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Zeolitic dehydration–rehydration of adipate-intercalated octacalcium phosphate

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Octacalcium phosphate (OCP); $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$) and adipate-intercalated OCP were investigated with respect to their dehydration-rehydration and related properties. The intercalation of adipate ions brought about increases in amount of zeolitic H_2O and in limiting the dehydration temperature for retaining the zeolitic character. Infrared spectroscopic and differential scanning calorimetric data also supported the zeolitic character. The basal spacing (d_{100}) of the OCP layer structure intercalated with and without adipate ions was contracted by dehydration and recovered by rehydration, and the variation in the d_{100} values was increased remarkably by the intercalation. The thermal stability of the layer structure was improved from 200 to 250° C to 400 to 450° C by the intercalation. Above these temperatures hydroxyapatite formed. The intermediately formed apatite could contain CO_3^{2-} and possibly $P_2O_7^{4-}$.

1. Introduction

Octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, Ca/P molar ratio 1.33; hereafter referred to as OCP), is not only of biological interest as a precursor in the formation of hydroxyapatite (HAp; stoichiometrically $Ca_{10}(PO_4)_6(OH)_2$, Ca/P = 1.67) *in vivo*, but also of material interest as well as HAp having already-wide biorestorative and industrial applications. The structure of OCP is built up of the alternative stacking of layers called the "apatitic layer" (A-layer) and the "hydrated layer" (B-layer) [1]. OCP contains two kinds of HPO_4^{2-} groups in the B-layer, i.e. one links to the A-layer and the other could be regarded as pillars [Ca–HPO_4–Ca] supporting the A-layers. Recently the pillar HPO_4^{2-} groups were found to be replaceable by various dicarboxylate ions ($^-OOCRCOO^-$, R = organic groups) [2, 3]. Fig. 1 shows a structural model for the intercalates [3]. According to this model the formula of the intercalates was ideally given by

$$Ca_8(HPO_4)(RC_2O_4)(PO_4)_4 \cdot mH_2O \qquad Ca/P = 1.60$$

However, prepared samples by the hydrolysis of $Ca_3(PO_4)_2$ apparently had the composition [3]

$$Ca_8(HPO_4)_{2-z}(RC_2O_4)_z(PO_4)_4 \cdot mH_2O \qquad z \leqslant 1$$

possibly due to predominant growth of the A-layer, or to insufficient hydrolysis of $Ca_3(PO_4)_2$. It was interesting to study what kind of change was brought about on OCP by such a replacement.

This work was done to investigate the influences of the intercalation of adipate ions (R; CH_2–CH_2–CH_2–CH_2) on the dehydration–rehydration and related behaviour of OCP.

2. Experimental procedure

Stoichiometric OCP and adipate-intercalated OCP (hereafter referred to as Adipate-OCP) were prepared by the hydrolysis of thermally synthesized $Ca_3(PO_4)_2$ in the absence and presence of adipate ions (R; CH_2–CH_2–CH_2CH_2), respectively [3]. The compositions of the samples so prepared were determined as

$$\text{OCP} \qquad Ca_8(HPO_4)_2(PO_4) \cdot 4.9H_2O$$

$$Ca/P = 1.34 \qquad d_{100} = 1.87\,\text{nm}$$

$$\text{Adipate-OCP}$$

$$Ca_8(HPO_4)_{1.07}(C_4H_8C_2O_4)_{0.93}(PO_4)_4 \cdot {\sim}6H_2O$$

$$Ca/P = 1.58 \qquad d_{100} = 2.36\,\text{nm}$$

by chemical analyses for calcium and phosphorus, isotachophoresis for adipate ions, thermogravimetry (TG) for H_2O, X-ray diffraction (XRD) and infrared (IR) spectroscopy. The d_{100} denotes the basal spacing of the OCP structure. Dehydrated samples were prepared by heating as-prepared samples to the desired temperatures at a heating rate (ϕ) of 10° C min^{-1}. Rehydrated samples were prepared by exposing dehydrated samples to saturated water vapour at room temperature (24 ± 1° C) and then leaving them in air at room temperature until equilibrium was established (about 40 min). These as-prepared, dehydrated and rehydrated samples were characterized by TG (ϕ = 10° C min^{-1}), differential scanning calorimetry (DSC; ϕ = 5° C min^{-1}), XRD, IR spectroscopy and BET area measurement.

