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First platinum(II)–alkaline-earth acetate-bridged complexes $Pt^{II}(\mu\text{-}OAc)_4M^{II}(AcOH)_4$ (M = Ca, Sr, Ba)

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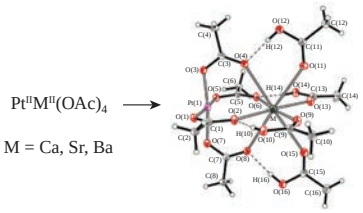
The first platinum(II)–alkaline-earth acetate-bridged complexes $Pt^{II}(\mu\text{-}OAc)_4M^{II}(AcOH)_4$ (M = Ca, Sr, Ba) were synthesized, structurally characterized using single-crystal synchrotron radiation X-ray diffraction analysis and tested for catalytic performance in homogeneous styrene hydrogenation under mild conditions.



Current studies in the chemistry of platinum focus attention on medicine[1] and catalysis[2] with an emphasis on Pt-based heterometallic compounds.[3–7] Here, we report on the synthesis, structure characterization and catalytic performance of Pt^{II}-based heterometallic acetate complexes containing Ca^{II}, Sr^{II} or Ba^{II} as complementary metals. It is likely that such complexes can be prepared in a similar way as the described[8] Pd^{II}-based analogues $Pd^{II}M^{II}(\mu\text{-}OAc)_4(AcOH)_4$ (M = Ca, Sr, Ba) from corresponding M^{II} and Pt^{II} acetates. However, platinum(II) acetate $Pt_4(OAc)_8$, unlike its palladium analogue $Pd_3(OAc)_6$, is poorly accessible and scarcely reactive towards metal(II,III) carboxylates.[9]

We proposed a new two-step protocol for the synthesis of Pt^{II}-based heterometallic complexes using convenient potassium hexahydroxoplatinate $K_2[Pt(OH)_6]$ as a starting material:

$$K_2[Pt^{IV}(OH)_6] + M^{II} \rightarrow M^{II}Pt^{IV}(OH)_6\downarrow + 2K^+ \quad (1)$$

$$M^{II}Pt^{IV}(OH)_6 + 6AcOH \rightarrow \{Pt^{IV}M^{II}(OAc)_6\} \rightarrow Pt^{II}M^{II}(OAc)_4(HOAc)_4 \quad (2)$$

Stage (1) is known to produce insoluble M^{II} hydroxoplatinates in aqueous solution.[10] We found that the alkaline-earth hydroxoplatinates thus obtained easily undergo reduction upon reflux in hot glacial acetic acid [stage (2)] to produce the alkaline-earth platinum(II) acetate-bridged complexes $Pt^{II}M^{II}(OAc)_4(AcOH)_4$ (M = Ca, Sr, Ba) in a high yield.†

These compounds can be formally considered as the salts of a $[Pt(OAc)_4]^{2-}$ anion and an M^{2+} cation. However, X-ray diffraction analysis‡ showed that the M^{2+} cation is covalently bound to the Pt^{II} acetate moiety by four acetate bridges to form a binuclear paddlewheel structure, while the coordination sphere of the M^{2+} cation containing four bridging acetate anions is augmented with four coordinated AcOH molecules [Figure 1(*a*)].

A similar structure was found earlier for the palladium(II) complexes $Pd^{II}M^{II}(\mu\text{-}OAc)_4(AcOH)_4$ (M = Ca, Sr, Ba).[6] In this work, we redetermined the structure of these complexes with

† $Pt(OAc)_4Ca(AcOH)_4$ **1**. An aqueous solution (50 ml) of $Ca(OAc)_2$ (158 mg, 1 mmol) was added to an aqueous solution (100 ml) of $K_2Pt(OH)_6$ (375.3 mg, 1 mmol) with stirring. The pale yellow precipitate of $CaPt(OH)_6$ was separated by centrifuging, washed with water and acetone and dried in a vacuum desiccator. Dry $CaPt(OH)_6$ was dissolved in boiling glacial acetic acid (50 ml) upon reflux. Then the solvent was evaporated *in vacuo*, the residue was dissolved in methylene chloride to give, after evaporation of the solvent, yellowish brown $CaPt(OAc)_4(AcOH)_{2.5}$. Recrystallization from hot acetic acid afforded yellow crystalline product **1** (640 mg, 90% based on Pt). Found (%): C, 26.93; H, 4.00; Pt, 27.40. Calc. for $PtCaC_{16}H_{28}O_{16}$ (%): C, 27.00; H, 3.96; Pt, 27.42. EAS (λ/nm): 370.

$Pt(OAc)_4Sr(AcOH)_4$ **2** was prepared similarly from $K_2Pt(OH)_6$ (375.3 mg, 1 mmol) and $Sr(OAc)_2\cdot0.5H_2O$ (214.6 mg, 1 mmol) to give yellow crystalline product **2** (610 mg, 91% based on Pt). Found (%): C, 25.42; H, 3.72; Pt, 25.64. Calc. for $PtSrC_{16}H_{28}O_{16}$ (%): C, 25.31; H, 3.69; Pt, 25.71. EAS (λ/nm): 312, 264.

$Pt(OAc)_4Ba(AcOH)_4$ **3** was prepared in a similar manner from $K_2Pt(OH)_6$ (375.3 mg, 1 mmol) and $Ba(OAc)_2\cdot3H_2O$ (309 mg, 1 mmol) to give green crystalline product **3** (752 mg, 93% based on Pt). Found (%): C, 19.80; H, 3.52, Pt, 24.10. Calc. for $PtBaC_{16}H_{28}O_{16}$ (%): C, 19.69; H, 3.46; Pt, 24.13. EAS (λ/nm): 260, 300.

