# Cyclophosphates as ligands for cobalt(III) in water†

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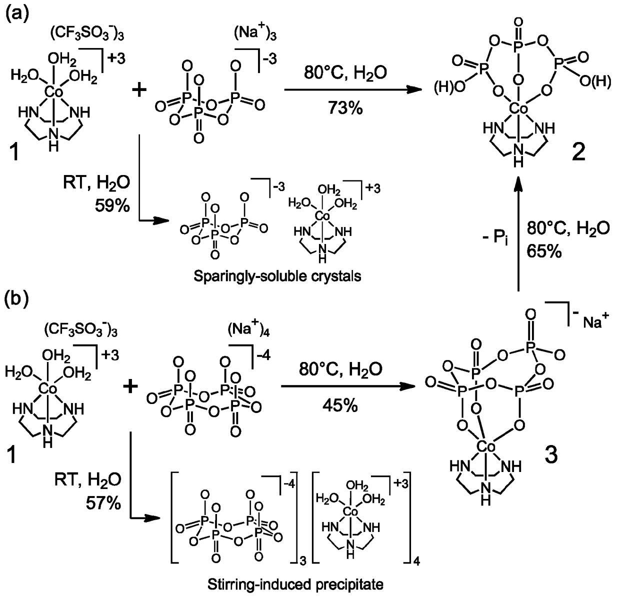
**Examination of cyclotriphosphate and cyclotetraphosphate as ligands for Co(III) in aqueous solutions revealed that cyclotetraphosphate affords stable complexes as a hemilabile ligand, while cyclotriphosphate exhibits facile hydrolysis.**

The utilization of inexpensive, readily available materials is essential for the development of cost-effective catalysts for renewable energy applications.[1] Important progress in this field was made by Kanan and Nocera with the discovery of a heterogeneous Co(III)-based water oxidation catalyst, which was electrodeposited from a neutral aqueous solution containing orthophosphate and simple Co(II) salts.[2] This discovery prompted us to examine condensed phosphate oligomers as low-cost, redox-stable polyanionic ligands for Co(III) in the context of water oxidation chemistry. As part of this effort, we have been investigating cyclophosphates,[3] which are the focus of this communication.

Cyclophosphates have received scant attention as ligands for cobalt, and only a handful of well-defined complexes are known,[4] all of which involve Co(II) and are based on solid-state data.[5] Herein, we describe the reactions of a cationic Co(III) precursor, $[Co(TACN)(H_2O)_3](CF_3SO_3)_3$ (complex **1**; TACN = 1,4,7-triazacyclononane),[6–8] with sodium salts of cyclotriphosphate ($P_3O_9^{-3}$) and cyclotetraphosphate ($P_4O_{12}^{-4}$) in aqueous solutions. These reactions facilitated a comparison of the two cyclophosphates as ligands for Co(III) under conditions relevant to water oxidation, and have also led to the isolation of the first Co(III)–cyclophosphato complexes.[4]

Cyclotriphosphate was initially sought as a tripodal capping ligand for Co(III), since it features facially-oriented terminal oxygen donor groups and is known to bind other transition metals in this fashion.[9] Nevertheless, our study yielded markedly different results, which are attributable to the use of water as a reaction medium rather than organic solvents, which served as reaction media for the other transition metals. As shown in Scheme 1a, when an aqueous solution of **1** was treated with one equivalent of $Na_3P_3O_9$ at room temperature, no coordination of the cyclophosphate was observed. Instead, the salt-metathesis product, $[Co(TACN)(H_2O)_3](P_3O_9)$, separated from the solution as red prismatic crystals (59% yield). The crystal structure of the salt, which was isolated as a trihydrate from a $D_2O$ solution, is shown in Fig. 1.[10] This structure exhibits an extensive network of hydrogen bonds that involves the water molecules, outer-sphere $P_3O_9^{-3}$ and TACN ligand. Similar hydrogen bonding between orthophosphate and Co(III)-bound water molecules may play an important role in Nocera's catalyst (*e.g.*, proton shuttling).



**Scheme 1** Reactions of $[Co(TACN)(H_2O)_3](CF_3SO_3)_3$ (**1**) with the cyclophosphates $Na_3P_3O_9$ (a) and $Na_4P_4O_{12}$ (b) in water. Yields refer to isolated material ($Li^+$ salts in the case of **2** and **3**), except for the reaction **3** → **2** for which NMR yield is cited. $P_i$ = orthophosphate.

When the reaction was repeated at 80 °C crystallization of the salt was prevented, but no $P_3O_9$-containing complexes were obtained. Instead, the solution contained the previously reported complex **2**[11] (Scheme 1a) as the major product. This was isolated from the reaction mixture using ion-exchange chromatography to afford the dilithium salt in 73% yield (or the diprotonated form in 61% yield).[12] The appearance of **2**, in which cobalt is not coordinated to $P_3O_9^{-3}$, but rather to the linear $P_3O_{10}^{-5}$ ligand (partially protonated in the reaction mixture),[13] clearly shows that the cyclophosphate ring had undergone hydrolytic P–O bond cleavage. The same result was obtained at room temperature when the reaction was carried out in buffered solutions with pH = 5.5–7.0,[14] wherein crystallization of the salt-metathesis product was prevented.

