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Reactivity of Peroxo- and Bis(μ-oxo)dicopper Complexes with Catechols**

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The aerobic oxidation of catechols to *o*-quinones mediated by copper ions is an important catalytic process in both synthetic and metalloprotein systems. Catechol oxidase[1] and tyrosinase,[2] both of which cycle through a (μ-η^2:η^2-peroxo)-dicopper active site intermediate, are capable of such catecholase activity, notwithstanding some controversy surrounding the involvement of discrete catechol intermediates in phenol oxidation by tyrosinase and model systems.[3] Many mechanistic studies of catalytic catechol oxidation by dissolved copper complexes have appeared, with copper–dioxygen species often postulated as being responsible for formation of quinone and H_2O_2 in the key reaction step [Eq. (1)].[4]

$$Cu^{II}(O_2^{2-})Cu^{II} + \text{catechol} \longrightarrow o\text{-quinone} + 2\,Cu^{I} + H_2O_2 \qquad (1)$$

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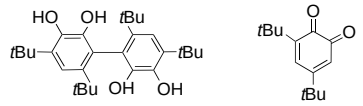
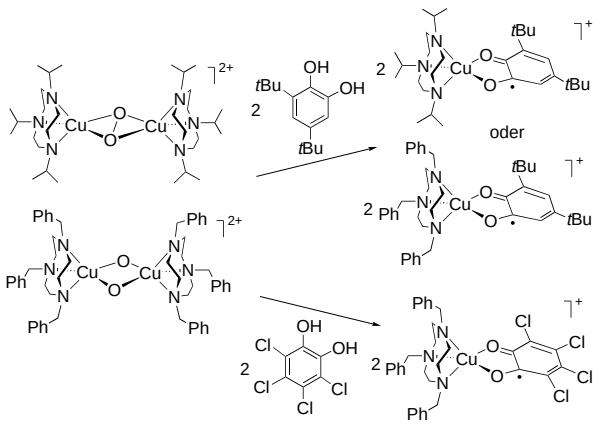
We have directly evaluated the feasibility of this transformation by examining the reaction of catechols with isolated (μ-η^2:η^2-peroxo)- and bis(μ-oxo)dicopper complexes[5] relevant to the tyrosinase and catechol oxidase active site species. In the only other reported study of this type,[6] a tris(pyrazolyl)hydroborate-capped (μ-η^2:η^2-peroxo)dicopper compound converted 3,5-di-*tert*-butylcatechol (dbcat) to the coupled product **1** under argon and to a mixture of **1** and the quinone **2** catalytically under O_2. Herein we report that instead of promoting these conversions or the reaction shown in Equation (1), complexes with isomeric $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O)_2]^{2+}$ and $[Cu_2(\mu\text{-}O)_2]^{2+}$ cores coordinated to amine macrocycles cleanly oxidize two equivalents of catechol to yield monocopper-semiquinone complexes by a heretofore unreported synthetic route to such species (Scheme 1).



1 **2**

Addition of two equivalents of dbcat to solutions[7] of orange $[\{Cu(L^{Bn_3})\}_2(\mu\text{-}O)_2](SbF_6)_2$ or red-brown $[\{Cu(L^{iPr_3})\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)](O_3SCF_3)_2$ in CH_2Cl_2 or THF at $-80\,^\circ C$ caused bleaching of their respective optical absorption features (L^{R_3} = *N*,*N*,*N*-trisubstituted 1,4,7-triazacyclononane). Upon subsequent warming and work-up, the deep green-brown complexes [Cu(L)(dbsq)]X (dbsq = 3,5-di-*tert*-butylsemiquinonato; $L = L^{Bn_3}$, $X = SbF_6$; $L = L^{iPr_3}$, $X = O_3SCF_3$) were isolated as crystalline solids in 93% and 81% yields, respectively. The complex $[Cu(L^{Bn_3})(Cl_4sq)]ClO_4$ (Cl_4sq = 3,4,5,6-tetrachlorosemiquinonato) was prepared analogously (90% yield of isolated product) from the ClO_4^- salt of the bis(μ-oxo)dicopper precursor and 3,4,5,6-tetrachlorocatechol monohydrate ($Cl_4cat \cdot H_2O$). When <2.0 equivalents of dbcat were added to the bis(μ-oxo) compound, $[Cu(L^{Bn_3})(dbsq)]^+$ was generated in the corresponding substoichiometric amount and **1** or **2** were not produced (monitored by ^1H NMR spectroscopy).[8]

