Inorganic Chemistry

Communication

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A Highly Efficient Luminescent Pt_2Tl_2 Chain with a Short Tl^I–Tl^I Interaction

Sirous Jamali,*[†] Mona M. Ashtiani,[†] Zahra Jamshidi,[‡] Elena Lalinde,[§] M. Teresa Moreno,[§] Hamidreza Samouei,[⊥] Eduardo Escudero-Adán,[⊥] and Jordi Benet-Buchholz[⊥]

[†]Chemistry Department, Sharif University of Technology, P.O. Box 11155-3516, Tehran, Iran
[‡]Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran
[§]Departamento de Química-Centro de Síntesis Química de La Rioja (CISQ), Universidad de La Rioja, 26006 Logroño, Spain
[⊥]Institute of Chemical Research of Catalonia (ICIQ), Tarragona 43007, Spain

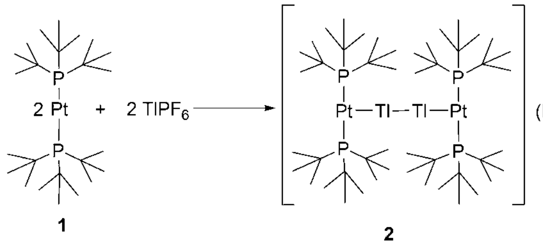
Supporting Information

ABSTRACT: The preparation of an unsupported tetranuclear cluster with a linear Pt^0–Tl^I–Tl^I–Pt^0 metal chain is described. The complex shows strong red emission in the solid state, having a quantum yield of 73%. Density functional theory (DFT) and time-dependent DFT calculations show that red emission originated from a platinum to thallium–thallium charge-transfer excited state.

Although metal–metal bonding interactions have been known for a long time, interesting developments over the decades keep them at the forefront of current research in the field of inorganic chemistry.[1] They are involved in many structures and tune optical, electrical, and magnetic properties of the extended array and self-assembled systems. In this area, molecular metal–metal-bonded discrete or extended chains have attracted attention for their unique structural features and also for their potential application as molecular electronic devices.[2] However, whereas metal–metal chain systems containing three or more metal atoms assisted by supporting bridging ligands have been well documented,[3] related unsupported metal–metal-bonded heteronuclear chains are still very rare.[4] Closed-shell interactions and metal–metal dative bonds have been used as attractive tools in the synthesis of heteronuclear discrete clusters and extended supramolecular networks.[5] Indeed, it has been demonstrated in many studies that the emission properties of polyheteronuclear metal complexes depend on the coligands, the nature of the metals, and the strength of the ligand–ligand and metal–metal interactions which involved. In particular, many heteronuclear systems involving d^{10}, d^8, and s^2 (Au^I, Ag^I, Pt^{II} and Tl^I) metal–metal contacts have been reported, of which most are stabilized by strong electrostatic contributions. For example, a series of discrete or extended platinum–thallium compounds have been prepared through neutralization reactions between anionic platinum(II) precursor complexes and thallium(I) salts.[6] Surprisingly, however, despite the well-known basicity of the soft low-valent platinum(0) complexes, the study of their reactivity toward acidic metal complexes has been less developed and, in particular toward thallium(I), rarely observed. Earlier examples have been reported by Catalano et al. using trigonal $16e^-$ precursors, showing that the initial emission of the precursor was quenched upon formation of bimetallic adducts $[PtL_3Tl]X$ (L = PPh_3, PPh_2Py; X = NO_3, AcO), and a similar behavior was also observed with related Pt_2Tl metallocryptands.[7] Recently, Braunschweig and co-workers have demonstrated that the encumbered $14e^-$ basic complex $[Pt(PCy_3)_2]$ (Cy = cyclohexyl) is also able to form interesting unsupported Pt–M (M = Al, Ag^I, Au^I, and Cu^I) bonded complexes, displaying final T-shaped coordination geometry around the Pt center.[8] Some of us have also recently reported the preparation of an extended thermochromic anionic chain $[-Pt^{II}-Tl^I-]_\infty$, formed by the discrete bimetallic fragment $[Pt(C_6F_5)_4Tl]^-$ linked by unsupported short Pt^{II}–Tl^I interactions.[9] On the basis of these precedents and continuing our interest in the synthesis of heteronuclear complexes and the study of their optical properties,[6b,c,9,10] we were intrigued to know whether a dicoordinate platinum(0) phosphine precursor would be able to form a final discrete binuclear Pt^0–Tl^I or an extended $[-Pt^0-Tl^I-]_\infty$ chain. Herein we describe the preparation of an unusual discrete tetranuclear metal chain $[(t\text{-}Bu_3P)_2PtTl_2Pt(t\text{-}Bu_3P)_2](PF_6)_2$ (**2**) containing a rare unusually short intermetallic thallophilic distance, which displays a strong red luminescence associated with this metallophilic interaction. Compound **2** was prepared under anaerobic and anhydrous conditions by the treatment of an acetone solution of $[Pt(t\text{-}Bu_3P)_2]$ (**1**) with 1 equiv of $TlPF_6$ at room temperature (Scheme 1).

