Extended rim redox active tris-metallodioxolene derivatives of cyclotricatechylene

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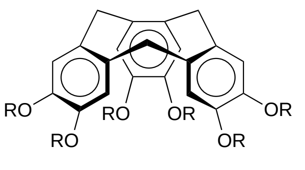
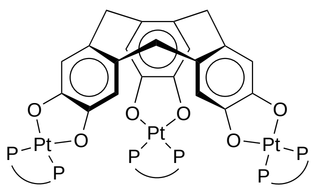
Triple metallation of cyclotricatechylene (CTC) results in new cavitands with significantly extended rims and three reversible redox couples as determined by single-crystal X-ray diffraction and electrochemistry.

Supramolecular constructs based on cyclotriveratrylene (CTV) **1** are versatile cavitands which form inclusion compounds for a diverse group of guests ranging from buckminsterfullerene[1] and carboranes[2] to halocarbons,[3] anions,[4] and cationic organometallic sandwich complexes.[5] As has been recently recognized, the solid state structures of these host–guest complexes are either columnar, with the guests often packing between the CTV units, much like a typical solvate, or, as in the case of the fullerene inclusion compounds, the cavity is fully utilized to maximize the non-covalent interactions in the $C_{60}\subset CTV$ aggregate.[1,5,6] One strategy to more fully utilize the cavitand scaffold offered by the CTV unit is to extend the rim by building off from the three catechol moieties; while a wide range of alkyl and pendant ligand derivatives have been so prepared,[7–9] we are unaware of any reports where transition metal complexes have been used to directly extend the rim of the CTV cavity. Herein, we describe (*i*) the preparation and characterization of two such derivatives; (*ii*) the structure of one as its bisdimethylacetamide (DMA) inclusion adduct; and (*iii*) the redox activity of these new hosts. These compounds provide unusual new examples of a redox active hosts where the redox units are incorporated directly into the framework of the host.

Cyclotriveratrylene, **1** was converted into the tris-catechol derivative, cyclotricatechylene **2** with boron tribromide.[10] Compound **2** was then treated for several hours in deoxygenated DMA solutions with a slight excess of $LPtCl_2$ [(L = diphenylphosphinobenzene (dppb) or diphenylphosphinoferrocene (dppfc)] in the presence of a methanol/potassium carbonate mixture acting as a base. The product was isolated as an orange solid collected by precipitation with diethyl ether and recrystallization from dichloromethane–acetone. The two materials, (CTC)[Pt(dppb)]$_3$ **3** and (CTC)[Pt(dppfc)]$_3$ **4**, were both obtained in moderate yields and appear indefinitely stable in air in the solid state; the latter slowly decomposes in solution after a few days.



R = Me **1**
R = H **2**



P P = dppb **3**
= dppfc **4**

Characterization† of these compounds has led to the formulation of the materials as the triply metallated platinum(II)–tris-catecholate species. Support for this assignment comes from the presence of a strong IR active band at 1270 cm^{-1} attributable to a ν(C–O–M) mode. In addition, the ^{31}P NMR spectral data for these species are indicative of complete substitution, showing only one phosphorus signal with corresponding platinum satellites. The ^{1}H NMR spectrum also shows this symmetrical substitution, indicated by a singlet representing the aromatic CTC protons. The geminal coupling of the protons on the methylene bridgehead carbons, characteristic CTC markers due to the rigid conformation of the bowl,[7] also suggests that the sterically bulky phosphine ligands do not significantly perturb the shape.

