[A([18]crown-6)2[Pt(CO)3] · 10 NH3 (A=K, Rb) – A crystal structure containing the long postulated [Pt(CO)3]2−

Susanne M. Tiefenthaler,[a] Florian Kleemiss,*[b] and Nikolaus Korber*[a]

On the occasion of the 60th birthday of Prof. Dr. Caroline Rühr.

Introduction

Due to their strong σ-bonding and π-back-bonding properties, carbonyl ligands are one of the predominant ligands in organometallic chemistry.[1] Especially transition metal complexes containing carbonyl groups have long since been a highly researched topic.[2]

Homoleptic carbonyl compounds of transition metals have been known since 1890, when Mond et al. synthesized Ni(CO)4 from the direct conversion of the metal and CO.[3] Ever since this entry into the field, numerous homoleptic single core carbonyl compounds of transition metals could be synthesized and characterized.[4] Especially the transition metals of the groups 6 to 9 exhibit a rich chemistry with respect to carbonylation, leading to single- and multi-nuclear complexes. Carbonyl complexes of the elements of group 10 however are few and far between, as the analogous neutral tetracarbonyl species of the heavier homologues palladium and platinum could to date only be synthesized as matrix isolated compounds and analyzed via IR and Raman spectroscopy.[5]

In addition to neutral complexes, also a number of carbonyl metalate anions are known.[6] While mononuclear carbonyl metalates are known for every metal of groups 3 to 9,[7] so far only the nickelate [Ni(CO)3]2− has been discovered out of the group 10 elements.[8]

Whereas the known mononuclear compounds are fairly limited, a number of less highly reduced multinuclear carbonyl platinates are known, most notably the so called Chini-clusters first described by Chini himself.[9] These clusters usually exhibit a triangular form made up of platinum atoms with terminal and bridging carbonyl groups and are either isolated or stacked.[10]

Solvated electrons are undeniably strong reducing agents, their occurrence has been linked to dissolved Zintl phases. The reductive nature of Zintl ions, especially polygermanides, in liquid ammonia has been demonstrated not only by the serendipitous emergence of the anion [Ni(CO)3]2−, but also through the detection of oxidized Zintl ions.[8,11] Sevov et al. determined the redox equilibrium between the nine atomic germanium clusters [Ge3]4+, [Ge3]5+, and [Ge3]6−, which results resulting in solvated electrons.[12] K3Rb2Ge17 contains [Ge3]6− as well as [Ge4]4− clusters.[13]

Results and Discussion

Crystal Structure of [A([18]crown-6)2[Pt(CO)3] · 10 NH3 (A=K, Rb)

Dark red, crystalline needles of [A([18]crown-6)2[Pt(CO)3] · 10 NH3 (A=K, Rb) could be obtained as a byproduct from a solution of K3Rb2Ge17, Pt(CO)3(PPh3)2, [2.2.2]-crypt (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) and [18]crown-6 (1,4,7,10,13,16-Hexaoxacyclooctadecane) in liquid ammonia.

The central moiety of the crystal structure consists of a platinum atom which is coordinated by three carbonyl ligands...
(see Figure 1). Both the Pt–C (1.869(6) Å – 1.898(5) Å), as well as the C–O bond lengths (1.154(6) Å – 1.178(7) Å) are in the expected range.\textsuperscript{13} The structure of the anion deviates only slightly from the expected trigonal planar shape, with the angles between the carbonyl groups ranging from 118.1(2)° to 122.3(2)°. As for the planarity of the complex, the maximal deflection from the plane amounts to 1°. Therefore, to ascribe $D_{3h}$ symmetry to the [Pt(CO)$_3$]$^+$ moiety can be considered an excellent approximation. Two crystallographically independent ([18]crown-6) (A=K/Rb) cation complexes compensate the twofold negative charge of the carbonyl platinate.

