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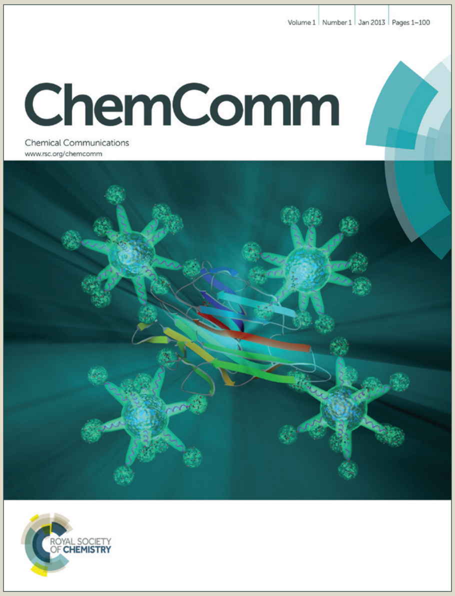

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Platinum polyoxoniobates

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Reaction of $[Nb_6O_{19}]^{8-}$ with $[Pt(OH)_4(H_2O)_2]$ upon heating yielded first characterized platinum polyniobates. A dimeric complex $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ (1) is produced in 1:1 molar ratio. Increasing the Pt/Nb_6 molar ratio to 1:2 yields a mixture of 1 and a sandwich-type complex $[Pt(Nb_6O_{19})_2]^{12-}$ (2).

The chemistry of noble metals polyoxometalates is a hot topic of modern inorganic chemistry.[1] The coordination chemistry of platinum has a long history and can be regarded as classics, but surprisingly little is known about coordination of Pt(IV) or Pt(II) to polyoxometalates (POM). Moreover, some reports on supposedly Pt-coordinated POM remain controversial. Well established examples of Pt containing POM are sparse and are essentially restricted to a series of Pt(IV)-containing Anderson-type structures differing in the degree of protonation.[2] Recently coordination of Pt(II) to $[W_5O_{18}]^{6-}$ and $[PW_{11}O_{39}]^{7-}$ units was reported.[3] A double Pt-substituted silicotungstate $(C(NH_2)_3)_8[SiPt_2W_{10}O_{40}]\cdot 6H_2O$ was reportedly prepared from $[Pt(OH)_6]^{2-}$, $[SiW_{11}O_{39}]^{8-}$ and guanidinium hydrochloride.[4] Later it was, however, suggested that this formulation was incorrect, the product being instead the guanidinium salt of monolacunary $[SiW_{11}O_{39}]^{8-}$.[5] Heating $[PtCl_4]^{2-}$ and $[PW_{11}O_{39}]^{7-}$ at pH = 4 resulted in a complex with molar ratio Pt/POM 2:1. It remains, however, inadequately characterized, and is unexplicably formulated as 1:1 complex in the abstract of the same paper.[6] $[WZnPt^{II}_2(ZnW_9O_{34})_2]^{12-}$ was prepared from $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ and $[PtCl_4]^{2-}$; it shows catalytic activity in oxidation reactions.[7] The claim for the preparation of individual $[Pt^{IV}(O)(OH_2)(PW_9O_{34})_2]^{16-}$ [8] has been withdrawn after more careful investigation and polemics.[9] Keggin-type heteropolyacids react with organoplatinum complexes bearing a Pt-CH_3 group, such as $[PtMe_2(COD)]$, leading to the methane evolution and grafting of the organometallic fragment (such as $\{PtMe(COD)\}^+$ on the polyacid, either as a tightly bound ionic pair, or by coordination to one of the POM oxygen atoms.[10] In the family of group 5 POM the only example of Pt-containing complex is provided by $[H_2Pt^{IV}V_9O_{28}]^{5-}$.[11] Hence the preparation and reliable characterization of Pt-containing POM (this is also more or less true for other noble metals) still remains a considerable challenge. No non-organometallic complexes of polyniobates (PONb) with noble metals have been reported other than those with $\{(p\text{-cym})Ru\}^{2+}$ [12,13] and $\{Cp^*Rh\}^{2+}$ [14] coordinated to $[Nb_6O_{19}]^{8-}$. Last, but not the least, niobium has diagonal relationship with titanium which explains photocatalytic activity of PONb, similar to that of TiO_2.[15] This potential use of PONb in photocatalysis has good prospects, but it needs a photoactivator, which role is typically fulfilled by H_2PtCl_6.[15b] From this point of view direct coordination of Pt(IV) to PONb is very desirable since Pt(IV), being octahedral and sufficiently oxophilic, could either substitute a Nb atom in the hexaniobate structure, similar to $[H_2Pt^{IV}V_9O_{28}]^{5-}$ which is simply a Pt(IV)-monosubstituted classical decavanadate, or be "grafted" as a capping atom.

