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# Proton-Coupled Electron Transfer from Phosphorus: A P–H/P–D Kinetic Isotope Effect of 178[**]

My Hang V. Huynh[*] and Thomas J. Meyer[*]

In the extensive redox chemistry of high oxidation state ruthenium(IV)–oxo,[1] osmium(VI)–nitrido,[2] osmium(IV–VI)–hydrazido,[3] osmium(IV)–cyanoimido,[4] and osmium(IV)–sulfilimido complexes,[5] multiple mechanistic pathways have been uncovered based on multiple electron and atom/group transfers. Examples include O atom,[6] $N^-$ ion,[7] $H^-$ ion,[8] and $NSC_6H_3Me_2^{2-}$ transfer.[9] Kinetic studies have revealed the existence of proton-coupled electron-transfer pathways based on bound oxo/hydroxo/aqua,[1, 10] dialkylhydrazido,[11] and sulfilimido[12] ligands that occur with large H/D kinetic isotope effects. Examples include $k_{\text{O-H}}/k_{\text{O-D}} = 30 \pm 1$[10a] for the oxidation of hydroquinone ($H_2Q$) to benzoquinone (Q) by *cis*-$[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$ (bpy = 2,2′-bipyridine and py = pyridine) [Eq. (1)].

$$cis\text{-}[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+} + \text{H}_2\text{Q} \rightarrow cis\text{-}[\text{Ru}^{\text{II}}(\text{bpy})(\text{py})(\text{H}_2\text{O})]^{2+} + \text{Q} \quad (1)$$

Other examples are $k_{\text{N-H}}/k_{\text{N-D}} \geq 41.4 \pm 1.3$[11] for the reduction of Q to $H_2Q$ by *trans*-$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{N(H)N(CH}_2)_4\text{O}\}]^+$ [Eq. (2); tpy = 2,2′:6′,2″-terpyridine], and $k_{\text{S-H}}/k_{\text{S-D}} \geq 31.1 \pm 0.2$[12] for the oxidation of *trans*-$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{NS(H)C}_6\text{H}_3\text{Me}_2\}]^+$ by Q [Eq. (3)].

$$2\,trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{N(H)N(CH}_2)_4\text{O}\}]^+ + \text{Q} \rightarrow 2\,trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2\{\text{NN(CH}_2)_4\text{O}\}]^+ + \text{H}_2\text{Q} \quad (2)$$

$$2\,trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{NS(H)C}_6\text{H}_3\text{Me}_2\}]^+ + \text{Q} \rightarrow 2\,trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NSC}_6\text{H}_3\text{Me}_2)]^+ + \text{H}_2\text{Q} \quad (3)$$

We report here the first example of proton-coupled electron transfer based on a phosphorus atom. Its existence may have important implications for the redox reactivity of organophosphorus compounds,[13] phosphoraniminato complexes,[14] and biologically active substances containing P–H acids.[15]

A rapid reaction occurs between the osmium(VI)–nitrido complex, $[\text{Os}^{\text{VI}}(\text{Tp})(\text{Cl})_2(\text{N})]$ ($\text{Tp}^-$ = tris(pyrazolyl)borate), and diethylphosphane ($HPEt_2$) in $CH_2Cl_2$ under nitrogen at room temperature to give the osmium(IV)–phosphoraniminato product, $[\text{Os}^{\text{IV}}(\text{Tp})(\text{Cl})_2\{\text{NP(H)Et}_2\}]$ ($\text{Os}^{\text{IV}}\text{NP(H)Et}_2$) [Eq. (4)].

$$[\text{Os}^{\text{IV}}(\text{Tp})(\text{Cl})_2(\text{N})] + \text{HPEt}_2 \rightarrow [\text{Os}^{\text{IV}}(\text{Tp})(\text{Cl})_2\{\text{NP(H)Et}_2\}] \quad (4)$$

The product was isolated (94 % yield) and characterized by elemental analysis,[16a] cyclic voltammetry,[16b] and UV/Vis,[16c] and infrared[16d] spectroscopies. Similar to other $d^4$ $\text{Os}^{\text{IV}}$–phosphoraniminato complexes,[17] $\text{Os}^{\text{IV}}\text{-NP(H)Et}_2$ is paramagnetic as shown by $^1$H NMR spectroscopy. Cyclic voltammetric measurements in 1:1 (v/v) $CH_3CN$:$H_2O$ ($\mu = 1.0\,\text{M}$ in $NH_4PF_6$) reveal that $E_{1/2}$ for the osmium(V/IV) couple decreases by 57 mV/pH unit from pH 0 ($E_{1/2} = 0.560$ V, versus sodium saturated calomel electrode (SSCE)) to 3.5 ($E_{1/2} = 0.360$ V, versus SSCE) and is pH independent above pH 3.5.[18] From these data, $\text{p}K_a = 3.52 \pm 0.04$ for the acid–base equilibrium shown in Equation (5), and Supporting Information Figure 1.

