DALTON
FULL PAPER

Reactivity of free and Co^{III}-co-ordinated phosphite; mechanisms of bromine oxidation and H/D exchange†

Sonya J. Carrington, David A. Buckingham, Jim Simpson, Allan G. Blackman* and Charles R. Clark*

The Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand.
E-mail: charles.clark@stonebow.otago.ac.nz

Received 17th August 1999, Accepted 23rd September 1999

The complexes *t*- and *p*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]ClO_4$ (**1**$\cdot ClO_4$ and **2**$\cdot ClO_4$, respectively) and *syn*$(OP(H)(O)_2)$, *anti*(OH_2)-$[Co(cyclen)(OH_2)\{OP(H)(O)_2\}]ClO_4$ (**3**$\cdot ClO_4$, cyclen = 1,4,7,10-tetraazacyclododecane) have been prepared. Single crystal structures have been determined for **1**$\cdot ClO_4\cdot 2H_2O$ and **3**$\cdot ClO_4\cdot 3H_2O$. In weakly acidic aqueous solution **3** equilibrates with its *syn*(OH_2),*anti*$(OP(H)(O)_2)$ isomer and the chelate $[Co(cyclen)\{O_2P(H)O\}]^+$. Kinetic studies of acid catalysed H/D exchange in H_2DPO_3 (**4**-D) and $[Co(NH_3)_5\{OP(D)(OH)O\}]^{2+}$ (**5**-D) in water (55.0 °C, $I = 1.0$ mol dm^{-3}, $NaClO_4$) showed that **4**-D ($k_{ex} = (1.6 \pm 0.2) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}) is four-fold more reactive than **5**-D ($k_{ex} = (4.0 \pm 0.5) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}) and that exchange likely involves $P(OH)_3$ and $[Co(NH_3)_5\{OP(OH)_2\}]^{2+}$ intermediates, respectively. Bromine oxidation of $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ (**5**-H, 25 °C, pH 1.22–4.34, $I = 1.0$ mol dm^{-3}, $NaClO_4$) follows the rate equation $k_{obs} = k^H K_a{}^H$ [**5**-H]$_T/(K_a{}^H + [H^+])(1 + K_{Br_3}[Br^-])$, where $K_a{}^H$ ($(4.2 \pm 0.5) \times 10^{-4}$ mol dm^{-3}) corresponds to the independently measured acid dissociation constant of the **5**-H conjugate acid, K_{Br_3} (17.6 dm^3 mol^{-1}) = $[Br_3{}^-]/[Br_2][Br^-]$, and where k^H (1316 ± 20 dm^3 mol^{-1} s^{-1}) represents the specific rate constant for reaction of Br_2 with **5**-H. For **5**-D as substrate $k^D = 560$ dm^3 mol^{-1} s^{-1} ($k_H/k_D = 2.4$). Similar studies with H_3PO_3 (**4**-H, 25 °C, pH 1.27–2.55, $I = 1.0$ mol dm^{-3}, $NaClO_4$) showed that bromine oxidation follows the rate equation: $k_{obs} = k^H K_{a1}{}^H K_{a2}{}^H$[**4**-H]$_T/([H^+]^2 + K_{a1}{}^H[H^+] + K_{a1}{}^H K_{a2}{}^H)(1 + K_{Br_3}[Br^-])$, with $K_{a1}{}^H$ (0.108 mol dm^{-3}) and $K_{a2}{}^H$ (1.67×10^{-6} mol dm^{-3}) corresponding to the independently measured first and second acid dissociation constants of **4**-H, and with k^H (2.1×10^5 dm^3 mol^{-1} s^{-1}) representing the specific rate constant for reaction of Br_2 with $HPO_3{}^{2-}$. For **4**-D as substrate $k^D = 1.22 \times 10^5$ dm^3 mol^{-1} s^{-1} ($k_H/k_D = 1.7$). NMR studies showed that there is no loss of ^{17}O label to solvent from $H_3P^{17}O_3$, either during H/D exchange or on bromine oxidation. Mechanisms for the reactions are discussed.

Introduction

There are surprisingly few examples of well defined phosphito complexes, and only two are complexes of Co^{III}. Sisley and Jordan,[1] and later Linn and Gould,[2] prepared $[Co(NH_3)_5\{OP(H)(OH)O\}]^{2+}$, and the latter were able to isolate and characterise its $ClO_4{}^-$ salt. Interest in this species, and in the related hypophosphito complex, $[Co(NH_3)_5\{OP(H)_2O\}]^{2+}$, derived principally from their electron transfer properties, and a number of studies examining this aspect of their chemistry have appeared.[1–3] More recently the phosphito dimer $[(NH_3)_5Co\{OP(H)(O)O\}Co(NH_3)_5]^{4+}$ has been synthesized and characterised by X-ray crystallography as both its free base and protonated (on the terminal O atom of the phosphito bridge) forms.[4] On treatment with aqueous bromine the dimer is oxidised cleanly to the corresponding phosphato complex, $[(NH_3)_5Co\{OP(OH)(O)O\}Co(NH_3)_5]^{4+}$. However, there have been only two detailed mechanistic studies on oxidation of free phosphorus oxyacids,[5,6] and in cases where halogens have been used as oxidants the nature of the reactive species has not been definitively established. Here we explore the mechanistic pathways operating for oxidation of free phosphite and see how reactivity is modified by co-ordination to an exchange inert cobalt(III) centre. Part of the present study has involved the preparation and characterisation of various complexes containing phosphite as a monodentate ligand, and crystal structures for two of these are described below. Also reported are data for H/D exchange in free and co-ordinated phosphite. However, primary interest was centred on elaborating the mechanism of bromine oxidation, and the bulk of this account details how this was achieved by using $[Co(NH_3)_5\{OP(H)(O)_2\}]ClO_4$ and H_3PO_3 as substrates.

Results and discussion

Synthesis and structure

The phosphito complexes *t*- and *p*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]^+$ ‡ may readily be obtained by treating aqueous solutions of the corresponding aqua complexes with H_3PO_3 and base at 70–75 °C for 4–5 h, with isolation by ion exchange (IE) chromatography on Sephadex and crystallisation. We were unable to detect (using IE methods) any $p \longrightarrow t$ or $t \longrightarrow p$ isomerisation during the reactions. Thus, anation occurs with retention as is usually the case.[7] A procedure similar to that above has been used to prepare $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$,[4] and was employed in the synthesis of its deuterio congener, $[Co(NH_3)_5\{OP(D)(O)_2\}]^+$. Essentially isotopically pure product (97% D by NMR spectroscopy) was obtained following the reaction of $[Co(ND_3)_5(OD_2)][ClO_4]_3$ with D_3PO_3 in D_2O, and work-up in normal water. The cobalt(III)–phosphito complexes were recovered in good yield as their $ClO_4{}^-$ salts and a crystal structure

---

† *Supplementary data available*: atomic coordinates and displacement parameters. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3809/, otherwise available from BLDSC (No. SUP 57651, 14 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

‡ tren = Tris(2-aminoethyl)amine; the *p* and *t* nomenclature for $[Co(tren)(NH_3)X]^{n+}$ species denotes whether X is positioned *trans* to primary (*p*) or tertiary (*t*) amine sites of the tetraamine ligand.