Red crystals of **2** were grown by the slow evaporation of a CH_2Cl_2 solution of **2** and structurally characterized using X-ray crystallography. Cluster complex **2** crystallizes in the monoclinic

Scheme 1



Received: July 22, 2013
Published: September 9, 2013

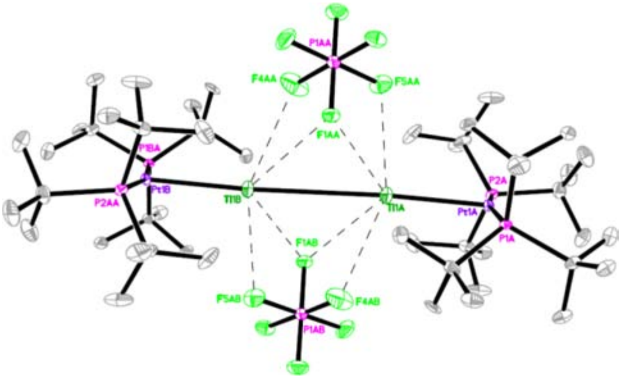


Figure 1. Molecular structure of complex **2**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1A–Tl1A, 2.707; Tl1A–Tl1B, 3.668; Pt1A–P1A, 2.320; Pt1A–P2A, 2.319; P1A–Pt1A–P2A, 166.29; P1A–Pt1A–Tl1A, 96.72; P2A–Pt1A–Tl1A, 96.6; Pt1A–Tl1A–Tl1B, 176.25.

system, in the space group $P2_1/c$. A view of the molecular structure of **2** and selected bond lengths and angles are shown in Figure 1. The most prominent feature is the formation of an unusual tetranuclear linear Pt–Tl–Tl–Pt (Pt–Tl–Tl 176.25°) cluster, generated through the presence of a relatively strong thallophilic interaction. The asymmetric unit of **2** comprises half of the cluster cation complex containing a very short Pt–Tl dative bond and a hexafluorophosphate counterion. Indeed, the Pt–Tl distance of 2.707 Å is comparable to the sum of the covalent radii of the two elements (2.75 Å). This distance is shorter than those found in previously reported platinum(0)–thallium(I) complexes (2.791–2.99 Å)[7,11] and in the reported range for platinum(II)–thallium(III) complexes (2.68–2.78 Å).[12] Each [$(t\text{-Bu})_3P)_2$PtTl] unit displays a slightly distorted T-shaped geometry around the Pt atom (P–Pt–P angle 166.3°) with the Tl–Pt vector roughly perpendicular to the P–Pt–P axis (tilted by 6.7° with respect to the normal line of the P–Pt–P axis). The Tl–Tl distance of 3.67 Å is comparable to those reported in other molecular compounds with thallous interactions such as substituted pyrazolylborate (3.7–3.9 Å)[13a] and thallene species $Tl_2\{\eta^5\text{-}C_5R_5\}$ (R = CH_2Ph; 3.63 Å)[13b] or in diverse coordination thallium(I) polymeric systems containing rhomboidal Tl_2O_2 motifs (3.594–3.669 Å).[13c] Polyheteronuclear complexes having Tl–Tl interactions are limited to various Au_2Tl_2 butterfly clusters[6a,14] or $[PtTl_2(C_6F_5)_2(C{\equiv}CFc)_2]_\infty$[6c] (3.602–3.715 Å). Further crystal structural analysis of this compound shows that the [$(t\text{-Bu})_3P)_2$PtTl] moieties are nearly coplanar (dihedral angle close to 0), and the Tl atoms display weak interactions with the F atoms of two PF_6 anions, which seem to wrap the thallophilic interaction.

