

are observed (Figure 1). The spectrum agrees well with those reported in the literature for PNB radical anion.¹⁵ The strongest signals are observed for **1**, **4**, and **5** (which have significant quantum yields of photodecarboxylation); the same signals are also observable for **2**, **3**, and **6**. Photolysis of phenylacetate anion ($\Phi \approx 0.01$)^{1,16} with PNB gave only very weak ESR signals. Photolysis of PNB alone or **1-6** in the absence of PNB does not give any ESR signal. It seems clear that **1-6** are sources of electrons on photolysis. We have ruled out a simple electron photoejection mechanism from the photoexcited carboxylate anions since carboxylate anions such as sodium benzoate—which do not photodecarboxylate—failed to give any ESR signal on photolysis with PNB. That the photogenerated carbanions are the sources of electrons is therefore implicated.

In summary, the results suggest that a simple "electron-count" rule applies for predicting the relative reaction efficiencies when dealing with photochemical reactions capable of generating charged conjugated cyclic arrays as intermediates. In the excited singlet state, a $4n$ -electron count is favored over the usual $4n + 2$ system commonly observed in the ground state.^{17,18}

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A Mixed-Valence Tetranuclear Platinum(I,II) Complex with a Pt(I)-Pt(I) Bond

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In the last two decades, dinuclear metal-metal bonded platinum(I) complexes have been the subject of numerous spectroscopic, structural, and electrochemical studies.¹ Almost all these diplatinum(I) compounds contain platinum-carbon bonds or

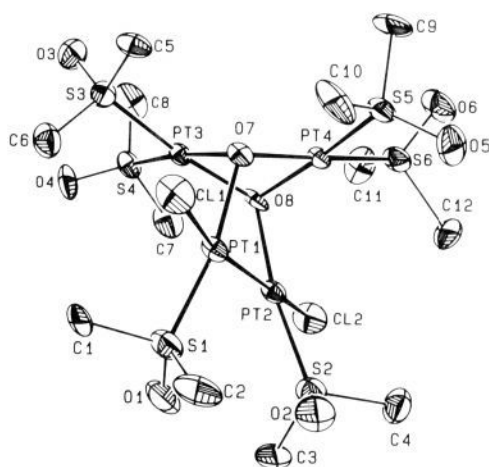
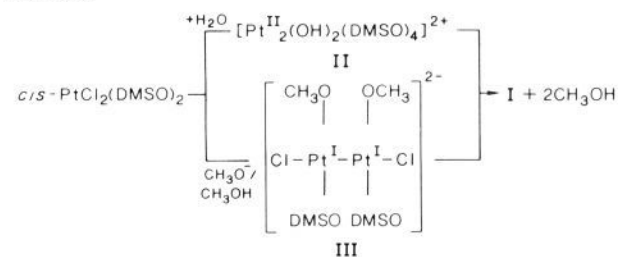


Figure 1. The structure of $[\text{Cl}_2\text{Pt}^{\text{I}}_2(\text{DMSO})_2(\mu_3\text{-O})_2\text{Pt}^{\text{II}}_2(\text{DMSO})_4]$, **1**, as found in **2**: average Pt^I-Cl 2.470 (5), Pt^I-S 2.169 (5), Pt^I-O 2.06 (1), Pt^{II}-O 2.03 (1), Pt^{II}-S 2.221 (5) Å.

Scheme 1



ligands such as phosphines and hydrides and are prepared under anaerobic conditions in nonaqueous solvents.

We report here the preparation and structural characterization of an unusual mixed-valence platinum(I,II) tetranuclear complex which contains a metal-metal bonded diplatinum(I) unit. Air stable compounds, containing the tetranuclear complex $[\text{Cl}_2\text{Pt}^{\text{I}}_2(\text{DMSO})_2(\mu_3\text{-O})_2\text{Pt}^{\text{II}}_2(\text{DMSO})_4]$, **1**, are easily prepared in solutions containing water and in the open.² A detailed X-ray analysis of three different solvates, $[\text{Pt}_4\text{Cl}_2\text{O}_2(\text{DMSO})_6]\cdot\text{X}$ ($\text{X} = 2\text{H}_2\text{O}$, **1**; $\text{X} = \text{H}_2\text{O}\cdot\text{DMF}$, **2**; $\text{X} = \text{CH}_2\text{Cl}_2$, **3**), showed that the structure and dimensions of **1** in **1-3** are almost identical.³ The tetranuclear complex, depicted in Figure 1, consists of a dimeric $\text{Pt}^{\text{I}}_2\text{Cl}_2(\text{DMSO})_2$ unit fused into a dimeric $\text{Pt}^{\text{II}}_2\text{O}_2(\text{DMSO})_4$ unit by the formation of two μ_3 -oxo bridges. Each oxygen atom bridges one Pt(I) and two Pt(II) atoms and the Pt_4O_2 unit can be described as a distorted cubane-type framework in which two oxygen atoms are missing. The O-Pt^I-Pt^I-O system deviates significantly from planarity with torsional angles of about 28°; the overall symmetry of **1** is therefore C_2 . The geometry about each platinum atom is nearly square planar. The two Pt(I) atoms in **1**, **2**, and **3** are bonded with Pt-Pt distances of 2.579 (1), 2.605 (1), and 2.569 (3) Å, respectively. These distances fall within the range of other Pt(I)-Pt(I) separations in other complexes which correspond to

