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Unexpected metal ion-assisted transformations leading to unexplored bridging ligands in Ni^{II} coordination chemistry: the case of PO₃F²⁻ group†

Despina Dermitzaki,^a Catherine P. Raptopoulou,^b Vassilis Psycharis,^b Albert Escuer,^c Spyros P. Perlepes*^a and Theocharis C. Stamatatos*^d

The initial 'accidental', metal ion-assisted hydrolysis of PF₆⁻ to PO₃F²⁻ has been evolved in a systematic investigation of the bridging affinity of the latter group in Ni^{II}/oximate chemistry; mono-, di- and trinuclear complexes have been prepared and confirmed both the rich reactivity of PO₃F²⁻ and its potential for further use as bridging ligand in high-nuclearity 3d-metal cluster chemistry.

One of the major current challenges in modern coordination chemistry is the utilization of new, flexible and relatively unexplored bridging ligands which would serve to link metal centers into unprecedented assemblies with beautiful structural motifs and interesting physical properties.¹ When the metal ions present are paramagnetic, the interest is mainly focused on the magnetic properties of the resulting oligo- or polynuclear coordination compounds.² For example, when the flexible carboxylate ions have been employed in high-oxidation state Mn chemistry the resulting [Mn^{III}₈Mn^{IV}₄O₁₂(O₂CR)₁₆(H₂O)₄] (R = various) family of coordination clusters was found to exhibit a significant energy barrier to reversal of the magnetization vector, and thus at low temperatures these Mn₁₂ molecules functioned as nanoscale magnetic particles.³ Such species were named single-molecule magnets (SMMs) and since their first discovery,⁴ numerous synthetic strategies have been developed and led to a remarkable database of different in nuclearity, structures and properties SMMs.²⁻⁴

Undoubtedly, the most successful route to date is the self-assembly which deals with the one-pot reaction of metal ion precursors with a combination of bridging and chelating

ligands.¹⁻³ Following the constructive use of carboxylate ions as bridging ligands in metal cluster chemistry,⁵ various groups have also employed ligands ranging from inorganic ones, such as pseudohalides (*i.e.* azides,⁶ cyanates,⁷ *etc.*) and sulfates,⁸ to more complex organic ones such as organophosphates⁹ and their derivatives. Still though, there is an increasing need for novel multifunctional bridging groups capable of bridging metal centers in a unique way and providing invaluable opportunities for new magnetic phenomena. Toward this end, exciting coordination compounds have been also resulted from unexpected, 'in situ' ligand transformations which have provided unprecedented groups with superior bridging abilities.^{2c,d,10} Such metal ion-assisted organic transformations have opened new avenues for crossing boundaries both inside and between the fields of inorganic/coordination chemistry, organic chemistry and homogeneous catalysis.

An additional fruitful strategy, slightly more controllable than the "serendipitous assembly",¹ is that of the "metal complexes as ligands";¹¹ in this approach, mononuclear or dinuclear 3d-metal complexes with uncoordinated O-donor groups are used as reactants and considered as "ligands" for further reactions with more oxophilic 3d'-metal ions or lanthanides (Ln).¹² To further develop this approach, and given the long-standing interest of our groups in the coordination and reactivity chemistry of 2-pyridyl oximes,¹³ we initially attempted to synthesize the [Ni(mpkoH)₃]²⁺ (mpkoH = methyl 2-pyridyl ketone oxime) metalloligand and employ it for the construction of Ni/Ln/mpko⁻ clusters and SMMs.

Thus, we performed the targeted 1:3:3 reaction between Ni(NO₃)₂·6H₂O, mpkoH and NH₄PF₆ in MeOH, which led to a dark orange suspension and upon filtration to the corresponding orange solution. Slow evaporation of the latter gave after 4 days blue crystals in 25% yield suitable for single-crystal X-ray diffraction studies.† Somewhat to our surprise, and in contrast to the expected "[Ni(mpkoH)₃](PF₆)₂", the resulting compound was the trinuclear [Ni₃(PO₃F)₂(mpkoH)₆](PF₆)₂·1.35MeOH·1.5H₂O (1·1.35MeOH·1.5H₂O)¹⁴ cluster comprising two PO₃F²⁻ bridging groups, six chelating mpkoH ligands and two PF₆⁻ counteranions. The low isolated yield of

^aDepartment of Chemistry, University of Patras, 265 04 Patras, Greece.