NMR and optical (see below) spectroscopies suggest dissociation of the thallophilic interaction in solution. Complex **2** showed the phosphorus resonance at 95 ppm in CD_2Cl_2, which is upfield-shifted in comparison to the precursor (102 ppm in CD_2Cl_2 for **1**), supporting that the Pt–Tl bond remained intact in solution. The remarkable reduction in the $^1J_{PtP}$ coupling constant ($^1J_{PtP}$ = 4420 Hz in **1** vs 3581 Hz in **2**) is also consistent with the increase in the coordination number of the Pt atom upon Tl^+ complexation.[7] The lack of an observable coupling between Tl and P atoms in **2** is not unprecedented and suggests that the Pt–Tl bond is dynamic on the NMR time scale.[7] Although the expected broadening of the phosphorus resonance was observed upon lowering of the temperature to −90 °C, no Tl–P coupling was resolved. Further characterization of **2** in solution could not be performed because of the dynamic nature of **2** and its decomposition to unknown products. Matrix-assisted laser desorption ionization time-of-flight mass spectrometric analysis of **2** was performed using DCTB as the matrix. Analysis in positive-ion mode revealed an intense signal at *m/z* 599 due to **1**+ and a low-intensity signal at *m/z* 804 due to the binuclear species $[(t\text{-Bu}_3P)_2PtTl]^+$, indicating that **2** is labile in the gas phase and undergoes dissociation via rupturing of thallophilic and Pt–Tl bonding interactions. Topological analysis of the electron density has been carried out on the experimental geometry (using the CAM-B3LYP method and def2-TZVPP basis set for Pt and Tl atoms and the 6-31+G(d,p) basis set for H, C, F, and P atoms) to identify the presence of weak interactions through the existence of a bond path connecting the bonded atoms. The value of the electron density $\rho(r)$ at bond critical points (BCPs) can be correlated to the bond strength. The electron density at the Tl–Tl BCP is about 0.9×10^{-2} au, and the estimated value of the bond energy is 1.57 kcal/mol. The positive values of the Laplacian of the electron density and energy density $H(r)$ at the Tl–Tl BCP indicate that this interaction has been classified as a closed-shell (electrostatic)-type bonding. The electron density and energy density at the Pt–Tl BCPs in the binuclear complex $[(t\text{-Bu}_3P)_2PtTl]PF_6$ [**3**; $\rho(r) = 0.061$ and $H(r) = -0.014$ au] are further than those observed for **2** [$\rho(r) = 0.045$ and $H(r) = -0.006$ au], indicating a decrease in the Pt–Tl bond strength upon formation of **2** via Tl–Tl interaction.

The electronic absorption spectrum of **2** in CH_2Cl_2 shows high-energy absorptions (at $\lambda < 380$ nm) ascribed to singlet metal-to-ligand charge-transfer (^{1}MLCT) transitions with some 5d → 6p character as in the starting complex **1**[15] and a new low-energy band at 460 nm reflecting the presence of the Pt–Tl bond in solution. In the solid state, an additional low-energy band centered at 508 nm (see the Supporting Information, SI) is resolved, which, according to time-dependent density functional theory (TD-DFT) calculations, is assigned to charge transfer from the Pt atoms to the two Tl centers (MM′CT). Unlike the previously reported platinum(0)–thallium(I) metallocryptands and unsupported platinum(0)–thallium(I) complexes that were nonemissive,[7] cluster **2** shows a long-lived (11.0 μs) and very intense red emission in the solid state at room temperature (645 nm and $\phi = 0.73$; Figure 2). Neither the platinum(0) precursor **1** nor $TlPF_6$ is luminescent at similar energies, suggesting that the emission stems from the Pt–Tl–Tl–Pt chromophore and Tl–Tl interaction. The emission is similar at 77 K, with only expected narrowing in the full-width half-maximum band and a slight increase in the lifetime (12.9 μs). Similar *rigidochromism* has been

