VIP Noble Metalates

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Synthesis and Characterization of the Dicopper(II)-Containing 22-Palladate(II)$[Cu^{II}_2Pd^{II}_{22}P^{V}_{12}O_{60}(OH)_8]^{20-}$**

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The recently discovered area of water-soluble noble-metal-based polyoxometalates (POMs)[1a] is currently developing fast, not only because of their interesting structures and properties but also because of the promising applications of these compounds.[1–5]

Currently polyoxopalladates(II) are the noble-metal-based polyanion family comprising the largest number of members. In 2008 the parent 13-palladate $[Pd^{II}_{13}As^{V}_8O_{34}(OH)_6]^{8-}$ ("$Pd_{13}As_8$") was reported, which consists of a cuboctahedral $\{Pd_{12}\}$ cage, a central Pd^{II} guest, and eight $\{AsO_4\}$ capping groups leading to an overall cubic shape of the polyanion.[1a] Later it was shown that the $\{As^{V}O_4\}^{3-}$ capping groups can also be replaced by $\{Se^{IV}O_3\}^{2-}$ or $\{PhAs^{V}O_3\}^{2-}$, which unexpectedly lead to coordination numbers of 6 (octahedral) and even 8 (cubic), respectively, for the central Pd^{II}.[1c] The 15-palladate $[Pd_{15}P_{10}O_{50}]^{20-}$ ("$Pd_{15}P_{10}$") was obtained in an attempt to replace the arsenate heterogroups in "$Pd_{13}As_8$" by phosphate ions.[2a] Delferro et al. reported $[Pd_{15}Se_{10}O_{40}Na]^{9-}$, which is the selenite analogue of "$Pd_{15}P_{10}$".[2b] Moreover, the central palladium ion in $[Pd_{13}(PhAs)_8O_{32}]^{6-}$ can be replaced by lanthanide and transition-metal ions, so that the more general formulation $MPd_{12}L_8$ (M = central metal ion, L = capping groups) is appropriate.[3] Very recently we reported the mixed-metal, bowl-shaped 6-vanado(V)-7-palladate(II) $[Pd^{II}_7V^{V}_6O_{24}(OH)_2]^{6-}$.[4b]

Herein we report a new structural type of noble metalates. In the course of studying the ability of the cubic $\{Pd_{12}L_8\}$ shell to incorporate different guest cations M and also heterogroups L we obtained a novel, double-cuboid-shaped copper(II)-containing polyoxo-22-palladate(II) $[Cu_2Pd_{22}P_{12}O_{60}(OH)_8]^{20-}$ ("$Pd_{22}Cu_2P_{12}$", (**1**), Figure 1). This polyanion contains the largest number of palladium ions yet found in polyoxopalladate chemistry. The bonding of each Cu^{II} ion involves the rare eightfold oxo-coordination. Polyanion **1** has been prepared by heating of $Pd_3(CH_3COO)_6$ and $Cu(CH_3COO)_2\cdot H_2O$ in sodium phosphate buffer (0.5 M, pH 6.9), and isolated as a hydrated sodium salt, $Na_{20}[Cu_2Pd_{22}P_{12}O_{60}(OH)_8]\cdot 58\,H_2O$ (Na-**1**), which is stable in the solid state under air and light, is soluble in water, and can be repeatedly recrystallized from aqueous solution.

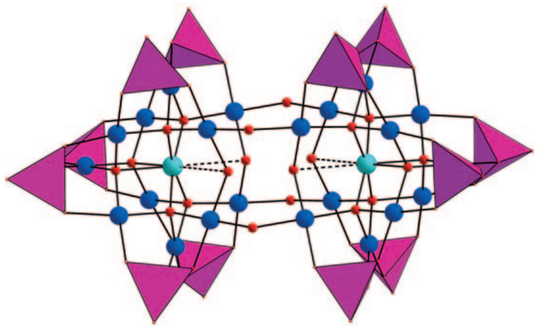

Figure 1. Combined ball-and-stick/polyhedral representation of **1**. Cu turquoise, Pd blue, O red balls, $\{PO_4\}$ purple tetrahedra. The very long Cu–O bonds (2.759(6)–2.839(6) Å) are indicated by dotted lines (see text for details).[15]