The reaction products were identified as Cu^{II}–semiquinonato species on the basis of spectroscopic comparisons to previously reported examples,[9] electrochemical properties, and X-ray crystallography. Notable diagnostic spectral features for the dbsq and Cl_4sq complexes include rich UV/Vis



Scheme 1. Oxidation of catechol to monocopper semiquinone complexes.

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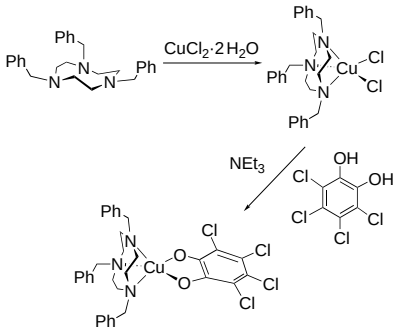
spectra with a pattern of multiple intense CT bands akin to literature data[9a–c] and EPR silence previously shown in a related complex[9d] to result from large zero-field splitting in the ferromagnetically coupled Cu^{II}-semiquinonato spin system. Paramagnetism is revealed by room temperature magnetic susceptibility (for $[Cu(L^{Bn_3})(dbsq)]SbF_6$, $\mu_{eff} = 2.8(1)\ \mu_B$, Evans method)[10, 11] and large downfield-shifted signals for the dbsq ligand in the ^1H NMR spectrum of $[Cu(L^{Bn_3})(dbsq)]SbF_6$ ($\delta = 32.2$, 39.5, 59.0, and 86.0). These signals were assigned by comparisons to the spectra of benzyl substituent deuterated and Cl_4sq analogues. Such paramagnetically shifted NMR spectral features have not been noted previously for compounds of this type.[9] Also consistent with the Cu^{II}–semiquinonato formulation, $[Cu(L^{Bn_3})(dbsq)]SbF_6$ shows reversible one-electron reduction ($E_{1/2} = -0.20$ V, $\Delta E_p = 80$ mV) and oxidation ($E_{1/2} = +0.80$ V, $\Delta E_p = 100$ mV) waves in its cyclic voltammogram indicative of stable Cu^{II}–catecholate and Cu^{II}–quinone/Cu^{I}–semiquinonato forms, respectively (data reported vs. SCE, 100 mV s^{-1}, Pt electrode, 25 °C, 0.2 M Bu_4NPF_6 in CH_2Cl_2). For the Cl_4sq analogue, both potentials are much higher, as expected, but the oxidation is irreversible ($E_{1/2} = +0.49$ V, $\Delta E_p = 80$ mV; $E_{pa} = +1.17$ V).

Definitive proof of the structural formulation of the reaction products was obtained by comparison of the X-ray structure of $[Cu(L^{Bn_3})(Cl_4sq)]ClO_4$ to that of its reduced congener prepared independently, the Cu^{II}–catecholate complex $[Cu(L^{Bn_3})(Cl_4cat)]\cdot CH_3CN$ (Scheme 2 and Figure 1).[12–14] Both complexes exhibit square-pyramidal copper ion geometries ($\tau < 0.03$).[15] A statistical analysis[16] of the bond lengths associated with the bound Cl_4sq^- and Cl_4cat^{2-} ligands confirmed their indicated redox states ($\Delta = -0.9(1)$ and $-1.9(1)$, respectively, where values of -0, -1, or -2 indicate quinone, semiquinone, or catecholate levels).