The observed hydrolysis of $P_3O_9^{-3}$ conforms to the known behavior of cyclophosphates in aqueous media, particularly under basic or acidic conditions,[15] but also in the presence of metal complexes.[15b,16] In our study, the experimental evidence strongly suggests that hydrolysis of $P_3O_9^{-3}$ is not acid-catalyzed, despite the weak acidity of **1**,[7] but is promoted by coordination to the Co(III) center. This conclusion is supported by the fact that **2** is

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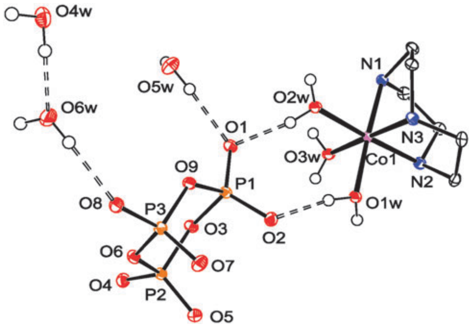


**Fig. 1** ORTEP drawing (50% probability level) of the asymmetric unit of the salt $[Co(TACN)(D_2O)_3](P_3O_9)\cdot 3D_2O$ (TACN H-atoms were omitted for clarity; dashed lines represent H-bonds).

obtained from **1** and $Na_3P_3O_9$ at pH = 5.5–7.0,[14] wherein acid catalysis is suppressed. In the absence of the cobalt precursor $P_3O_9^{-3}$ exhibits no significant hydrolysis under the same conditions.

The facile hydrolysis of $P_3O_9^{-3}$ in the presence of **1** led us to explore its larger congener, cyclotetraphosphate ($P_4O_{12}^{-4}$), as a more hydrolytically stable alternative.[15] Indeed, mixing equimolar amounts of **1** and $Na_4P_4O_{12}$ at room temperature led to formation of $P_4O_{12}$-containing complexes. However, this reaction proceeded very slowly (over several days) and was hampered by stirring-induced precipitation of the salt $[Co(TACN)(H_2O)_3]_4(P_4O_{12})_3$ (57% yield), in a manner reminiscent of $Na_3P_3O_9$. Nevertheless, heating at 80 °C prevented precipitation and significantly accelerated the reaction, leading within minutes to the formation of the complex $[Co(TACN)(\kappa^3\text{-}P_4O_{12})]Na$ (**3**; Scheme 1b) as the predominant product.

The new complex was purified by ion-exchange chromatography to afford its lithium salt in 45% yield. Its $^{31}P$ NMR spectrum in $D_2O$ features three signals at −11.80 (t, $^2J_{PP}$ = 20.5 Hz), −14.70 (dd, $^2J_{PP}$ = 26.8 Hz, $^2J_{PP}$ = 20.5 Hz) and −26.81 ppm (t, $^2J_{PP}$ = 26.8 Hz).[17] These signals, which exhibit a 1 : 2 : 1 integral ratio, are consistent with a $C_s$-symmetrical structure, bearing a tridentate $P_4O_{12}^{-4}$ ligand. This proposed structure was corroborated by X-ray crystallographic analysis (see below). To the best of our knowledge, this is the first documented case of a Co(III)–cyclophosphato complex, as well as the first case in which $P_4O_{12}^{-4}$ binds to a transition metal in a tridentate fashion.[4,18]

The crystal structure of **3**[19] (Fig. 2) features a cobalt ion situated in an octahedral environment defined by the facially-coordinated TACN and $P_4O_{12}^{-4}$ ligands. Interestingly, the structure also exhibits a trihydrated lithium counter-cation which is bound to one of the coordinated $PO_3^-$ moieties, rather than to the non-coordinated $PO_3^-$ fragment. Nevertheless, this "free" $PO_3^-$ group is fully engaged in hydrogen bonding, as part of an extensive network that also involves the N–H moieties, water molecules and non-coordinated terminal oxygen atoms of the cyclophosphato ligand.

Complex **3** is stable in the solid state for months under normal ambient conditions. More importantly, it also exhibits notable stability in water, as only minor cyclophosphate hydrolysis is observed over several days at room temperature, and even at 80 °C complete consumption of the complex requires prolonged heating (*e.g.*, 16 h for $[\mathbf{3}]_0$ = 4.5 mM).