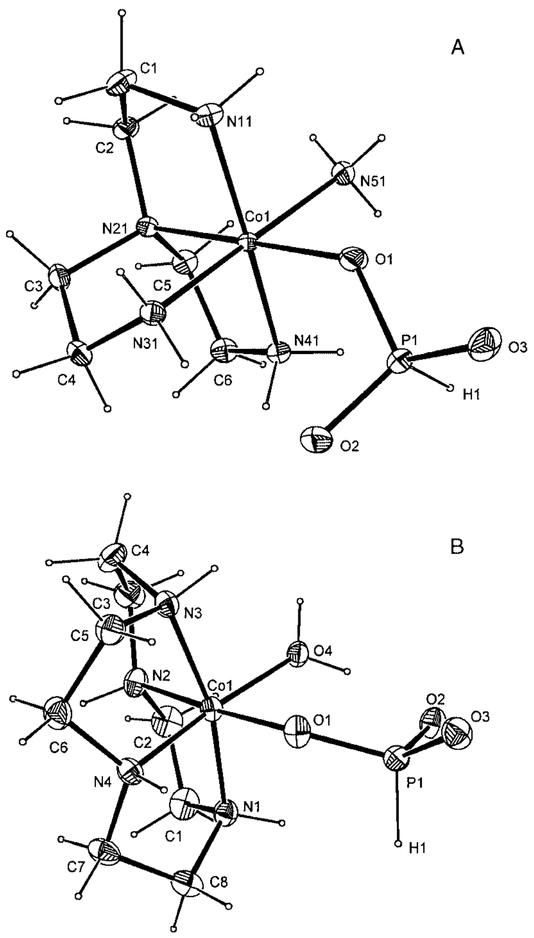


Fig. 1 Molecular structures of the *t*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]^+$ **A** and *syn*$(OP(H)(O)_2)$,*anti*(OH_2)-$[Co(cyclen)(OH_2)\{OP(H)(O)_2\}]^+$ **B** cations. Thermal ellipsoids are drawn at the 50% probability level.

was obtained for *t*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]ClO_4{\cdot}2H_2O$. The structure of the *t*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]^+$ cation is shown in Fig. 1A.

Syn$(OP(H)(O)_2)$,*anti*(OH_2)-$[Co(cyclen)(OH_2)\{OP(H)(O)_2\}]$-$ClO_4{\cdot}3H_2O$ (cyclen = 1,4,7,10-tetraazacyclododecane) was obtained following acid hydrolysis of $[Co(cyclen)(O_2CO)]ClO_4$, treating the resultant diaqua complex with Na_2HPO_3, and crystallisation from aqueous $LiClO_4$. The *syn*$(OP(H)(O)_2)$,*anti*-(OH_2) stereochemistry was established by crystallography (*cf.* Fig. 1B). This isomer appears to crystallise preferentially since ^{31}P NMR monitoring shows that in aqueous solution it equilibrates to give a mixture of species. At pH 5.4 the reaction is rapid ($t_{1/2} \approx 4$ min) and the final spectrum consists of three doublets (δ, J^{PH}/Hz = 13.79, 604; 15.09, 601; 27.23, 626) of intensity ratio *ca.* 2 : 1 : 2. The signal at highest field corresponds to the starting material while that at δ 15.09 is assigned to *anti*-$(OP(H)(O)_2)$,*syn*(OH_2)-$[Co(cyclen)(OH_2)\{OP(H)(O)_2\}]^+$. The signal at lowest field is presumed to arise from the chelate, $[Co(cyclen)\{O_2P(H)O\}]^+$, which is also likely to be present as the *syn*,*anti* isomer. Facile isomer interconversion *via* OH^- catalysed meridional amine proton exchange in $[Co(cyclen)$-$X(Y)]^{n+}$ complexes is now well documented,[8,9] with *syn*,*syn* and *anti*,*anti* isomers appearing to be appreciably less stable than their *syn*(X),*anti*(Y) or *anti*(X),*syn*(Y) counterparts.[9] The isomeric possibilities are shown schematically in Fig. 2. Attempts to prepare phosphito chelates *via* reaction of Na_2-HPO_3 with other $[Co(N_4)(OH_2)(OH)]^{2+}$ species (N_4 = tren or 2en) at neutral pH resulted in the production of complex mixtures which were not investigated further.

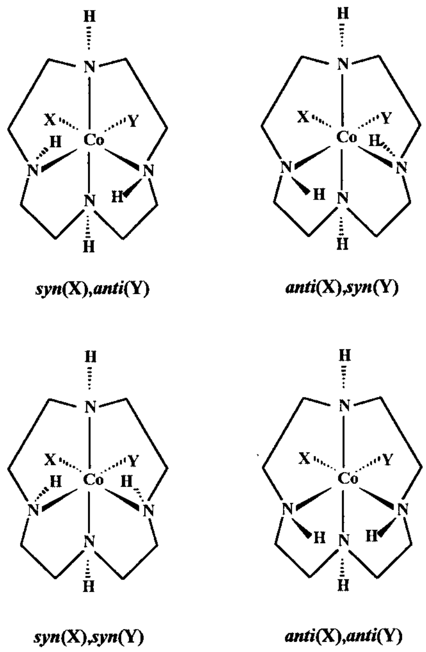


Fig. 2 Isomer possibilities in the $[Co(cyclen)X(Y)]^{n+}$ system.

^{31}P NMR spectroscopy appears to give a good indication of co-ordination mode; the ^{31}P NMR chemical shift of free phosphite is δ 3 ± 1 (*e.g.* H_2O solvent, δ, J^{PH}/Hz = 4.25, 663 (H_3PO_3); 2.59, 630 ($H_2PO_3^-$); 3.05, 611 (HPO_3^{2-})), whereas chemical shifts of *ca.* δ 13 are observed for a complex with one Co–O bond and δ 20 to 22 for $[(NH_3)_5Co\{OP(H)(O/H)O\}$-$Co(NH_3)_5]^{4+/5+}$, species which have two.[4] This supports the assignment of the δ 27.2 signal seen in the Co–cyclen system as arising from the chelate and a similar correlation is now well established for cobalt(III)–phosphate complexes, with each Co–O(P) bond contributing *ca.* 10 ppm to a downfield shift in the ^{31}P resonance.[10] Such shifts also appear to be largely independent of additional protonation (*cf.* free phosphite, see above).

The structure of the *t*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]^+$ cation (Fig. 1A) consists of a central cobalt ion bonded to all four nitrogen atoms of a tren ligand, with approximately octahedral co-ordination completed by a NH_3 ligand and a monodentate $OP(H)(O)_2^-$ group in a *cis* configuration. A perchlorate anion balances the charge, and two waters of crystallisation are also present. The Co–N bond lengths in the cation range from 1.938 to 1.989 Å, with that to the ammonia ligand being the longest. The P–O bond involving the co-ordinated oxygen (1.546 Å) is significantly longer than the terminal P–O bonds (1.516 and 1.506 Å) and the similarity in these latter distances is not consistent with a P=O formulation of either bond. The P–H bond distance (1.336 Å) resembles those found in structurally characterised salts of phosphorous acid, as well as in the free acid itself (*cf.* ref. 4). Extensive hydrogen bonding occurs within the crystal lattice, mediated by the perchlorate counter ions and the waters of crystallisation. The monodentate phosphito ligand is involved in hydrogen bonding with the two waters of crystallisation, with the terminal phosphite oxygen atom, O16, 2.773 Å from O22 and the co-ordinated phosphite oxygen, O15, 2.722 Å from O23. The perchlorate anion is involved in weak hydrogen bonding with both C–H and N–H protons, while the phosphorus-bound hydrogen has no close intermolecular contacts.