Previously reported preparative routes to Cu^{II}–semiquinonato complexes include 1) reaction of dicopper(II) complexes with dbcat with generation of a Cu^{I} coproduct and 2) reduction of an *o*-benzoquinone by a Cu^{I} complex.[9] Little mechanistic information is available for the reactions reported herein, but the existence of an intermediate (currently under investigation) is implicated by UV/Vis monitoring at −75 °C which showed bleaching of bis(μ-oxo)dicopper features *before* the appearance of final product Cu^{II}–semiquinonato absorptions that grew in only upon subsequent warming. The reactions we have discovered are new; indeed, we had anticipated conversion of catechols to *o*-benzoquinones with generation of bis(μ-hydroxo)dicopper(II) complexes on the basis of the propensity of the latter to be formed upon decomposition of (μ-η^2:η^2-peroxo)- and bis(μ-oxo)-dicopper compounds.[7,17] Evidently, in the synthetic systems the mononuclear Cu^{II}–semiquinonato complexes are particularly stable thermodynamically. In contrast, the restrictive confines of the dicopper protein active sites of catechol oxidase or tyrosinase might be expected to inhibit the reaction pathway we have observed, leaving as a feasible enzymatic route the reaction of a single catechol with either a $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$ or a $[Cu_2(\mu\text{-}O)_2]^{2+}$ core to afford *o*-benzoquinone.[19]



Scheme 2. Synthesis of $[Cu(L^{Bn_3})(Cl_4cat)]\cdot CH_3CN$.

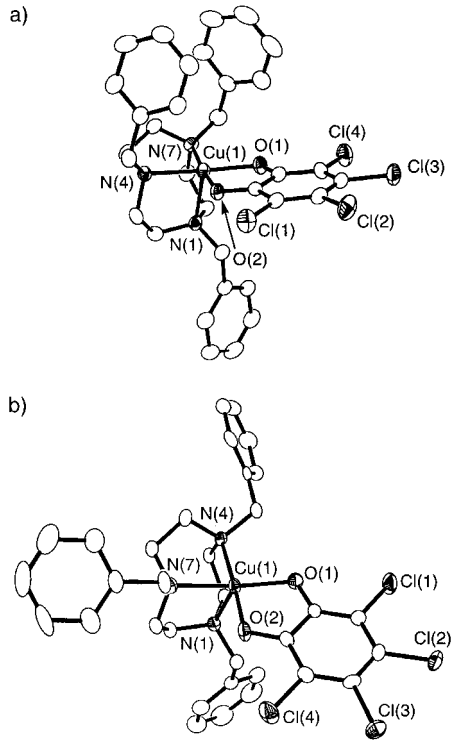


Figure 1. Representations of the X-ray crystal structures of a) the cationic portion of $[Cu(L^{Bn_3})(Cl_4sq)]SbF_6$ and b) $[Cu(L^{Bn_3})(Cl_4cat)]\cdot CH_3CN$ without the CH_3CN solvate molecule, showing non-hydrogen atoms as 30% and 50% thermal ellipsoids, respectively. Selected bond lengths [Å] and angles [°] for (a): Cu(1)–O(1) 1.989(4), Cu(1)–O(2) 2.001(4), Cu(1)–N(1) 2.203(4), Cu(1)–N(4) 2.028(4), Cu(1)–N(7) 2.024(4), O(1)–Cu(1)–O(2) 82.1(2); O(1)-Cu(1)-N(4) 174.0(2), N(7)-Cu(1)-O(2) 172.4(2), O(1)-Cu(1)-N(7) 96.2(2), O(2)-Cu(1)-N(4) 93.7, N(4)-Cu(1)-N(7) 87.4(2), O(1)-Cu(1)-N(1) 99.8(2), O(2)-Cu(1)-N(1) 101.0(2), N(7)-Cu(1)-N(1) 86.6(2), N(4)-Cu(1)-N(1) 85.2(2). Selected bond lengths [Å] and angles [°] for (b): Cu(1)–O(1) 1.940(4), Cu(1)–O(2) 1.915(4), Cu(1)–N(1) 2.254(4), Cu(1)–N(4) 2.058(40, Cu(1)–N(7) 2.079(4); O(1)-Cu(1)-O(2) 86.6(2), O(1)-Cu(1)-N(7) 168.3(2), O(1)-Cu(1)-N(4) 97.0(2), O(2)-Cu(1)-N(1) 98.2(2), N(4)-Cu(1)-N(1) 84.1(2), O(2)-Cu(1)-N(4) 174.8(2), O(2)-Cu(1)-N(7) 90.3(2), N(4)-Cu(1)-N(7) 85.4(2), O(1)-Cu(1)-N(1) 108.0(2), N(7)-Cu(1)-N(1) 83.6(2).