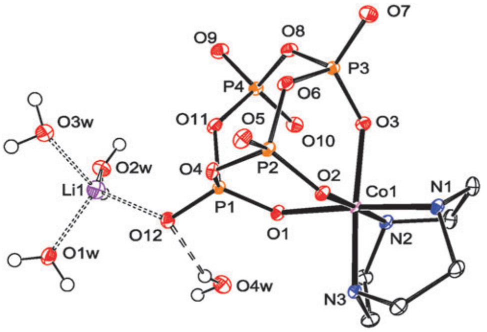


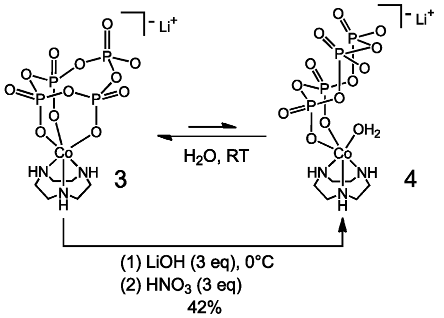
**Fig. 2** ORTEP drawing (50% probability level) of the asymmetric unit of complex **3** (TACN H-atoms were omitted for clarity; a dashed line represents an H-bond and dotted lines represent Li–O dative bonds).

Moreover, **3** was found to be surprisingly stable under highly acidic conditions, exhibiting a hydrolytic half-life of 146 min in 1 M $HNO_3$ at 40 °C, which is close to that of the parent cyclophosphate $Na_4P_4O_{12}$ ($t_{\frac{1}{2}}$ = 174 min).[20] As shown in Scheme 1, hydrolytic decomposition of **3** involves loss of orthophosphate with concomitant formation of **2** as a major product (*e.g.*, *ca.* 65% yield[21] in pure water at 80 °C).

Significantly different behavior was observed under basic conditions. When **3** was treated at room temperature with excess LiOH (*e.g.*, 3 equiv.) the complex was fully consumed within minutes, mainly due to displacement of intact $P_4O_{12}^{-4}$ (*ca.* 80% yield),[21] rather than its hydrolysis. This reaction is reversible, as neutralization of the reaction mixture with $HNO_3$, followed by heating at 80 °C, regenerated **3** (albeit in *ca.* 50% yield[21] due to hydrolysis of $P_4O_{12}^{-4}$). It is important to stress that the rapid reaction of **3** with hydroxide stands in marked contrast to its relative substitutional inertness in non-basic aqueous solutions, wherein cyclophosphate dissociation occurs to only a small extent over several hours at room temperature (see below). These observations imply that the hydroxide-promoted extrusion of $P_4O_{12}^{-4}$ occurs *via* the dissociative conjugate base (**D**$_{\mathbf{CB}}$) mechanism, whereby N–H group deprotonation induces dissociation of $P_4O_{12}^{-4}$. This type of anionic ligand dissociation is well documented for Co(III) complexes bearing nitrogen donor ligands with N–H bonds.[22]

When **3** was dissolved in water a small amount of a new species appeared within a few hours at room temperature. The new species, which was identified as the complex $[Co(TACN)(\kappa^2\text{-}P_4O_{12})(H_2O)]Na$ (**4**; Scheme 2), gives rise to two identical multiplets at −14.51 and −24.89 ppm in the $^{31}P$ NMR spectrum ($D_2O$, 5 °C). These multiplets exhibit a 1 : 1 integral ratio and their pattern is consistent with an $AA'XX'$ spin system (downfield multiplet: $^2J_{AA'}$ = 23 Hz, $^2J_{AX}$ = $^2J_{A'X'}$ = 25 Hz; upfield multiplet: $^2J_{XX'}$ = $^2J_{AX}$ = $^2J_{A'X'}$ = 25 Hz). This, in turn, is commensurate with a $P_4O_{12}^{-4}$ ligand which is coordinated in a bidentate fashion *via* two vicinal $PO_3^-$ moieties (1,5-chelate).[23] The remaining coordination site on Co(III) is most likely occupied by a water molecule.[24]

Interestingly, **4** could be generated as the predominant species by treating **3** with LiOH (3 equiv.) at 0 °C, and then neutralizing the cold solution within a few minutes using $HNO_3$ (Scheme 2). The complex was then purified by ion-exchange chromatography and isolated in 42% yield. When **4**



**Scheme 2** Equilibrium between complexes **3** and **4** in water. A preparative pathway for converting **3** to **4** is also shown.

was dissolved in water it slowly reverted to **3**, reaching a constant molar ratio **3** : **4** ≈ 10 : 1 within a few days at room temperature. The same ratio was obtained when a pure sample of **3** was dissolved in water, clearly demonstrating the existence of equilibrium between **3** and **4** (Scheme 2), wherein **3** is thermodynamically preferred. This establishes $P_4O_{12}{}^{-4}$ as a hemilabile ligand that alternates between tri- and bidentate binding modes. Such hemilability is highly desirable for catalytic systems, in which reversible coordinative unsaturation of the metal center is crucial.[25]

In conclusion, we have shown that precursor **1** reacts with $Na_4P_4O_{12}$ in water to afford the first reported complexes of Co(III) with $P_4O_{12}{}^{-4}$. In contrast, complexes of $P_3O_9{}^{-3}$ could not be obtained due to facile hydrolysis of the cyclo-triphosphate ring. These results highlight the inadequacy of $P_3O_9{}^{-3}$ as a ligand for Co(III) in aqueous media, while demonstrating the potential of using $P_4O_{12}{}^{-4}$ under these conditions, which are relevant to water oxidation chemistry.

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