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Synthesis, Characterization, and Crystal Structure of the Water Soluble Copper(I) Complex with Trisulfonated Triphenylphosphine

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Introduction

Aqueous soluble copper(I) complexes stable toward valence disproportionation are rare.[1] Thus, in addition to the seminal complex $[Cu(NH_3)_3]^+$ isolated in 1901 by G. Bodlaender[2] and recently reinvestigated by Lamble et al.,[3] only salts of $[Cu(CN)_3]^{2-}$ [4] and of $[Cu(DMP)_2]^+$ (DMP = 2,9-dimethyl-1,10-phenantroline)[5] appear to have been isolated and characterized as solid species. In contrast, a plethora of lipophilic Cu^{I} complexes have been synthesized and thoroughly investigated in organic media.[6] In this connection, it is noted that the availability of water- and air-stable soluble copper(I) complexes featured by a substantial coordinative unsaturation might provide valuable starting compounds for developing aqueous inorganic and bioinorganic chemistry of copper(I), barely explored so far.[1,7]

Tris(*m*-sulfonatophenyl)phosphine (TPPTS) trisodium salt is a soft ligand whose coordination ability toward a variety of transition metals has been demonstrated by Herrmann et al. in the late 80s.[8] Syntheses performed in aqueous media include metal centers such as Mn^{I}, Fe^{0}, Ru^{II}, Co^{I,0}, Rh^{I}, Ir^{I}, Ni^{0}, Pd^{0}, Pt^{II,0}, Ag^{I}, and Au^{I}, but not Cu^{I}.

In the frame of our ongoing interest for Cu^{I}/Cu^{II} coordination chemistry with phosphines, phosphine oxides and chalcogenides, and phosphinoamines,[9−16] we report here the synthesis and characterization, including the X-ray structure, of the complex $\{Na_5[Cu(TPPTS)_2]\cdot 5H_2O\cdot {}^1/_2EtOH\}_n$, **1**·$^1/_2$EtOH, where TPPTS is $[P(C_6H_4\text{-}m\text{-}SO_3)_3]^{3-}$. For the synthesis we have utilized a two-phase approach, taking advantage of the lability of the $[Cu(MeCN)_4]^+$ precursor and of the capability of TPPTS to extract the copper ion into the aqueous phase through the formation of a very stable complex, which combines high water solubility with unusual redox stability.

Experimental Section

TPPTS[17] and $[Cu^{I}(MeCN)_4]BF_4$ [9] were prepared according to published procedures. The ^{31}P CPMAS spectra were obtained with a Bruker DSX 500 spectrometer and referenced to external $NH_4H_2PO_4$. Solution-state NMR measurements were performed in D_2O at 293 K on a Bruker AC 200 spectrometer.

Synthesis of $\{Na_5[Cu(TPPTS)_2]\cdot 5H_2O\}_n$ (1). Complex **1** was obtained upon reacting a 25 mL dichloromethane solution of $[Cu(MeCN)_4]BF_4$ (0.344 g, 1.09 mmol) with a 25 mL water solution of TPPTS (1.60 g, 2.80 mmol) under vigorous stirring. The slight ligand excess over the 2:1 stoichiometry took into account the ca. 20% TPPTS oxide present in the starting crude material. After 30 min, the colorless organic phase was removed and a raw glassy material was collected from the aqueous phase after solvent removal. Pure **1** was obtained upon redissolution with a lesser amount of water (ca. 10 mL) followed by gradual addition of ethanol (ca. 50 mL). The white product was recovered by filtration, washed with ethanol, and dried under vacuum to constant weight. Yield: 1.25 g (90%). Found: C, 33.5; H, 2.7; S, 15.0; Cu, 4.9; Na, 9.6. Anal. Calcd for $C_{36}H_{34}CuNa_5O_{23}P_2S_6$ (**1**): C, 34.1; H, 2.7; S, 15.2; Cu, 5.0; Na, 9.1. ^{1}H NMR: δ 7.36 (d, H-γ, ^3J = 7.5 Hz), 7.46 (t, H-β, ^3J = 7.6 Hz), 7.77 (s, H-α'), 7.87 (d, H-α, ^3J = 7.8 Hz) ppm. ^{13}C NMR: 130.79 (C4), 132.64 and 132.87 (C2 and C5), 134.83 (C1), 138.96 (C6), 146.55 (C3). ^{31}P NMR (D_2O/CD_3OD 1:1, 243 K): δ −2.2 (s, $\gamma_{1/2}$ = 55 Hz). ^{31}P CPMAS: δ −8.2 ppm (q, J_{PCu} = 1.05 kHz). Molar conductivity in water (1.00 mmol dm^{-3}): Λ_M 496 ohm^{-1} cm^2 mol^{-1}, a value corresponding to the range expected for a 5:1 electrolyte in which noncomplex cations are balanced by a complex anion of much lower ionic mobility. For comparison, the uncoordinated TPPTS ligand was found to have $\Lambda_M = 270\ \Omega^{-1}$ cm^2 mol^{-1}, a reasonable value for bulky tris-univalent electrolyte type. Thermal analysis: loss of water from 60 to 170 °C = 8.7% (vs 7.9 calcd). The dehydrated complex is stable up to 600 °C. Electrospray mass spectra (ESI) obtained from H_2O/MeOH solutions, in the presence of trifluoroacetic acid, reveal a major signal centered at 1200.5 (*m*/*z*) corresponding to (**1** + Na$^+$ − 5H_2O).

