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$[K([2.2.2]\text{-crypt})]K[Pt_3(\mu^2\text{-CO})_3(PPh_3)_3]\cdot 3NH_3$ – A New *Chini*-Type Platinum Carbonyl Complex

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Dedicated to Professor Thomas Schleid on the occasion of his 65th birthday.

The titular compound $[K([2.2.2]\text{-crypt})]K[Pt_3(\mu^2\text{-CO})_3(PPh_3)_3]\cdot 3NH_3$ (**1**) ([2.2.2]-crypt = 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) contains a triangular platinum complex, the approximate D_3 symmetry of which is only broken by the phenyl substituents of the PPh_3 ligands.. The dianionic complex represents only the second triangular carbonyl platinate characterized via single crystal X-ray diffraction in monomeric form. The compound crystallizes in the space group $P\bar{1}$ with the unit cell parameters a = 13.8826 Å, b = 14.2899 Å and c = 21.3254 Å. For the formation of the platinate, liquid ammonia seems to play a crucial role as a solvent for the polygermanide used for the reduction as well as for the stabilization of the dianion.

Introduction

Transition metal carbonyl complexes have been a intensively researched topic, ever since the discovery of the first heteroleptic carbonyl platinum compound by *Schützenberger* in 1868.[1] Since then, a large number of hetero- and homoleptic carbonyl compounds of single- and multicore transition metal complexes have been characterized.[2]

In the case of platinum clusters, two main types of neutral triangular carbonyl complexes are known, with either terminal or edge capping carbonyl ligands.[3,4] Predominantly phosphine ligands have been employed to complete the platinum coordination spheres.[5] In many cases, the platinum triangle is additionally capped by another transition metal atom, such as Tl, Cu, Ag, Au, Zn or Hg.[4,6]

Chini and *Longoni* first described the motif of triangular platinum anions containing carbonyl ligands in literature, when they published their findings on $[Pt_3(CO)_6]_n^{2-}$ (n = 2–5) in 1974.[7] Just two years later they expanded the number of $[Pt_3(CO)_6]_n^{2-}$ oligomers with n = 6 and ~10 by spectroscopically analyzing the reaction products of various platinum compounds with alkali metals in the presence of carbon monoxide.[8] In addition to the oligomeric species, they also report on the detection of the monomer $[Pt_3(CO)_6]^{2-}$ through IR and UV spectroscopy. Due to the first author's involvement in establishing platinate clusters of this type, they are often colloquially referred to as "*Chini*-Clusters".[9]

Recently the group of *Figueroa* succeeded in synthesizing a *Chini*-type cluster with isocyanide ligands instead of phosphine as the terminal group.[10] By treating the neutral triangular complex with KC_8, they were able to reduce the platinum atoms, resulting in the dianion $[Pt_3(\mu\text{-CO})_3(CNAr^{Dipp2})_3]^{2-}$. This compound represents the first monomeric *Chini*-Cluster characterized via single crystal X-ray diffraction. *Figueroa et al.* reasoned that the stabilization from the extended π-system allows for the reduction of the platinum atoms. This is in reference to the proposition of *Ciabatti et al.* that due to the weak π-accepting properties of triorganophosphines, dianionic clusters with these ligands are difficult to synthesize, due to their weak reactivity.[11] Nontheless, a few examples of mostly extended compounds of this nature have been found.[17]

Results and Discussion

Red crystals of the titular composition could be found from the reaction of $K_6Rb_6Ge_{17}$, $Pt(CO)_2(PPh_3)_2$ and [2.2.2]-crypt in liquid ammonia after three months storage. The central moiety of the compound $K([2.2.2]\text{-crypt})]K[Pt_3(\mu^2\text{-CO})_3(PPh_3)_3]\cdot 3NH_3$ (**1**) is represented by the anionic triangular platinum complex $[Pt_3(\mu^2\text{-CO})_3(PPh_3)_3]^{2-}$ (**1 a**) (see Figure 1). Each of the triangular sides is bridged by a carbonyl ligand, while each platinum atom carries a terminal PPh_3 ligand. The Pt–Pt bond lengths vary between 2.6326(3) Å and 2.6423(3) Å, which is in good agreement with known Pt–Pt distances.[9,10] With lengths between 2.001(5) Å and 2.077(5) Å the Pt–C bonds are in the expected range as well, as are the C–O bonds with distances from 1.188(6) Å to 1.199(5) Å.[9,10]