The pH value of the reaction mixture is a crucial factor for the formation of Na-**1**. For example, at slightly lower pH values (6.0–6.2), we observed the formation of dark-red, octahedral crystals of a hydrated sodium salt of a compound with a $\{CuPd_{12}P_8\}$ core,[5] the crystal structure and properties of which will be presented elsewhere. At the intermediate pH range 6.2–6.9, a mixture of the two compounds was obtained. In the absence of copper(II) ions, a similar synthetic

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procedure leads to the star-shaped polyoxo-15-palladate(II) "$Pd_{15}P_{10}$".[2a]

Single-crystal X-ray analysis showed that **1** consists of two $\{CuPd_{11}P_6O_{32}\}$ fragments, which are connected by four hydroxo bridges (Figure 1).[6] The structure of each $\{CuPd_{11}P_6O_{32}\}$ building block is reminiscent of the parent "$Pd_{13}L_8$" structure, with the central Pd^{II} ion being replaced by Cu^{II} and a $\{PdP_2O_8\}$ edge of the cube missing. The structure of **1** can also be viewed as two fused "lacunary" $\{CuPd_{11}P_6O_{32}\}$ units. As found for the entire "$Pd_{13}L_8$" family, the two Cu^{II} ions in **1** are encapsulated in a distorted cubic $\{O_8\}$ ligand field. Owing to the symmetry of **1**, the $\{O_8\}$ cube is disproportionately stretched along one of its diagonal planes (the horizontal O_4 plane in Figure 1). Thus the Cu–O distances are very long for the two *cis* oxygen atoms of this diagonal plane (Cu–O89 and Cu–O011, 2.759(6), 2.839(6) Å), somewhat elongated for the other two oxygen atoms in the same plane (2.274(6), 2.290(6) Å), and are in the usual range of 2.032(6)–2.066(6) Å for the remaining four oxygen atoms of the $\{O_8\}$ cuboid motif. The coordination sphere of the Cu^{II} ions in **1** can be described as a strongly distorted cube (with coordination number 8), or if the very long Cu–O bonds are ignored, as a trigonal prism (coordination number 6) with the Cu^{II} ions displaced towards one of the square faces (the distance Cu^{II}–$\{O_4$ face$\}$ is 0.166(2) Å).

Regarding the linkage of the Pd^{II} ions to the oxygen atoms of the $\{O_8\}$ cuboid, the oxygen atoms can be divided into two groups: six μ_4-bridging oxygen atoms, each of which is coordinated by a Cu^{II} and three Pd^{II} ions (Pd–O 1.929(6)–2.012(6) Å), and two μ_2-bridging oxygen atoms coordinated by two Pd^{II} centers (Pd–O 2.008(6)–2.034(6) Å). All Pd^{II} ions within the $\{CuPd_{11}P_6O_{32}\}$ fragment have the expected square-planar coordination geometry and coordinate two oxygen atoms of the inner $\{O_8\}$ motif. Seven of the eleven Pd^{II} ions in each $\{Pd_{11}CuP_6O_{32S}\}$ half unit complete their square-planar coordination with oxygen atoms of two neighboring tetrahedral phosphate groups (Pd–O 2.015(6)–2.070(6) Å; P–O 1.532(6)–1.573(7) Å). The remaining four Pd^{II} centers complete their square-planar coordination geometry with an oxygen atom of a phosphate heterogroup (Pd–O 2.005(6)–2.021(6) Å; P–O 1.547(6)–1.568(7) Å) and a μ_2-bridging oxygen atom of the hydroxo group (see below) linking the two $\{CuPd_{11}P_6O_{32}\}$ fragments (Pd–O 2.026(6)–2.035(6) Å).

In the solid state, individual polyanions of **1** are surrounded by sodium countercations and water molecules linked together through a framework of strong hydrogen bonds as well as $Na^+\cdots OH_2$ and $Na^+\cdots OPO_3$ interactions. Both X-ray diffraction and elemental analysis are consistent with the presence of a total of 20 Na^+ ions in Na-**1**. Eight additional protons are thus required to balance the negative charges of **1**. By using bond valence sum (BVS) calculations[7] four of the eight protons in the structure of **1** can be unambiguously associated with the four μ_2-oxygen atoms linking the two $\{CuPd_{11}P_6O_{32}\}$ units (see Figure 1, and also the Supporting Information for details). One more proton is most likely located at the inversion center of **1**, being surrounded by a square of four oxygen atoms (O89, O011 and their inversion-related counterparts) separated from each other by 2.53 and 2.69 Å. This description is consistent with the observation of electron density at the inversion center in the difference Fourier map. The remaining three protons are disordered over the terminal oxygen atoms of ten of the twelve phosphate capping groups (P–O 1.513(6)–1.533(7) Å).