The hexanuclear Lindqvist-type polyoxoniobate $[Nb_6O_{19}]^{8-}$ is a convenient starting material for preparation of various PONb.[16] Thus unprecedented PONb with Keggin-type anions $[XNb_{12}O_{40}]^{n-}$ were isolated and structurally characterized. [17-19] Lacunary type PONb $Na_{14}[H_2Si_4Nb_{16}O_{56}]\cdot 45.5H_2O$ [20] and $Na_{15}[(PO_2)_3PNb_9O_{34}]\cdot 22H_2O$, [21] which have no analogues among the polymolybdates and polytungstates have been reported. L. Cronin et al. succeeded in generation of the pentagonal building block $\{(Nb)Nb_5\}$ based on niobium from $K_7H[Nb_6O_{19}]$, which offers links with the chemistry of giant keplerates.[22]

Under the less drastic conditions hexaniobate $[Nb_6O_{19}]^{8-}$ is stable in the alkaline solutions and acts as tridentate ligand towards various metal cations and labile cationic complexes because of the presence of basic $\{Nb_3O_3\}$ sites. There are several examples of complex formation between $[Nb_6O_{19}]^{8-}$ and non-organometallic transition metal ions, such as Mn(IV), Ni(IV) [23] or Co(III).[24] Typically the coordination leads to a "sandwich"-type complex with D_{3d} point group symmetry, $[M(Nb_6O_{19})_2]^{n+}$, where the central cation is octahedrally coordinated by the oxide bridges of two hexaniobates, acting in tridentate mode. Formation of monomeric or dimeric complexes with a transition metal cation incorporated into the Lindqvist anion also occurs.[25, 26] Basic conditions, necessary to prevent hydrolysis of hexaniobate and precipitation of niobium oxide, severely limit the choice of suitable metal precursors if the list of existing PONb complexes is to be expanded. In this respect Pt(IV) is a good choice since it forms a well-defined and stable hydroxo complexes, such as $[Pt(OH)_4(H_2O)_2]$ and $[Pt(OH)_6]^{2-}$.

We have found that reaction of $[Pt(OH)_4(H_2O)_2]$ with $K_7H[Nb_6O_{19}]\cdot 13H_2O$ in 1:1 molar ratio at 150 °C gives a yellow solution, which has only one signal in ^{195}Pt NMR spectrum at 3189 ppm ($[Pt(OH)_4(H_2O)]$ in these conditions demonstrates signal at 3308 ppm). Slow evaporation of this solution in air yielded aggregates of needle-like yellow crystals of $Cs_2K_{10}[Nb_6O_{19}\{Pt(OH)_2\}]_2\cdot 13H_2O$ (**Cs_2K_{10}-1**) (Fig. 1), which were characterized with X-ray structural analysis (for experimental details see Table S1, crystal packing Fig. S1).