While two of the carbonyl ligands only deviate slightly from the platinum plane (2.0(3)° and 3.5(5)°), the angle of the C1–O1 moiety is 7.8(5)°. This can be explained by a hydrogen bond

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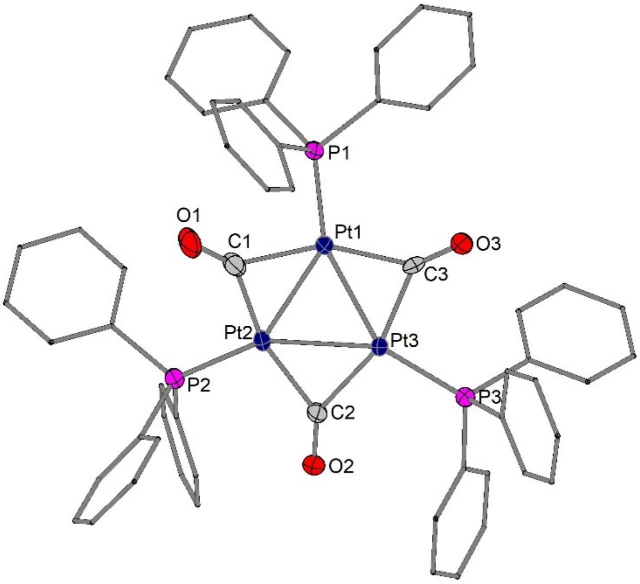

Figure 1. $[Pt_3(\mu^2\text{-}CO)_3(PPh_3)_3]^{2-}$ (**1 a**) in compound **1**. To increase the visibility, C-atoms of the phenyl rings are displayed as wires/sticks. Thermal ellipsoids at 50 % probability.

between O1 and one of the hydrogen atoms of the neighboring phenyl rings.

To compensate the twofold negative charge from the platinate, two potassium cations are present in the crystal structure. One of these cations is sequestered in a [2.2.2]-crypt molecule. The other cation (K1) is located off-center above the platinum plane closer to the P2–Pt3 bond in the range between 3.3202(12) Å and 3.8613(13) Å. K1 also has contacts to three ammonia molecules of crystallization. Through an inversion center in the structure, two of these entities form a dimer, which is shown in Figure 2.

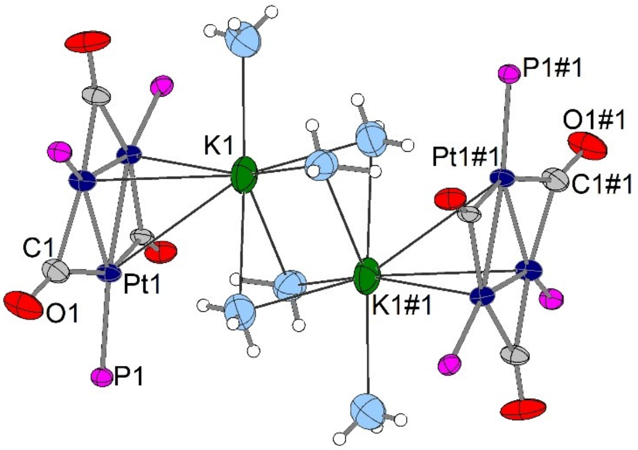

Figure 2. Potassium cation and ammonia bridged dimer of $[Pt_3(\mu^2\text{-}CO)_3(PPh_3)_3]^{2-}$ (**1 a**) in **1**. To increase the visibility, phenyl rings are not displayed. Thermal ellipsoids at 50 % probability.

The reduction itself is facilitated by the Zintl-type compound $K_6Rb_6Ge_{17}$. *Zintl*-anions and *Zintl*-phases have been shown to possess reducing properties, which in this case result in the emergence of the presented palatinate.[12] Liquid ammonia as a solvent is known to be metastable for a long time against reduction at the low temperature employed (233 K) and has proven to be an excellent solvent for multiply charged cluster anions.

