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An Organometallic Tetranuclear Complex of μ_4-PO$_4$: [{(Cp*Cr)$_2$(μ-OMe)$_2$}$_2$(μ_4-PO$_4$)]X (X = I, PF$_6$)

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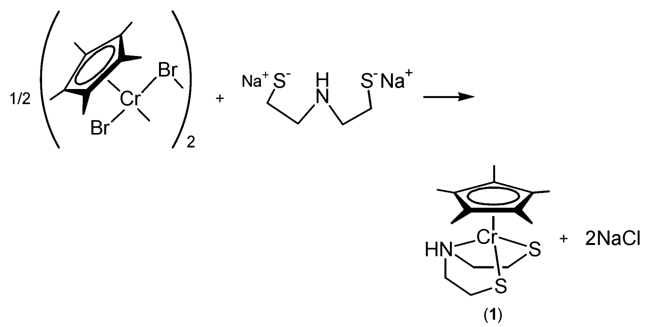
*Summary: The first discrete organometallic tetranuclear μ_4-PO$_4$ complex, [{(Cp*Cr)$_2$(μ-OMe)$_2$}$_2$(μ_4-PO$_4$)]$^+$ (**5**; Cp* = η^5-C$_5$Me$_5$), was isolated as the iodide and PF$_6$ salts from the reaction between NaH$_2$PO$_4$ and [Cp*Cr(μ-OMe)I]$_2$ (**2**), which was derived from thiolate methylation of [Cp*Cr{η^3-HN(CH$_2$CH$_2$S)$_2$}] (**1**) with MeI in MeOH.*

Phosphate compounds of most metals are known.[1] The last two decades have witnessed an explosive growth in their studies on account of their relevance to a variety of functional materials.[2] Crystallographic determinations show that most of these phosphates contain framework structures, in which the phosphate anions ligate in various bonding modes, ranging from mondentate (η^1-O) and chelating (η^2-O,O′) to the predominant bridging (μ_2,η^1-O:η^1-O′) mode or combinations thereof. μ_3 and μ_4 bonding of PO$_4$ is very rare, whether in open-framework or discrete polynuclear complexes. The only examples of the latter have been three recently reported tetranuclear coordination compounds: viz. the Fe(III) complex [{Fe$_2$(tren)$_2$(μ-O)}$_2$(μ_4-PO$_4$)]$^{5+}$ (**A**; tren = tris(2-aminoethyl)amine), formed in an unexpected hydrolysis of 4-nitrophenyl phosphate in its reaction with Fe(III) and tren, in an attempt to synthesize a model complex of transition-metal-containing glycoproteins, the purple acid phosphatases,[3] the Cu(II) complex [{CuL(MeCN)}$_4$(μ_4-PO$_4$)]$^{5+}$ (**B**; L = a terdentate N-donor ligand, isolated as "small numbers of crystals"), wherein the PO$_4$ moiety was presumed to come from complete hydrolysis of PF$_6$ anion,[4] and a second Cu(II) complex, [Cu$_4$L$_2$(μ_4-PO$_4$)]$^{3+}$ (**C**; L = pyrazole-bridged bis(1,4,7-triazacyclononane), formed from interaction of Cu^{2+} ions with L and NaH$_2$PO$_4$ at pH 5.5.[5]

Scheme 1



Despite the wealth and wide applicability of microporous metal phosphate compounds, organometallic phosphate complexes are hardly known, except for polymeric {(Bu$_4$N)Ir(COD)(PO$_4$H)}$_n$, which was characterized by mass spectroscopy.[2i] Our entry into this area was incidental: the μ_4-PO$_4{}^{3-}$ complex **5**(PF$_6$) was the unexpected outcome of a NH$_4$PF$_6$ metathesis exchange reaction following methylation of [Cp*Cr{η^3-HN(CH$_2$CH$_2$S)$_2$}] (**1**; Cp* = η^5-C$_5$Me$_5$).

Compound **1** was obtained in 66% yield from the reaction of [Cp*Cr(Br)$_2$]$_2$ with HN(CH$_2$CH$_2$SNa)$_2$ as an air-sensitive, very dark green solid (Scheme 1).[6] After our unusual findings resulting from alkylation of the thiolate S atoms in [Cp*Ru{η^3-X(CH$_2$CH$_2$S)$_2$}] (X = S, NH),[7] we were interested in a comparative study of **1**.