The alkali metal cation position closer to the platinum atom (K1/Rb1) is split, with each of the split positions being occupied by either potassium (88.5 %) or rubidium (11.5 %), whereas the second cation position is partially occupied with 23.4 % by either potassium (88.5 %) or rubidium (11.5 %), whereas the second cation position is partially occupied with 23.4 % by potassium and 76.6 % rubidium. Through contacts to three ammonia molecules, which in turn exhibit contacts to the cation K2/Rb2, sandwich like complexes are formed. The earlier discovered nickel analogue exhibits the same structural motif.\textsuperscript{8} Voids in the unit cell are filled by additional ammonia molecules of crystallization. While one of the ammonia molecules shows no preferred direction for the hydrogen atoms, by investigating the N–N distances, as well as the direct surroundings of the nitrogen atom, an amide or hydroxide molecular anion can be excluded.

Theoretical investigations

Quantum mechanical structure optimizations were performed to gain further insight on the electronic structure and bonding situation of the central anionic species. The results of the non-symmetrized geometry optimization in an ammonia continuum solvation model are in good agreement with the structure observed by X-ray diffraction, with Pt–C bond lengths of 1.7445 Å and C–O distances between 1.1903 Å and 1.1905 Å. Additionally, the calculations confirm the planar nature of the anion. The analysis of the ELF shows a partial $\pi$-bond over and under the carbonyl plane. As the $\pi$-bonding is less pronounced than in the nickel analogous species,\textsuperscript{9} a stronger localization of the electrons at the central atom is inferred. This is reflected by the QTAIM charges of +0.254 for Pt\textsuperscript{13} in contrast to the charge of +0.311 of Ni at the same level of theory. Similarly, ELI–D basins of lone pairs found at Pt have a much higher integrated electron density compared to the Ni analogn.\textsuperscript{13} (0.227 for Pt, 0.152 for Ni). In agreement with the stronger isolation of the platinum atom from the ligands the disynaptic basin of the C–Pt bond cannot be found, the ELI–D basin is monosynaptic, therefore interpreted as a lone pair (compare two regions above and below Pt–C direction in the ELF, Figure 2b). In the Ni analogon the bond was still disynaptic. The shape of the HOMO (shown in Figure 2c) once again indicates a distribution of electrons parallel to the carbonyl plane.

Conclusion

The compound [([18]crown-6)][Pt(CO)$_3$]$^-$·10 NH$_3$ (A=K, Rb) contains the trigonal planar carbonyl platinate dianion, which has been postulated for a long time and has now been found. To the best of our knowledge, this represents the first mononuclear carbonyl platinate, as well as only the second mononuclear carbonyl metallacone of a group 10 element.

Experimental Section

All operations were carried out under argon atmosphere using standard Schlenk and glovebox techniques. Liquid ammonia was dried and stored over sodium for at least 96 hours, with constant cooling by an EtOH/CO$_2$ cooling bath. Crown ether was purified by sublimation before use.

Synthesis of K$_6$Rb$_5$Ge$_{17}$: 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 5 K/min. The product was dried and stored over sodium for at least 96 hours, with constant cooling by an EtOH/CO$_2$ cooling bath. Crown ether was purified by sublimation before use.

Figure 1. Asymmetrical and nominal unit of [([18]crown-6)][Pt(CO)$_3$]$^-$·10 NH$_3$ (A=K, Rb). Thermal ellipsoids at 50 % probability.

Figure 2. Isosurfaces of the ELF of [Pt(CO)$_3$]$^-$ at $\eta_a=0.7$ (a) and $\eta_a=0.875$ (b) as well as the HOMO (c) and LUMO (d). Positive (blue) and negative (red) isosurfaces are shown at a level of 0.1 for the MOs.
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)$_3$(PPh)$_3$:** The compound was synthesized following the directions of Chini and Longoni from K$_2$PtCl$_6$, PPh$_3$ and CO.$^{[15]}$

**Synthesis of [Al(18-crown-6)]$_2$[Pt(CO)$_3$]·10 NH$_3$ (A=K, Rb):** K$_6$Rb$_2$Ge$_{17}$, Pt(CO)$_3$(PPh)$_3$, [18-crown-6 and [2.2.2]-crypt were weighed into a heated Schlenk vessel in the stoichiometric ratio of 1:1:1.5:2.5. 5 mL of liquid ammonia were condensed onto the reactants, resulting in a red solution. After storage of the vessel at 233 K for five weeks, dark red needles of the titular compound could be isolated and analysed 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 selection 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.$^{[16]}$ ShelXT was used for structure solution, with ShelXL for refinement.$^{[16]}$ For visualization purposes Olex2 1.3 was employed, while the figures were drawn up with Diamond 4.$^{[20]}$