Experimental Section

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.

$[Cu(L^{Bn_3})(dbsq)]SbF_6$: A solution of $[(L^{Bn_3}Cu)_2(\mu\text{-}O)_2](SbF_6)_2$ in CH_2Cl_2 (10 mL) at −80 °C was prepared as described previously (0.20 g, 0.27 mmol scale of Cu^{I} precursor).[7b,c] After removal of excess dioxygen by purging N_2 at −80 °C for 10 min, a solution of dbcat (0.06 g, 0.27 mmol) in CH_2Cl_2

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(≈0.5 mL) was added, resulting in an instantaneous color change from orange-brown to intense brown-green. The reaction mixture was stirred at −80 °C for 30 min and then warmed to room temperature. After concentrating the solution to ≈2 mL by evaporation under vacuum, Et_2O (20 mL) was added to induce precipitation of a brown-green microcrystalline solid which was collected by filtration, washed with Et_2O, and air-dried. The product was obtained as dark brown-green crystals by diffusing Et_2O into a 1:1 CH_2Cl_2/Et_2O solution at room temperature (0.23 g, 93 %). FT-IR (KBr): $\tilde{\nu}$ = 1476 (C–O), 656 (SbF_6^-) cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 382 (2300), 441 (1400), 558 (720), 750 sh, 844 (340), 990 sh nm; EPR (CH_2Cl_2, 77 K): silent; ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 3.6 (br, 12H), 8.1 (3H), 8.9 (6H), 12.2 (br, 6H), 32.2 (br, 9H), 39.5 (br, 1H), 59.0 (br, 9H), 86.0 (very br, 1H); ISP-MS (CH_2Cl_2): *m/z* (%): 682.4 (100) [M^+]; elemental analysis calcd for $C_{41}H_{53}N_3O_2CuSbF_6$ (%): C 53.64, H 5.82, N 4.58; found: C 53.07, H 5.76, N 4.54. Samples of $[Cu([D_{21}]L^{Bn_3})(dbsq)]ClO_4$ were prepared similarly starting with $[Cu([D_{21}]L^{Bn_3})(CH_3CN)]ClO_4$. FT-IR (KBr): $\tilde{\nu}$ = 1475 (s, C–O), 1100 (vs, ClO_4^-), 624 (s, ClO_4^-) cm^{-1}; EPR (CH_2Cl_2, 77 K) silent; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 3.4 (br, 12H), 32.4 (br, 9H), 39.8 (br, 1H), 59.5 (br, 9H), 86.0 (very br, 1H).

$[Cu(L^{Bn_3})(Cl_4sq)]ClO_4$: This compound was prepared analogously to $[Cu(L^{Bn_3})(dbsq)]SbF_6$,except by treating $[\{Cu(L^{Bn_3})\}_2(\mu\text{-}O)_2](ClO_4)_2$ with $Cl_4cat \cdot H_2O$ (0.24 g, 90 %). FT-IR (KBr): $\tilde{\nu}$ = 1498 (s, C–O), 1451 (s, C–O), 1090 (vs, ClO_4^-), 624 (s, ClO_4^-) cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 331 (12400), 434 sh (3300), 444 (3400), 626 (1100), 988 (400) nm; EPR (CH_2Cl_2, 77 K): silent; ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.6 (br, s, 12H), 8.1 (s, 3H), 9.0 (s, 6H), 12.8 (br, s, 6H); elemental analysis calcd for $C_{33}H_{33}N_3O_6Cl_5Cu$ (%): C 49.19, H 4.13, N 5.22; found: C 49.25, H 4.27, N 5.14.