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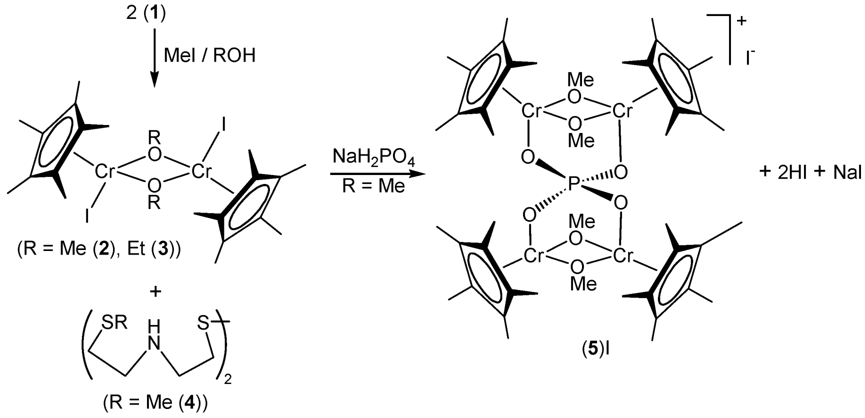
[6] *Synthesis of [(η^5-C$_5$Me$_5$)Cr{η^3-NH(CH$_2$CH$_2$S) $_2$}]* (**1**). To a suspension of sodium methoxide (freshly generated from sodium (142 mg, 6.17 mmol) and evacuated to dryness) in THF (25 mL) was injected bis(2-mercaptoethyl)amine (0.35 mL, 2.80 mmol), and the mixture was stirred for 12 h. To the white gel-like suspension was added solid [Cp*Cr(Br)$_2$]$_2$ (405 mg, 0.58 mmol), and the mixture was stirred at ambient temperature. The color gradually changed from dark blue to dark green over a period of 3.5 h, after which the reaction mixture was evacuated to dryness and the residue triturated with ether (5 × 10 mL) to extract out unreacted chromium substrate (50 mg, 0.072 mmol). The black residue was then dissolved in acetonitrile (5 × 10 mL) and filtered to give a dark green filtrate. Addition of ether (15 mL) gave black crystalline solids (216 mg, 66%) of [Cp*Cr{η^3-NH(CH$_2$CH$_2$S)$_2$}] (**1**) after 24 h at −30 °C. ^{1}H NMR (δ; CD$_3$CN): −12.04 (br s, $\nu_{1/2}$ ca. 390 Hz). IR (ν, cm^{-1}; KBr): 3120 m (N−H), 2909 s, 2861 msh, 1483 m, 1446 s, 1376 m, 1330 w, 1305 m, 1289 m, 1235 m, 1212 m, 1200 m, 1160 w, 1085 s, 1069 s, 1028 s, 970 m, 954 m, 921 w, 792 w, 766 w, 681 w, 435 s, 419 s. FAB$^+$-MS (m/z): 322 [M]$^+$. Anal. Found: C, 52.36; H, 7.00; N, 4.57; S, 20.15. Calcd for C$_{14}$H$_{24}$NCrS$_2$: C, 52.14; H, 7.50; N, 4.34; S, 19.89.

10.1021/om048974d CCC: $30.25

Scheme 2



Treatment of **1** with MeI in MeOH resulted in a dark blue product solution, from which was obtained moderately air-stable blackish purple cubic crystals of $[\{(\mathrm{Cp^*Cr})_2(\mu\text{-OMe})_2\}_2(\mu_4\text{-PO}_4)]\mathrm{PF}_6$, **5**($\mathrm{PF}_6$), in 64% yield, after metathesis with excess $\mathrm{NH_4PF_6}$, which we subsequently analyzed to contain ca. 15% of $\mathrm{(NH_4)H_2PO_4}$ impurity (see the Supporting Information). We therefore sought to delineate the reaction pathway for the formation of **5**.