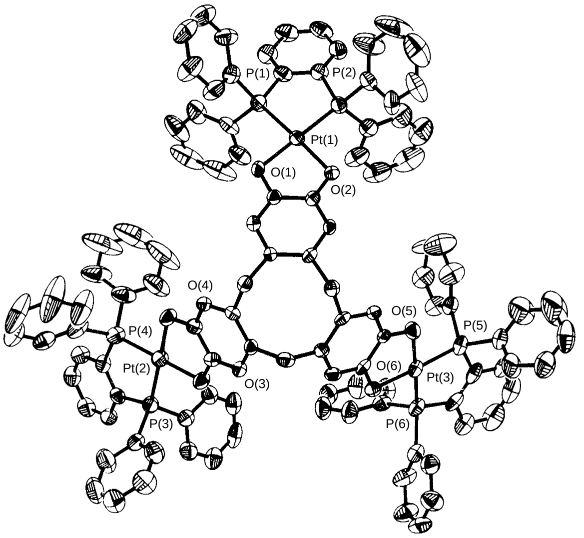


Fig. 1 Structure of (CTC)[Pt(dppb)]$_3$ **3** viewed looking down from the top of the bowl, ORTEP (50% thermal ellipsoids); solvent and hydrogens removed for clarity. Average Pt–Pt distance 9.85 Å.

Structural characterization of **3** by single-crystal X-ray diffraction‡ confirms that the tris-catecholate complex retains the original bowl structure of the cavitand (Fig. 1). Moreover, the square planar coordination of the platinum centers within the molecule and their metrical data are consistent with the formulation of the compound as a Pt^{II} catecholate.[11] As shown in the graphical abstract a crystallographic inversion center leads to the formation of a cage in the solid state. The resulting shell incorporates four DMA molecules, disordered over eight positions, within its interior. While this is expected from the known ability of CTV compounds to form inclusion type complexes,[7,8] what is especially striking is that the guests are now completely enclosed within the rim of the host; derivatization at the rim of the CTV bowl with LPt extends the depth of the cavity while also maintaining the host character of the parent compound.

The electrochemical properties of the two compounds, **3** and **4**, were examined by cyclic voltammetry.§ Upon sweeping the voltage to oxidizing potentials, a three wave voltammogram (Fig. 2) appears, with the first oxidation taking place at approximately 50 mV (*vs.* NHE). These reversible oxidations corresponds to the three separate one-electron oxidations of each catecholate (cat) moiety of the CTC unit to a semiquinoid (sq) species (Table 1). This behavior is quite different to that of the parent CTV compound which shows two irreversible waves

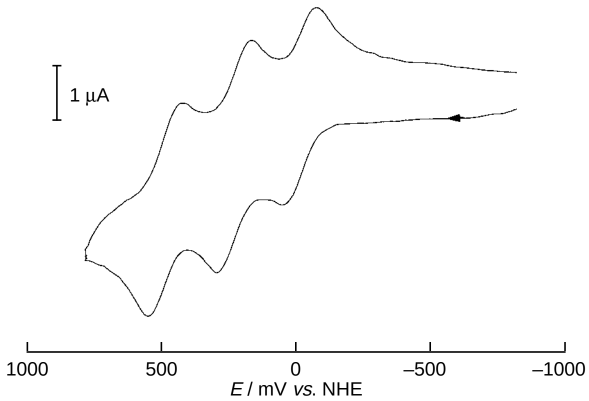


Fig. 2 Cyclic voltammogram of (CTC)[Pt(dppfc)]$_3$ **4** reversible cat–sq couples. Referenced *vs.* NHE, scan rate = 100 mV s^{-1}. See Table 1 for experimental conditions.

Table 1 Electrochemical data

Compound	$E_{1/2}{}^a$/mV	Assignment
3	40	cat–sq
	240	
	490	
	≈ 1050 (irr.)	sq–quin (decomp.)
4	60	cat–sq
	230	
	470	
	≈ 1150 (irr.)	sq–quin (decomp.)