$[Cu(L^{iPr_3})(dbsq)]CF_3SO_3$: A deep red-brown solution of $[(L^{iPr_3}Cu)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)](CF_3SO_3)_2$ in CH_2Cl_2 (10 mL) at −80 °C was prepared as described previously (0.13 g, 0.26 mmol scale of Cu^I precursor).[7a] To this solution was added a solution of dtbc (0.057 g, 0.26 mmol) in CH_2Cl_2 (1 mL) which resulted in an instantaneous color change from red-brown to brown-green. After stirring at −80 °C for 15 min, the solution was allowed to warm to room temperature and the solvent was removed under vacuum. Recrystallization of the resulting solid by pentane diffusion into a THF solution at room temerature resulted in the deposition of the product as brown-green crystals (0.142 g, 81 %). FT-IR (KBr): $\tilde{\nu}$ = 1476 (s, C–O), 1226 ($CF_3SO_3^-$), 1151 ($CF_3SO_3^-$), 1030 ($CF_3SO_3^-$), 638 ($CF_3SO_3^-$) cm^{-1}; EPR (1:1 CH_2Cl_2/toluene, 77 K) silent; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 380 (2100), 444 (1450), 548 (730), 750 (350), 840 sh (330), 980 sh (200) nm; FAB-MS (MNBA): *m/z* (%): 538 (100) $[M - CF_3SO_3]^+$; elemental analysis calcd for $C_{30}H_{53}N_3O_5F_3SCu$ (%): C 52.35, H 7.76, N 6.10; found: C 52.10, H 7.66, N 6.00.

$[Cu(L^{Bn_3})(Cl_4cat)] \cdot CH_3CN$: To a solution of L^{Bn_3} (0.20 g, 0.50 mmol)[18] in CH_2Cl_2 (10 mL) was added a suspension of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.50 mmol) in CH_2Cl_2 (10 mL). Addition of excess Et_2O (≈25 mL) to the resulting yellow-green solution induced deposition of a pale green microcrystalline product formulated as $L^{Bn_3}CuCl_2$ (0.22 g, 82 %). UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 396 (1250), 710 (100) nm; EPR (CH_2Cl_2, 77 K, 9.46 G Hz): $g_{\|}$ = 2.25, $A_{\|}$ = 146 G, $g_{\perp}$ = 2.04; elemental analysis calcd for $C_{27}H_{33}N_3CuCl_2$ (%): C 60.89, H 6.25, N 7.89; found: C 60.33, H 6.27, N 7.75. To a solution of $L^{Bn_3}CuCl_2$ (0.15 g, 0.20 mmol) in CH_2Cl_2 (10 mL) was added $Cl_4cat \cdot H_2O$ (0.054 g, 0.20 mmol) and Et_3N (0.02 g, 0.20 mmol). The reaction mixture was stirred for 15 min during which time its green color slowly intensified. Addition of excess Et_2O resulted in the deposition of the product as green microcrystals (0.13 g, 89 %). X-ray quality crystals were obtained by slow evaporation of a CH_2Cl_2/CH_3CN solution. FT-IR (KBr): $\tilde{\nu}$ = 1462 (vs, C–O) cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 265 (13000), 307 (7200), 485 (50), 634 (40), 990 (20) nm; EPR (CH_2Cl_2/Toluene, 77 K, 9.44 G Hz): g_1 = 2.24, g_2 = 2.05, g_3 = 2.01, A_1 = 177 G; elemental analysis calcd for $C_{35}H_{36}N_4O_2Cl_4Cu$ (%): C 56.22, H 4.86, N 7.50; found: C 55.79, H 4.73, N 7.10.

