Synthesis and Crystallographic Characterization of the Planar Tetraethynylplatinum Complex $(NBu_4)_2[Pt(OBET)_2]$ and its Double-Tweezer Mercury Dichloride Complex $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$

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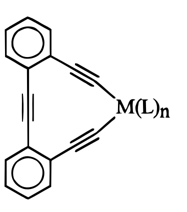
Summary: The tetralkynylplatinum complex $(NBu_4)_2[Pt(OBET)_2]$*, with two tweezers and two pockets, has been synthesized. Reaction of* $(NBu_4)_2[Pt(OBET)_2]$ *with* $HgCl_2$ *affords the heterotrimetallic double-tweezer complex* $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$*. Both* $(NBu_4)_2[Pt(OBET)_2]$ *and* $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$ *have been characterized by X-ray crystallography.*

We recently reported the heterocyclynes $M(L)_n(OBET)$ of general structure **1**[1] and metal complexes of **1** in which M′ resides in the pocket, as indicated in **2**. Most relevant to the work described herein are the complexes **1** in which M is platinum, $Pt(PR_3)_2(OBET)$.[2] The $Pt(OBET)P_2$ fragment is planar in these complexes.



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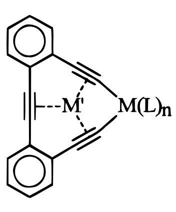

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We have had a long-term interest in the synthesis of new conducting compounds based on cyclic polyalkynes,[3] particularly those that may fit Little's criteria for a high-temperature excitonic superconductor.[4] Planar dianions with two OBET ligands bound to platinum of the general form $[Pt(OBET)_2]^{2-}$ would appear to fit many of Little's criteria. The advantage of using OBET over other acetylides, such as those in the known $[Pt(C{\equiv}CR)_4]^{2-}$ (R = *t*-Bu, $SiMe_3$, Ph),[5] is that the benzo-ring substituents in OBET are confined to be within the plane defined by the platinum atom and the acetylide carbon atoms. Planarity is an essential feature in stacked conducting systems such as metallophthalocyanines, Krogmann salts, TTF-TCNQ, and the Bechgaard salts.[4,6] A complex such as $[Pt(OBET)_2]^{2-}$ would contain two regions for binding additional metals: the two pockets and the two tweezers. These two regions are expected to provide different complexation selectivity toward metal species according to their size and coordination geometry preferences, with the possibility of forming complexes with one type of metal in the pockets and another type of metal bound to the tweezers. We report here the high-yield syntheses and X-ray crystal structures of $(NBu_4)_2[Pt(OBET)_2]$ and its complex $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$. In the latter complex $[Pt(OBET)_2]^{2-}$ functions as a double tweezer[7,8] toward the two $HgCl_2$ moieties while the two pockets defined by the OBET ligands remain vacant. These are among the first tetraalkynylplatinum complexes to have been crystallographically characterized.[9]

The syntheses of $(NBu_4)_2[Pt(OBET)_2]$ and $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$ are shown in Scheme 1. $Li_2[Pt(OBET)_2]$ was formed by the addition of $Li_2(OBET)$[1] in 100 mL of THF, generated *in situ* from $(OBET)H_2$[10] (1.46 g, 6.45 mmol) and *n*-BuLi (12.908 mmol in hexane), to $PtCl_2(tht)_2$ (1.43 g, 3.23 mmol; tht = tetrahydrothiophene) in THF (30 mL). Yellow solid $(NBu_4)_2[Pt(OBET)_2]$[11] (3.64 g) was prepared in 72% yield by dissolving $Li_2[Pt(OBET)_2]$ in deoxygenated water and treating the aqueous solution with NBu_4Br (2.1 g, 6.45 mmol) in 2.5 mL of isopropyl alcohol. Crystals suitable for single-crystal X-ray crystallography were formed by slow evaporation of THF. Reaction of $HgCl_2$ (0.024 g, 0.088 mmol) with $(NBu_4)_2[Pt(OBET)_2]$ (0.050 g, 0.044 mmol) in acetone gave $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$[12]