Our experiments showed that the reaction of **1** with MeI in ROH resulted in cleavage of the "NS$_2$" ligand after methylation at one of the thiolate S atoms, leading to isolation of very air-sensitive, blackish blue crystals of $[\mathrm{Cp^*Cr}(\mu\text{-OR})\mathrm{I}]_2$ (R = Me (**2**), Et (**3**)) in 69 and 71% yields, respectively, together with white solids of $[\mathrm{MeS(CH_2)_2HN(CH_2)_2S^-}]_2$ (**4**) (isolated from the reaction in MeOH).[8] Treatment of the product solution in MeOH (after removal of excess MeI) with $\mathrm{NaH_2PO_4}$ gave (**5**)I in 65% yield (Scheme 2).[9]

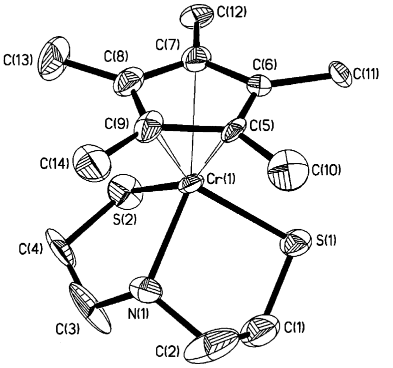


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)−S(1) = 2.346(4), Cr(1)−S(2) = 2.306(4), Cr(1)−N(1) = 2.119(10); S(1)−Cr(1)−S(2) = 102.93(15), S(1)−Cr(1)−N(1) = 87.7(3), S(1)−Cr(1)−N(1) = 85.5(3).

The molecular structure of **1** shows Cr coordinated to η^5-Cp* and $\eta^3\text{-HN(CH_2CH_2S^-)_2}$ (Figure 1). **2** and **3** are dinuclear $\eta^5\text{-Cp^*Cr^{III}I}$ species containing bis(μ-alkoxy) bridges (Figure 2 and S1 (Supporting Information)). A close structural analogy to these Cr(III) complexes is the complex $\mathrm{Cp_2Cr_2}(\mu\text{-OBu}^t)_2\mathrm{I_2}$, containing a weak M−M bond (2.967(2) Å).[10] The $[\mathrm{Cp^*Cr}(\mu\text{-OR})]_2$ moiety remains intact as two units are assembled together in the process of nucleophilic displacement of the iodo ligands by the phosphate oxygens of $\mathrm{PO_4}^{3-}$, producing **5** with the molecular structure illustrated in Figure 3. There is a slight decrease of Cr···Cr distance from **2** (3.094 Å) to **5** (2.957, 2.954 Å) and a slight increase in the Cr−O(Me) distances from 1.970(3) Å to

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(8) *Syntheses of* **2** *and* **3**: *Reaction of* **1** *with MeI in MeOH and EtOH*. Into a stirred solution of **1** (20 mg, 0.062 mmol) in MeOH (10 mL) was injected MeI (20 μL, 0.32 mmol). The solution was stirred for 3 h, resulting in a gradual color change from dark green to dark blue. The reaction mixture was then evacuated to dryness and the residue extracted with THF (3 × 2 mL) and filtered from white solids of $[\mathrm{MeS(CH_2)_2HN(CH_2)_2S^-}]_2$ (**4**). The dark blue filtrate was concentrated to half volume, and addition of ether gave blackish blue cubic crystals of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Cr}(\mu\text{-OMe})\text{I}]_2$ (**2**; 12 mg, 69% yield) after 3 days at −30 °C. The complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Cr}(\mu\text{-OEt})\text{I}]_2$ (**3**) was similarly obtained as blackish blue cubic crystals (13 mg, 71% yield) from the reaction of **1** (20 mg, 0.062 mmol) with MeI (20 μL, 0.32 mmol) in EtOH (15 mL). **2** and **3** are stable both in the solid state and in solution under an inert atmosphere but are very air sensitive even in the solid state, decomposing immediately on exposure to air. Data for **2** are as follows. ^{1}H NMR (δ; CD$_3$CN): −29.56 (br s, $\nu_{1/2}$ ca. 1650 Hz), −40.53 (br s, $\nu_{1/2}$ ca. 600 Hz) (Figure S2 in the Supporting Information). IR (ν, cm^{-1}; KBr): 2947 msh, 2941 s, 2853 m, 2820 m, 1482 m, 1426 m, 1375 m, 1261 w, 1159 w, 1071 s, 1018 m (C−O), 955 w, 907 w, 794 m, 669 w, 548 msh, 517 vs (Cr−O), 481 msh, 421 w. Data for **3** are as follows. ^{1}H NMR (δ; CD$_3$CN): −4.36 (br s, $\nu_{1/2}$ ca. 150 Hz), −10.93 (br s, $\nu_{1/2}$ ca. 270 Hz), −19.50 (br s, $\nu_{1/2}$ ca. 180 Hz) (Figure S3 in the Supporting Information). IR (ν, cm^{-1}; KBr): 2954 ssh, 2918 vs, 2853 ssh, 2792 s, 2744 msh, 2633 w, 2565 w, 2403 w, 2368 w, 2342, 1479 msh, 1427 s, 1380 s, 1321 w, 1261 w, 1148 wsh, 1085 s, 1050 vs, 1023 ssh (C−O), 958 w, 891 m, 808 w, 554 m (Cr−O), 461 m. Data for **4** are as follows. ^{1}H NMR (δ; CD$_3$OD): HNCH_2, unresolved multiplets centered at 3.41 (4H), 3.27 (4H); SCH_2, unresolved multiplets centered at 3.09 (4H), 2.83 (4H); SCH_3, 2.16 (6H). ^{13}C NMR (δ; CD$_3$OD): HNCH$_2$, 47.53, 47.47; SCH$_2$, 34.2, 30.8; SCH$_3$, 15.0. ESI$^+$-MS (m/z): 301 [M]$^+$. EI-MS (m/z): 254 [M − SMe], 183 [M − SMe − (CH$_2$)$_4$ − NH], 150 [M − SMe − S(CH$_2$)$_4$ − NH − H].