3. Results and discussion

3.1. Zeolitic H_2O

Fig. 2 shows the TG curves for the as-prepared and rehydrated samples. The hatched areas indicate reversible H_2O; that is, zeolitic H_2O. Zeolitic H_2O for OCP was observed below 200° C and lost at almost 250° C. Up to 200° C about three H_2O moles volatilized, and the remaining two moles up to 400° C. On the other hand, for Adipate-OCP it extended remarkably as follows:

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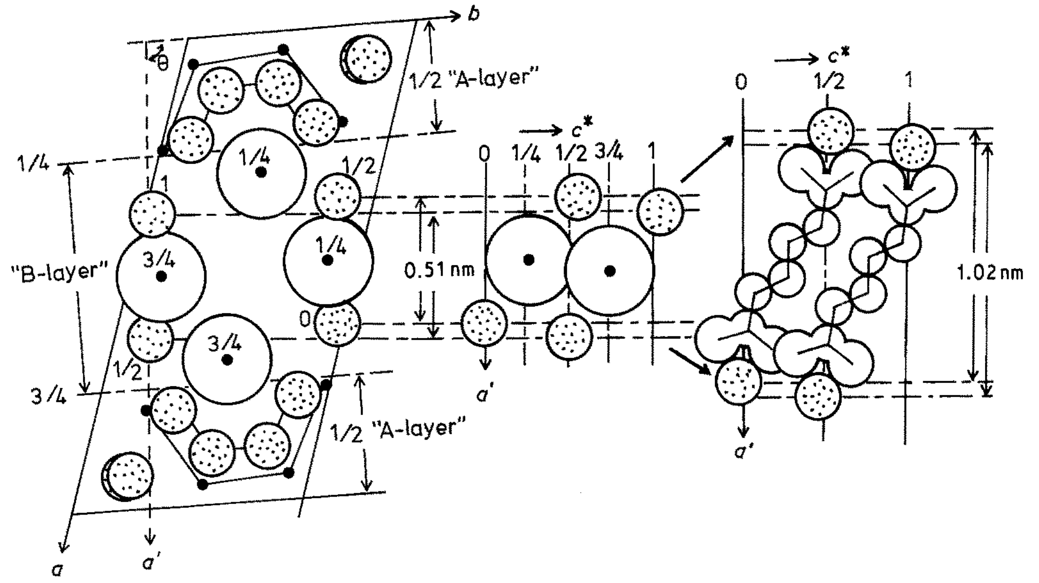

Figure 1 Simplified OCP structure (left), illustrated according to the literature data [1], and the side views of the configurations of HPO_4^{2-} (middle) and intercalated adipate ions (right) [2]. (●) P, (◎) Ca, (◎) HPO_4, c^*, perpendicular to the a–b plane, $\theta = 94°$. Oxygen atoms in the A-layer and H_2O molecules are omitted.

Step I (room temperature to 200° C): 100% zeolitic H_2O
Step II (200 to 420° C): 85 to 95% zeolitic H_2O
Step III (420 to 700° C): rapid loss of zeolitic H_2O

The TG changes in the ranges 420 to 500, 500 to 700 and 700 to 900° C seemed to be common features of the thermal decomposition of organic calcium salts. Subsequent gradual decreases above 900° C were probably due to CO_2 liberation from CO_3^{2-}-containing HAp [4].