$$[\text{Os}^{\text{IV}}(\text{Tp})(\text{Cl})_2\{\text{NP(H)Et}_2\}] \overset{K_a}{\rightleftharpoons} [\text{Os}^{\text{IV}}(\text{Tp})(\text{Cl})_2(\text{NPEt}_2)]^- + \text{H}^+ \quad (5)$$

Reminiscent of the $[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2\{\text{NN(CH}_2)_4\text{O}\}]^+$/$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{N(H)N(CH}_2)_4\text{O}\}]^+$ and $[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NSC}_6\text{H}_3\text{Me}_2)]^+$/$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{NS(H)C}_6\text{H}_3\text{Me}_2\}]^+$ couples,

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[*] Dr. T. J. Meyer
Associate Laboratory Director for Strategic Research
Los Alamos National Laboratory, MS A127
Los Alamos, NM 87545 (USA)
Fax: (+1) 505-667-5450
E-mail: tjmeyer@lanl.gov

Dr. M. H. V. Huynh
Director-Funded Postdoctoral Fellow
Los Alamos National Laboratory, Chemistry Division MS J514
Los Alamos, NM 87545 (USA)
Fax: (+1) 505-667-9905
E-mail: huynh@lanl.gov

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we have found clear kinetic evidence for proton-coupled electron transfer based on phosphorus for the $[Os^{V}(Tp)(Cl)_2(NPEt_2)]/[Os^{IV}(Tp)(Cl)_2\{NP(H)Et_2\}]$ couple.

When $[Os^{IV}(Tp)(Cl)_2\{NP(H)Et_2\}]$ and Q are mixed in 1:1 (v/v) $CH_3CN:H_2O$ (pH 1.5 and $\mu = 1.0$ M in $NH_4PF_6$), a rapid reaction occurs in which Q is reduced to $H_2Q$, and $[Os^{IV}(Tp)(Cl)_2\{NP(H)Et_2\}]$ is oxidized to $[Os^{V}(Tp)(Cl)_2(NPEt_2)]$ [Eq. (6)]. From redox potential measurements, $\Delta G^{\circ} = -0.03$ eV for this reaction.[18]

$$2[Os^{IV}(Tp)(Cl)_2\{NP(H)Et_2\}] + Q \xrightarrow{\Delta G^{\circ}=-0.03\,\mathrm{eV}} 2[Os^{V}(Tp)(Cl)_2(NPEt_2)] + H_2Q \quad (6)$$

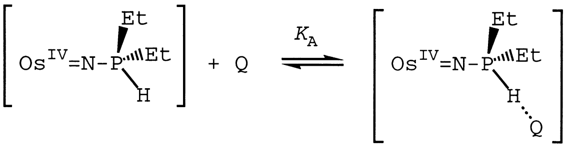
As found for the oxidation of *trans*-$[Os^{IV}(tpy)(Cl)_2\{N(H)N(CH_2)_4O\}]^+$ and *trans*-$[Os^{IV}(tpy)(Cl)_2\{NS(H)ArMe_2\}]^+$ by Q, the oxidation of $[Os^{IV}(Tp)(Cl)_2\{NP(H)Et_2\}]$ by Q is pH dependent, consistent with the rate law in Equations (7a) and (7b) at $[Q] < 3.05 \times 10^{-3}$ M with $k_1(H_2O) = (1.48 \pm 0.01) \times 10^{1}\,M^{-1}s^{-1}$, $k_2(H_2O) = (3.95 \pm 0.04) \times 10^{2}\,M^{-1}s^{-1}$, and $K_a = 3.2 \times 10^{-4}$. This rate law is consistent with competing pathways, and the oxidation of $Os^{IV}-NP(H)Et_2$ ($k_1$) and of $Os^{IV}-NPEt_2^-$ ($k_2$) by Q.