Conclusion

The compound $[K([2.2.2]\text{-crypt})]K[Pt_3(\mu^2\text{-}CO)_3(PPh_3)_3]\cdot 3NH_3$ contains the new monomeric *Chini*-type dianion $[Pt_3(\mu^2\text{-}CO)_3(PPh_3)_3]^{2-}$. Its existence shows that triorganophosphines are indeed strong enough ligands to stabilize such clusters, but the stabilizing effect of liquid ammonia towards negatively charged species might also be crucial to their formation.

Experimental Section

All steps were performed under argon atmosphere using standard Schlenk and glovebox techniques. Liquid ammonia was dried and stored over sodium metal, with constant cooling from a EtOH/CO_2 cooling bath. Crown ether was purified before use by sublimation.

Synthesis of $K_6Rb_6Ge_{17}$: Potassium (236.7 mg, 6.06 mmol), rubidium (517.5 mg, 6.06 mmol) and germanium (1245.7 mg, 17.16 mmol) were weighted into a tantalum ampoule, which was subsequently welded shut under argon. The ampoule was encased in an evacuated quartz-glass tube and heated to 1223 K with a heating rate of 50 K/h. After being held for two hours, the temperature was lowered to 298 K with 20 K/h.

Synthesis of $Pt(CO)_2(PPh_3)_2$: The compound was synthesized following the directions of *Chini* and *Longoni* from K_2PtCl_4, PPh_3 and CO.[13]

Synthesis of $[K([2.2.2]\text{-crypt})]K[Pt_3(\mu^2\text{-}CO)_3(PPh_3)_3]\cdot 3NH_3$: $K_6Rb_6Ge_{17}$, $Pt(CO)_2(PPh_3)_2$ and [2.2.2]-crypt were weighed into a heated Schlenk tube, after which 5 mL of ammonia were condensed onto the reactants. The mixture was stored at 233 K for three months, a yield of approximately 20 percent of dark needle-like crystals of the titular compound could be isolated and analyzed via single crystal X-ray diffraction.

X-ray diffraction studies: Due to the moisture-, air- and heat-sensitivity of the compound, the crystals had to be cooled and preserved in oil for the duration of picking and measurement. To achieve this, perfluoroether oil was cooled in a stream of nitrogen, into which the crystals were transferred from the reaction vessel. During the transport from the oil to the diffractometer liquid nitrogen was employed for cooling.

The software *CrysAlisPro* (Version 41_64.83a) was used for the data reduction.[14] *ShelXT* was used for structure solution, with *ShelXL* for refinement.[15] For visualization purposes *Olex² 1.3* was employed, while the figures were drawn up with *Diamond 4*.[16]

Crystal data for $[A@[18]crown\text{-}6]_2[Pt(CO)_3]\cdot 10\,NH_3$ ($A = K, Rb$): $M = 1961.89\ g\,mol^{-1}$, space group $= P\bar{1}$, $a = 13.8826(3)$ Å, $b = 14.2899(3)$ Å, $c = 21.3254(3)$ Å, $\alpha = 75.474(2)°$, $\beta = 89.8370(10)°$, $\gamma = 65.082(2)°$, $V = 3688.53(14)$ Å³, $Z = 2$, $\rho_{calc} = 1.766\ g\,mol^{-1}$, $\mu = 12.528\ mm^{-1}$, $F(000) = 1926.0$, 158087 measured reflections, 14739 independent reflections, $R_{int} = 5.02\,\%$, $R_1 = 3.23\,\%$, $\omega R_2 = 8.10$ for $I >$

$2\sigma(I)$, $R_1=3.47\%$, $\omega R_2=8.24$ for all data, GooF = 1.056, $\Delta\rho_{mac}=1.87\ e\text{Å}^{-3}$, $\Delta\rho_{min}=-2.20\ e\text{Å}^{-3}$.

Crystallographic data for the compound have been deposited in the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-2104004 (Fax: +44-1223-336-033, E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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