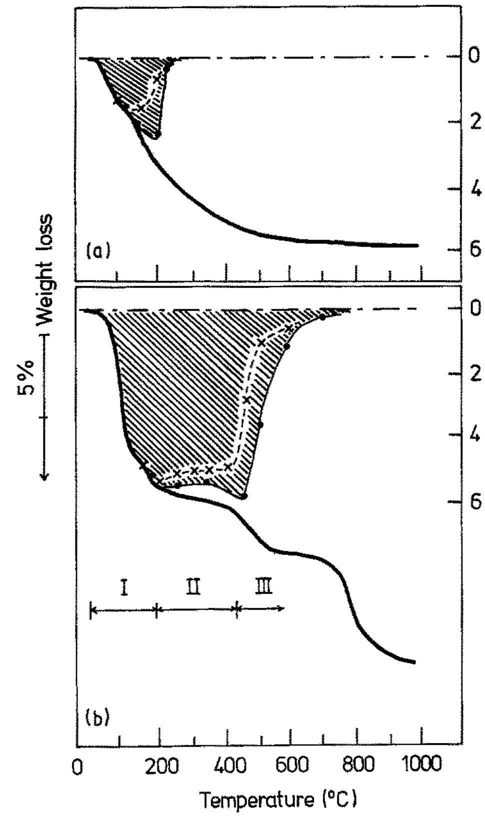

Figure 2 Heating weight loss curves for (a) OCP and (b) Adipate-OCP with a heating rate of 10° C min^{-1}. (——) TG curves for as-prepared samples, (—●—) TG losses for samples exposed to air at room temperature after TG heating once to various temperatures, (— —x— —) TG losses for samples exposed to air at room temperature after heating for 30 min at various temperatures. Hatched regions show parts of zeolitic reversible H_2O.

Consequently, loss of the reversibility of H_2O must be related to collapses of the pillars; that is, thermal decomposition of pillared HPO_4^{2-} in OCP and adipate ions in Adipate-OCP.

3.2. Reversible change in d_{100}

The basal spacings (d_{100}) of OCP and Adipate-OCP were contracted by dehydration, and recovered to the

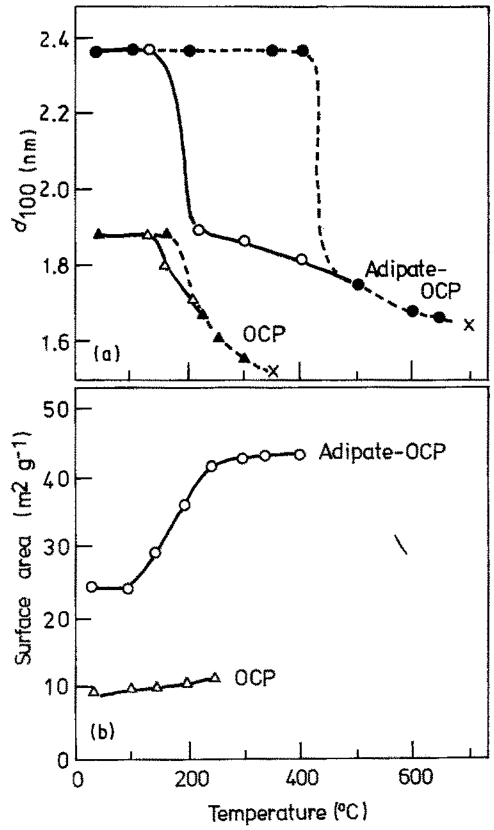

Figure 3 Changes in (a) the basal spacing d_{100} and (b) the specific surface area of OCP and Adipate-OCP with a heating rate of 5° C min^{-1}. (——) Just after heating and (- - -) exposed to air at room temperature after heating.