[a] Experiments were carried out using CH_2Cl_2 as the solvent with 0.1 M $NBu^n{}_4PF_6$ as the supporting electrolyte, Pt disc working and Pt wire auxiliary electrodes, and an Ag–$AgNO_3$ non-aqueous reference electrode. Half-cell potentials were calibrated against an internal Fc–Fc$^+$ standard. Reported values are referenced *vs.* NHE.

at much higher potential, 1670 and 1830 mV (*vs.* NHE).[12] Though the electrochemical properties of **3** and **4** are very different from **1**, the first oxidation potentials are similar to those observed for the first oxidation of simple platinum catecholate derivatives.[13] Sweeping to greater oxidizing potentials produces a fourth irreversible couple resulting in decomposition of the CTC complex. This fourth oxidation is observed at *ca.* 1100 mV and most likely is attributed to quinoid formation and loss of coordination of the CTC moiety to the platinum center. For **4**, this oxidation and decomposition appears to be coincident with oxidation of the ferrocene moiety of the chelating phosphine. The three cat–sq waves indicate communication between the metal centers; since the potential is characteristic of CTC based catecholate oxidations, this communication is likely to be mediated primarily by the CTC framework itself, either through a through-space interaction from the increased charge density on the aromatic ring, or from a through-bond interaction at the bridging methylene spacers. The electron rich CTV based cryptophanes are known to form radical cations which are thought to be stabilized through extended delocalization of the unpaired electron over the CTV units.[12] The communication observed between the redox centers of **3** and **4** may be attributed to a similar phenomenon.

This set of compounds extends the family of known CTC derivatives to include the new dioxolene species which incorporate a previously unexamined aspect of metallated host–guest chemistry. Current efforts are directed towards exploring the range of complexes that can be created and characterizing their binding and catalytic properties.

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Footnotes and References

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† *Selected spectroscopic data*: IR **3**, 1271 cm^{-1}; **4**, 1274 cm^{-1} (aryl C–O–M stretch). NMR [$CDCl_3$–CD_3OD (5 : 1), 23 °C]: **3**, δ(^{1}H) 6.7 (s, 6 H, CTV aromatic), 4.6 (d, J 12 Hz, 3 H, CTV methylene bridge), 3.3 (d, J 12 Hz, 3 H, CTV methylene bridge). δ(^{31}P) 33.2 ($^1J_{PPt}$ 3492 Hz). **4**, δ(^{1}H) 6.7 (s, 6 H, CTV aromatic), 4.8 (d, J 12 Hz, 3 H, CTV methylene bridge), 3.4 (d, J 12 Hz, 3 H, CTV methylene bridge). δ(^{31}P) 10.2 ($^1J_{PPt}$ 3640 Hz). Complete details are available in supplementary data available from the authors.

‡ *Selected crystallographic data* for **3** (193 K): $C_{143}H_{156}N_8O_{14}P_6Pt_3$, dark orange rhombus from DMA–isopropyl alcohol, triclinic, space group $P\bar{1}$, a = 17.2442(3), b = 20.98140(10), c = 21.3249(3) Å, α = 69.876(1), β = 85.997(1), γ = 66.325(1)°, U = 6613.8(2) Å^3, Z = 2; R_1 (wR_2) [$I > 2\sigma(I)$] = 0.046 (0.095), All non-hydrogen atoms refined anisotropically. Complete details are available in supplementary material available from the authors. CCDC 182/725.

§ Anaerobic dichloromethane solutions of **3** and **4**, with 0.1 M $NBu^n{}_4PF_6$ as supporting electrolyte, were examined using a Pt disk working electrode, a Pt wire auxiliary electrode, and a nonaqueous Ag/$AgNO_3$ reference electrode. Potentials and corresponding currents were examined at various scan rates, ranging from 25 to 1000 mV s^{-1}. Reversibility was determined by examination of cathodic and anodic peak current ratios as well as peak symmetry and by examination of the linearity of plots of $\Delta E = E_{ox} - E_{red}$ *vs.* the square root of the scan rate. Measured potentials were calibrated through the use of an internal Fc–Fc$^+$ standard, with the reported values referenced against NHE.

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