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[8] Treatment of THF solutions of $[\{Cu(L^{Bn_3})_2\}(\mu\text{-}O)_2](SbF_6)_2$ (≈0.07 mM) that had been purged of excess O_2 with N_2 with 1.5, 1.0, or 0.5 equiv (per dicopper complex) of dbcat at −71 °C followed by warming to ambient temperature produced $[Cu(L^{Bn_3})(dbsq)]SbF_6$ [plus unidentified copper(II) products] in yields stoichiometrically consistent with the amount of dbcat introduced, as indicated by the intensity of the unique 454 (ε 1300 $M^{-1}cm^{-1}$) nm absorption band. Only a trace amount of **2** (<5 %) was detected after removal of solvent and ^1H NMR analysis of the Et_2O-extracted residue (even when only 0.5 equiv dbcat per dicopper complex was added).

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[10] We have been unable to interpret preliminary magnetic susceptibility data obtained (courtesy of Prof. J. Miller and J. Manson, University of Utah) for a powdered sample of $[Cu(L^{Bn_3})(dbsq)]SbF_6$ (4.2 – 350 K, SQUID magnetometer), which showed an anomalously high μ_{eff} of ≈3.6 μ_B at 300 K (2.8 μ_B at 5 K). Intermolecular magnetic interactions in this sample appear to be operative, but further experiments are necessary in order to fully analyze the system.

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[12] Crystal data for $[Cu(L^{Bn_3})(Cl_4sq)]ClO_4$: $C_{33}H_{33}N_3O_6Cl_5Cu$, M_r = 808.46, crystal size 0.35 × 0.30 × 0.12 mm, triclinic, space group $P\bar{1}$, a = 10.181(2), b = 10.638(2), c = 16.529(3) Å, α = 77.80(3), β = 86.91(3), γ = 79.00(3)°, V = 1717.5(6) Å^3, Z = 2, ρ_{calcd} = 1.563 g cm^{-3}, T = 293(2) K, radiation $Mo_{K\alpha}$ (λ = 0.71073 Å), 2θ max = 49.9°. Data were collected on an Enraf-Nonius CAD4 diffractometer and the structure was solved by direct methods using SHELXTL-Plus V5.0 on an SGI INDY R4400-SC computer. All non-hydrogen atoms were

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refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined as riding atoms with fixed isotropic displacement parameters. For 6017 independent reflections with $I > 2\sigma(I)$ and 433 parameters, $R1 = 0.058$ and $wR2 = 0.1181$.

[13] Crystal data for $[Cu(L^{Bn_3})(Cl_4cat)] \cdot CH_3CN$: $C_{35}H_{36}N_4O_2Cl_4Cu$, $M_r = 750.06$, crystal size $0.50 \times 0.35 \times 0.07$ mm, monoclinic, space group $P2_1/n$, $a = 9.802(2)$, $b = 27.759(5)$, $c = 13.049(2)$ Å, $\beta = 104.39(2)^\circ$, $V = 3439.2(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.447$ g cm^{-3}, $T = 173(2)$ K, radiation $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), 2θ max $= 50.10^\circ$. Data were collected on Siemens SMART system and the structure was solved by direct methods using SHELXTL-Plus V5.0 on an SGI INDY R4400-SC computer. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined as riding atoms with fixed isotropic displacement parameters. For 6038 independent reflections with $I > 2\sigma(I)$ and 444 parameters, $R1 = 0.0735$ and $wR2 = 0.1391$.

[14] Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408633 and -408634.

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Synthesis and Characterization of the Tetrahydroxyphosphonium Hexafluorometalates $P(OH)_4^+MF_6^-$ (M = As, Sb)

Rolf Minkwitz* and Stefan Schneider

The existence of the tetrahydroxyphosphonium ion, $P(OH)_4^+$ **1**, has been discussed for more than 60 years. The investigations were initiated by Hantzsch who erroneously postulated that nitratacidium perchlorate, $(HO)_2NO^+ClO_4^-$ **2**, was a product of the reaction of HNO_3 with $HClO_4$, but which actually yielded a nitryl salt.[1, 2] In 1937 Arlman studied the behavior of phosphorous acid, H_3PO_4 **3**, towards perchlorous acid on the assumption that **2** existed. He obtained a solid that he presumed had the formula $P(OH)_4^+ClO_4^-$, in analogy to Hantzsch, but gave no evidence for the constitution.[3] It was not until 1952 that the results were supported by Raman spectroscopic investigations.[4] In the following years **1** was proved to exist also in HNO_3, H_2SO_4, FSO_3H, and superacidic FSO_3H/SbF_5 solutions, but it was not possible to isolate it.[5–9] Finally, in 1995 **1** was assumed to be a structural element in a modification of KH_2PO_4, which was prepared at pH 10.[10] The formation of **1** can nevertheless hardly be imagined under these conditions.