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(2) Crystals of **1** were obtained by slow evaporation (2 weeks) of a solution containing K_2PtCl_4 (25 mg), NaOCH_3 (30 mg) in MeOH (30 mL), DMSO (6 mL), and DMF (1 mL) in an open beaker. Compound **2** was obtained by using the same reactants but with 6 mL of DMF. Crystals of **3** were obtained by recrystallization of **2** from CH_2Cl_2 . All solvents were used undried. The bright orange crystals were collected and washed with small amounts of acetone and dried under vacuum.

(3) Compound **1**: $[\text{Pt}_4\text{O}_2\text{Cl}_2(\text{DMSO})_6]\cdot 2\text{H}_2\text{O}$; space group $P2_1/c$, $a = 9.960$ (1) Å, $b = 17.315$ (2) Å, $c = 20.588$ (2) Å, $\beta = 100.73$ (3)°, $V = 3488$ (1) Å³, $d_{\text{calcd}} = 2.644$ g cm⁻³, $Z = 4$, $R = 0.059$, $R_w = 0.068$. Compound **2**: $[\text{Pt}_4\text{O}_2\text{Cl}_2(\text{DMSO})_6]\cdot\text{DMF}\cdot\text{H}_2\text{O}$; space group $P1$, $a = 11.591$ (1) Å, $b = 14.509$ (2), $c = 10.697$ (1) Å, $\alpha = 90.35$ (3), $\beta = 95.78$ (3), $\gamma = 93.77$ (2)°, $V = 1786$ (1) Å³, $d_{\text{calcd}} = 2.684$ g cm⁻³, $Z = 2$, $R = 0.046$, $R_w = 0.053$. Compound **3**: $[\text{Pt}_4\text{O}_2\text{Cl}_2(\text{DMSO})_6]\cdot\text{CH}_2\text{Cl}_2$; space group $P1$, $a = 11.109$ (1), $b = 16.184$ (2), $c = 10.121$ (1) Å, $\alpha = 94.43$ (3), $\beta = 97.72$ (3), $\gamma = 72.04$ (3)°, $V = 1714$ (1) Å³, $d_{\text{calcd}} = 2.784$ g cm⁻³, $Z = 2$, $R = 0.058$, $R_w = 0.071$.

a single bond.¹ The $\nu(\text{Pt}^{\text{I}}-\text{Pt}^{\text{I}})$ Raman frequency found in **2**, 149 cm^{-1} , is in good agreement with other complexes containing a Pt_2^{I} system.⁴ The oxygen atoms in the coordination sphere of the $\text{Pt}(\text{I})$ atoms deviate by about 0.5 Å from the planes defined by the central metal atom and the four surrounding atoms, i.e., Pt_2OCl_2 .

The interplanar angle about the $\text{Pt}-\text{Pt}$ bonds is 52.0°, 45.1°, and 54.9° in **1**, **2**, and **3**, respectively. These values are similar to those found in other diplatinum(I) systems and close to the optimal value of 45°.^{1c,d,f} The dimensions of the $\text{Pt}_2\text{O}_2(\text{DMSO})_4$ fragment in **1** are very similar to those reported for $[\text{Pt}^{\text{II}}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$, **II**.⁵ The main difference is in the dihedral angle between the two PtO_2 planes which is about 35° in **I** compared with the planar Pt_2O_2 system in the di- μ -hydroxo compound. The formation of **I** from K_2PtCl_4 is obviously a multistage process. The first stage is the formation of *cis*- $\text{PtCl}_2(\text{DMSO})_2$.⁶ Colorless crystals of this compound are precipitated and are redissolved when DMF is added to the reaction mixture. When K_2PtCl_4 was replaced by *cis*- $\text{PtCl}_2(\text{DMSO})_2$ as a starting material, the same product, **I**, was obtained. Scheme I is proposed for the formation of **I** from *cis*- $\text{PtCl}_2(\text{DMSO})_2$. The formation of **II** from *cis*- $\text{PtCl}_2(\text{DMSO})_2$ in the presence of water was previously reported,⁵ and the postulated Pt_2^{I} species, **III**, may be formed by the reduction of Pt^{II} by the $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$ mixture as found in other systems.^{1a,f} The attraction of the dinegative intermediate **II** to the dipositive intermediate **III** may promote their fusion into the product **I**.