$$\mathrm{Rate} = k_{obs}[Q][Os^{IV}]_T \quad (7a)$$

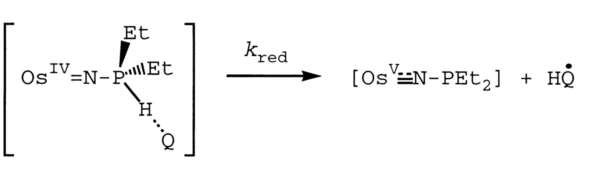
$$k_{obs} = \{\frac{2k_1[H^+] + 2k_2K_a}{[H^+] + K_a}\} \quad (7b)$$

As in the reaction between *trans*-$[Os^{IV}(tpy)(Cl)_2\{N(H)N(CH_2)_4O\}]^+$ and Q, there is evidence in the $k_1$ pathway for an $Os^{IV}-NP(H)Et_2\cdots Q$ intermediate. This conclusion is based on the appearance of saturation kinetics in [Q] (Figure 1) and by the direct observation of the intermediate. At $[Q] = 1.2 \times 10^{-3} - 1.2 \times 10^{-2}$ M, a shift occurs in the characteristic $\lambda_{max}$ for $Os^{IV}-NP(H)Et_2$ in $CH_3CN:H_2O$ at pH 1.5 from 366 nm to 382 nm. This feature subsequently disappears to give the spectrum of $[Os^{V}(Tp)(Cl)_2(NPEt_2)]$ with $\lambda_{max} = 396$ nm.

These observations and that the reaction is dominated (~80%) at pH 1.5 by the $k_1$ pathway are consistent with the mechanism in Equations (8a)–(8c). Related mechanisms involving pre-association with formation of H-bonded adducts have been found in the oxidations of *trans*-$[Os^{IV}(tpy)(Cl)_2\{N(H)N(CH_2)_4O\}]PF_6$[11] and *trans*-$[Os^{IV}(tpy)(Cl)_2\{NS(H)C_6H_3Me_2\}]PF_6$[12] by Q.



$$[Os^{IV}{=}N{-}P(H)Et_2] + Q \underset{}{\overset{K_A}{\rightleftharpoons}} [Os^{IV}{=}N{-}P(Et_2)H\cdots Q] \quad (8a)$$



$$[Os^{IV}{=}N{-}P(Et_2)H\cdots Q] \xrightarrow{k_{red}} [Os^{V}{\equiv}N{-}PEt_2] + H\dot{Q} \quad (8b)$$

$$Os^{IV}-NP(H)Et_2 + HQ^{\bullet} \xrightarrow{\mathrm{rapid}} Os^{V}-NPEt_2 + H_2Q \quad (8c)$$

From the plots of $k_{obs}$ versus [Q] and of $1/k_{obs}$ versus 1/[Q] (Figure 1) $k_{red}$ in $H_2O$ is $(1.54 \pm 0.02) \times 10^{-2}\,s^{-1}$, and $K_A(H_2O)$ is $(2.15 \pm 0.02) \times 10^{3}\,M^{-1}$.

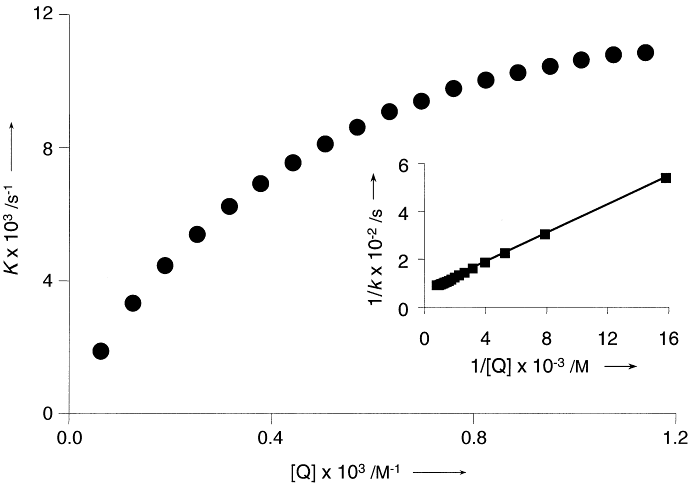


Figure 1. Plot of $k_{obs}$ versus [Q] for the reaction between Q and $[Os^{IV}(Tp)(Cl)_2(NP(H)Et_2)]$ in 1:1 (v/v) $CH_3CN:H_2O$ (25.0 ± 0.1 °C, $[H^+] = 3.2 \times 10^{-2}$ M, and $\mu = 1.0$ M in $NH_4PF_6$). A plot of $1/k_{obs}$ versus 1/[Q] is shown in the inset.