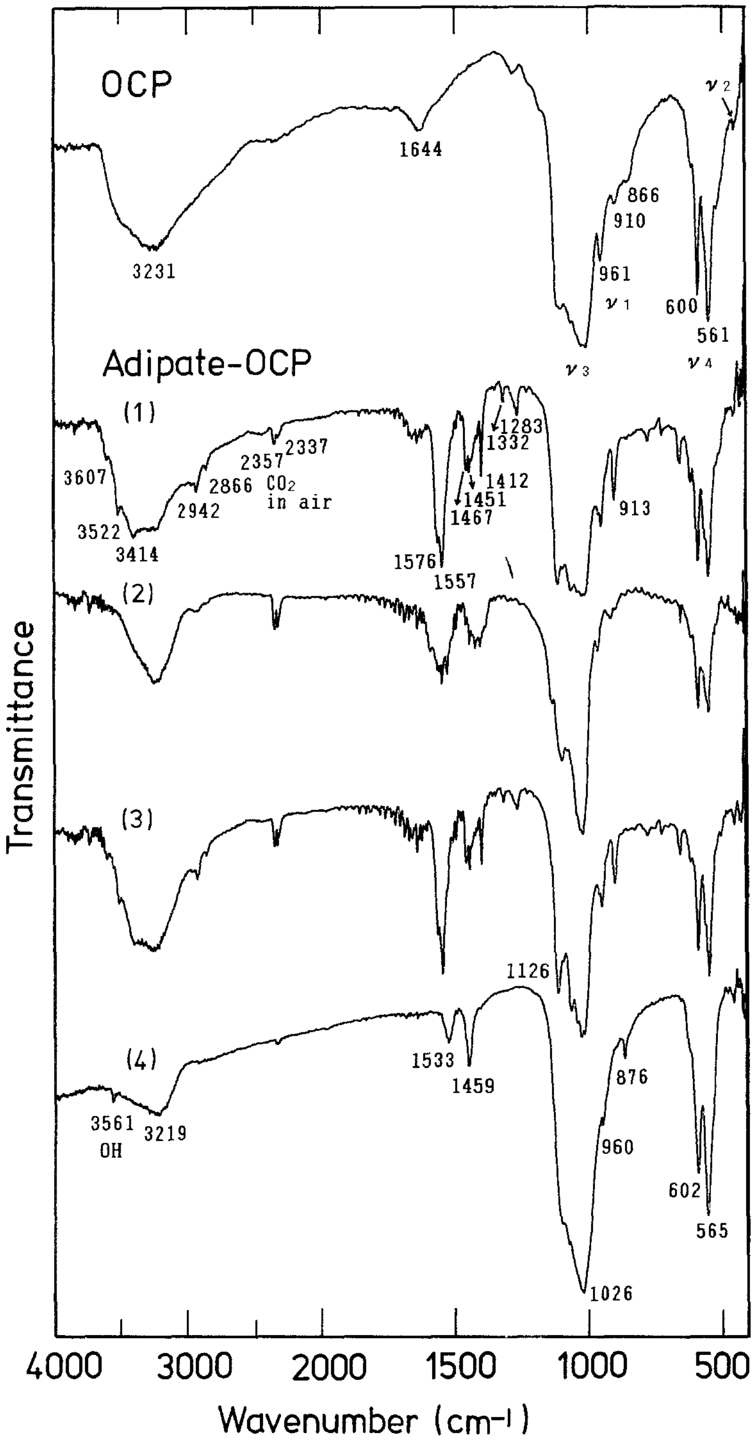

Figure 4 IR spectra at room temperature for OCP and Adipate-OCP. (1) Unheated, (2) just after heating to 400° C, (3) exposed to air at room temperature after heating to 400° C and (4) heated to 900° C.

original spacing by rehydration as shown in Fig. 3a. The recovering temperature ranges were in accord with the ranges for H_2O reversibility (Fig. 2). The difference between the contracted and recovered d_{100}-values was large for Adipate-OCP and small for OCP. Such a large contraction of Adipate-OCP suggested the bending–recovery of the zig-zag chain of intercalated adipate ions. The dehydration was accompanied by increases in the BET specific area as shown in Fig. 3b. So, nitrogen molecules with a molecular cross-section of $0.162\,nm^2$ (77 K) and radius of 0.227 nm adsorbed probably in the inside surface of cavities formed around the pillars between A-layers by the dehydration. Similarly, H_2O molecules with $0.108\,nm^2$ cross-section (25° C) and 0.185 nm radius could enter the cavities, and resulted in the recovery of the d_{100}.

3.3. Phase change by heating

Table I shows thermal changes in phase and ionic species of OCP and Adipate-OCP. OCP changed similarly to the well-known conventional data:

200 to 250° C $\quad HPO_4^{2-} \rightarrow \frac{1}{2}P_2O_7^{4-} + \frac{1}{2}H_2O$

decomposition of OCP and formation of HAp

600 to 700° C $\quad$ decomposition of HAp

$(\rightarrow 2Ca_3(PO_4)_2 + Ca_2P_2O_7)$

No $Ca_2P_2O_7$ phase was recognized as a distinct phase in the temperature range below 600° C. Therefore, the intermediate HAp was speculated to have a formula like $Ca_8\square_2(P_2O_7)_{1.5}(PO_4)_3(OH, \square)_2$ containing $P_2O_7^{4-}$ ions and lattice vacancies. Similar $P_2O_7^{4-}$-containing

HAp had been proposed also to form in the course of heating of non-stoichiometric HAp [5].