**Crystal data for [Al(18-crown-6)]$_2$[Pt(CO)$_3$]·10 NH$_3$ (A=K, Rb):** M = 1097.06 g·mol$^{-1}$, space group $P2_12_12_1$, $a = 14.09789(10)$ Å, $b =$ 8.88557(7) Å, $c =$ 38.0486(3) Å, $\beta =$ 109.7675(7), $V =$ 4765.86(6) Å$^3$, $Z = 4$, $\mu_\text{abs} = 1.525$ g·mol$^{-1}$, $\mu =$ 0.034 mm$^{-1}$, F(000) = 2235.0, 80461 measured reflections, 9795 independent reflections, $R_\text{int} = 7.25\%$, $R_\text{exp} = 4.75\%$, $\omega R_\text{exp} = 12.43$ for $I > 2\sigma(I)$, $R_1 = 5.10\%$, $\omega R_1 = 12.63$ for all data, GooF = 1.095, $\Delta p_{\text{max}} = 1.88$ eÅ$^{-3}$, $\Delta p_{\text{min}} = -1.34$ eÅ$^{-3}$.

Crystallographic data for the compound has 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-2103387 (Fax: +44-1223-336-033, E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Theoretical calculations:** The calculations were performed using ORCA (Version 4.2.1) employing a level of theory of D3H2-BLYP-D3BJ/TZP-DKH using a CPCM model of ammonia.$^{[21]}$ Generation of grids was performed using cuQCT,$^{[22]}$ visualization done using VMD,$^{[23]}$ QTAIM analysis was performed using AIMAll.$^{[24]}$ Calculation of ELI-D and its analysis was performed using DGrid Version 5.2.$^{[23]}$

**Acknowledgements**

F. K. acknowledges funding from the DFG by the Walter-Benjamin program number KL3500/1-1. N. K. acknowledges funding from the DFG in the RTG 2620. Open Access funding enabled and organized by Projekt DEAL.

**Conflict of Interest**

The authors declare no conflict of interest.

---

**Data Availability Statement**

The data that support the findings of this study are openly available in Cambridge Crystallographic Data Centre, CCDC at http://www.ccdc.cam.ac.uk, reference number 2103387.