The presence of bridging hydroxo groups in **1** supports the important role of the pH value in the formation of this polyanion. The availability of OH^- ions appears to drive the dimerization of "lacunary" $\{CuPd_{11}P_6O_{32}\}$ motifs derived from the recently characterized $\{CuPd_{12}P_8\}$ species.[5] We are trying to isolate and characterize the $\{CuPd_{11}P_6O_{32}\}$ intermediate as we believe that this formally "monolacunary" ion may exhibit a chemistry as rich and diverse as that of the monolacunary $\{XW_{11}\}$ (X = P, Si, Ge, etc.) Keggin ions.

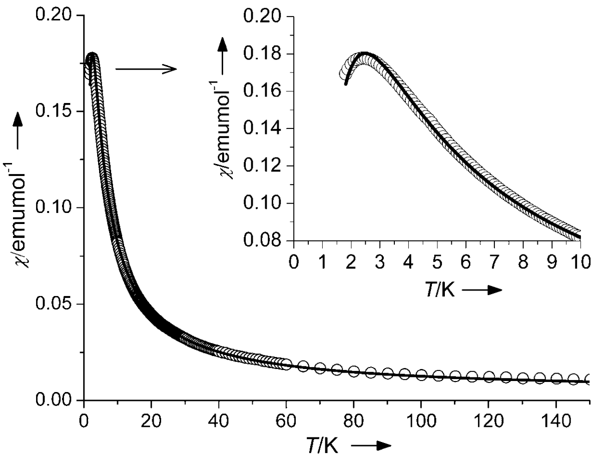

Figure 2. Temperature dependence of magnetic susceptibility (χ) of a polycrystalline powder of Na-**1** at a constant magnetic field $H = 500$ Gauss. Inset: low-temperature region magnified for clarity. The solid line represents the fit to the Bleaney–Bowers equation.

Since the geometry of the Cu^{II} ions is unique, involving eight oxo bonds, we carried out magnetic susceptibility (χ) measurements over 1.8–280 K, and EPR at frequencies of 9.65, 35, and 240 GHz in a temperature range of 3.7–330 K. The measurements yielded quite unexpected results. As shown in Figure 2, χ goes through a maximum at about 2.4 K, providing direct evidence for a significant antiferromagnetic interaction between the two Cu^{II} ions ($d_{Cu\cdots Cu} = 7.4$ Å) within the double-cuboid polyanion. The plot could be well fitted to the standard equation for a Cu^{II}–Cu^{II} dimer in copper acetate, with a diamagnetic ($S = 0$) ground state and $S = 1$ (triplet) excited state separated by the energy J, using the Bleaney–Bowers formula [Eq. (1)][8]

$$\chi = \chi_0 + \frac{4C}{T(3 + \exp(-J/k_B T))} \tag{1}$$

where χ_0 is the term due to temperature-independent paramagnetism (TIP), C the Curie constant, J the exchange coupling constant corresponding to the spin Hamiltonian $\hat{H}_{exchange} = -J\hat{S}_1\hat{S}_2$ and k_B the Boltzmann constant. The fitting yielded $J = -4.0(1)$ K (ca. 2.8(1) cm^{-1}), $g_{av} = 1.869(2)$ and $\chi_0 = 4\times10^{-3}$ emu mol^{-1}, with an R value of 0.9997. The coupling J is surprisingly large, when considering that the two Cu^{II}

centers are 7.4 Å and six bonds apart (or four if coupling is through the central proton). The largest antiferromagnetic coupling reported[9] for two Cu^{II} ions interacting through an exchange pathway involving a diamagnetic Pd^{II} center is 72 cm^{-1}. In this case the two Cu^{II} centers are about 7.6 Å apart, but in contrast to **1**, the Cu^{II} ions are in a distorted square-pyramidal coordination environment, bound by three nitrogen and two oxygen atoms. Hence, this complex is not comparable to our polyanion.