E-mail: perlepes@upatras.gr

^bInstitute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, NCSR "Demokritos", 153 10 Agia Paraskevi Attikis, Greece

^cDepartament de Química Inorgànica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain

^dDepartment of Chemistry, 500 Glenridge Ave, Brock University,

L2S 3A1 St. Catharines, Ontario, Canada. E-mail: tstatamatatos@brocku.ca

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1 together with the intense orange coloration of the filtrate led us to retain the solution for a prolonged slow evaporation. Hence, after two weeks orange crystals were deposited and crystallographically characterized as the 'desired' $[\text{Ni}(\text{mpkoH})_3](\text{PF}_6)(\text{NO}_3)$ (**2**) complex in yields as high as 60% (based on Ni).[†] Of synthetic interest is the fact that the two compounds never co-crystallize and always **1** precipitates before **2**, under a wide variety of different synthetic and crystallization conditions.

The structure of the cation of **1** (Fig. 1) consists of three Ni^{II} ions held together by two $\eta^1:\eta^1:\eta^1:\mu_3$ PO_3F^{2-} bridging groups in a triangular conformation, emphasizing the bridging flexibility of the PO_3F^{2-} group and its ability to connect multiple metal ions. The PO_3F^{2-} ions are the exclusive bridging ligands in **1** and lie above and below the Ni_3 plane (Fig. S1[†]); the $\text{Ni}^{\text{II}}\cdots\text{Ni}^{\text{II}}$ separations are 4.749 ($\text{Ni1}\cdots\text{Ni2}$), 4.592 ($\text{Ni2}\cdots\text{Ni3}$) and 4.645 Å ($\text{Ni1}\cdots\text{Ni3}$). Peripheral ligation about the three distorted octahedral Ni^{II} ions is provided by six N,N' -chelating mpkoH molecules, two on each Ni^{II} ion, with their neutral $=\text{N}-\text{OH}$ groups hydrogen-bonded to the O-atoms of PO_3F^{2-} groups. The cation of **2** (Fig. S2[†]) comprises a distorted octahedral Ni^{II} ion capped by three N,N' -bidentate chelating mpkoH ligands and counterbalanced by a PF_6^- and a NO_3^- ions. The latter are strongly H-bonded with the oxime functionalities of **2**, thus leading to a supramolecular 1-D chain extended parallel to the crystallographic c axis (Fig. S3[†]).

The PO_3F^{2-} group in **1** arises from the partial hydrolysis of the PF_6^- ion ($\text{PF}_6^- + 4\text{H}_2\text{O} \rightarrow \text{PO}_3\text{F}^{2-} + 5\text{HF} + \text{H}_3\text{O}^+$)^{15,16} as confirmed by the simultaneous presence of both groups in the first and second coordination spheres, respectively (*vide infra*).