On the other hand, Adipate-OCP was thermally much more stable than OCP, i.e. the reaction $HPO_4^{2-} \rightarrow \frac{1}{2}P_2O_7^{4-} + \frac{1}{2}H_2O$ occurred at 400 to 450° C, transformation into HAp at 600 to 700° C, and decomposition of HAp at 700 to 800° C. The intermediate HAp was the so-called A-type carbonated HAp having IR bands around 1540, 1465 and 880 cm^{-1} [6], and it might contain $P_2O_7^{4-}$ as well as the above idea. In addition, considering sample colour changes such as slight brown at 450° C, deep black at 600 to 900° C and white at 1000° C, the following reactions must occur: thermal decomposition of adipate and formation of carbon at 450 to 500° C, $C + O_2$ (in air) $\rightarrow CO_2$ at 700 to 900° C. The temperatures and products for the thermal decomposition of Adipate-OCP were almost the same as those for succinate-intercalated OCP [7]. As the reaction $HPO_4^{2-} \rightarrow P_2O_7$ is known to begin from 200 to 300° C in various HPO_4^{2-}-containing materials (e.g. $CaHPO_4$ 270° C, $ZnHPO_4$ 200 to 230° C, OCP 200° C, HAp (Ca/P < 1.67) 250° C) and to proceed rapidly above about 400° C. Consequently, the structure and HPO_4^{2-} content of Adipate-OCP could be said to be stabilized by the intercalation of adipate ions.

Fig. 4 shows IR spectra of as-prepared, dehydrated and rehydrated samples. A band at 910 cm^{-1} for OCP is reported to be assigned to the in-plane deformation mode of O–H of a strongly hydrogen bonded HPO_4^{2-} ion, and a band at 866 cm^{-1} to the P–O(H) symmetrical streching of HPO_4^{2-} [8]. On the other hand, Adipate-OCP lost the band corresponding to 866 cm^{-1}. Loss of the band 866 cm^{-1} might be related to the fact that OCP contained two kinds of HPO_4^{2-} and the intercalation of adipate ions removed one kind of them, i.e. replaceable HPO_4^{2-} in the B-layer. The intercalation of adipate ions into OCP caused the appearance of characteristic bands of the carboxyl group in the range 1600 to 1250 cm^{-1} and a number of weak peaks or splitting on the whole (Fig. 4(1)). In particular, the bands around 3700 to 2800 and 1600 to 1250 cm^{-1} related to H_2O and carboxyl groups, respectively, were remarkable. Such a complicated spectrum became smooth after the thermal dehydration treatment (Fig. 4(2)); however, it returned to the original spectrum after the rehydration treatment (Fig. 4(3)). The spectrum for Adipate-OCP heated to 900° C showed the formation of A-type carbonated HAp having characteristic bands at 3561 cm^{-1} for OH^- and 1533, 1459 and 876 cm^{-1} for CO_3^{2-} contained in HAp [6].

