Hexafluoridophosphate partial hydrolysis leading to the one-dimensional coordination polymer [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$]

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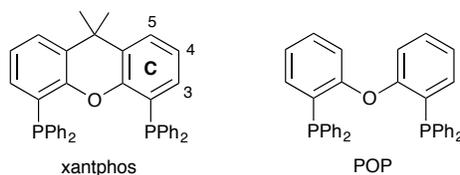*Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland*

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Abstract

The one-dimensional coordination polymer [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$] (xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) is reported, the first in which copper(I) centres are linked by μ-PO$_2$F$_2$ units.

Keywords: Coordination polymer; copper(I); hexafluoridophosphate hydrolysis; crystal structure; P^P chelate; μ-PO$_2$F$_2$ units

The hexafluoridophosphate, [PF$_6$]$^-$, counterion is a ubiquitous choice in preparative inorganic chemistry due to a broad range of favourable properties including its weak coordination and straightforward handling. This counterion has become well-established in materials with applications including ionic liquids and batteries [1,2,3]. Nonetheless, hydrolysis of [PF$_6$]$^-$ is not unprecedented [4] and can lead to unexpected complexes containing [PO$_2$F$_2$]$^-$ or [PO$_3$F]$^{2-}$ groups [5,6,7,8,9]. Hydrolysis is catalysed by certain metal salts [10] and has also been observed under electrolytic conditions [11]. We report here the fortuitous formation of a one-dimensional coordination polymer consisting of chains of {Cu(μ-O$_2$PF$_2$)} units.

Scheme 1. Structures of xantphos and POP. Ring labelling in xantphos is for NMR assignments; Ph ring = D.

The attempted synthesis of [Cu(xantphos)(6,6'-(CF$_3$)$_2$bpy)][PF$_6$] (xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) from equimolar amounts of [Cu(MeCN)$_4$][PF$_6$], xantphos and 6,6'-bis(trifluoromethyl)-2,2'-bipyridine (6,6'-(CF$_3$)$_2$bpy) following procedures used for related complexes [12,13] yielded a slightly orange solid, in contrast to the intense

yellow or orange which is characteristic of [Cu(xantphos)(N^N)][PF$_6$] complexes (N^N = derivative of bpy) [13]. Crystal growth by layering yielded colourless crystals as the dominant product, in addition to some orange crystals. Parallel studies identified these as [Cu(6,6'-(CF$_3$)$_2$bpy)$_2$][PF$_6$] [14]. The failure to obtain [Cu(xantphos)(6,6'-(CF$_3$)$_2$bpy)][PF$_6$] is probably related to the electronic and steric factors of the two CF$_3$ groups combined with the bulky xantphos ligand. The related complex [Cu(POP)(6,6'-Me$_2$bpy)][PF$_6$] (POP = bis(2-diphenylphosphinophenyl)ether, 6,6'-Me$_2$bpy = 6,6'-dimethyl-2,2'-bipyridine) can be isolated [12], and the increased demands of CF$_3$ versus CH$_3$ are consistent with the larger Tolman cone angle of P(CF$_3$)$_3$ (137°) versus PMe$_3$ (118°) [15]. Single crystal X-ray diffraction revealed the colourless crystals to be the one-dimensional coordination polymer [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$]. The NMR spectroscopic data were consistent with the presence of [PO$_2$F$_2$]$^-$ rather than [PF$_6$]$^-$. The solvent from the crystallization tube was carefully removed, and the orange crystals manually separated from the colourless crystals. The latter were washed with Et$_2$O, dried in air and dissolved in CD$_2$Cl$_2$. Signals in the ^{1}H NMR spectrum [16] are consistent with the {Cu(xantphos)} unit. The ^{19}F NMR spectrum shows a broad doublet at δ −82.6 ppm (J_{PF} = 964 Hz) characteristic of [PO$_2$F$_2$]$^-$ [4]. In the ^{31}P NMR spectrum (Figure 1) there is a coincidental overlap of a singlet arising from the {Cu(xantphos)} unit (δ −16.81 ppm) and the middle of the triplet assigned to the [PO$_2$F$_2$]$^-$ ion (δ −16.98 ppm, J_{PF} = 962 Hz). The electrospray mass spectrum (positive mode) showed a peak envelope at m/z 641.4 arising from [Cu(xantphos)]$^+$; although the [PO$_2$F$_2$]$^-$ anion was not observed in the negative mode, the spectrum showed a peak at m/z 63 assigned to [PO$_2$]$^-$ which is a characteristic fragment [17, 18].
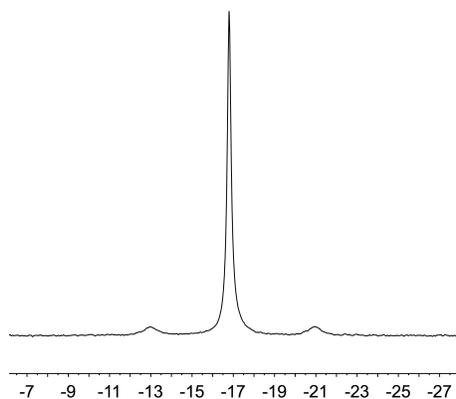