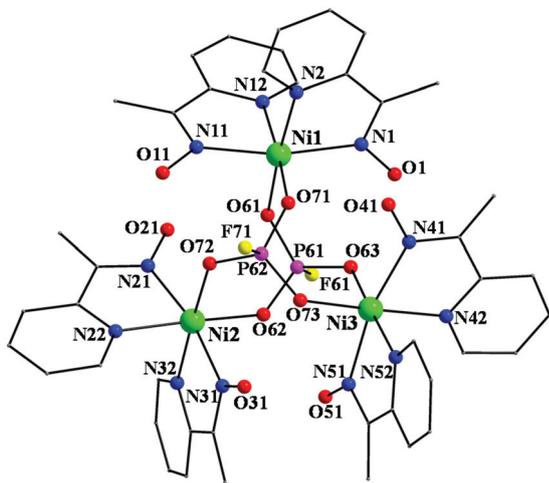


Fig. 1 Labelled plot of the trinuclear cation present in complex **1**. Color scheme: Ni^{II} green, O red, N blue, C gray, P purple, F yellow. H-atoms are omitted for clarity. Selected bond distances (Å): $\text{Ni1}-\text{N1}$ 2.098(5), $\text{Ni1}-\text{N2}$ 2.095(5), $\text{Ni1}-\text{N11}$ 2.070(4), $\text{Ni1}-\text{N12}$ 2.095(4), $\text{Ni1}-\text{O61}$ 2.076(3), $\text{Ni1}-\text{O71}$ 2.068(4), $\text{Ni2}-\text{N21}$ 2.089(5), $\text{Ni2}-\text{N22}$ 2.087(5), $\text{Ni2}-\text{N31}$ 2.089(5), $\text{Ni2}-\text{N32}$ 2.085(5), $\text{Ni2}-\text{O62}$ 2.057(3), $\text{Ni2}-\text{O72}$ 2.070(4), $\text{Ni3}-\text{N41}$ 2.077(6), $\text{Ni3}-\text{N42}$ 2.096(5), $\text{Ni3}-\text{N51}$ 2.077(6), $\text{Ni3}-\text{N52}$ 2.088(5), $\text{Ni3}-\text{O63}$ 2.076(4), $\text{Ni3}-\text{O73}$ 2.065(4), $\text{P61}-\text{O61}$ 1.523(3), $\text{P61}-\text{O62}$ 1.522(4), $\text{P61}-\text{O63}$ 1.541(4), $\text{P62}-\text{O71}$ 1.512(4), $\text{P62}-\text{O72}$ 1.533(4), $\text{P62}-\text{O73}$ 1.527(3).

We believe that the presence of Ni^{II} is necessary for the promotion of hydrolysis; presumably, the role of Ni^{II} is to activate the H_2O molecule while the resulting H_3O^+ from the hydrolysis reaction of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ can catalyze the hydrolysis of PF_6^- . The coordination of the resulting PO_3F^{2-} ion to the Ni^{II} center most likely fosters the termination of hydrolysis. Given the limited number of structurally characterized metal complexes bearing PO_3F^{2-} as bridging ligand^{15,17} and the fact that **1** is the first PO_3F^{2-} -bridged paramagnetic metal cluster ever reported, we undertook the challenge to initiate a program aiming at the in-depth exploration of its coordination and bridging abilities in conjunction with other chelates such as the 2-pyridyl oximes.

Therefore, by using the $\text{Na}_2\text{O}_3\text{PF}$ precursor in reactions with $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, mpkoH and NH_4PF_6 , in a 2:3:6:2 molar ratio in MeOH, we have been primarily able to isolate blue crystals of **1** in yields higher than 80% depending on the crystallization process. As part of the chemical reactivity studies of **1**, we then decided to perform the same reaction but in the absence of PF_6^- ions. Thus, the 2:3:6 reaction of $\text{Na}_2\text{O}_3\text{PF}$, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and mpkoH in MeOH gave a bluish suspension which was filtered and the resulting filtrate was left to slowly evaporate at room temperature. After ten days, light blue plate-like crystals of the new dinuclear $[\text{Ni}_2(\text{PO}_3\text{F})_2(\text{mpkoH})_4]\cdot 2\text{H}_2\text{O}$ ($3\cdot 2\text{H}_2\text{O}$) complex were precipitated and collected in ~55% yield.[†] The centrosymmetric structure of **3** (Fig. 2)¹⁴ consists of two distorted octahedral Ni^{II} ions bridged by two $\eta^1:\eta^1:\mu$ PO_3F^{2-} groups to form a dimer with a $\text{Ni}\cdots\text{Ni}'$ separation of 5.237 Å. Similar to **1**, peripheral ligation is provided by a total of four N,N' -bidentate chelating mpkoH ligands. The third, dangling O-atom of each PO_3F^{2-} group in **3** is actually 'blocked' for metal coordination due to its participation in two strong intramolecular H-bonds with the protonated hydroxyl groups of the oxime moieties (Fig. 2). Their dimensions are: $\text{O1}\cdots\text{O5}$ 2.620 Å, $\text{H}(\text{O1})\cdots\text{O5}$ 1.825 Å, $\text{O1}-\text{H}(\text{O1})\cdots\text{O5}$ 177.4° and $\text{O2}\cdots\text{O5}'$ 2.570 Å, $\text{H}(\text{O2})\cdots\text{O5}'$ 1.722 Å, $\text{O2}-\text{H}(\text{O2})\cdots\text{O5}'$ = 172.9°.

