49 \pm 3$ cm$^{-1}$, $\Delta E_2 = 323 \pm 25$ cm$^{-1}$, $k_1 = 1.29 \pm 0.03 \times 10^4$ s$^{-1}$, $k_2 = 1.56 \pm 0.16 \times 10^6$ s$^{-1}$, and $k_3 = 3.3 \pm 0.5 \times 10^7$ s$^{-1}$ where $\Delta E_1$ and $\Delta E_2$ represent the energy separations between the middle and the lowest and highest levels, respectively. $k_1$, $k_2$, and $k_3$ represent the decay rates from the lowest, middle, and highest levels, respectively.

## Electronic Structures

The electronic structure of $Tl_2Pt(CN)_4$ was determined from a relativistic extended Hückel calculation. The highest occupied molecular orbital (HOMO) is of $a_{1g}$ symmetry and consists of 82% Pt $5d_{z^2}$ and 18% $CN^-$ character. The lowest unoccupied molecular orbital (LUMO) is of $a_{2u}$ symmetry and is composed of 33% Tl $6p_z$ and 66% $CN^-$ $\pi^*$ character. These results are consistent with a recent relativistic density functional calculation on $Tl_2Pt(CN)_4$.[7] However, the Hückel calculation does indicate a smaller amount of Tl-Pt bonding compared to the density functional calculation.

The electronic structure of an isolated $Tl[Au(CN)_2]$ molecule ($C_{2v}$ point group) was also determined by a relativistic extended Hückel calculation. The HOMO is of $a_1$ symmetry and consists of 60% Au (45% $5d_{z^2}$, 15% 6s) and 25% $CN^-$ character. The LUMO is of $b_2$ symmetry and consists of 78% $CN^-$ $\pi^*$ character, the remaining contributions coming from Tl $6p_z$ and Au $6p_z$ orbitals. The Tl-Au overlap population was calculated to be 0.31. Substantial Tl-Au interactions involving the filled 6s and empty $6p_z$ orbitals on each leads to a lowering of the HOMO-LUMO energy gap and explains why the absorption and luminescence of $Tl[Au(CN)_2]$ occur at lower energy than for the isostructural $Cs[Au(CN)_2]$,[4,5] which does not show such covalent interactions. Relativistic effects are especially important in influencing the energies of the 6s orbitals involved. Further details of this and other results of the electronic structure calculations are reported elsewhere.[6]

The spectroscopic results are similar to those reported for other compounds of $Pt(CN)_4^{2-}$[1] and $Au(CN)_2^-$.[4,5] Replacing adjacent $Pt(CN)_4^{2-}$ anions, present in columnar forms of this compound, with $Tl^+$ cations in $Tl_2Pt(CN)_4$ appears to result in similar electronic properties. This is because the frontier orbitals of $Tl^+$ are isolobal with those of $Pt(CN)_4^{2-}$, the filled 6s and empty $6p_z$ orbitals of $Tl^+$ playing a role analogous to the filled $5d_{z^2}$-based and empty $6p_z$-based orbitals of $Pt(CN)_4^{2-}$. Similar comments apply to the role of $Tl^+$ in $Tl[Au(CN_2]$, where the filled Au 6s orbital is involved instead of $5d_{z^2}$.

## CONCLUSIONS

Both the luminescence behavior and the electronic structure calculations for $Tl_2Pt(CN)_4$ and $Tl[Au(CN)_2]$ reveal that direct covalent interactions between Tl and Pt and Au, respectively, are present in these compounds. In fact $Tl^+$ appears to mimic both $Pt(CN)_4^{2-}$ and $Au(CN)_2^-$ electronically by virtue of having frontier orbitals which are similar in energy, symmetry, and shape.

Thus $Tl^+$ can be considered isolobal with both anions. This explains why the luminescence properties of $Tl_2Pt(CN)_4$, with direct Tl-Pt interactions, are similar to those observed for columnar compounds of $Pt(CN)_4^{2-}$,[1] which involve Pt-Pt interactions. Therefore $Tl_2Pt(CN)_4$ can also be considered as a molecular model for such columnar compounds. The isolobal analogy explains also why the absorption and luminescence of $Tl[Au(CN)_2]$ are lower in energy than for the isostructural $Cs[Au(CN)_2]$.[3-6]

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