**Keywords:** Platinum · Carbonyl · Anion · Zintl Phases · Liquid ammonia

---

[1] W. Hieber, *Adv. Organomet. Chem.* 1970, 8, 1–28.
[2] a) S. D. Ding, M. B. Hall, in: *Chemical Bond I: 100 Years Old and Getting Stronger*, Vol. 169 (Ed.: D. M. P. Mingos), Springer, New York, 2016, pp. 199–248; b) R. J. Cross, *Annu. Rep. Progr.Chem. Sect. A-Phys. & Inorg. Chem.* 1974, 71, 291–344; Inorg. Chem. 1974, 71, 291–344.
[3] L. Mond, C. Langer, F. Quincke, *J. Chem. Soc. Trans.* 1890, 57, 749–753.
[4] a) E. W. Abel, F. G. A. Stone, *Q. Rev. Chem. Soc.* 1969, 23, 325–371; b) E. W. Abel, F. G. A. Stone, *Q. Rev. Chem. Soc.* 1970, 24, 498–552.
[5] a) P. Kündig, M. Moskovits, G. A. Ozin, *J. Mol. Struct.* 1972, 14, 137–144; b) J. H. Darling, J. S. Ogden, *J. Chem. Soc., Dalton Trans.* 1973, 1079–1085.
[6] J. E. Ellis, *Organometallics* 2003, 22, 3322–3338.
[7] a) J. E. Ellis, *Organometallics* 2003, 22, 3322–3338; b) J. E. Ellis, P. T. Barger, M. L. Winzenburg, G. F. Warnock, *J. Organomet. Chem.* 1990, 383, 521–530; c) G. L. Rochfort, J. E. Ellis, *J. Organomet. Chem.* 1983, 250, 265–276; d) J. E. Ellis, C. P. Parnell, G. P. Hagen, *J. Am. Chem. Soc.* 1978, 100, 3605–3607; e) J. E. Ellis, P. T. Barger, M. L. Winzenburg, *J. Chem. Soc. Chem. Comm.* 1977, 686–687.
[8] C. Lorenz, M. Kaas, N. Korber, *Z. Anorg. Allg. Chem.* 2018, 644, 1678–1680.
[9] a) G. Longoni, P. Chini, *J. Am. Chem. Soc.* 1976, 98, 7225–7231; b) J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni, S. Martinengo, *J. Am. Chem. Soc.* 1974, 96, 2614–2616.
[10] a) I. Ciabatti, C. Femoni, M. C. Iapalucci, G. Longoni, S. Zacchini, *J. Cluster Sci.* 2013, 25, 115–146; b) C. Cesari, J. H. Shon, S. Zacchini, L. A. Berben, *Chem. Soc. Rev.* 2011, 50, 9503–9539; c) B. Bertl, C. Femoni, M. C. Iapalucci, S. Ruggieri, S. Zacchini, *Eur. J. Inorg. Chem.* 2018, 3285–3296.
[11] J. M. Goicoechea, S. C. Sevov, *Inorg. Chem.* 2005, 44, 2654–2658; J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* 2004, 126, 6860–6861.
[12] A. Ugrino, S. C. Sevov, *Chem. Eur. J.* 2004, 10, 3727–3733.
[13] C. Hoch, M. Wendorff, C. Rohr, *J. Alloys Compd.* 2004, 366, 309–309.
[14] B. R. Barnett, A. L. Rheindorf, J. S. Figueuera, *Angew. Chem.* 2016, 128, 9399–9404; *Angew. Chem. Int. Ed.* 2016, 55, 9253–9258.
[15] R. F. W. Bader, *Atoms in molecules: a quantum theory*, Oxford: Claredon press, Oxford, 1990.
[16] M. Kohout, *Faraday Discuss.* 2007, 135, 43–54.
[17] P. Chini, G. Longoni, *J. Chem. Soc. A* 1970, 1542–1542.
[18] 171.41.83a 64-bit ed., Rigaku Oxford Diffraction, Oxford, England, 2020.
[19] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2015, 71, 3–8; b) G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, 71, 3–8; c) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, 64, 112–122; d) SHELXL-97, University of Göttingen 1997, Sheldrick, G. M.
[20] a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, 42, 339–341; b) K.
[21] a) F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* **2020**, *152*, 224108–224108; b) F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327; c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465; d) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104–154104; e) L. S. C. Martins, F. E. Jorge, S. F. Machado, *Mol. Phys.* **2015**, *113*, 3578–3586; f) F. E. Jorge, A. C. Neto, G. G. Camiletti, S. F. Machado, *J. Chem. Phys.* **2009**, *130*, 064108–064108; g) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001.

[22] L. A. Malaspina, E. K. Wieduwilt, J. Bergmann, F. Kleemiss, B. Meyer, M. F. Ruiz-Lopez, R. Pal, E. Hupf, J. Beckmann, R. O. Piltz, A. J. Edwards, S. Grabowsky, A. Genoni, *J. Phys. Chem. Lett.* **2019**, *10*, 6973–6982.

[23] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics* **1996**, *14*, 33–38.

[24] T. A. Keith, 19.10.12 ed., TK Gristmill Software, Overland Park, KS, USA, 2019.

[25] M. Kohout, Program DGrid, version 5.1, Dresden, Germany, 2021.
Dr. S. M. Tiefenthaler, Dr. F. Kleemiss*, Prof. Dr. N. Korber*

1 – 5

\[\text{[Al\{18\text{crown-6}\}\text{H}\text{[Pt\{CO\}3]}\cdot 10 \text{NH}_3 (A=K, Rb) – A crystal structure containing the long postulated [Pt-\{CO\}3]}^2^-}\]