The $[Co(cyclen)(H_2O)\{OP(H)(O)_2\}]^+$ cation (Fig. 1B) consists of a central cobalt ion bonded to the four mutually *cis* nitrogen atoms of a cyclen ligand. Monodentate *cis* aqua and $OP(H)(O)_2^-$ ligands complete the co-ordination sphere, while a perchlorate anion balances the charge. Three waters of crystallisation are also present. Deviations from ideal octahedral geometry about the cobalt(III) ion are observed, with the N2–Co1–N4 and N1–Co1–N3 bond angles of 97.90 and 166.45° being the most significant of these. Similar deviations have been reported in other structurally characterised cobalt(III)

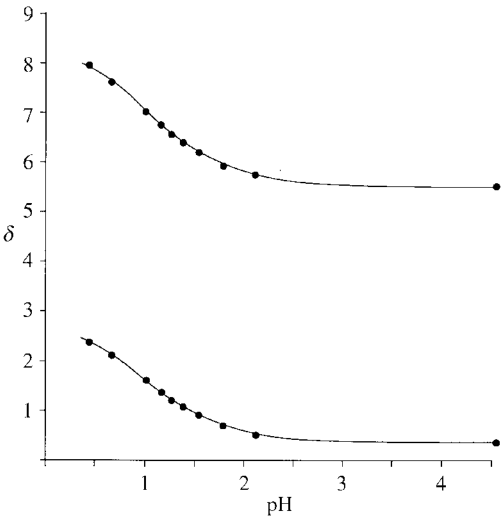


Fig. 3 Plot of ^{31}P chemical shift, δ_{obs}, *versus* pH for H_3PO_3 in water, 25 °C, $I = 1.0$ mol dm^{-3} ($NaClO_4$). The points represent experimental values and the lines are calculated according to eqn. (1) for δ^1_{obs} data, $\delta_{H_2A} = 5.536$, $\delta_{H_3A} = 8.868$, $K_{a1} = 0.106$ mol dm^{-3}; δ^2_{obs} data, $\delta_{H_2A} = 0.377$, $\delta_{H_3A} = 3.034$, $K_{a1} = 0.111$ mol dm^{-3}.

complexes containing cyclen[11–14] and appear to be the result of geometric constraints imposed by the macrocyclic cyclen ligand. The P1–O3 bond length (1.512(2) Å) is slightly shorter than the other P–O distances (1.528(3) Å), but is again not consistent with a formal P=O description. The monodentate $OP(H)(O)_2^-$ ligand is hydrogen bonded to all three waters of crystallisation, with O···O distances being 2.705, 2.838 and 2.842 Å. Of particular note is a short intramolecular contact of 2.593 Å between O2 of the $OP(H)(O)_2^-$ ligand and O4 of the co-ordinated water molecule, which presumably involves hydrogen bonding. This interaction may in part account for the slight lengthening of the P1–O2 bond relative to P1–O3.

Acidity and proton exchange

Potentiometric titration established $pK_a = 3.3 \pm 0.1$ and 3.5 ± 0.1 for *p*- and *t*-$[Co(tren)(NH_3)\{OP(H)(OH)O\}]^{2+}$, respectively (25.0 °C, electrolyte absent). These values appear typical for monodentate cobalt(III)–phosphito complexes; Linn and Gould[2] report $pK_a = 3.06 \pm 0.06$ (23 °C, electrolyte absent) for $[Co(NH_3)_5\{OP(H)(OH)O\}]^{2+}$, while we find $pK_a = 3.38 \pm 0.05$ for this substrate and 3.35 ± 0.06 for $[Co(NH_3)_5\{OP(D)(OH)O\}]^{2+}$ (25 °C, $I = 1.0$ mol dm^{-3} $NaClO_4$). Thus, substituting D for H on phosphorus leads to little change in acidity. Similarly, potentiometric data gave $pK_{a2} = 5.78 \pm 0.03$ for H_3PO_3 and 5.86 ± 0.02 for H_2DPO_3 (25 °C, $I = 1.0$ mol dm^{-3} $NaClO_4$). The value of pK_{a1} for H_3PO_3 in water was determined using ^{31}P chemical shift data (δ^1_{obs}, δ^2_{obs}; *cf.* Fig. 3) for 0.20 mol dm^{-3} solutions in the pH range 0.46–4.5 (25 °C, $I = 1.0$ mol dm^{-3} $NaClO_4$). Least squares fitting of the δ_{obs} data using eqn. (1) gave $K_{a1} = 0.108 \pm 0.009$ mol dm^{-3}, corresponding to $pK_{a1} = 0.97 \pm 0.04$.

$$\delta_{obs} = \frac{\delta_{H_2A}K_{a1} + \delta_{H_3A}[H^+]}{K_{a1} + [H^+]} \qquad (1)$$

Table 1 Rate constants for isotopic H/D exchange in H_2DPO_3[a] and $[Co(NH_3)_5\{OP(D)(O)_2\}]^+$:[b] aqueous solution, 55 °C, $I = 1.0$ mol dm^{-3} ($NaClO_4$)

$[H^+]$/mol dm^{-3}	10^5k_{obs}/s^{-1}
0.150	2.35[a]
0.250	3.15[a]
0.350	4.65[a]
0.500	6.30[a]
0.750	9.90[a]
1.00	14.3[a]
1.00	4.17[b]
0.150	7.06[c]

[c] For D_2HPO_3 in D_2O solution.

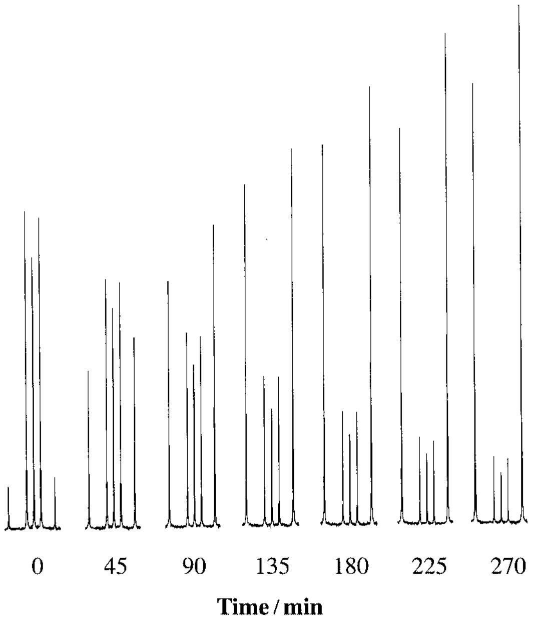


Fig. 4 Variation of the ^{31}P NMR spectrum with time for D_3PO_3 (0.10 mol dm^{-3}) in 0.75 mol dm^{-3} $HClO_4$, 55 °C, $I = 1.0$ mol dm^{-3} ($NaClO_4$). Every third spectrum shown.

The P–H bond in $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ is kinetically robust. No detectable H–D exchange at this site occurs during alkaline hydrolysis in 1.0 mol dm^{-3} NaOD–D_2O at 25 °C (eqn. (2), $t_{1/2} \approx 2$ h), nor was any observed during slow aquation of

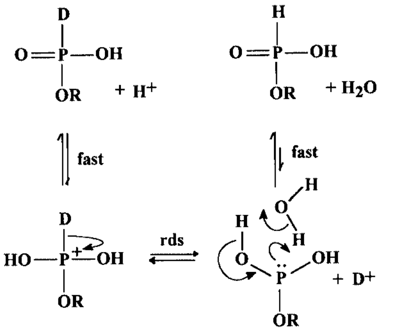
$$[Co(NH_3)_5\{OP(H)(O)_2\}]^+ \xrightarrow{D_2O\text{–}OD^-} [Co(ND_3)_5(OD)]^{2+} + HPO_3^{2-} \qquad (2)$$

the complex in D_2O (<10% reaction after 3 h at 60 °C and pD 1.4). This behaviour contrasts with the relatively facile exchange observed for H_3PO_3 in 0.15 mol dm^{-3} $DClO_4$ at 55 °C ($t_{1/2} = 195$ min) and effectively precluded direct H/D exchange on $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ as a viable route to its deuterio analogue (see above). The H/D exchange in free phosphite was studied for solutions of D_3PO_3 in water as a function of H^+ concentration (55 °C, $I = 1.0$ mol dm^{-3} $NaClO_4$). Reactions were followed using ^{31}P NMR spectroscopy (*cf.* Fig. 4 for reaction in 0.75 mol dm^{-3} $HClO_4$) and essentially identical rate constants (±7%) were obtained irrespective of whether P–D signal decay or P–H signal growth was monitored. Rate constants are given in Table 1. Under the conditions ($[H^+] = 0.15$–1.0 mol dm^{-3}) the substrate is present essentially as H_2DPO_3 and the reaction follows the second-order rate law: rate = $k_{ex}^D[H_2DPO_3][H^+]$ with $k_{ex}^D = (1.6 \pm 0.2) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. An early study by Martin[15] using Raman techniques and concentrated H_3PO_3–D_2O solutions (*ca.* 33–50% w/w, 23 °C) failed to establish the rate law for isotopic exchange. However, Samuel and Silver§ have reported $k_{ex}^H = 1.8 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} for the exchange process observed for phosphorous acid in acidified D_2O solution at 80 °C. Exchange does not involve P–O scission, as might be expected considering the generally robust nature of P–O bonds.[17] This fact was demonstrated by ^{17}O NMR monitoring of a solution of ^{17}O-enriched H_3PO_3 in 0.15 mol dm^{-3} $DClO_4$ at 55 °C ($I = 1.0$ mol dm^{-3} $NaClO_4$) where no appreciable loss of