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Table 1. Crystallographic Data of the Copper Complex **1**$\cdot{}^{1}/_{2}$EtOH

chem formula $C_{37}H_{37}CuNa_5O_{23.5}P_2S_6$	fw 1290.5
$a = 16.480(3)$ Å	space group $C2/m$ (No. 12)
$b = 28.321(6)$	$T = 21$ °C
$c = 12.969(3)$	$\lambda = 0.710\ 73$ Å
$\beta = 110.28(2)°$	$\rho_{calcd} = 1.510$ g cm^{-3}
$V = 5678(2)$ Å^3	μ(Mo Kα) = 7.74 cm^{-1}
$Z = 4$	$R(F)$,[a] 8.64%
	$R(wF^2)$,[b] 23.16%

[a] $R = \sum||F_o| - |F_c||/\sum |F_o|$. [b] $R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Synthesis of $\{Na_5[Ag(TPPTS)_2]\cdot 5H_2O\}_n$ (2). Complex **2** was prepared upon treating $AgNO_3$ (0.082 g, 0.48 mmol) with TPPTS (0.700 g, 1.23 mmol) in water (10 mL). The resulting solution was stirred at room temperature for 1 h, and crude **2** was collected as a glassy material after solvent removal. The solid was recrystallized as for **1**, affording colorless microcrystals. Yield: 0.51 g (80%). Found: C, 32.2; H, 2.8; S, 14.0. Anal. Calcd for $C_{36}H_{34}AgNa_5O_{23}P_2S_6$: C, 33.0; H, 2.6; S, 14.7. ^{1}H NMR: δ 7.37 (d, H-γ, $^3J = 7.7$ Hz), 7.50 (t, H-β, $^3J = 7.7$ Hz), 7.82 (s, H-α'), 7.87 (d, H-α, $^3J = 7.9$ Hz) ppm. ^{31}P NMR (D_2O/CD_3OD 1:1, 243 K): δ 10.5 ppm (dd, $^1J_{107AgP} = 438$ and $^1J_{109AgP} = 506$ Hz). ^{31}P CPMAS: δ 5.1 ppm (d, $^1J_{AgP} = 541$ Hz).

Crystallography. Single crystals of the copper complex were grown by layering ethanol onto the sample solution in water. A colorless transparent crystal of approximate dimensions 0.4 mm × 0.3 mm × 0.2 mm was mounted inside a Lindemann capillary with some mother liquor and used for data collection. The crystal data and refinement parameters are summarized in Table 1.

Data were measured on a Nicolet R3m/V four-circle diffractometer in $2 \leq \theta \leq 25°$. A total of 5277 reflections were collected of which 3660 with $I \geq 2\sigma(I)$ were judged observed. The structure was solved by heavy-atom methods, completed by subsequent difference Fourier syntheses, and refined on F^2 by full-matrix least-squares procedures, using the SHELX suite of programs.[18] Much of the high-angle data collected were flagged as weak and bore negative intensity; refinement was improved by omitting the 833 reflections with negative intensity from the final refinement cycles. Attempts to treat Cu, S, P, Na, and phenyl C atoms anisotropically were successful, while refinement in the alternative space groups $C2$ and Cm did not improve the model. Final residuals were $R = 0.086$ (observed data) and 0.098 (all data). The maximum residual electron densities (up to 1.1 e Å^{-3}) have no chemical significance. Nonetheless, refinement of the crystal structure was not satisfactory and was severely hampered by many factors. First, the crystal batch had inherent handling difficulties and the only remotely suitable sample for a single-crystal structure determination was substandard, as quickly manifested in broad scan widths during early search routines on the diffractometer. Second, six of the nine SO_3 oxygen atoms (those at S(1B) and S(1C) of Figure 2) were each disordered over two positions; the site occupancy factors of the disordered atoms were refined, the total value for each set being constrained to unity. In all cases the refined value approaches $^3/_5$. Moreover, the complex contains half a molecule of ethanol with high thermal parameters indicative of some positional disorder, and unfortunately, the Na^+ ions, along with the water molecules, were also seen to be severely disordered into a number of partially occupied sites. The occupancies assume the values $^3/_4$, $^1/_2$, or $^1/_4$ and the isotropic U value was always ca. 0.14 Å^2. Diligent efforts to model the disorder for the H_2O molecules were unsuccessful, and we believe that the unresolved disorder is responsible for the high R values. Consequently, only the bond distances and angles in the inner core of complex **1**$\cdot{}^1/_2$EtOH are to be considered reliable data (see caption of Figure 2).