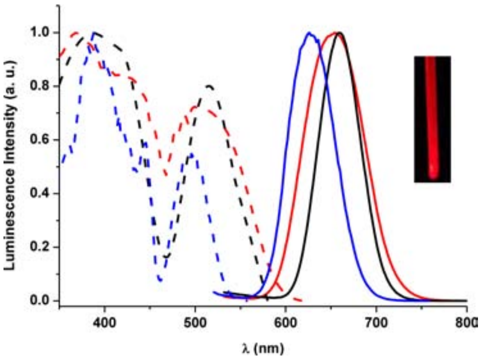
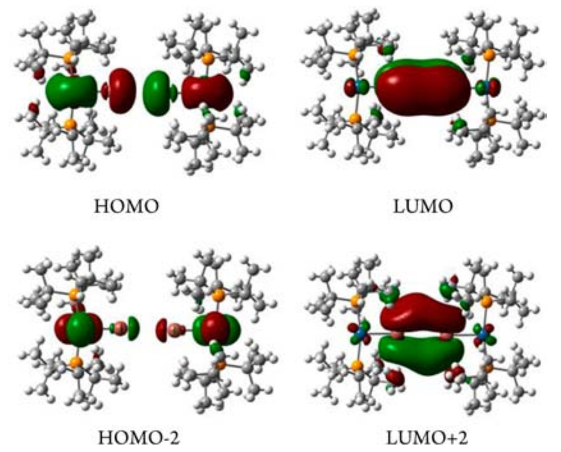


Figure 2. Excitation and emission spectra of complex **2** in the solid state (298 K, red; 77 K, black) and in the glassy CH_2Cl_2 solution (blue).


HOMO LUMO

HOMO-2 LUMO+2

Figure 3. Selected HOMO and LUMO plots for **2**.

reported in other polyheteronuclear clusters[14] exhibiting particularly very short metal−metal interactions, suggesting that a further influence of the temperature on the transition gap is negligible. The emission and excitation profile spectrum in a glassy solution is only slightly blue-shifted (630 nm) in relation to that have seen in the solid state. This fact points to the formation of similar tetranuclear Pt−Tl−Tl−Pt chromophoric units, likely with slightly longer metallic distances, in the frozen process.

In light of the above-mentioned results, DFT calculations on the tetranuclear complex **2** and its binuclear analogue platinum−thallium, **3**, were performed at the B3LYP level of theory based on experimental geometries. As shown in Figure 3 and according to Mulliken population analysis (Tables S1 and S2 in the SI), the HOMOs and LUMOs of **2** are mainly confined on the metallic Pt−Tl−Tl−Pt chain. In contrast to the binuclear platinum−thallium complex **3**, which shows the HOMOs and LUMOS localized on both Pt and Tl atoms (see the SI), for **2**, the HOMOs are mostly contributed from the Pt centers with a minor contribution of the Tl atoms, while the LUMOs are mainly located on the two Tl atoms. According to the results of TD-DFT at the optimized ground-state geometry (Table S3 in the SI), the low-lying excited states S_1 ($S_0 \rightarrow S_1 = 409$ nm; $f = 0.433$) and T_1 ($S_0 \rightarrow T_1 = 586$ nm) are derived from HOMO → LUMO and HOMO−2 → LUMO transitions, being associated with charge transfer from Pt orbitals to an orbital having Tl−Tl bonding character. The emission, therefore, originates from the Tl−Tl interaction, which keeps the two $[(t\text{-Bu}_3\text{P})_2\text{PtTl}]$ units together.

In summary, we report the first tetranuclear cluster that contains a rare linear short metallic $\text{Pt}^0\text{−Tl}^\text{I}\text{−Tl}^\text{I}\text{−Pt}^0$ chain by using the basic low-valent $14e^-$ complex **1** as the precursor. Besides the unusual structure and bonding pattern, the complex displays a strong red emission derived from a platinum to thallium−thallium charge-transfer excited state. Replacement of the monodentate phosphine by other potential bridging phosphine ligands or the Tl metal centers by bare closed-shell ions would open new perspectives to study emissive systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental details, spectroscopy, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sjamali@sharif.ir.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Sharif University of Technology Research Council, the Iran National Science Foundation (Grant 91000888), and the Spanish MICINN (Project CTQ2008-06669-C02-02/BQU) for financial support. We also thank Dr. Eddy Martin for his help with X-ray crystallography measurements.

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