Products $Pd^{II}(\mu\text{-}OAc)_4M^{II}(AcOH)_4$ **4**–**6** were prepared from $Pd_3(OAc)_6$ and Ca, Ba and Sr acetates according to published protocols.[6]

‡ *Crystallographic data for* **1**–**6**. X-ray diffraction data were collected on the 'Belok' beamline of the National Research Center 'Kurchatov Institute' using a Rayonix SX165 CCD detector. Total of 720 images for each of compounds were collected using an oscillation range of 1.0° and φ scan mode and corrected for absorption using the Scala program.[12] The data were indexed, integrated and scaled using the iMOSFLM utility in the CCP4 program.[13] For details, see Table S1, Online Supplementary Materials. The structures were determined by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms of the OH groups were localized in the difference Fourier map and included in the refinement within a riding model with fixed isotropic displacement parameters. The other hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [$U_{iso}(H) = 1.5U_{eq}(C)$]. All calculations were carried out using the SHELXTL program.[14]

CCDC 1563825–1563830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

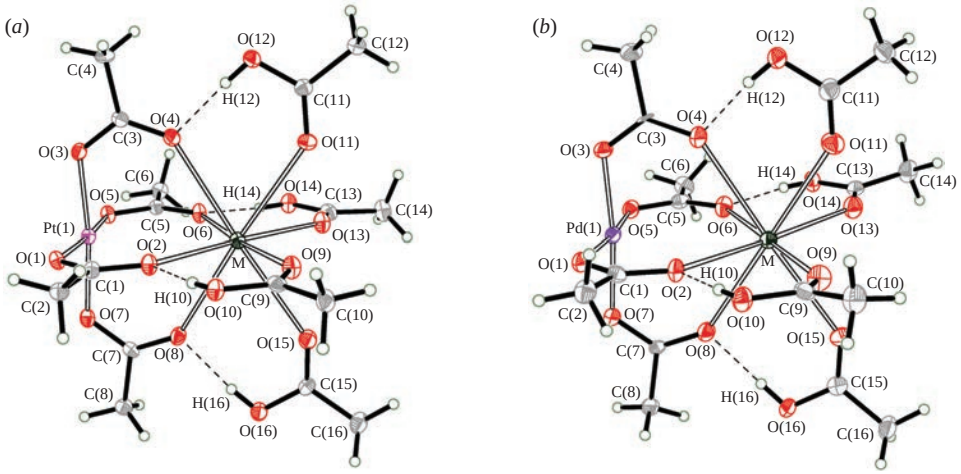


Figure 1 Molecular structure of the complexes (*a*) $Pt^{II}(\mu\text{-}OAc)_4M^{II}(AcOH)_4$ **1**–**3** and (*b*) $Pd^{II}(\mu\text{-}OAc)_4M^{II}(AcOH)_4$ **4**–**6** (M = Ca, Sr, Ba).

the same synchrotron radiation X-ray diffraction low-temperature technique as we used for platinum(II) complexes **1**–**3**. The refined results [Figure 1(*b*)] showed a close similarity between the structures of **1**–**3** and **4**–**6**.

Complexes **1**–**3** demonstrated unusual performance in the homogeneous catalysis of alkene hydrogenation. Generally, monometallic platinum(II) complexes are easily reduced to metallic platinum just upon feeding gaseous hydrogen, and the catalytic reaction proceeds over the metallic platinum.[11]

We also found that complexes **1**–**3** were reduced by H_2 in solution; however, no reduction to Pt metal was observed when an alkene was preliminarily added to the reaction solution, while alkene hydrogenation occurred under homogeneous conditions without the formation of Pt metal [Figure 2(*a*),§(*b*)¶]. Styrene acts as a π ligand, which stabilizes an active heterometallic complex; therefore, its complete hydrogenation results in the reduction of Pt^{II} to Pt metal. The catalytic activity of heterometallic complexes decreased in the order **3** > **2** > **1**.

Hence, our study demonstrated that heterometallic platinum(II) complexes can be catalytically active in not only heterogeneous[15] but also homogeneous catalysis.

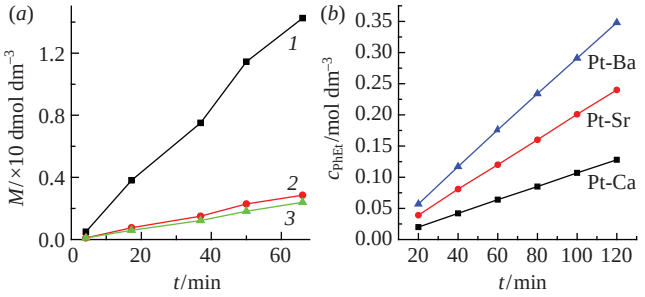


Figure 2 Ethylbenzene accumulation curves during styrene hydrogenation (H_2, 1 atm; 20 °C) catalyzed by (*a*) complex **3** (1 mmol dm^{-3}) in (*1*) AcOH, (*2*) EtCOOH and (*3*) DMF; (*b*) complexes **1**–**3** (2 mmol dm^{-3}) in acetic acid.

§ A solution of styrene (210 mg, 2 mmol) in 5.0 ml of propionic or acetic acid or DMF containing $Pt(OAc)_4Ba(AcOH)_4$ (8 mg, 0.01 mmol) was stirred under hydrogen (1 atm) at 20 °C to 100% styrene conversion into ethylbenzene, while the reaction solution remained clear, and no platinum metal sediment or mirror was observed.

¶ A solution of syrene (315 mg, 3 mmol) in 5.0 ml of acetic acid containing $Pt(OAc)_4M(AcOH)_4$ (0.01 mol) was stirred under hydrogen (1 atm) at 20 °C to 100% styrene conversion into ethylbenzene.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.031.

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