---

§ D. Samuel and B. L. Silver, unpublished work; quoted by Reuben *et al.*[16]

^{17}O label to solvent (<5%) was detected in a time (690 min) corresponding to $>3t_{1/2}$ for hydrogen-exchange (see above). Acid-catalysed isotopic H/D exchange in $[Co(NH_3)_5\{OP(D)(OH)O\}]^{2+}$, $k_{ex} = 4 \times 10^{-5}$ dm^3 mol^{-1} s^{-1} (Table 1), occurs *ca.* four times less rapidly than in free phosphorous acid. This is presumably related to the poorer electron withdrawing ability of the $Co(NH_3)_5$ group when compared to H^+, resulting in its lesser effectiveness in diminishing P–H bond strength. Also, even though there may be significant contributions from secondary effects, the magnitude of the measured $k_H:k_D$ ratio (3.0 : 1, Table 1) for isotopic exchange in D_2HPO_3 (in D_2O) and H_2DPO_3 (in H_2O) suggests that phosphorus–hydrogen bond breaking is rate determining, Scheme 1. Such a process gives rise to a three-co-ordinate intermediate corresponding to the minor tautomeric form of the phosphito species (*i.e.* $P(OH)_3$ or $Co(NH_3)_5\{OP(OH)_2\}^+$). Rapid proton redistribution within this species, either directly or *via* participation of solvent (as shown), allows the exchange cycle to be completed. The mechanism is analogous to that proposed by Jenkins and Yost[18] to account for acid-catalysed exchange in hypophosphorous acid, H_3PO_2. The non-lability of the phosphito P–H bond under all but strongly acidic conditions emphasises that phosphites are best regarded as phosphorus(V) hydrides rather than as compounds of P^{III}.



Scheme 1

Bromine oxidation

Phosphito species are readily oxidised to the corresponding phosphato species on treatment with aqueous bromine. In the present case this was demonstrated by sequential additions of $Br_2(aq)$ to D_2O solutions of either $[Co(NH_3)_5\{OP(H)(O)_2\}]ClO_4$ or H_3PO_3. Product appearance was monitored using ^{31}P NMR spectroscopy and final spectra were identical to those obtained using authentic $[Co(NH_3)_5(OPO_3)]$ or H_3PO_4, respectively. Treatment of $[(NH_3)_5Co\{OP(H)(O)O\}Co(NH_3)_5]^{4+}$ with $Br_2(aq)$ has similarly been shown to give $[(NH_3)_5Co\{OP(OH)(O)O\}Co(NH_3)_5]^{3+}$.[4] For an acidic solution of $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ (0.05 mol dm^{-3} in 1.0 mol dm^{-3} HBr) in the presence of $Br_2(aq)$ (0.10 mol dm^{-3}) conversion was achieved with $t_{1/2} = 13$ min at 25 °C, Fig. 5, and without the accumulation of a detectable intermediate. Precise kinetic data for oxidation of $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ and H_3PO_3, and their monodeuterio congeners, were obtained spectrophotometrically (UV-vis, 400 nm) under pseudo first-order conditions. In all cases the phosphito reagent was present in at least a 25-fold excess over Br_2, and studies were carried out over extensive pH ranges. Tables 2 and 3 give data for oxidation of $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ at constant $[Br^-]$ (0.10 mol dm^{-3}) and variable pH (1.22–4.34), and at constant pH (3.52 ± 0.02) and variable $[Br^-]$ (0.025–0.200 mol dm^{-3}), respectively (25.0 °C, $I = 1.0$ mol dm^{-3}, $NaClO_4$). Included in Table 2 are more limited data on bromine oxidation of $[Co(NH_3)_5\{OP(D)(O)_2\}]^+$. The observed rate constants (k_{obs}) for reaction of the protio substrate follow eqn. (3), and least-squares fitting

$$k_{obs} = k^H K_a^H[\text{phosphite}]_T/(K_a^H + [H^+])(1 + K_{Br_3}[Br^-]) \quad (3)$$

Table 2 Rate constants for bromine oxidation of $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ and $[Co(NH_3)_5\{OP(D)(O)_2\}]^+$ at 25 °C and $[Br^-] = 0.10$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$)

pH	$[Co]_T$[a]/mol dm^{-3}	$[H^+]$/mol dm^{-3}	k_{obs}/s^{-1}	k_{calc}[b]/s^{-1}
1.22	0.0250	9.00×10^{-2}	0.0534	0.0556
1.34	0.0250	6.82×10^{-2}	0.0746	0.0733
1.49	0.0250	4.82×10^{-2}	0.107	0.104
1.78	0.0250	2.48×10^{-2}	0.209	0.200
2.30	0.0250	7.48×10^{-3}	0.638	0.637
3.39	0.0100	6.08×10^{-4}	2.08	1.96
3.45	0.0150	5.30×10^{-4}	3.47	3.18
3.48	0.0200	4.94×10^{-4}	4.68	4.40
3.50	0.0250	5.22×10^{-4}	5.37	5.63
3.54	0.0050	4.30×10^{-4}	1.46	1.18
3.67	0.0250	3.19×10^{-4}	6.54	6.79
3.84	0.0250	2.16×10^{-4}	7.74	7.90
4.04	0.0250	1.36×10^{-4}	9.17	9.03
4.34	0.0250	6.82×10^{-5}	10.2	10.3
3.46	0.0195[c]	5.18×10^{-4}	1.85	1.85
3.69	0.0156[c]	3.05×10^{-4}	1.79	1.89
4.02	0.0132[c]	1.43×10^{-4}	2.13	2.04

[a] Protio substrate unless otherwise stated. [b] Calculated using eqn. (3) and the values of the constants given in the text. [c] Deuterio substrate.

Table 3 Rate constants for bromine oxidation of $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ at constant pH (3.52 ± 0.02) and variable $[Br^-]$, 25 °C, $I = 1.0$ mol dm^{-3} ($NaClO_4$), $[Co]_T = 0.025$ mol dm^{-3}

pH	$10^4\,[H^+]$/mol dm^{-3}	$[Br^-]$/mol dm^{-3}	k_{obs}/s^{-1}	k_{calc}[a]/s^{-1}
3.54	4.30	0.025	11.2	11.3
	4.30	0.050	8.62	8.65
3.52	4.51	0.075	7.04	6.85
	4.51	0.100	5.77	5.76
3.53	4.40	0.125	5.06	5.03
3.52	4.51	0.150	4.36	4.37
	4.51	0.175	3.86	3.90
3.50	4.72	0.200	3.44	3.44

[a] Calculated using eqn. (3) and the values of the constants given in the text.