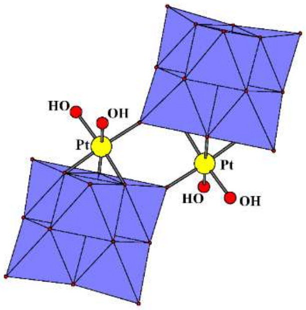

Figure 1. Structure of $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$

This is a unique dimeric complex, first of this type in the chemistry of polyniobates, which consists of two Pt(IV) coordinated each by three oxygen atoms from a $\{Nb_3O_3\}$ face of a hexaniobate ($d(Pt\text{-}O)_{av}$ 2.028(13), 2.010(14), and 2.124(14) Å), a terminal oxygen of the adjacent $[Nb_6O_{19}]^{8-}$ anion (d(Pt-O) 1.998(11) Å), and bearing two terminal OH groups (d(Pt-O) = 2.015(16) and 1.994(14) Å). For comparison, $H_2[Pt(OH)_6]$ has Pt-O distances in the range of 1.994-2.006 Å.[27] In $[(dach)Pt(OH)_4]$ (dach = trans-(±)-1,2-diaminocyclohexane) the Pt-OH distances are 1.96(2)–2.01(2) Å.[28] In the crystal structures of different isomers of $[PtCl_2(NH_3)_2(OH)_2]$ the Pt-O distances are 2.000(5)-2.010(7) Å.[29] By the contrary, Pt-H_2O distances in $[(PtMe_3(H_2O))_2SO_4]_\infty$ are rather long, 2.322(9) and 2.363(8) Å. [30] Hence, according to the literature data and the charge balance, the Pt-O distances in **1** correspond to coordinated OH rather than to H_2O.

In a freshly prepared aqueous solution of a pure **Cs_2K_{10}-1** sample single signal appears in ^{195}Pt NMR spectrum at 3189 ppm, the same as in mother liquor, indicating that no dissociation of the dimer $[Nb_6O_{19}\{Pt(OH)_2\}]_2$ occurs in solution. The resonance at 3189 ppm for **Cs_2K_{10}-1** is rather close to 3275 ppm, reported for $[Pt(OH)_6]^{2-}$.[31] This means that the observed chemical shift of 3189 ppm agrees well with expected all-oxygen environment around Pt(IV).

The negative ESI mass spectrum of aqueous solutions of **Cs_2K_{10}-1** strongly suggests that the integrity of the dimeric $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ polyanion is preserved in solution (see Figure S3). Two groups of signals featuring 4- and 3- charge states are observed, which correspond to **1** associated with cations of the general formula $[(Nb_6O_{19}\{Pt(OH)_2\}_2 + cat_8]^{4-}$ and $[(Nb_6O_{19}Pt(OH)_2)_2 + cat_9]^{3-}$ (where cat stands indiscriminately for H^+, K^+ or Cs^+; see fig. S2 for full peak assignments).

Reaction of $[Pt(OH)_4(H_2O)_2]$ and $K_7H[Nb_6O_{19}]\cdot 13H_2O$ in the 1:2 molar ratio at 160-190°C gives a yellow solution, which has two signals in ^{195}Pt NMR spectra at 3189 and 3422 ppm with relative intensities 0.75/0.25 (Fig. S2). Slow evaporation of this solution, even in the presence of Cs^+, produces light-yellow polyhedra of $Na_2K_{10}[Pt(Nb_6O_{19})_2]\cdot 18H_2O$ (**Na_2K_{10}-2)** as the first crop. This is not uncommon since the solubility of niobates and tantalates are lowest for Na^+ and highest for Cs^+. The sandwich-type anion $[Pt(Nb_6O_{19})_2]^{12-}$ (**2**) is a structural analog of well-known $[M(Nb_6O_{19})_2]^{n+}$ (M = Mn, Ni, Co) complexes (Fig. 2). All Pt-O distances are equivalent, being 2.042(1) Å. **Na_2K_{10}-2** is isotypic to $K_6Na_2[Co^{III}H_5(Nb_6O_{19})_2]\cdot 26.5H_2O$ salt and has similar crystal packing pattern of the polyoxoanions.[24]

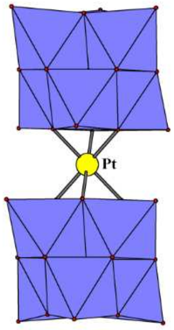

Figure 2. Structure of $[Pt(Nb_6O_{19})_2]^{12-}$

Further evaporation of the solution gives a mixture of **Cs_2K_{10}-1** and crystals with analogous unit cell parameters as **Na_2K_{10}-2**, but with different cationic composition (close to K_{12}) due to sodium salts of polyoxoniobates having very low solubility.[16] The Na^+ in **Na_2K_{10}-2** comes from leaching from the glass container in the alkaline solution. Slow increase in Na^+ concentration by leaching is beneficial for obtaining X-ray quality single crystals. If crystallization does not occur, stoichiometric amount of NaOH may be added. If 2M NaOH is used instead of 2 M CsOH, isostructural Na_5K_6H-**2** separates rapidly.