The pH-dependent experiments were repeated from pH 0.0–2.5 ($\mu = 1.0$ M in $NH_4PF_6$) in 1:1 (v/v) $CH_3CN:H_2O$ and 1:1 (v/v) $CH_3CN:D_2O$ at 25.0 ± 0.1 °C at relatively low [Q] ($\leq 3.04 \times 10^{-3}$ M) under conditions where the $k_1$ pathway is first order in [Q]. At these conditions, $[H^+]$ is much larger than $K_a$, and it follows from Equation (7b) that $K_{obs}$ is given by Equation (9).

$$k_{obs} = 2k_1 + \frac{2k_2K_a}{[H^+]} \quad (9)$$

From the plots of $k_{obs}$ versus $1/[H^+]$ in Figure 2, $k_1(H_2O) = (1.48 \pm 0.01) \times 10^{1}\,M^{-1}s^{-1}$ and $k_2(H_2O) = (3.95 \pm 0.04) \times 10^{2}\,M^{-1}s^{-1}$ and $k_1(D_2O) = (8.30 \pm 0.07) \times 10^{-2}\,M^{-1}s^{-1}$ and $k_2(D_2O) = (1.16 \pm 0.01) \times 10^{2}\,M^{-1}s^{-1}$. Based on these data, $k_1(H_2O)/k_1(D_2O) = 178.3 \pm 7.5$ and $k_2(H_2O)/k_2(D_2O) = 3.41 \pm 0.01$.

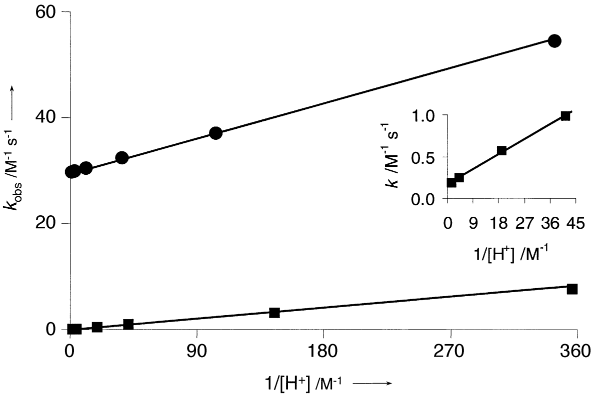


Figure 2. pH dependence of $k_{obs}$ for the reaction between $[Os^{IV}(Tp)(Cl)_2(NP(H)Et_2)]$ and Q from pH 0.0 to 2.5 in 1:1 (v/v) $CH_3CN:H_2O$ ($\mu = 1.0$ M in $NH_4PF_6$) at $T = 25.0 \pm 0.1$ °C and $CN_3CN:D_2O$. A plot of the same reaction under the same conditions in $CH_3CN:D_2O$ from pH 0.0 to 1.6 is shown in the inset.

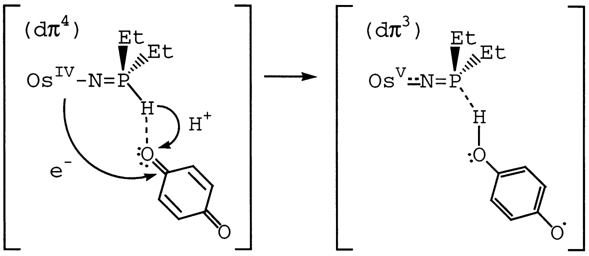
The observation of a kinetic isotope effect of 178.3 ± 7.5 for $k_1$ is remarkable. Given the mechanism in Equations (8a) and (8b), $k_1$ is the product $k_{red}K_A$. A series of experiments was conducted at pH = 1.5 (pD = 1.1) at high concentration of Q, up to $1.46 \times 10^{-3}$ M. Under these conditions, saturation kinetics in [Q] were observed for the $k_1$ pathway, consistent with the rate law in Equations (10a) and (10b).

$$\text{Rate} = k_{obs}[\mathrm{Os^{IV}}]_T \tag{10a}$$

$$k_{obs} = \frac{k_{red}K_A[\mathrm{Q}] + k_2\frac{K_a}{[\mathrm{H^+}]}[\mathrm{Q}]}{K_A[\mathrm{Q}] + 1} \tag{10b}$$

From plots of $1/k_{obs}$ versus 1/[Q] (Supporting Information Figure 2), $K_A(D_2O) = (2.10 \pm 0.02) \times 10^3\,\mathrm{M^{-1}}$ and $k_{red}(D_2O) = (1.96 \pm 0.03) \times 10^{-4}\,\mathrm{s^{-1}}$. Based on this result, $K_A(H_2O)/K_A(D_2O) = 1.02 \pm 0.02$ and $k_{red}(H_2O)/k_{red}(D_2O) = 175.1 \pm 0.9$. This fact shows that the isotope effect appears largely in the redox step, $k_{red}$, and the large isotope effect points to a proton-coupled electron-transfer mechanism.