Results and Discussion

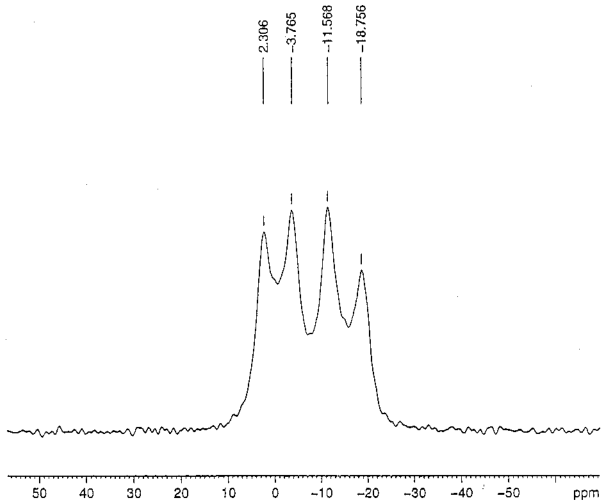

Figure 1. ^{31}P CPMAS spectrum of **1**.

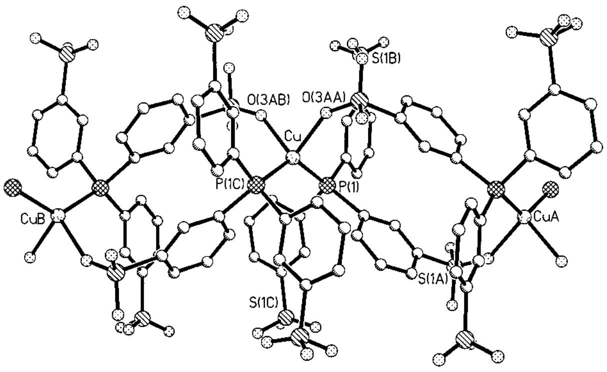

Figure 2. PLUTO diagram showing the polymeric nature of the anion of **1**$\cdot{}^1/_2$EtOH. For the sake of clarity the Na^+ cations, the water, and EtOH molecules have not been shown. Selected bond lengths [Å] and angles [deg] are the following: Cu−P(1) 2.269(1); Cu−O(3A*A*) 2.136(6); P(1)−Cu−O(3A*A*) 107.1(2); P(1)−Cu−O(3A*B*) 109.2(2); O(3A*A*)−Cu−O(3A*B*) 87.8(3); P(1)−Cu−P(1*C*) 128.8(1). Symmetry transformations used to generate equivalent atomsare the following: (*A*) $^1/_2 - x$, $^1/_2 - y$, $1 - z$; (*B*) $x - {}^1/_2$, $^1/_2 - y$, z; (*C*) $-x$, y, $1 - z$.