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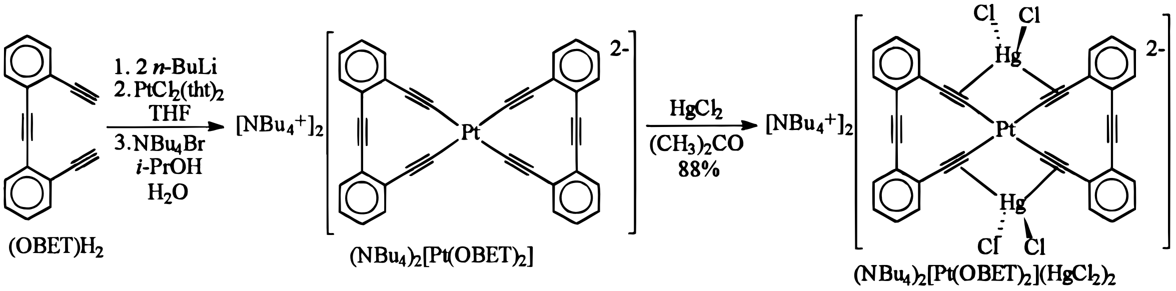
[11] Anal. Calcd for $(NBu_4)_2[Pt(OBET)_2]$ $(C_{68}H_{88}N_2Pt)$: C, 72.37; H, 7.86. Found: C, 71.69; H, 7.58. FDMS: *m/e* 1126 (M^+, ^{194}Pt). Mp: decomposed at 180 °C. IR (Nujol): $\nu(C{\equiv}C)$ 2063 cm^{-1}. ^1H NMR (300 MHz): δ (vs $CDCl_3$) 7.50 (dd, 4H), 7.43 (dd, 4H), 7.15 (dt, 4H), 7.04 (dt, 4H), 3.47−3.52 (m, 16H), 1.51−1.54 (m, 16H), 1.32−1.40 (m, 16 H), 0.757 (t, 24H). ^{13}C NMR (75 MHz): δ (vs $CDCl_3$) 132.51, 131.34, 130.98, 127.86, 126.53, 122.84, 122.51 (α-C, coupled to ^{195}Pt, $J = 991$ Hz), 104.92 (β-C, coupled to ^{195}Pt, $J = 290$ Hz), 93.24, 59.68, 24.93, 19.93, 13.98.

[12] Anal. Calcd for $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$ $(C_{68}H_{88}Cl_4Hg_2N_2Pt)$: C, 48.86; H, 5.31. Found: C, 48.96; H, 5.20. Mp: decomposed at 128 °C. IR (Nujol): $\nu(C{\equiv}C)$ 2052 cm^{-1}. ^1H NMR (300 MHz): δ (vs $CDCl_3$) 7.88−7.80 (dd, 4H), 7.64−7.57 (dd, 4H), 7.37−7.30 (dt, 4H), 7.29−7.22 (dt, 4H), 3.38−3.28 (m, 16H), 1.50−1.65 (m, 16H), 1.30−1.18 (m, 16H), 0.65 (t, 24H). ^{13}C NMR (75 MHz): δ (vs $CDCl_3$) 132.20, 131.04, 128.51, 127.36, 126.78, 126.09, 116.33, 98.28, 93.07, 59.07, 24.41, 19.87, 13.75.

S0276-7333(97)00009-5 CCC: $14.00

Scheme 1



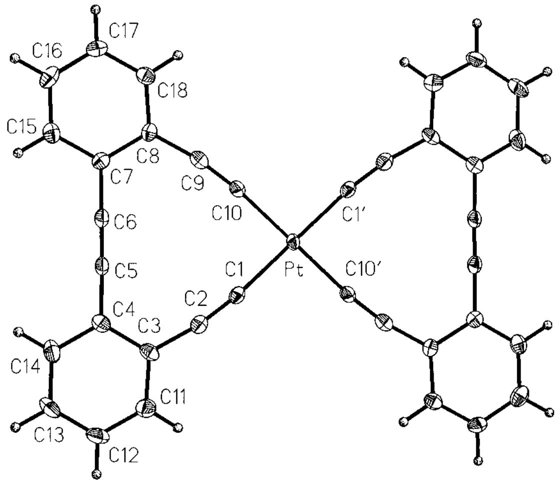


Figure 1.

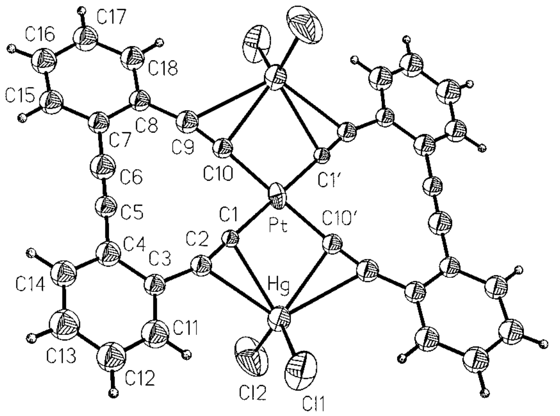


Figure 2.