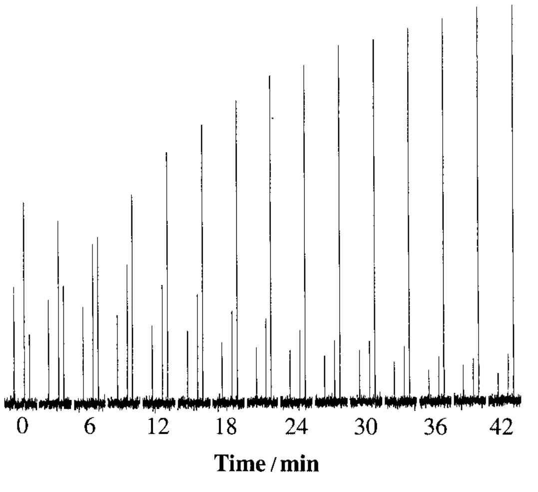


Fig. 5 Variation of the ^{31}P NMR spectrum with time for $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$ (0.05 mol dm^{-3}) in 1.0 mol dm^{-3} HBr following addition of $Br_2(aq)$ (0.10 mol dm^{-3}), 25 °C.

gave excellent agreement between observed and calculated data for $k^H = 1316 \pm 20$ dm^3 mol^{-1} s^{-1} when the known values of K_a^H (= (4.2 ± 0.5) × 10^{-4} mol dm^{-3}, $pK_a^H = 3.38 \pm 0.05$; see above) and K_{Br_3} (= $[Br_3^-]/[Br_2][Br^-] = 17.6$ dm^3 mol^{-1}, 25.0 °C, $I = 1.06$ mol dm^{-3})[18] were inserted as fixed parameters, and where $[\text{phosphite}]_T = [Co(NH_3)_5\{OP(H)(O)_2\}^+] + [Co(NH_3)_5\{OP(H)(OH)O\}^{2+}]$. Data for the corresponding reaction of the deuterio-complex gave $k^D = 560$ dm^3 mol^{-1} s^{-1} with use of the

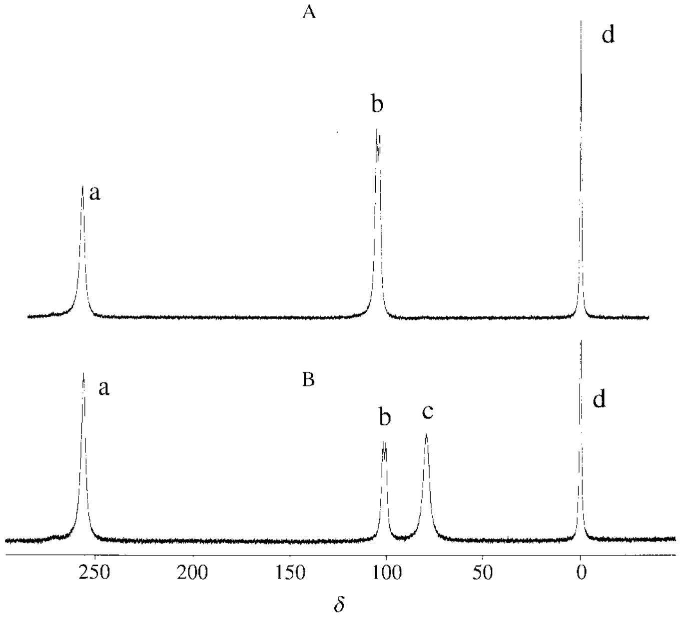


Fig. 6 ^{17}O NMR spectra for $H_3P^{17}O_3$ (0.174 mol dm^{-3}, *ca.* 10 atom% ^{17}O) in 50% v/v D_2O–H_2O before (A) and after (B) reaction with added Br_2 (0.1 mol dm^{-3}). Signals are: a, external ^{17}O labelled CH_3CO_2H as integration reference, δ 256; b, H_3PO_3, δ 102, coupling to the spin $\frac{1}{2}$ ^{31}P nucleus apparent; c, H_3PO_4, δ 79; d, H_2O, δ 0.0. The peak area ratios are: a : b = 1.20 : 1.76 in A, a : b : c = 1.20 : 0.73 : 1.0 in B.

Table 4 Rate constants for bromine oxidation of H_3PO_3 and H_2DPO_3 at 25 °C and $[Br^-] = 0.10$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$)

pH	$[H_3PO_3]_T$ [a]/mol dm^{-3}	$[H^+]$/mol dm^{-3}	k_{obs}/s^{-1}	k_{calc} [b]/s^{-1}
1.27	0.100	8.02×10^{-2}	0.283	0.296
1.42	0.100	5.67×10^{-2}	0.432	0.462
1.56	0.080	4.10×10^{-2}	0.530	0.550
1.62	0.100	3.58×10^{-2}	0.786	0.811
1.63	0.060	3.49×10^{-2}	0.499	0.500
1.74	0.040	2.72×10^{-2}	0.453	0.447
1.94	0.100	1.72×10^{-2}	1.87	1.85
1.96	0.020	1.64×10^{-2}	0.406	0.394
2.17	0.010	1.01×10^{-2}	0.365	0.330
2.24	0.050	8.58×10^{-3}	1.89	1.96
2.35	0.050	6.67×10^{-3}	2.57	2.55
2.55	0.050	4.21×10^{-3}	4.15	4.11
1.39	0.0515 [c]	6.07×10^{-2}	0.104	0.105
1.45	0.0515 [c]	5.30×10^{-2}	0.118	0.124
1.57	0.0515 [c]	4.02×10^{-2}	0.166	0.174
1.65	0.0515 [c]	3.34×10^{-2}	0.208	0.217
1.86	0.0515 [c]	2.06×10^{-2}	0.360	0.376
2.25	0.0515 [c]	8.39×10^{-3}	0.947	0.990
2.45	0.0515 [c]	5.30×10^{-2}	1.64	1.60

[a] Protio substrate unless otherwise stated. [b] Calculated using eqn. (4) and the values of the constants given in the text. [c] Deuterio substrate.

measured value of $K_a^D = 4.5 \times 10^{-4}$ mol dm^{-3} ($pK_a^D = 3.35$; see above). Thus $k_H/k_D = 2.4$, a value clearly indicating that the oxidation reaction involves rate determining P–H bond breaking. The observed rate law is consistent with Br_2, rather than HOBr or Br_3^-, being the active oxidant, and with $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$, rather than its conjugate acid, being the kinetically important form of the cobalt(III) reactant. Our failure to detect a pathway for reaction of $[Co(NH_3)_5\{OP(H)(OH)O\}]^{2+}$ indicates that it must be at least 6×10^3 less reactive than $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$.

Data for the similar oxidation of free phosphite (*cf.* Table 4 for the protio and deuterio substrates) follow eqn. (4), with

$$k_{obs} = k^H K_{a1}^H K_{a2}^H [\text{phosphite}]_T / \\ ([H^+]^2 + K_{a1}^H[H^+] + K_{a1}^H K_{a2}^H)(1 + K_{Br_3}[Br^-]) \quad (4)$$