Within the concept of chemical reactivity on coordination compounds, another important synthetic factor that is worthy

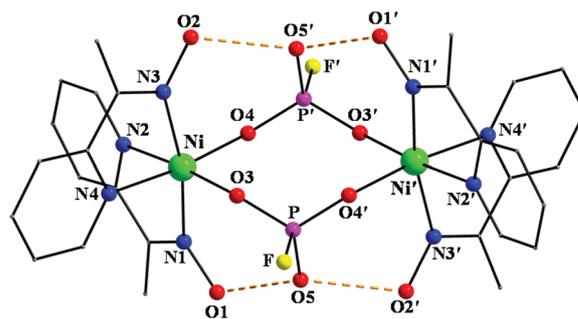


Fig. 2 Labelled plot of the dinuclear complex **3**. Color scheme as in Fig. 1. H-atoms are omitted for clarity. The orange dashed lines highlight the intramolecular H-bonds discussed in the text. Primed atoms are related to the non-primed ones by the symmetry operation: $1 - x, -y, 1 - z$. Selected bond distances (Å): $\text{Ni}-\text{N1}$ 2.080(2), $\text{Ni}-\text{N2}$ 2.089(2), $\text{Ni}-\text{N3}$ 2.094(2), $\text{Ni}-\text{N4}$ 2.095(2), $\text{Ni}-\text{O3}$ 2.043(2), $\text{Ni}-\text{O4}$ 2.027(2), $\text{P}-\text{O3}$ 1.505(2), $\text{P}-\text{O4}'$ 1.488(2), $\text{P}-\text{O5}$ 1.518(2).

of investigation is the effect of the solvent on the structural identity of the complexes. Toward that end, the reaction that led to complex **3** was repeated in MeCN (instead of MeOH) under exactly the same *ambient conditions*. The resulting turquoise suspension was filtered and the filtrate afforded after 20 days purple plate-like crystals in 15% yield.† X-ray diffraction studies revealed the unusual $[\text{Ni}(\text{P}_2\text{O}_5\text{F}_2)(\text{mpkoH})_2] \cdot 0.6\text{MeCN} \cdot 0.65\text{H}_2\text{O}$ ($4 \cdot 0.6\text{MeCN} \cdot 0.65\text{H}_2\text{O}$) compound resulted from an unprecedented metal-ion assisted transformation of $\text{PO}_3\text{F}_2^{2-}$ to $\text{P}_2\text{O}_5\text{F}_2^{2-}$. Note that such type transformations are of precedent in *orthophosphoric acid* chemistry albeit under high-temperature conditions ($>400^\circ\text{C}$).¹⁸ The $\text{P}_2\text{O}_5\text{F}_2^{2-}$ group can be considered as the symmetrical difluoro analogue of the *pyrophosphate* anion ($\text{P}_2\text{O}_7^{4-}$).