(9) *Synthesis of* **5**(*I*): *Reaction of* **1** *with MeI in MeOH followed by NaH*$_2$*PO*$_4$. Into a stirred solution of **1** (20 mg, 0.062 mmol) in MeOH (10 mL) was injected MeI (20 mL, 0.32 mmol). The solution was stirred for 3 h, resulting in a gradual color change from dark green to dark blue. The reaction mixture was then evacuated to dryness to remove excess MeI and the dark blue residue redissolved in MeOH (8 mL). NaH$_2$PO$_4$ (3 mg, 0.025 mmol) was added and the solution stirred for 30 min. The dark purplish blue solution was evacuated to dryness and the product extracted with CH$_3$CN (3 × 2 mL). The dark purplish blue extract was filtered and evacuated to dryness and the residue recrystallized in 1/1 toluene/THF and ether. Blackish purple cubic crystals of $[\{\mathrm{Cp^*Cr}(\mu\text{-OMe})\}_4(\mu_4\text{-PO}_4)]\mathrm{I}$ (**5**(I); 11 mg, 65% yield) were obtained after 2 days at −30 °C. ^{1}H NMR (δ; CD$_3$CN): −12.64 (br s, $\nu_{1/2}$ ca. 170 Hz). IR (ν, cm^{-1}; KBr): 2919 m, 2821 w, 1377 w, 1262 w, 1058 vs (P−O), 1032 vs (P−O), 803 w, 563 m, 512 s (Cr−O), 483 m. ESI$^+$-MS (m/z): 968 [M − I]$^+$. ESI$^-$-MS (m/z): 127 [I]. Anal. Found: C, 49.54; H, 6.70. Calcd for $\mathrm{C_{44}H_{72}O_8Cr_4IP\cdot{}^1/_2C_7H_8}$: C, 50.0; H, 6.71. The salt is stable both in the solid state and in solution under an inert atmosphere. On exposure to air, the solution is stable for a few minutes, but the solid remains unchanged for up to several days.

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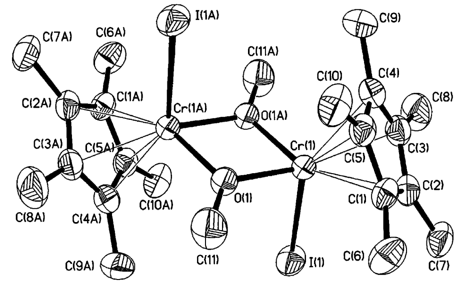

Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)−O(1) = 1.973(3), Cr(1)−O(1A) = 1.970(3), Cr(1)−I(1) = 2.6960(8), O(1)−C(11) = 1.404(5), Cr(1)···Cr(1A) = 3.094; O(1)−Cr(1)−O(1A) = 76.64(12), I(1)−Cr(1)−O(1) = 95.63(9), I(1)−Cr(1)−O(1A) = 97.34(9), Cr(1)−O(1)−Cr(1A) = 103.36(12), Cr(1)−O(1)−C(11) = 127.7(3). Cr(1)O(1)Cr(1A)O(1A) is planar.