(0.065 g) in 88% yield upon refrigeration in the form of crystals which were suitable for study by single-crystal X-ray diffraction.

The thermal ellipsoid plots of the single-crystal structures of $(NBu_4)_2[Pt(OBET)_2]$ and $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$ are shown in Figures 1 and 2, respectively.[13,14] In both complexes the platinum atom is on a center of inversion. The differences between the $[Pt(OBET)_2]^{2-}$ portions of the two salts are insignificant. The distorted-square-planar geometry at platinum for both $(NBu_4)_2[Pt(OBET)_2]$ and $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$ is shown by the C(1)−Pt−C(10) (85.8(2) and 85.8(7)°) and C(1)−Pt−C(10′) (94.2(2) and 94.2(7)°) angles. The discrepancy in the C(1)−Pt−C(10′) and C(1)−Pt−C(10) angles is one indication of the larger binding site presented to a metal by the tweezer portion of $[Pt(OBET)_2]^{2-}$ as compared to the pockets. The alkyne ligands in both $(NBu_4)_2[Pt(OBET)_2]$ and $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$ show quasi-linear geometries, as indicated by the C(2)−C(1)−Pt (174.1(3) and 179(2)°), C(9)−C(10)−Pt (174.1(3) and 175(2)°), C(1)−C(2)−C(3) (171.2(2) and 171.3(4)°), and C(10)−C(9)−C(8) (162(2) and 167(2)°) angles. The geometry at mercury is distorted tetrahedral. The Cl−Hg−Cl angle is 121.2(3)°. The C(1)−Hg and C(10)−Hg distances are 2.55(2) and 2.51(2) Å, and the C(2)−Hg and C(9)−Hg distances are 2.70(2) and 2.77(2) Å. Only one other bis(η^2-alkyne)mercury(II) compound has been crystallographically characterized: $[NBu_4]_2[\{cis\text{-}Pt(C_6H_5)_2(C{\equiv}CSiMe_3)_2\}HgBr_2]$. The mercury in this complex is more tightly bound to the alkynes than in $(NBu_4)_2[Pt(OBET)_2](HgCl_2)_2$, as shown by the Hg−C distances to the alkyne carbons α (2.57(2) and 2.64(2) Å) and β (2.41(2) and 2.46(2) Å) to the platinum and the smaller C(alkyne)−Pt−C(alkyne) angle (88.0(9)°).[9b] The two mercury complexes lend support to the proposal that solvomercuration of alkynes may involve mercury alkyne complexes.[15] The $(NBu_4)_2[Pt(OBET)_2]$ salt forms an integrated stack system with alternating layers of anions and cations.

We are currently exploring the preparation of $[Pt(OBET)_2]^{2-}$ salts with a variety of cations and the packing behavior of these salts in regards to the formation of segregated stack conducting systems when appropriately doped. We are also studying the pocket and tweezer complexation of $[Pt(OBET)_2]^{2-}$ with a variety of metals.

Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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(13) Crystal data for $C_{68}H_{88}N_2Pt$: $M_r = 1128.50$, monoclinic, space group $P2_1/n$, $a = 8.361(3)$ Å, $b = 24.169(7)$ Å, $c = 14.481(4)$ Å, $\beta = 101.82(2)°$, $V = 2864(1)$ Å^3, $Z = 2$, $\mu = 2.491$ mm^{-1}, $F(000) = 1176$, $T = 145$ K, semiempirical absorption correction. Refinement for data with $I > 2\sigma(I)$ (4995 reflections) gave R1(F) = 0.0247 and wR2(F^2) = 0.0589. Crystal data for $C_{68}H_{88}Cl_4Hg_2N_2Pt$: $M_r = 1670.90$, orthorhombic, space group $Pbca$, $a = 18.300(5)$ Å, $b = 18.692(4)$ Å, $c = 18.987(5)$ Å, $V = 6495(3)$ Å^3, $Z = 4$, $\mu = 7.067$ mm^{-1}, $F(000) = 3264$, $T = 139$ K, semiempirical absorption correction. Refinement for data with $I > 2\sigma(I)$ (4248 reflections) gave R1(F) = 0.0496 and wR2(F^2) = 0.1545.

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