The mononuclear compound **4** (Fig. 3)¹⁴ features a distorted octahedral Ni^{II} ion surrounded by four N-atoms from two bidentate chelating mpkoH ligands and two O-atoms from the $\text{P}_2\text{O}_5\text{F}_2^{2-}$ group. The latter has never been seen before in any coordination compound and it acts as an *O,O'*-bidentate chelating ligand, forming a stable six-membered chelate ring around Ni^{II} . It can be also considered as the ‘dimeric’ form of the $\text{PO}_3\text{F}_2^{2-}$ precursor, with an O-atom (O23) shared between the two adjacent $-\text{PO}_2\text{F}$ pendants. The P1–O23–P2 angle is 125.8° and the $\text{P}_2\text{O}_5\text{F}_2^{2-}$ ion adopts an overall staggered conformation similar to that in the previously reported organic salt $[\text{DMAPH}]_2[\text{P}_2\text{O}_5\text{F}_2]^{19}$ where DMAPH^+ stands for the $(\text{CH}_3)_2\text{NC}_5\text{H}_4\text{N}^+$ cation. The phosphorus environments are near tetrahedral and the resulting 1,2-difluorodiphosphate anion has a virtual C_2 symmetry. Two strong intramolecular H-bonds involving the uncoordinated O-atoms of $\text{P}_2\text{O}_5\text{F}_2^{2-}$ and the $-\text{OH}$ groups of the mpkoH ligands contribute to the thermodynamic stability of **4**. Their dimensions are: O1...O22 2.680 Å, H(O1)...O22 1.831 Å, O1–H(O1)...O22 157.6° and O11...O25 2.641 Å, H(O11)...O25 1.639 Å, O11–H(O11)...O25 154.4° .

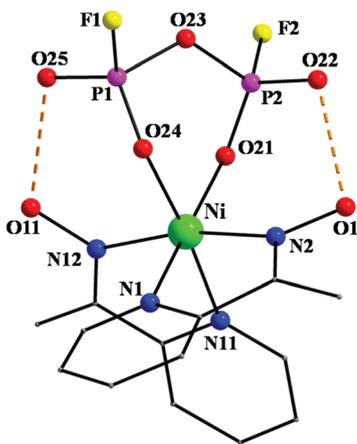


Fig. 3 Labelled plot of complex **4**. Color scheme as in Fig. 1. H-atoms are omitted for clarity. The orange dashed lines highlight the intramolecular H-bonds discussed in the text. Selected bond distances (Å): Ni–N1 2.071(8), Ni–N2 2.064(9), Ni–N11 2.102(9), Ni–N12 2.066(8), Ni–O21 2.063(6), Ni–O24 2.034(6), P1–O23 1.686(9), P1–O24 1.473(6), P1–O25 1.525(7), P2–O21 1.460(6), P2–O22 1.482(7), P2–O23 1.632(6).

A detailed mechanistic perspective of the $\text{PO}_3\text{F}_2^{2-}$ to $\text{P}_2\text{O}_5\text{F}_2^{2-}$ transformation is currently beyond our scope and requires solution kinetic studies which are hindered by the paramagnetic nature of the Ni^{II} -containing complex. To our opinion, a simplistic reaction scheme may include the initial metal-ion assisted single protonation of two $\text{O}=\text{PF}(\text{O}^-)(\text{O}^-)$ ions to the corresponding $\text{O}=\text{PF}(\text{OH})\text{O}^-$ groups, with the required protons mainly provided by the hydrolysis reaction of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. Subsequently, nucleophilic attack of the negatively charged O-atom of $\text{O}=\text{PF}(\text{OH})\text{O}^-$ to the P-atom of a neighboring $\text{O}=\text{PF}(\text{OH})\text{O}^-$ unit generates the intermediate, unstable compound $[\text{O}=\text{PF}(\text{OH})]_2\text{O}-[(\text{OH})(\text{O}^-)\text{FP}=\text{O}]$ which undergoes water elimination and results in the formation of stable $[\text{O}=\text{PF}(\text{O}^-)]_2\text{O}-[(\text{O}^-)\text{FP}=\text{O}]$ species (*a condensed fluorophosphate*, $\text{P}_2\text{O}_5\text{F}_2^{2-}$).^{19,20}