A freshly prepared solution of pure **Na_2K_{10}-2** demonstrates only one, slightly broadened, signal at 3422 ppm. There are few examples of ^{195}Pt signals with such a large positive chemical shift: $[(OH)_4Pt(\mu\text{-}OH)_2Pt(OH)_4]^{2-}$ [32] (3570 ppm) and TBA$^+$ and K^+ salts of $[H_2SiPtW_{11}O_{40}]^{4-}$ (3666 and 3616 ppm respectively). [33] Aged solutions of **Na_2K_{10}-2** give rise to increasingly intense signal at 3189 ppm, corresponding to the formation of **1**.

This experimental evidence points towards a dynamic behavior of the species in the $Nb_6O_{19}^{8-}$ / Pt(IV) system, where dimeric $[Pt(Nb_6O_{19})_2]^{12-}$ complex interconverts with $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$. Taking advantage of the versatility and high sensitivity of the ESI-MS technique for tracing solution speciation in the POM chemistry,[34] we recorded ESI-MS spectrum of aqueous solution of **Cs_2K_{10}-1** equilibrated for one week. ESI-MS results suggest coexistence of at least four different species in solution. Both dimeric $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ (**1**) and monomeric $[Pt(Nb_6O_{19})_2]^{12-}$ (**2**) polyanions were identified (see figures S3-S5); moreover, the ESI-MS data allow us to suggest the presence of free Lindqvist $[Nb_6O_{19}]^{8-}$ polyanion, with an additional species that corresponds to the $[Nb_6O_{19}Pt(OH)_3]^{7-}$ anion whose structure might correspond to capping of $[Nb_6O_{19}]^{8-}$ with a C_{3v}-$\{Pt(OH)_3\}^+$ group.

It seems that the formation of **1** and **2** are favored regardless of the Pt /$Nb_6O_{19}^{8-}$ ratio. Thus, reaction of $[Nb_6O_{19}]^{8-}$ with $[Pt(H_2O)_2(OH)_4]$ at 170 C in 1:4 molar ratio gives only an equimolar mixture of $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ and $[Pt(Nb_6O_{19})_2]^{12-}$, as deduced from ^{195}Pt NMR. Again, after keeping mother liquor for 6 months this ratio increases to 6:1, and signal from $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ broadens, which may imply appearance of the monomeric $[Nb_6O_{19}\{Pt(OH)_3\}]^{7-}$ species whose chemical shift should only slightly differ form that of $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$.

Compound **Cs_2K_{10}-1** exhibits electrocatalytic activity for water oxidation in 0.1 M Na_2SO_4. Oxidation process generates a significant rise in the current consistent with catalytic process mediated by **Cs_2K_{10}-1** (Fig. S8). The current for **Cs_2K_{10}-1** (upper curve at Fig. S8) is several times higher compared to that for the blank solution (bottom curve). This electrochemical behavior is similar to the polyoxotungstate with tetrarhodium-oxo core. [35]

Conclusions

This work reports first examples of coordination of Pt(IV) to a polyniobate. We have isolated and characterized two Pt/Nb_6O_{19} complexes (1:1 and 1:2 molar ratio) with x-ray, EDX and ^{195}Pt NMR. The 1:1 complex has a new coordination type of a transition metal to Lindqvist-type anions. According to ESI-MS data, complex 1:1 is more stable in solution and retains its structure, but complex 1:2 undergoes a rapid evolution into several species with 1:1 product being the dominant product. Complex **Cs_2K_{10}-1** demonstrates electrocatalytic activity for water oxidation in 0.1 M Na_2SO_4.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental section, X-ray crystallography, ESI-MS experiments, Xrpd patterns, cyclic voltammogram of **Cs_2K_{10}-1** in 0.1 M Na_2SO_4 at the glassy carbon electrode. See DOI: 10.1039/c000000x/

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