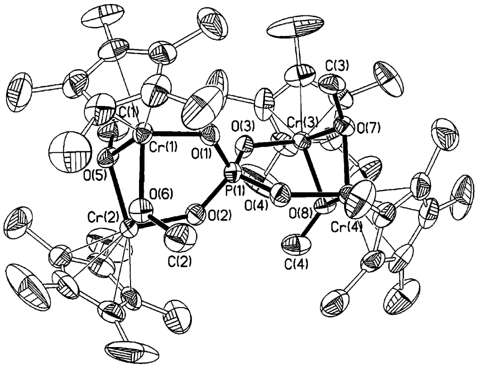

Figure 3. Molecular structure of the cation of **5**(I). Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)···Cr(2) = 2.957, Cr(3)···Cr(4) = 2.954, P(1)−O(1) = 1.537(4), P(1)−O(2) = 1.539(4), P(1)−O(3) = 1.531(4), P(1)−O(4) = 1.531(4); O(1)−P(1)−O(2) = 109.92(19), O(1)−P(1)−O(3) = 109.4(2), O(1)−P(1)−O(4) = 108.8(2), O(2)−P(1)−O(3) = 108.7(2), O(2)−P(1)−O(4) = 109.4(2), O(3)−P(1)−O(4) = 110.6(2). Dihedral angles (deg): between Cr(1)Cr(2)O(5) and Cr(1)Cr(2)O(6), 29.0; between Cr(3)Cr(4)O(7) and Cr(3)Cr(4)O(8), 28.3.

a range of 1.971(4)−1.986(3) Å. The P atom is tetrahedrally coordinated by the O atoms (O−P−O angles being 108.7(2)−110.6(2)°). The μ_4-bridging mode of PO_4 is the first of its kind for Cr and for an organometallic compound. In the μ_4-PO_4 inorganic coordination compounds reported, **A** contains singly oxo-bridged pairs of the Fe atoms, with P in an ideal tetrahedral geometry,[3] while the Cu complex **B** possesses S_4 symmetry with P located on the S_4 axis and the Cu atoms in an approximate square-pyramidal arrangement[4] and complex **C** contains two dinuclear [Cu_2L] units, in which one Cu atom exhibits a distorted-trigonal-bipyramidal coordination and the other a distorted-square-pyramidal geometry.

Complexes **1**−**3** and **5** belong to the class of 15-electron Cr(III) complexes. Although **5** contains four d^3 centers, its observed EPR signal is extremely weak, indicative of probable pairing of odd electrons on the metals in shared molecular orbitals. Cyclic voltammetry shows reversible oxidation and reduction processes (see the Supporting Information).

As far as we are aware, complex **5** is the first example of a discrete μ_4-PO_4 organometallic species. The present findings impinge on an unexplored area of organometallics. It is yet to be uncovered whether such organometallics will be as useful as microporous metal phosphates in the wide arena of materials or in the biological area, where current studies on the interactions of the antitumor-active complexes Cp_2MX_2 (M = Ti, V, Nb, Mo, Re) with phosphates and DNA have yielded crystallographic evidence of η^1 and η^2 bonding of the PO_4R moiety in the nucleotides to Cp_2M (M = Ti, Mo).[11] Our work will be extended to like systems of the group 6 metals and different classes of phosphates.

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Supporting Information Available: Crystal data for **1**−**3** and **5** (Table S1) and full crystallographic data as CIF files, selected metric data of **5** (Table S2), an ORTEP diagram of **3** (Figure S1), the ^1H NMR spectra of **2** and **3** (Figures S2 and S3, respectively), and text giving general experimental procedures and details for initial isolation and EPR and cyclic voltammetry of **5**(PF_6) (including Table S3 and Figures S4 and S5). This material is available free of charge via the Internet at http://pubs.acs.org.

OM048974D

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