Variable-temperature dc magnetic susceptibility measurements were performed on vacuum-dried samples of **1** and **3** in the temperature range 2.0–300 K in an applied field of 1 kG (0.1 T). The data are shown as $\chi_{\text{M}}T$ versus T plots in Fig. 4. The values of the $\chi_{\text{M}}T$ product at 300 K are 4.24 (**1**) and 2.19 (**3**) $\text{cm}^3 \text{mol}^{-1} \text{K}$, slightly higher than and very close to the 3.63 and $2.42 \text{ cm}^3 \text{mol}^{-1} \text{K}$ values (calculated with $g = 2.2$) expected for complexes of three and two non-interacting Ni^{II} ($S = 1$) atoms, respectively. For both **1** and **3**, the value of $\chi_{\text{M}}T$ remains constant in the 300–40 and 300–50 K ranges, respectively, and then decreases rapidly with decreasing T to reach the values of 2.27 (**1**) and 1.53 (**3**) $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 2 K. The data and shape of plots indicate negligible magnetic exchange interactions in the higher- T regime (>40 K) which turn to moderate antiferromagnetic upon lowering the temperature, thus suggesting small or zero ground state spin values for the reported compounds.

In order to quantify the nature of the magnetic exchange within **1** and **3**, and evaluate the ‘magnetic potency’ of $\text{PO}_3\text{F}_2^{2-}$ bridge, theoretical expressions of χ_{M} as a function of T were derived and fit to the experimental data. For both **1** and **3**, Heisenberg spin-Hamiltonians (using the atomic numbering in Fig. 1 and 2), eqn (1) and (2), were considered. Hence, in **1** the data were primarily fit using an isosceles, 2- J model, but the fitting was equally good and accurate when an 1- J model was

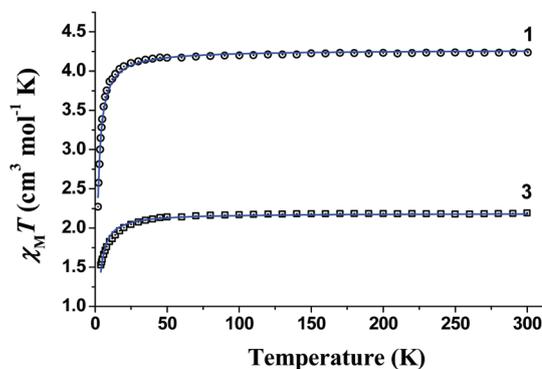


Fig. 4 $\chi_{\text{M}}T$ versus T plots of **1** and **3** in a 1 kG field. The blue solid lines are the fits of the data; see the text for the fit parameters.

employed assuming a C_3 equilateral triangle, in consistency also with the structural features of the compound, namely the same $\text{Ni}^{\text{II}}-(\mu\text{-O}_3\text{PF})_2\text{-Ni}^{\text{II}}$ pathways. As an approximation, zero-field splitting (ZFS) parameters, usually small in these types of systems, were not included in the models.

$$\mathcal{H}_{\text{Ni}3} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_3) \quad (1)$$

$$\mathcal{H}_{\text{Ni}2} = -J(\hat{S}_1 \cdot \hat{S}_{1'}) \quad (2)$$

The best set of parameters for **1** are: $J = -0.61(1) \text{ cm}^{-1}$ and $g = 2.38(2)$, and for **3**: $J = -1.40(1) \text{ cm}^{-1}$ and $g = 2.09(3)$, both indicating weak-to-moderate antiferromagnetic interactions between the Ni^{II} centers. Triangular metal complexes are ideal candidates for the study of spin frustration effects which emerge from the competing antiferromagnetic interactions that prevent (frustrate) the preferred antiparallel spin alignments.²¹ Such studies for complex **1** are currently in progress and will be reported in an upcoming full paper of this work.