As shown in Equation (11), proton-coupled electron transfer in this case involves $d\pi(\mathrm{Os^{IV}}) \rightarrow n\pi^*(\mathrm{Q})$ electron transfer coupled to $sp^3(\mathrm{P}) \rightarrow sp^2(\mathrm{O})$ proton transfer from the $\mathrm{Os^{IV}}$ donor to the benzoquinone acceptor.



(11)

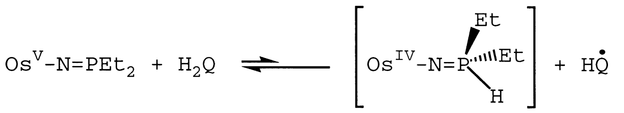
Hydrogen-atom transfer with both electron and proton transferred from $sp^3$(P–H) would lead to the high energy, ligand-oxidized intermediate, $\mathrm{Os^{IV}{-}NP^{\bullet}Et_2}$.

The magnitude of the kinetic isotope effect points to the importance of tunneling and a large tunneling distance which occurs by the coupling of a $\nu$(P–H) mode in the donor and a $\nu$(O–H) mode in the $\mathrm{HQ^{\bullet}}$ product.

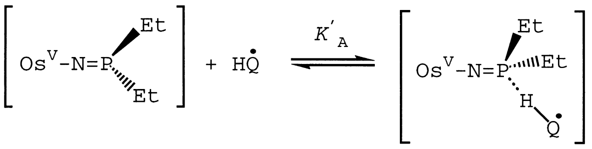
The driving force for the reaction in Equation (6) is −0.03 eV, and the reaction is measurably reversible.[19] The results of an initial kinetic study on the oxidation of $H_2Q$ by $[\mathrm{Os^V(Tp)(Cl)_2(NPEt_2)}]$ reveal the rate law shown in Equation (12).

$$\frac{-d[\mathrm{Os^V}]}{dt} = k_{obs}\frac{[\mathrm{Os^V - NPEt_2}]^2[\mathrm{H_2Q}]}{[\mathrm{Os^{IV} - NP(H)Et_2}]} \tag{12}$$

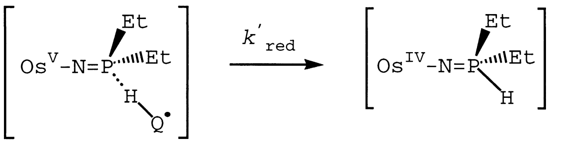
This result is consistent with the reverse of the mechanism in Equations (8a)–(8c) and rate-limiting proton-coupled electron transfer between $\mathrm{HQ^{\bullet}}$ and $\mathrm{Os^V{-}NPEt_2}$. The initial reaction between $H_2Q$ and $\mathrm{Os^V{-}NPEt_2}$ is a rapid pre-equilibrium. Initial results at high $[H_2Q]$ have provided direct evidence for the intermediate, $\mathrm{Os^V{-}NPEt_2 \cdots HQ^{\bullet}}$, and the mechanism for the reverse reaction shown in Equations (13a)–(13c).



(13a)



(13b)



(13c)

In conclusion, our study provides the first documented example of proton-coupled electron transfer involving a phosphorus atom that is not directly bonded to a metal. The large magnitude of the kinetic isotope effect is also remarkable and opens the possibility of observing giant isotope effects in related reactions where proton-coupled electron transfer is the dominant mechanism.