The susceptibility results were fully supported by the variable frequency EPR data. Figure 3 shows a typical X-band spectrum (9.647 GHz) from a powder of **1**. The structure that is visible in the low-field part of the spectrum consists of a combination of fine structure (zero-field splitting) and a septet hyperfine structure with intensity rations 1:2:3:4:3:2:1 from two coupled $I = 3/2$ nuclei. This finding clearly shows that the spin state is a $S = 1$ triplet state, and a computer simulation[10] yields a zero-field splitting parameter D of 1.7 mT and a hyperfine splitting $A_{\parallel}$ of 3.9 mT, which is reasonable.[9,11] These results were fully supported by the Q-band and 240 GHz data (shown in Figure S7 of the Supporting Information). The g-values obtained are $g_z = 2.4674$, $g_y = 2.0797$, and $g_x = 2.0706$.

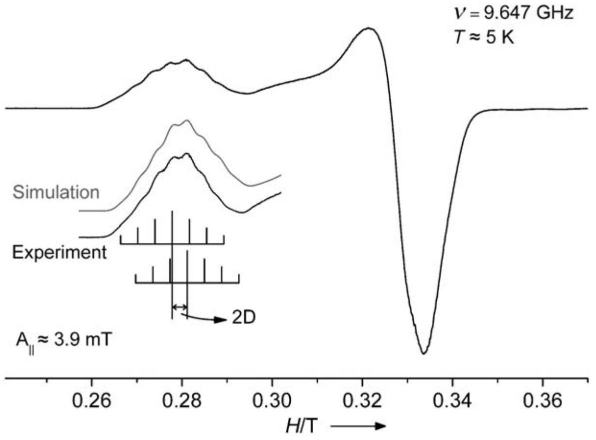

Figure 3. X-band powder EPR spectrum of Na-**1** measured at 5 K. Inset: the enlarged low-field part of the spectrum and its computer simulation in which the bars show a schematic construction of the hyperfine splitting and relative intensities.

To our knowledge, Figure 3 represents the first report of an EPR spectrum of a Cu^{II} ion in an eightfold oxo-coordination. There is a report of a g-value for a possibly very distorted eightfold oxo-coordination in the Ca–Cu acetate lattice,[11] but no high-field EPR data was reported. Also a g_z value as high as the 2.4674 exhibited by Na-**1** has not been reported for any Cu^{II} complex. The fact that $g_{\parallel} > g_{\perp}$ indicates that in the Cu^{II} ion the $d_{x^2-y^2}$ orbital is dominant.

It seems clear that our synthesis of the Cu^{II}–Cu^{II} dimer **1** opens up a new avenue for studying Cu^{II} dimers with control of their interionic distance and bonding parameters. This control should provide a new, quantitative basis for testing the accuracy of theoretical models of Cu–Cu magnetic interactions, which is of interest because many solids and biological materials contain such dimers.

Owing to its relative insolubility in most useful electrolytes, the electrochemistry of Na-**1** was studied in the solid-state by entrapping it in a perfluorinated polymer (Nafion), in a carbon paste (CPE), or a room-temperature ionic liquid (BMImBF$_4$; BMIm = 1-butyl-3-methylimidazol). These matrices are widely used for hybrid electrode materials. The modified electrode preparations are described in detail in the Supporting Information. Na-**1** is suitable for a very facile incorporation in all these films and the modified electrodes remain remarkably stable even after hundreds of voltammetric cycles in a large potential domain (from hydrogen evolution to Pd redox processes). Figure S4 in the Supporting Information is representative of the voltammograms recorded in a pH 7.1 medium. A well-defined hydrogen sorption/desorption pattern was observed just before the electrolyte reduction. The two well-resolved oxidation peaks arising from absorbed and adsorbed hydrogen at −0.540 V and −0.385 V (versus the saturated calomel electrode (SCE)) are the "fingerprint" of palladium nanoparticles (Supporting Information, Figure S4). Note that such distinct waves indicate that the Pd particles remain well-dispersed.[13] Thus, Na-**1** opens the way for the fabrication of smoothly distributed Pd nanostructures in various conditions. This observation is important because palladium nanostructures and palladium nanocomposites are among the more attractive electrocatalysts for various reduction and oxidation electrode processes. However, the major challenge remains the facile preparation of efficient electrodes based on thin films of well-dispersed Pd nanoparticles. The modified electrodes based on Na-**1** meet these requirements probably because this precursor is a well-characterized and palladium-rich discrete oxide. Given that oxides are the favorite supports for most heterogeneous catalysts, these observations could lead to the preparation of new electrocatalysts.