-7   -9   -11   -13   -15   -17   -19   -21   -23   -25   -27

Figure 1. 243 MHz ^{31}P NMR spectrum of a CD$_2$Cl$_2$ solution of dissolved crystals of [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$] showing overlapping singlet and triplet (J_{PF} = 962 Hz). Chemical shifts in δ / ppm.

The coordination polymer [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$] crystallizes in the monoclinic space group $P2_1/c$ [19]; the structure of the repeat unit is shown in Figure 2 and part of one polymer chain in Figure 3. The copper atom is in a distorted tetrahedral environment, bonded by the two P atoms of the xantphos ligand and two O atoms of different μ-O$_2$PF$_2$ groups. The PF$_2$ unit of the bridging {PO$_2$F$_2$} group is disordered and has been modelled over two sites with fractional occupancies of 70 and 30%. Both orientations were constrained to be tetrahedral; only the major orientation is discussed below. Although the ability of [PO$_2$F$_2$]$^-$ to function as a bridging ligand is known (25 hits in a search of the Cambridge Structural Database, version 5.36 with February 2015 updates [20] using Conquest version 1.1.7 [21]), [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$] is the first reported coordination polymer of {PO$_2$F$_2$} connecting copper(I) centres. In the Cu(xantphos) unit, the Cu–P distances and P–Cu–P bond angle are in accord with literature values [**Error! Bookmark not defined.**]. Although xantphos is a relatively rigid ligand compared to POP (Scheme 1), the fused ring domain in xantphos (Scheme 1) undergoes a conformational change associated with the sp^3 carbon of the CMe$_2$ unit (C17–C19–C23 = 106.9(3)°). The C–O–C angle of 114.2(2)° coupled with the C–O bond distances of 1.387(4) and 1.397(4) Å are consistent with some π-localization across the C–O–C unit. In free xantphos, the corresponding angle is 117.4° [22]. Despite the π-contribution, the heterocyclic ring tends to adopt a boat conformation (survey of 173 structures containing xantphos in the CSD, version 5.36 with February 2015 updates [[20]]); the conformation is variable and is affected if the O atom is involved in coordination [23]. In [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$], the angle between the planes containing atoms C18, O1 and C28 and atoms C17, C18, C23 and C28 is 31.9° and that between the planes containing atoms C17, C18, C23 and C28 and C17, C19 and C23 is 32.3°. The corresponding internal angles of the boat in free xantphos are 20.8° and 24.34°.

The one-dimensional polymer chain is propagated by a screw axis running parallel to the crystallographic *b*-axis, and the Cu...Cu separation of adjacent copper atoms in a chain is 5.9590(9) Å. The copper atoms and connecting O–P–O motifs in a chain are essentially coplanar (deviation from a least squares plane through these atoms <0.14 Å), and the O atom of the xantphos ligand also lies in this plane. Polymer chains are related by a glide plane with a distance between the planes containing the Cu(μ-O–P–O) units of 9.3214(5) Å. The chains are packed