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# A New Crystal Modification of Chromium Tetrafluoride: $\beta$-$CrF_4$**

Primož Benkič, Zoran Mazej,* and Boris Žemva

*In memoriam Karel Lutar*

Part of the investigations into reactions between chromium fluorides ($CrF_2$, $CrF_3$, $CrF_5$) and xenon fluorides ($XeF_2$, $XeF_6$) was a search for appropriate starting materials for the preparation of pure solid $CrF_4$.[1, 2] It was found that solid $XeF_2 \cdot CrF_4$ is quickly solvolyzed in anhydrous hydrogen fluoride (aHF) to give amethyst $CrF_4$.[1] Although the obtained $CrF_4$ was of very low crystallinity, its X-ray powder diffraction pattern indicated that it has a different crystal structure than $CrF_4$ prepared by direct fluorination of elemental chromium with an aHF/$F_2$ mixture at 573 K.[3] However, efforts to prepare single crystals of the new form of $CrF_4$ were plagued by the same preparative difficulties that prevent the growth of suitable single crystals of higher binary fluorides (high reactivity, moisture sensitivity, tendency to disproportionate, and thermal decomposition to lower valent compounds and elemental fluorine). Because of their reactivity they can be handled only in a few solvents, and their low solubility makes the preparation of single crystals from saturated solutions infeasible. For these reasons the preparation of single crystals of each 3d transition metal tetrafluoride represented a special challenge, and different preparation conditions were required in each case. We found that slow thermal decomposition of $CrF_5$ at 403 K yields large, beautiful, dark red-violet single crystals. Their color, vibrational data (see Supporting Information), and chemical analysis (see Experimental Section) confirmed that single crystals of $CrF_4$ were obtained. The presence of lower chromium fluorides ($CrF_2$, $Cr_2F_5$, or $CrF_3$) or oxyfluorides ($CrF_2O$, $CrF_3O$, $CrF_4O$, or $CrF_2O_2$) was excluded.

The crystal structures of the lower chromium fluorides ($CrF_2$,[4] $Cr_2F_5$,[5] $CrF_3$[6]) have long been known, and the crystal structure of $CrF_4$ was reported recently.[3] Here we report on a new crystal modification of $CrF_4$, which we named $\beta$-$CrF_4$ to distinguish it from the already known $\alpha$-$CrF_4$.[3]

The tetrafluorides $MF_4$ can be divided into five groups. The first group contains $MF_4$ of larger $M^{4+}$ ions (M = Hf, Ce, Pr, Tb, Th–Bk),[7] isostructural to $\beta$-$ZrF_4$;[7] the second the structurally related $MF_4$ (M = Rh, Os, Ir, Pt, Pd, Re);[8, 9] the third the structurally related $NbF_4$,[10, 11] $SnF_4$,[12] $PbF_4$,[12] $VF_4$,[10] and $RuF_4$;[11] and the fourth $SeF_4$ and $TeF_4$.[13] The fifth group includes $TiF_4$,[14] $\alpha$-$MnF_4$,[15] $\beta$-$MnF_4$,[15] $\alpha$-$ZrF_4$,[16] and $\alpha$-$CrF_4$,[3] which represents unique examples. $\beta$-$CrF_4$ crystallizes in a new structural type. The basic unit of the crystal structure consists of four corner-sharing $CrF_6$ octahedra (Figure 1). Tetrameric rings are thus formed in which four Cr atoms are connected by *cis* bridging fluorine atoms. The coordination sphere around Cr atoms is completed by two *cis* terminal fluorine atoms and two *trans* bridging fluorine atoms

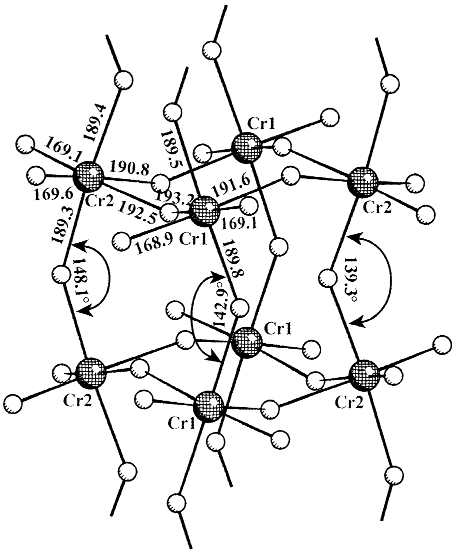

Figure 1. Section of the crystalline structure of $\beta$-$CrF_4$ showing tetrameric rings with bond lengths [pm] and angles [°].

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[*] Dr. Z. Mazej, Dipl.-Chem. P. Benkič, Prof. Dr. B. Žemva
Jožef Stefan Institute
Jamova 39, SI-1000 Ljubljana (Slovenia)
Fax: (+386) 1-423-2125
E-mail: zoran.mazej@ijs.si

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