The hydrogen-evolution reaction (HER) was selected to study the electrocatalytic behavior of electrodes modified with Na-**1**. Tafel analysis was performed on the HER wave to determine the kinetic parameters of this reaction (Supporting Information, Figure S5). The Tafel parameters ($\eta = a + b \log i$) with the exchange current density, i_0, expressed in A cm^{-2} and b in mV were: for pH 7.1: $\log i_0 = -4.1 \pm 0.1$; $b = 65 \pm 5$ mV; correlation coefficient $R = 0.995$. These values compare favorably with those recently reported for Pd nanoparticles synthesized in aqueous toluene medium (pH 5), then embedded in Nafion films.[14] The absence of Cu^{II} redox processes is mainly due to 1) Cu^{II} reduction is more difficult than that of Pd^{II}, 2) the percentage of Cu^{II} is small compared to Pd, and 3) the copper wave is obscured by the efficient hydrogen evolution reaction in the presence of even a tiny amount of Pd.

In conclusion, we have prepared a novel, discrete, solution-stable, double-cuboid-shaped copper(II)-containing polyoxo-22-palladate(II), $[Cu^{II}_2Pd^{II}_{22}P^{V}_{12}O_{60}(OH)_8]^{20-}$ (**1**) using a simple, one-pot procedure in aqueous solution and mild reaction conditions. The salt $Na_{20}[Cu^{II}_2Pd^{II}_{22}P^{V}_{12}O_{60}(OH)_8]\cdot 58H_2O$ (Na-**1**) was characterized by single-crystal X-ray diffraction, elemental analysis, IR, UV/Vis, and EPR spectroscopy, thermogravimetric analysis, electrochemistry, and magnetic susceptibility measurements. The pH value and the presence of Cu^{II} ions play a key role in the formation of **1**. This compound has afforded, to our knowledge, the first detailed EPR measurements on Cu^{II} ions in this octa oxo geometry. In addition, the magnetic exchange interaction between the two Cu^{II} ions in **1** is found to be unexpectedly large, possibly opening up a new area for theoretical investigations of magnetic interactions on Cu^{II} and other complexes under controlled coordination and bonding parameters. Moreover, **1** could be used for the preparation of electrocatalysts. Also, we have already prepared the monocuboid $\{CuPd_{12}P_8\}$ containing polyoxopalladate, as well as several other derivatives of this type with various d-block transition-metal ion guests and capping groups. These results will be reported elsewhere.

Experimental Section

Na-**1**: $Pd_3(CH_3COO)_6$ (0.140 g, 0.208 mmol) and $Cu(CH_3COO)_2{\cdot}H_2O$ (0.021 g, 0.104 mmol) were dissolved in 0.5 M NaH_2PO_4 buffer (5 mL; pH 6.9). Under stirring, the solution was heated to 80 °C. During the first 30 min, the pH value of the reaction mixture was adjusted to 6.9–7.2 by addition of 1 M NaOH. The resulting solution was heated at 80 °C for 1 h. Then it was cooled to room temperature, filtered, and allowed to crystallize in an open vial. Needle-like orange-red crystals were obtained after several days, which were collected by filtration and air dried. Yield: 0.039 g (25 % based on Pd).

Elemental analysis calcd (%): Na 8.45, Cu 2.34, Pd 43.03, P 6.83; found: Na 8.53, Cu 2.29, Pd 42.45, P 6.99. IR (2 % KBr pellet): $\tilde{\nu}$ = 1634 (m), 1087 (s), 973 (s), 934 (s), 678 (sh), 614 (s), 580 (sh), 551 (m), 444 cm^{-1} (m). UV/Vis (H_2O, λ_{max}): 250–254 and 396–400 nm. The thermogram (25–900 °C) and electrochemistry of Na-**1** are discussed in the Supporting Information. The UV/Vis spectrum is also shown in the Supporting Information (Figure S3). The EPR spectra were obtained with a Bruker Elexsys 680 instrument and the high-field spectrometers[16] at the NHMFL EPR facility.

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[5] Unit cell of the hydrated sodium salt of $\{CuPd_{12}P_8\}$: tetragonal, space group $P4/m$, $a = 14.9249(8)$, $c = 20.1530(9)$ Å, $V = 4480.11(63)$ Å^3, $T = 173(2)$ K.

[6] Crystal data and details of the X-ray diffraction experiment are in the Supporting Information. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-422151 and -422152 (SQUEEZEd. data).

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[15] Figure 1 was generated by Diamond Version 3.2 (copyright Crystal Impact GbR).

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