Phosphorus acids with the general composition H_3PO_n in hydrogen fluoride yield fluorophosphorane for $n = 2$ and 3 [Eqs. (1) and (2)] and in the case of **3** ($n = 4$) they yield monofluorophosphoric acid **4** and water [Eq. (3)].[11, 12]

$$H_3PO_2 + 3\,HF \rightleftharpoons H_2PF_3 + 2\,H_2O \quad (1)$$

$$H_3PO_3 + 4\,HF \rightleftharpoons HPF_4 + 3\,H_2O \quad (2)$$

$$\underset{\mathbf{3}}{H_3PO_4} + HF \rightleftharpoons \underset{\mathbf{4}}{H_2PO_3F} + H_2O \quad (3)$$

In the superacidic systems HF/MF_5 (M = As, Sb), which are suitable for the isolation of thermolabile salts,[13–17] these acids show a differing reaction behavior. H_3PO_3 yields tetrafluorophosphorane [Eq. (2)] and hydronium salts.[18] A hydronium salt, as well as **4**, can also be expected for an analogous reaction of **3**. However, in contrast to this expectation we find only a singlet at $\delta = -2.4$ (δ^1H 7.1)[5–9] in the ^{31}P NMR spectrum (in SO_2 at $-40\,^\circ$C), and only the signals of the MF_6^- ions in the ^{19}F NMR spectrum. It follows that the reaction with **3** does not proceed according to Equation (3) but yields **1**-MF_6 [Eq. (4), M = As, Sb].

$$\underset{\mathbf{3}}{H_3PO_4} + HF/MF_5 \longrightarrow \underset{\mathbf{1}\text{-}MF_6}{P(OH)_4^+MF_6^-} \quad (4)$$

The presence of **1** in HF/MF_5 at $-60\,^\circ$C can be directly proved as an intermediate in the reaction of **3** to **4.** Before **4** can be formed water has to be removed from **1**, which proceeds after a 1,3 proton transfer, for which a considerable energy barrier of 200 kJ mol^{-1} was calculated.[19]

With the HF/MF_5 system not only was proof for **1**-MF_6 obtained but also its isolation and crystallization were achieved (Figure 1, Table 1). The crystal structural investigation shows that all P – O bond lengths (152.9(2) to 153.6(2) pm) are equivalent within the accuracy of the measurement. In comparison to **3** (154.7(4) to 155.1(4) pm) the bond lengths are shortened.[20, 21] Compound **1** shows almost S_4 symmetry, with O-P-O angles between 101.2(1)° and

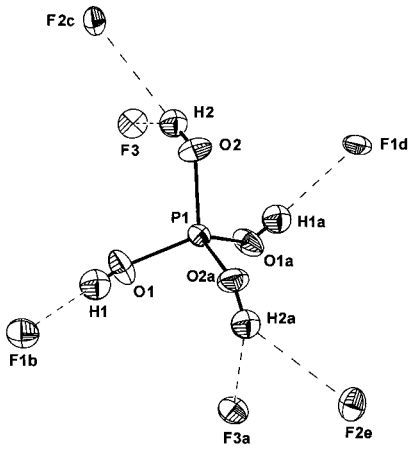

Figure 1. View of the structure of **1** showing the H ··· F contacts and atom labels. Selected bond lengths [pm]: F2c ··· H2 218(4), F3 ··· H2 220(4), F1d ··· H1a 199(4), F2e ··· H2a 218(4), F3a ··· H2a 220(4), F1b ··· H1 199(4).

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