$[\text{phosphite}]_T = [H_3PO_3] + [H_2PO_3^-] + [HPO_3^{2-}]$ and where K_{a1}^H and K_{a2}^H refer to the first and second acid dissociation constants of phosphorous acid, eqn. (5). For the protio substrate an excellent fit between observed and calculated data is

$$H_3PO_3 \overset{K_{a1}^H}{\rightleftharpoons} H^+ + H_2PO_3^- \overset{K_{a2}^H}{\rightleftharpoons} H^+ + HPO_3^{2-} \quad (5)$$

found for $k^H = 2.12 \times 10^5$ dm^3 mol^{-1} s^{-1} using the measured values for K_{a1}^H and K_{a2}^H (0.108, 1.67×10^{-6} mol dm^{-3} respectively; $pK_{a1}^H = 0.97$, $pK_{a2}^H = 5.78$, $I = 1.0$ mol dm^{-3}, $NaClO_4$). Such agreement implies that only the most basic form of the substrate (*i.e.* HPO_3^{2-}) reacts with Br_2 which is in line with observations for co-ordinated phosphite (see above). However, since the dianion comprises only *ca.* 0.001–0.01% of $[\text{phosphite}]_T$ in the pH range 1.27–2.55 it must be extraordinarily reactive compared to both $H_2PO_3^-$ and H_3PO_3. In the event that either of these were reactants (*via* k_1^H, k_2^H, respectively) k_{obs} would vary according to eqns. (6) and (7), respectively. The

$$k_{obs} = k_1^H K_{a1}^H [\text{phosphite}]_T / ([H^+] + K_{a1}^H)(1 + K_{Br_3}[Br^-]) \quad (6)$$

$$k_{obs} = k_2^H [H^+][\text{phosphite}]_T / ([H^+] + K_{a1}^H)(1 + K_{Br_3}[Br^-]) \quad (7)$$

$[H^+]$ dependence of the reaction rate therefore clearly distinguishes HPO_3^{2-} as the reactive entity.¶ Data for oxidation of the deuterio-substrate in water, Table 4, also give a satisfactory fit using eqn. (4) for $k^D = 1.22 \times 10^5$ dm^3 mol^{-1} s^{-1} and $K_{a1}^D = 0.16$ mol dm^{-3} when the measured value of K_{a2}^D ($(1.38 \pm 0.06) \times 10^{-6}$ mol dm^{-3}, 25.0 °C, $I = 1.0$ mol dm^{-3}) is inserted as a fixed parameter. Thus, for oxidation of HPO_3^{2-} the primary kinetic isotope effect is $k_H/k_D = 1.7$, a somewhat lower value than that observed in the $[Co(NH_3)_5\{OP(H/D)(O)_2\}]^+/Br_2$ reaction, but similarly indicative of a significant contribution from P–H bond rupture in the rate determining step. Martin[15] has calculated that an isotope effect (k_H/k_D) of 5.1 corresponds to complete loss of the phosphorus–hydrogen stretch vibration in the transition state.

The reaction occurs without oxygen exchange. Fig. 6 shows ^{17}O NMR spectra obtained for ^{17}O-labelled H_3PO_3 (0.174 mol

---

¶ However, Agarwal *et al.*[20] report that bromine oxidation of phosphorous acid involves only $H_2PO_3^-$ and H_3PO_3 as reactants, but the crucial data describing the dependence of rate on pH are not given in this paper.

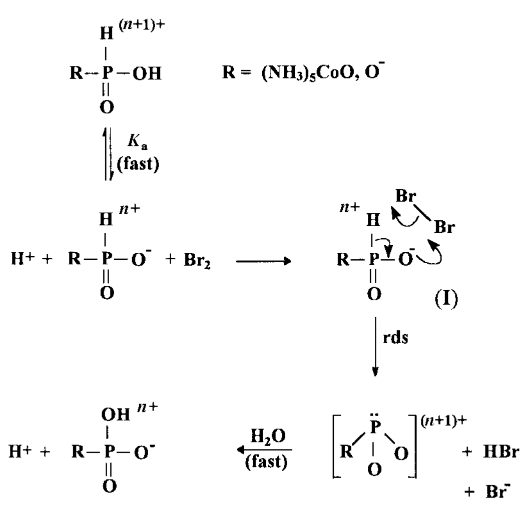
dm^{-3}, 1.0 cm^3, 1.74 × 10^{-4} mol) prior to (A), and following (B), addition of a less than stoichiometric amount of Br_2 (1.0 × 10^{-4} mol). Peak area comparisons, taken relative to external $CH_3C^{17}O_2H$, are consistent with conversion into H_3PO_4 occurring *via* the stoichiometry indicated in eqn. (8), and with no loss

$$H_3P^{17}O_3 + Br_2 + H_2{}^{16}O \longrightarrow H_3P^{17}O_3{}^{16}O + 2HBr \qquad (8)$$

of ^{17}O label during oxidation in normal water. Reactivity differences are large, since Br_2 reacts with $HPO_3{}^{2-}$, $[Co(NH_3)_5\{OP(H)(O)_2\}]^+$, and $[(NH_3)_5\{OP(H)(O)O\}Co(NH_3)_5]^{4+}$[4] at rates spanning five orders of magnitude (second-order rate constants: $k^H = 2.1 \times 10^5$, 1300, 1.0 dm^3 mol^{-1} s^{-1}, respectively, 25.0 °C, $I = 1$ mol dm^{-3}, $NaClO_4$). These are strongly correlated with substrate O-atom basicity, since the pK_a values of the acid conjugates are 5.78, 3.38 and 1.05 respectively.|| The Brønsted relationship (9) holds, and this relationship supports the idea

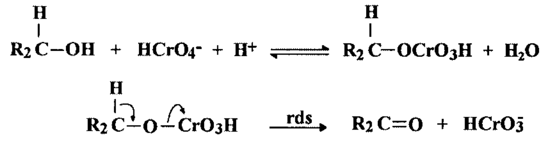
$$\log k = 1.16\, pK_a - 1.1 \qquad (9)$$

that the reactions involve attack by Br_2 at the most basic site available, which in all cases is a phosphite O atom. We prefer the mechanism shown in Scheme 2, with the rate determining step



Scheme 2

in bromine oxidation involving electron redistribution within the 'cyclic' intermediate, **I**. Accordingly, P–H bond cleavage is synchronous with Br_2 attack, and rapid capture of the resulting metaphosphate species by H_2O results in the phosphato product. This mechanism is analogous to that currently accepted[21] for the H^+ catalysed oxidation of primary and secondary alcohols by $HCrO_4{}^-$ originally proposed by Westheimer,[22] Scheme 3. The data are certainly not in accord with reaction *via* phos-



Scheme 3

phito minor tautomeric forms since the rates of H/D exchange at phosphorus are slower than oxidation by several orders of magnitude.** It should be noted that, as is the case for alcohols, the chromium(VI) promoted oxidation of phosphite requires acid catalysis,[6] whereas bromine oxidation does not. Such features may relate to the facilitation of Cr–O bond cleavage in a $(HO)P(H)(O)OCrO_3H$ intermediate, and Cr–O bond rupture in chromium(VI) oxyanions is certainly extremely slow in all but their conjugate acids.[24] In the practical sense this means that while chromium(VI) oxidation of phosphite is relatively sluggish (minutes), even in 1.0 mol dm^{-3} [H^+] solution bromine oxidation is facile (milliseconds) under much less forcing conditions (*i.e.* neutral to weakly acidic solution). A standard undergraduate text states that oxidants react slowly with phosphorous acid,[25] but this is clearly not the case for the reaction with bromine.

Finally, it may be noted that chiral phosphites, $RP(H)(^{17}O)(OR')$, are in prospect (for R = octahedral cobalt(III), diastereomers are also contemplated), and that oxidation of these will allow the stereochemistry of the reaction to be probed. Such experiments are in hand.

Experimental

CAUTION: Although no problems were encountered in the synthesis and handling of the materials described below, those containing perchlorate are potentially explosive and should be handled with great care.

Preparations

$[Co(ND_3)_5(OD_2)][ClO_4]_3$. This complex was prepared from $[Co(NH_3)_5(OH_2)][ClO_4]_3$[26] (5.0 g, 0.108 mol) by carrying out four cycles of dissolution in D_2O (99.9 atom% D, 20 cm^3) at 80 °C for 10 min ($CaCl_2$ guard tube), and evaporation to dryness.