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Supplementary Material Available: Tables of atomic positional parameters for **1**, **2**, and **3** (3 pages). Ordering information is given on any current masthead page.

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The First X-ray Crystalline Structure of the Bis(monoazacrown ether) Complex.

A Bis(crown ether) or a Lariat Ether?

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The bis(crown ether) is one of the macrocyclic polyethers which has been designed to improve the cation-binding properties.¹ Extraction behaviors and homogeneous stability constants have provided conclusive demonstrations for the cooperation of the two crown units in many bis(crown ether)s in the complexation with the cations being larger than their hole size.² To date, however, there is no unequivocal evidence on how the two crown rings

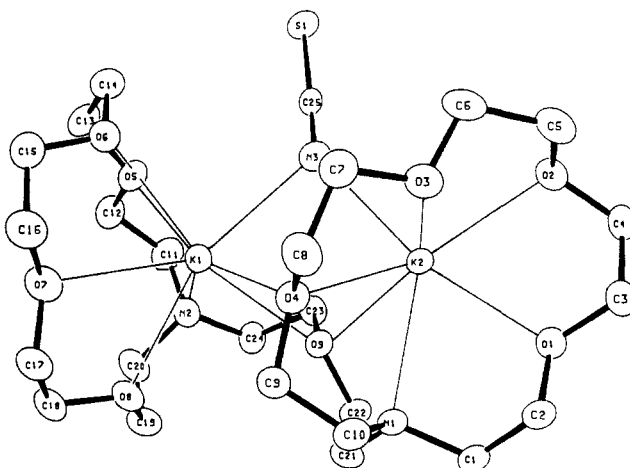
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K1-O5	2.731(4)	K2-O1	2.718(4)	K1-N2	2.951(4)
K1-O6	2.840(5)	K2-O2	2.758(3)	K1-N3	2.820(5)
K1-O7	2.874(5)	K2-O3	2.819(4)	K2-N1	2.939(4)
K1-O8	2.837(4)	K2-O4	2.985(4)	K2-N3	2.742(6)
K1-O9	2.967(5)	K2-O9	2.827(3)	K1-O4	2.916(4)

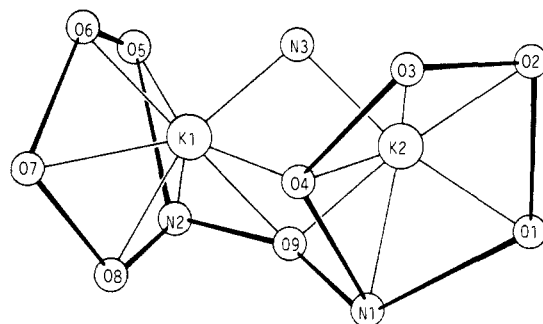


Figure 1. Perspective (top) and skeletal (bottom) drawings of $\text{BOA15C5}\cdot 2\text{KSCN}\cdot \text{H}_2\text{O}$, along with the coordination bond distances (Å).

cooperate in the complexation, although many X-ray analytical results on mono(crown ether) complexes have been reported³ and Gokel et al. gave the evidence for the side-arm participation in the crystalline lariat ether complexes.⁴ X-ray analyses of the bis(monoaza-15-crown-5)potassium thiocyanate complex presented here show that the bis(crown ether) can bind two K^+ cations and that the oxygen atom in the bridging chain interacts directly with both ring-bound cations.

The structure of the KSCN complex of 1,5-bis(*N*-monoaza-15-crown-5)-3-oxapentane (BOA15C5) is shown in Figure 1 along with a skeletal drawing of the donor atoms and metal ions in which their relative arrangements were depicted.⁵ The whole molecule

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(5) $\text{C}_{22}\text{H}_{48}\text{N}_2\text{O}_9\cdot 2\text{KSCN}\cdot \text{H}_2\text{O}$, a white crystalline solid, mp 132-133 °C; IR (Nujol) 3490, 3390, 2060, 2040, 1120, 1080, 940, 850 cm^{-1} ; Crystal data: triclinic $P\bar{1}$, $a = 12.071(5)$ Å, $b = 16.619(4)$ Å, $c = 9.817(2)$ Å, $\alpha = 106.67(5)^\circ$, $\beta = 99.80(9)^\circ$, $\gamma = 72.03(9)^\circ$, $V = 1787$ Å³, $Z = 2$, $d_c = 1.341$ g cm^{-3} , $R = 0.074$ for 6690 data. Anal. Calcd for $\text{C}_{22}\text{H}_{50}\text{N}_4\text{O}_{10}\text{K}_2\text{S}_2$: C, 43.31; H, 6.99; N, 7.77. Found: C, 43.35; H, 6.93; N, 7.93. No effort has been made to locate the hydrogen atoms.