Complex **1** is obtained in high yield upon stirring a dichloromethane solution of $[Cu(MeCN)_4]BF_4$ with a 2 to 1 molar excess of TPPTS dissolved in water. The crude product, obtained from the aqueous phase upon solvent removal, is in agreement with the formulation $\{Na_5[Cu(TPPTS)_2]\cdot 5H_2O\}_n$ as determined by elemental analysis, ESI mass spectrometry, conductivity measurements, and ^{1}H and ^{13}C NMR spectroscopy. In particular, the ^{31}P NMR spectrum in D_2O exhibits a slightly broadened signal (without multiplicity) centered at δ −2.2 ppm ($\gamma_{1/2} = 55$ Hz) compared with the sharp singlet at −5.1 ppm ($\gamma_{1/2} = 8$ Hz) exhibited by uncoordinated TPPTS. Furthermore, the ^{31}P CPMAS spectrum shows an asymmetrical quartet (Figure 1), as expected for the coupling of a set of equivalent phosphorus nuclei with the $I = {}^3/_2$ ^{63}Cu and ^{65}Cu nuclei. The asymmetrical pattern reflects the distortion from spherical symmetry in the coordination environment of **1** (vide infra), as already reported for copper(I) phosphine complexes with low symmetry.[19] Bowmaker et al.,[20] for the case of Cu, and Muetterties et al.,[21] for the case of silver, indicate that the scalar coupling constant for the ^{31}P−metal bond appears to depend only on the number of phosphine ligands coordinated to the metal(I) center. In our case, the mean value of $^1J_{CuP}$ is between the reported values

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for two-coordinated and three-coordinated phosphinocopper(I) complexes.[20] In attempts to elucidate completely the stoichiometry of **1**, prolonged efforts of recrystallization of crude **1** from water/ethanol mixtures led to white microcrystals suitable for X-ray determination. The molecular structure of the title complex is depicted in Figure 2.

The copper(I) center lies on a 2-fold axis, and it is coordinated by two phosphorus atoms [P(1) and P(1C)], achieving a distorted tetrahedral configuration thanks to the coordination of two oxoanion atoms O(3A*A*) and O(3A*B*), one from the unit at $^1/_2 - x$, $^1/_2 - y$, $1 - z$ and the other from that at $x - {}^1/_2$, $^1/_2 - y$, z. Thus, TPPTS turns out to behave as a bridging ligand to produce an intricate lattice architecture in which the empty space between the coils is filled with sodium ions, water molecules, and also molecules of ethanol coming from the crystallization solvent. The coils are aligned and propagate along the crystallographic *a* axis. The Cu−P distance (2.269 Å) is slightly longer than the mean sum of the covalent radii (2.23 Å)[22] and agrees well with previous data;[9−16] the Cu−O distance (2.136 Å) is only slightly longer than the mean value (2.11 Å) observed in complexes containing $\mathrm{Cu^I{-}ONO_2}$ bonds.[22−27] The major distortion from tetrahedral geometry arises from the wider P−Cu−P angle (128.8°) and the narrower O−Cu−O one (87.8°). To the best of our knowledge, **1** is the fourth reported structure of a metal−TPPTS complex besides $[\mathrm{W(CO)_5(TPPTS)}]^{3-}$,[28] dinuclear $[\mathrm{Co_2(CO)_6(TPPTS)_2}]$,[29] and $\mathrm{Cs_8[Au(TPPTS)_3]}$.[30]

The isolation of the Cu−complex **1** prompted us to verify the reactivity of TPPTS with the second-row congener silver by using a synthetic procedure identical to that employed for **1**. Instead of the reported tris-substituted $\mathrm{Ag^I}$ [8] (and also $\mathrm{Au^I}$ [30,31]) TPPTS species, we collected the silver analogue of **1**, $\{\mathrm{Na_5[Ag(TPPTS)_2]\cdot 5H_2O}\}_n$ (**2**), as established by NMR spectroscopy. In fact, ^{31}P NMR at −30 °C displays two doublets centered at 10.5 ppm with $^1J_{\mathrm{107AgP}} = 438$ and $^1J_{\mathrm{109AgP}} = 506$ Hz, values in agreement with a 1:2 Ag/P ratio.[21] The corresponding values for the tricoordinated species[8] are different (i.e., 314 and 358 Hz), and the magnitude of *J* clearly accounts for a 1:3 metal/ligand ratio. As a further support of the two-phosphorus coordination, the ^{31}P CPMAS spectrum of **2** exhibits a doublet at δ 5.1 ppm with $^1J_{\mathrm{AgP}}$ equal to 541 Hz.

As for the solution state of complex **1** in water, its FT-IR spectrum is virtually superimposable with that of aqueous TPPTS in the sulfonate regions. This is in contrast with the pattern in the solid state, where detectable differences between the sulfonate absorption bands of free and Cu(I)-coordinated TPPTS are observed. This result suggests lability of coordinated sulfonate groups, thereby generating vacancies in the coordination sphere (likely filled by still labile water molecules). Preliminary multinuclear NMR investigations reveal that aqueous **1**, while retaining the P−Cu(I)−P moiety, readily incorporates small molecules such as acetonitrile and physiologically relevant imidazole and histamine.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $\mathbf{1}\cdot{}^1/_2\mathrm{EtOH}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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