D_3PO_3. To a stirred, cooled solution of freshly distilled PCl_3 (50.9 g, 0.37 mol) in distilled CCl_4 (200 cm^3), and under a nitrogen atmosphere, D_2O (99.9 atom% D, 22.2 g, 1.10 mol) was added dropwise over 1 h while the temperature was maintained at 0 °C (ice-bath). Cooling was discontinued and the two phase reaction mixture stirred for 1.5 h during which time the product crystallised; D_2O (15 cm^3) was then added, the CCl_4 layer discarded and the aqueous phase extracted with further CCl_4 (2 × 50 cm^3). The aqueous solution was evaporated at 50 °C (rotavap) to a viscous residue, which crystallised on vacuum desiccation (1 mmHg) to give the D_3PO_3 product (>99% isotopic purity); ^{31}P NMR (20% D_2O in water): δ 4.85, t, J^{PD} 102 Hz.

$H_3P^{17}O_3$. This was prepared by the dropwise addition of $H_2{}^{17}O$ (0.36 cm^3, 1.67 × 10^{-2} mol, 10 atom% ^{17}O, Yeda) to a stirred, cooled solution of PCl_3 (0.755 g, 5.50 × 10^{-3} mol) in CCl_4 (3 cm^3). The two-phase solution was stirred for 1.5 h, evaporated to dryness (rotavap) and the crystalline product obtained on storage over P_2O_5 in a vacuum desiccator (1 mmHg).

$[Co(NH_3)_5\{OP(D)(O)_2\}]ClO_4{\cdot}H_2O$. The synthesis of this complex was carried out under an atmosphere of dry nitrogen. A solution of D_3PO_3 (7.0 g), $[Co(ND_3)_5(OD_2)][ClO_4]_3$ (2.5 g) and 2,6-dimethylpyridine (4.6 g) in D_2O (10 cm^3, 99.9 atom% D) was heated at 70–75 °C with stirring and guard-tube protection for 5 h. The product was then isolated by the method described for $[Co(NH_3)_5\{OP(H)(O)_2\}]ClO_4{\cdot}H_2O$;[4] yield 1.20 g (67%, isotopic purity 95% according to ^{31}P NMR). A preparation carried out using the above conditions but with 2,6-dimethylpyridine absent gave a lower yield (0.75 g, 42%), but somewhat higher isotopic purity (97 atom% D).

***p*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]ClO_4$ and *t*-$[Co(tren)(NH_3)\{OP(H)(O)_2\}]ClO_4{\cdot}2H_2O$.** A solution containing either *p*-$[Co(tren)(NH_3)(OH_2)][ClO_4]_2NO_3$ or *t*-$[Co(tren)(NH_3)(OH_2)][ClO_4]_3$[27] (1.0 g, 2 × 10^{-3} mol) in water (10 cm^3) with H_3PO_3 (2.0 g, 2.4 × 10^{-2} mol) and NaOH (1.0 g, 2.5 × 10^{-2} mol) was

---

|| The latter pK_a refers to the acidity of the (formally) phosphoryl-O protonated species; see ref. 4.

** Silver and Luz,[23] interpret the slow (hours) depletion of iodine from acidic solutions of phosphorous acid as oxidation by I_2 *via* the $P(OH)_3$ tautomer.

heated at 75 °C for 4 h. Water (50 cm^3) was added and the filtered solution loaded onto Dowex 50W × 2 (pyridinium form). The product was recovered on elution of the column with pyridinium acetate (0.2 to 1.0 mol dm^{-3}) and rotary evaporation of the 1+ fraction. It was isolated as the ClO_4^- salt by treating an aqueous solution (3 cm^3) with $LiClO_4$ (1.0 g), then EtOH (30 cm^3) and ice cooling. Found for the *p* isomer: C, 18.20; H, 5.54; Cl, 8.73; N, 17.20; P, 7.77. $C_6H_{22}ClCoN_5O_7P$ requires C, 17.94; H, 5.52; Cl, 8.83; N, 17.44; P, 7.71%. ^{31}P NMR (D_2O): δ 11.98, d, J^{PH} 599 Hz. UV-vis: λ_{max}/nm (1.0 mol dm^{-3} $HClO_4$) 498 (ε/dm^3 mol^{-1} cm^{-1} 106) and 356 (90). Found for the *t* isomer: C, 16.30; H, 5.97; Cl, 7.86; N, 15.81; P, 6.86. $C_6H_{22}ClCoN_5O_7P{\cdot}2H_2O$ requires C, 16.46; H, 5.99; Cl, 8.10; N, 16.00; P, 7.07%. ^{31}P NMR (D_2O): δ 13.40, d, J^{PH} 592 Hz. UV-vis: λ_{max}/nm (1.0 mol dm^{-3} $HClO_4$) 517 (ε/dm^3 mol^{-1} cm^{-1} 157) and 357 (117). Crystals suitable for structural determination were obtained on layering an aqueous solution with EtOH.

***syn*(OP(H)(O)$_2$),*anti*(OH$_2$)-[Co(cyclen)(OH$_2$){OP(H)(O)$_2$}]-ClO$_4$·3H$_2$O.** To a warm (50 °C) solution of [Co(cyclen)(O_2-CO)]$ClO_4{\cdot}H_2O$[28] (0.408 g, 1.0 × 10^{-3} mol) in water (5 cm^3) was added $HClO_4$ (1.0 mol dm^{-3}, 2.5 cm^3, 2.5 × 10^{-3} mol). Once CO_2 evolution was complete $Na_2HPO_3{\cdot}5H_2O$ (0.27 g, 1.25 × 10^{-3} mol) was added and after 10 min the solution was filtered. Lithium perchlorate (1.0 g) then EtOH (10 cm^3) were added and the solution was allowed to stand for 24 h at 4 °C. The purple crystals which deposited were of crystallographic quality; these were filtered off, washed with EtOH and air dried. Found: C, 20.11; H, 6.12; N, 11.46; P, 6.33. $C_8H_{23}ClCoN_4O_8P{\cdot}3H_2O$ requires C, 19.91; H, 6.06; N, 11.61; P, 6.42%. ^{31}P NMR in weakly acidified D_2O: δ 14.11, d, J^{PH} 604 Hz.

Physical measurements

The pK_a values for *p*- and *t*-[Co(tren)(NH_3){OP(H)(OH)O}]$^{2+}$, [Co(NH_3)$_5${OP(H)(OH)O}]$^{2+}$, [Co(NH_3)$_5${OP(D)(OH)O}]$^{2+}$, $H_2PO_3^-$ and $HDPO_3^-$ were determined by potentiometric titration using standard methods.[29] The first acid dissociation constant of H_3PO_3 (pK_{a1}^H) was obtained by ^{31}P NMR titration. Values are reported as concentration constants; $K_a = [A^-][H^+]/[HA]$, with $[H^+] = a_{H+}/\gamma_\pm$, and $a_{H+} = 10^{-pH}$ for $\gamma_\pm = 0.67$ ($I = 1.0$ mol dm^{-3}, $NaClO_4$).[30] Bromine oxidation kinetics were followed using a Durrum D110 stopped-flow spectrometer coupled to a North Star Horizon computer running Olis software.[31] Rate data (25.0 °C, $I = 1.0$ mol dm^{-3}, $NaClO_4$) were collected using pseudo first-order conditions, with Br_2 as the limiting reagent for both variable (0.025–0.200 mol dm^{-3}) and constant $[Br^-]_T$ (0.10 mol dm^{-3}). Solutions were unbuffered. Reactions were followed over at least four half-lives by monitoring the decay of the Br_3^- absorption at 400 nm and first-order rate constants obtained from least squares fits of the resulting absorbance–time data. Errors in the first-order constants are estimated to be ±3% (oxidation reactions) or ±10% (H/D exchange processes). pH Determinations were carried out on completion of the reactions. There was no detectable difference in pH (±0.02) between the reaction mixtures and 'blanks' of identical composition, but without added Br_2. The ^{31}P NMR spectra were recorded using a Varian VXR-300 spectrometer operating at 121.4 MHz. Chemical shifts are given relative to external H_3PO_4 in water (δ 0.00). The ^{17}O NMR spectra were recorded either using the VXR-300 spectrometer equipped with a 10 mm probe and operating at 40.662 MHz, or a Varian Inova-500 2-channel spectrometer equipped with a 5 mm probe and operating at 67.751 MHz. Chemical shifts are given relative to water (δ 0.00) and peak areas were determined relative to external ^{17}O-labelled CH_3CO_2H (δ 256.3). The UV-vis spectra were recorded using a Cary 219 spectrometer. pH Measurements were made using a Radiometer 82 pH meter equipped with K4040 (calomel) and G2040B (glass) electrodes. The system was standardised with use of 0.025 mol dm^{-3} Na_2HPO_4–0.025 mol dm^{-3} KH_2PO_4, 0.0100 mol dm^{-3} potassium hydrogenphthalate and 0.050 mol dm^{-3} $KHC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O$ buffers.