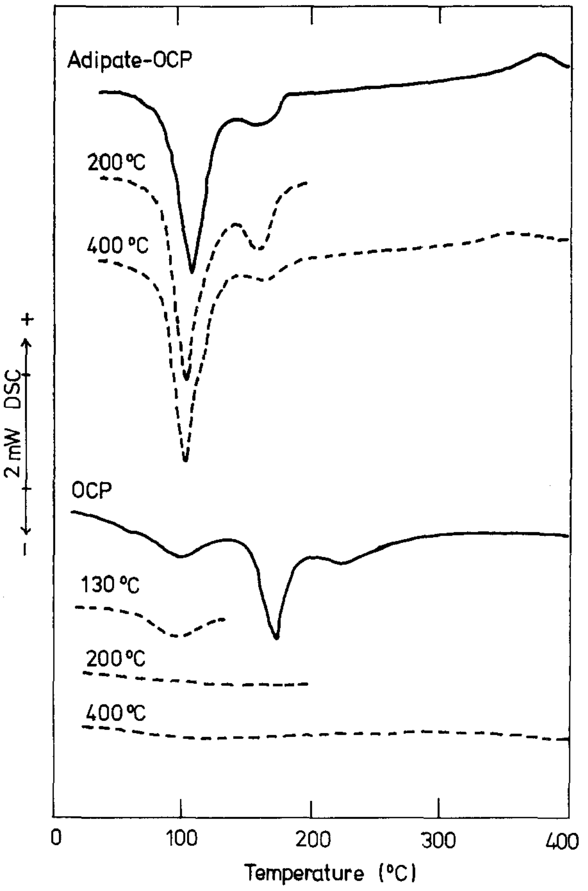

Figure 5 DSC curves for OCP (8.40 mg) and Adipate-OCP (9.45 mg) at a heating rate of 5° C min^{-1}. (——) As-prepared and (– – –) exposed to air at room temperature after DSC heating once or twice to the temperatures written near the curves.

3.4. DSC change

Fig. 5 shows DSC curves for as-prepared and rehydrated samples. As-prepared OCP had three DSC

TABLE I Thermal changes of Adipate-OCP and OCP

Temperature (° C)	Reaction products after heating*			
	Adipate-OCP		OCP	
	XRD	IR	XRD	IR
Room temperature	OCP	COO, HPO_4	OCP	HPO_4
150	OCP	COO, HPO_4	OCP	HPO_4
200	OCP	COO, HPO_4	OCP	OH, HPO_4
250	OCP	COO, HPO_4	OCP	OH, HPO_4, P_2O_7
300	OCP	COO, HPO_4	A	OH, P_2O_7
350	OCP	COO, HPO_4	A	OH, P_2O_7
400	OCP	COO, HPO_4	A	OH, P_2O_7
450	OCP	COO, HPO_4, P_2O_7	A	OH, P_2O_7
500	OCP	OH, CO_3	A	OH, P_2O_7
600	OCP	OH, CO_3	A, T	OH, P_2O_7
700	A	OH, CO_3, P_2O_7	A, T, Py	OH, P_2O_7
800	A, T	OH, CO_3, P_2O_7	T, Py	P_2O_7
900	A, T	OH, CO_3	T, Py	P_2O_7

*A, HAp; T, $Ca_3(PO_4)_2$; Py, $Ca_2P_2O_7$; COO, in adipate; CO_3, in A-type carbonated HAp; OH in HAp.

endothermic bands around 94, 170 and 225° C. When OCP was heated to each end-temperature of each band, the first band with the liberation of 1.0 mol H_2O was reproducible after the rehydration treatment, whereas the second, with loss of 2.0 mol H_2O, and the third were not reproducible. The heats of the dehydration reactions were $22 \pm 2\,\mathrm{kJ\,mol^{-1}}$ (OCP) for the first band and $70 \pm 8\,\mathrm{kJ\,mol^{-1}}$ (OCP) for the second band.

Adipate-OCP had two reproducible endothermic bands around 100 and 140 to 180° C. About 5.5 mol H_2O were liberated up to 180° C. The first band was reproducible by the rehydration treatment even after heating to 400° C. A band at around 350 to 400° C seemed to be exothermic, but further significant information was not obtained. The total heat for the two endothermic dehydration reactions was $235 \pm 10\,\mathrm{kJ\,mol^{-1}}$ (Adipate-OCP), which could convert to $43\,\mathrm{kJ\,mol^{-1}}$ (H_2O). The value was comparable with the heat of vaporization of H_2O ($40.66\,\mathrm{kJ\,mol^{-1}}$ (H_2O)). It was therefore suggested that the interlayer H_2O exited as loosely bound H_2O, and the liberation of the H_2O caused basically little change in the OCP layer structure.

4. Conclusions

The intercalation of adipate ions into OCP brought about an increase in the amount of zeolitic H_2O and a remarkable extension of the limiting dehydration temperature for retaining the zeolitic character. IR spectroscopic and DSC data supported the reversibility of H_2O.

The basal spacing of the OCP layer structure intercalated with and without adipate ions was contracted and recovered by the dehydration and rehydration treatment, and the variation between the contraction and recovery was increased remarkably by the intercalation.

The thermal stability of the layer structure was improved from 200 to 250° C for OCP to 400 to 450° C for Adipate-OCP by the intercalation. Above these temperatures hydroxyapatite formed. The apatite could contain CO_3^{2-} and possibly $P_2O_7^{4-}$.

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