Conclusions

In this preliminary report, we have shown that our initial unsuccessful attempt to isolate Ni^{II} /oxime complexes as metal-ligands has led to the unexpected formation of a triangular Ni_3 cluster bearing PO_3F^{2-} bridging ions. The latter were resulted from a metal-ion assisted hydrolysis of PF_6^- ions, primarily employed to counterbalance the charge of the targeted “[$\text{Ni}(\text{mpkoH})_3$]²⁺” compound. This *in situ* ligand transformation has stimulated us to initiate a different program aiming at the systematic investigation of the chemical reactivity of the $\text{Ni}^{\text{II}}/\text{PO}_3\text{F}^{2-}/\text{mpkoH}$ system, under bench-top conditions, seeking ways to unveil the bridging capability of the O-rich PO_3F^{2-} group. By changing several synthetic variables, we have been able to isolate a PO_3F^{2-} -bridged Ni_2 dimer and a mononuclear Ni^{II} compound with an exciting and unprecedented $\text{PO}_3\text{F}^{2-} \rightarrow \text{P}_2\text{O}_5\text{F}_2^{2-}$ transformation presumably derived from a combination of hydrolysis, nucleophilic attack and condensation reactions. We believe that this work presages a rich new area of metal-assisted reactivity of fluorophosphates and deserves to be further explored with a variety of metal ions and ancillary chelating ligands, and under different reaction conditions. For example, we are currently undertaking reactions in the presence of an external base to deprotonate the mpkoH ligand and consequently break the strong intramolecular H-bonding interactions which seem responsible for confining a higher bridging affinity of PO_3F^{2-} , thus hindering the formation of polynuclear cluster compounds.

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- 14 Anal. Calcd (Found) for **1–4** (all solvent-free): **1**: C 34.11 (34.37), H 3.27 (3.42), N 11.37 (11.16); **2**: C 37.42 (37.32), H 3.59 (3.51), N 14.54 (14.72); **3**: C 39.20 (39.45), H 3.76 (3.87), N 13.06 (12.85); **4**: C 32.91 (33.06), H 3.17 (3.27), N 10.97 (10.80). Crystal structure data for **1**·1.35MeOH·1.5H₂O: C_{43.35}H_{56.4}F₁₄N₁₂Ni₃O_{14.85}P₄, *M_w* = 1549.21, monoclinic, space group *P2₁/n* with *a* = 17.3467(3), *b* = 17.1048(3), *c* = 24.5607(4) Å, β = 107.689(1)°, *V* = 6942.9(2) Å³, *T* = 183(2) K, *Z* = 4, *R1/wR2* [*I* > 2σ(*I*)] = 0.0796/0.2380. Crystal structure data for **2**: C₂₁H₂₄F₆N₇NiO₆P, *M_w* = 674.15, monoclinic, space group *P2₁/c* with *a* = 13.4305(2), *b* = 13.7894(2), *c* = 15.9761(2) Å, β = 112.968(1)°, *V* = 2724.19(7) Å³, *T* = 183(2) K, *Z* = 4, *R1/wR2* [*I* > 2σ(*I*)] = 0.0493/0.1296. Crystal structure data for **3**·2H₂O: C₂₈H₃₆F₂N₈Ni₂O₁₂P₂, *M_w* = 894.01, monoclinic, space group *P2₁/n* with *a* = 10.3339(1), *b* = 12.9700(1), *c* = 13.7335(2) Å, β = 104.312(1)°, *V* = 1783.58(3) Å³, *T* = 160(2) K, *Z* = 2, *R1/wR2* [*I* > 2σ(*I*)] = 0.0350/0.0880. Crystal structure data for **4**·0.6MeCN·0.65H₂O: C_{15.2}H_{19.1}F₂N_{4.6}NiO_{7.65}P₂, *M_w* = 547.30, monoclinic, space group *P2₁/c* with *a* = 11.9266(6), *b* = 18.0040(11), *c* = 13.3621(8) Å, β = 111.294(1)°, *V* = 2673.3(3) Å³, *T* = 293(2) K, *Z* = 4, *R1/wR2* [*I* > 2σ(*I*)] = 0.1065/0.2618.
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