Table 5 Crystal data and structure refinement for *t*-[Co(tren)(NH_3)-{OP(H)(O)$_2$}]$ClO_4{\cdot}2H_2O$ and *syn*(OP(H)(O)$_2$),*anti*(OH$_2$)-[Co(cyclen)-(OH$_2$){OP(H)(O)$_2$}]$ClO_4{\cdot}3H_2O$

Chemical formula	$C_6H_{26}ClCoN_5O_9P$	$C_8H_{29}ClCoN_4O_{11}P$
Formula weight	437.67	482.70
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
μ(Mo-Kα)/mm^{-1}	1.422	1.244
T/K	168(2)	158(2)
a/Å	7.7245(8)	7.715(3)
b/Å	7.9011(7)	9.047(3)
c/Å	13.5297(7)	13.478(3)
α/°	77.282(5)	78.51(2)
β/°	84.402(7)	83.63(2)
γ/°	77.001(12)	81.03(3)
V/Å^3	783.84(11)	907.5(5)
Z	2	2
Reflections measured	3978	3963
Unique reflections	3738 [*R*(int) = 0.0180]	3180 [*R*(int) = 0.0283]
Final *R*1, *wR*2		
[$I > 2\sigma(I)$]	0.0275, 0.0675	0.0385, 0.0888
(all data)	0.0326, 0.0699	0.0528, 0.0925

Crystal structures

Diffraction data for *t*-[Co(tren)(NH_3){OP(H)(O)$_2$}]ClO_4 and [Co(cyclen)(OH_2){OP(H)(O)$_2$}]ClO_4 were collected on a Siemens P4 diffractometer, processed, and empirical absorption corrections applied using programs from the SHELXTL package.[32] The structures were solved by direct methods using the TREF option in SHELXS 97,[33] with the resulting Fourier map revealing the location of all non-hydrogen atoms. Weighted full matrix refinement on F^2 was carried out using SHELXL 97[34] with all non-hydrogen atoms being refined anisotropically.

***t*-[Co(tren)(NH$_3$){OP(H)(O)$_2$}]ClO$_4$·2H$_2$O.** All hydrogen atoms except H1 were included in calculated positions and refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters; H1 was located and refined to a distance of 1.336 Å from P1. The goodness of fit was 1.094 and maximum $\Delta/\sigma = 0.001$. A final Fourier-difference map showed the highest peak to be 0.480 e Å^{-3}.

[Co(cyclen)(OH$_2$){OP(H)(O)$_2$}]ClO$_4$·3H$_2$O. All hydrogen atoms were included in calculated positions, except for H1 which was fixed at a distance of 1.300 Å from P1, and refined as described above. The goodness of fit was 0.965 and maximum $\Delta/\sigma = 0.000$. The highest peak in the final Fourier-difference map was 0.410 e Å^{-3}.

Selected crystal and refinement data for both structures are given in Table 5.

CCDC reference number 186/1661.

References

1 M. J. Sisley and R. B. Jordan, *Inorg. Chem.*, 1987, **26**, 273.

2 D. E. Linn and E. S. Gould, *Inorg. Chem.*, 1987, **26**, 3442.

3 D. E. Linn and E. S. Gould, *Inorg. Chem.*, 1988, **27**, 3140.

4 C. R. Clark, D. A. Buckingham, A. G. Blackman and G. B. Jameson, *Inorg. Chim. Acta*, in the press.

5 A. Moondra, A. Mathur and K. K. Banerji, *Int. J. Chem. Kinet.*, 1991, **23**, 669.

6 G. P. Haight, Jr., M. Rose and J. Preer, *J. Am. Chem. Soc.*, 1968, **90**, 4809.

7 M. J. Gaudin, C. R. Clark and D. A. Buckingham, *Inorg. Chem.*, 1986, **25**, 2569.

8 D. A. Buckingham, C. R. Clark, A. J. Rogers and J. Simpson, *Inorg. Chem.*, 1998, **37**, 3497.

9 D. A. Buckingham, C. R. Clark and A. J. Rogers, *J. Am. Chem. Soc.*, 1997, **119**, 4050.

10 G. P. Haight, *Coord. Chem. Rev.*, 1987, **79**, 293.

11 D. A. Buckingham, C. R. Clark and A. J. Rogers, *Aust. J. Chem.*, 1998, **51**, 461.

12 J. H. Kim, J. Britten and J. Chin, *J. Am. Chem. Soc.*, 1993, **115**, 3618.

13 Y. Iitaka, M. Shina and E. Kimura, *Inorg. Chem.*, 1974, **13**, 2886.

14 J. H. Loehlin and E. B. Fleischer, *Acta Crystallogr., Sect. B*, 1976, **32**, 3063,

15 R. B. Martin, *J. Am. Chem. Soc.*, 1958, **81**, 1574.

16 J. Reuben, D. Samuel and B. L. Silver, *J. Am. Chem. Soc.*, 1963, **85**, 3093.

17 D. E. C. Corbridge, *Phosphorus. An Outline of its Chemistry, Biochemistry and Uses*, 5th edn., Elsevier, Amsterdam, 1995, p. 51.

18 W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, 1959, **11**, 297.

19 A. G. Blackman, D. A. Buckingham and C. R. Clark, *Aust. J. Chem.*, 1991, **44**, 981.

20 S. Agarwal, A. Mathur and K. K. Banerji, *J. Indian Chem. Soc.*, 1992, **69**, 433.

21 J. March, *Advanced Organic Chemistry*, 4th edn., Wiley, New York, 1992, p. 1170.

22 F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419; F. Holloway, M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, 1951, **73**, 65.

23 B. Silver and Z. Luz, *J. Phys. Chem.*, 1962, **66**, 1356.

24 N. E. Brasch, D. A. Buckingham, A. B. Evans and C. R. Clark, *J. Am. Chem. Soc.*, 1996, **118**, 7969.

25 F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, 6th edn., Wiley, New York, 1999, p. 412.

26 E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, 1964, **86**, 1318.

27 D. A. Buckingham, C. R. Clark and W. S. Webley, *Aust. J. Chem.*, 1980, **33**, 263.

28 C. R. Clark and D. A. Buckingham, *Inorg. Chim Acta.*, 1997, **254**, 339.

29 A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases*, Methuen, London, 1963, p. 151.

30 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd edn., Butterworths, London, 1959, p. 492.

31 OLIS, On-line Instrument Systems, Inc., Bogart, GA, 1985.

32 G. M. Sheldrick, SHELXTL PLUS, Structure determination software programs, Siemens Analytical X-Ray Instruments Inc, Madison, WI, 1990.

33 G. M. Sheldrick, SHELXS 97, Program for the solution of crystal structures, University of Göttingen, 1997.

34 G. M. Sheldrick, SHELXL 97, Program for the refinement of crystal structures, University of Göttingen, 1997.

Paper 9/06670E