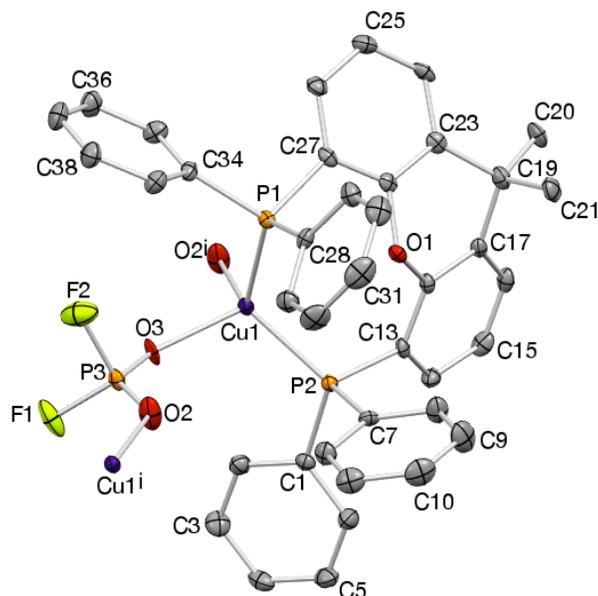closely together with no solvent-accessible voids; interactions between adjacent chains are dominated by H…H contacts.

Figure 2.   The repeat unit (including atoms defining polymer connectivity) in [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$]; H atoms omitted and ellipsoids plotted at 40% probability. Symmetry codes: i = 1–x, $^1/_2$+y,$^3/_2$–z. Selected bond parameters: Cu1–O2i = 2.167(2), Cu1–O3 = 2.063(2), Cu1–P1 = 2.2434(10), Cu1–P2 = 2.2299(9), O3–P3 = 1.450(4), O2–P3 = 1.407(5), F2–P3 = 1.617(3), F1–P3 = 1.547(5) Å; O2i–Cu1–P1 = 105.55(8), O2i–Cu1–P2 = 110.04(8), P1–Cu1–P2 = 117.64(4), O2i–Cu1–O3 = 97.83(8), P1–Cu1–O3 = 110.92(7), P2–Cu1–O3 = 112.76(8), F2–P3–F1 = 98.4(3), F2–P3–O3 = 104.8(2), F1–P3–O3 = 108.9(3), F2–P3–O2 = 105.0(3), F1–P3–O2 = 112.6(3), O3–P3–O2 = 123.7(3)^o.
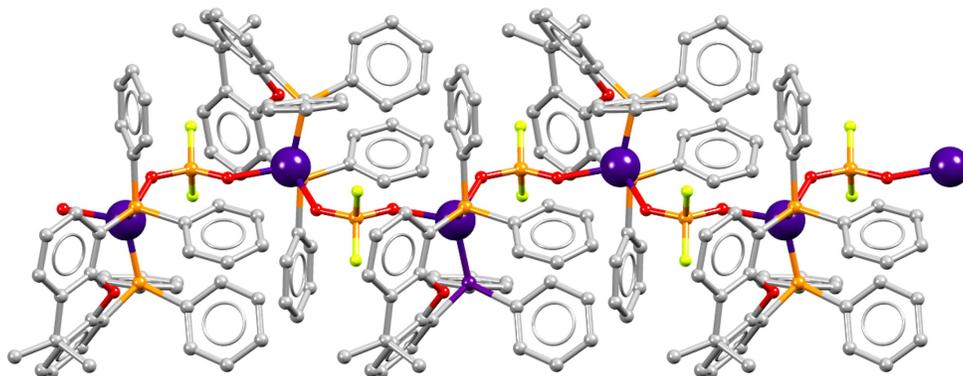

Figure 3. Part of one polymer chain in [{Cu(xantphos)(μ-PO$_2$F$_2$)}$_n$] viewed down the c-axis; the chain follows the *b*-axis.

Given the general application of [PF$_6$]$^−$ as a counterion in our work over many years, particularly in the isolation of [Cu(N^N)(POP)][PF$_6$] [24] and [Cu(N^N)(POP)][PF$_6$] complexes (N^N = bpy derivatives) [12,25], the hydrolysis of [PF$_6$]$^−$ to [PO$_2$F$_2$]$^−$ was unexpected. We attribute it to a

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combination of adventitious water and to the catalytic action of copper(I), possibly in the presence of the xantphos ligand.

Acknowledgements

Appendix A. Supplementary data

CCDC 1053233 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk)

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