Homochiral column structure of *rac*- and Λ-[$M^{III}(tn)_3$]P_3O_9 (M = Co, Cr; tn = 1,3-diaminopropane; P_3O_9 = cyclotriphosphate(3−)) produced by multiple hydrogen bonds†

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Received (in Montpellier, France) 12th April 2010, Accepted 7th July 2010
DOI: 10.1039/c0nj00270d

The crystal structures of *rac*- and Λ-[$M^{III}(tn)_3$]$P_3O_9 \cdot nH_2O$ (M = Co, Cr; tn = 1,3-diaminopropane = trimethylenediamine; P_3O_9 = cyclotriphosphate(3−)) were determined by single-crystal X-ray analyses. In *rac*-[$Co(tn)_3$]$P_3O_9 \cdot 7.3H_2O$, the [$Co(tn)_3$]$^{3+}$ cations with the same absolute configuration (Δ or Λ) and the $P_3O_9{}^{3-}$ anions are alternately arrayed and connected by multiple NH···O hydrogen bonds to form a homochiral columnar structure. Adjacent homochiral columns with opposite chirality are connected by intercolumn hydrogen bonds to form a racemic pair of columns. The crystal structure of *rac*-[$Cr(tn)_3$]$P_3O_9 \cdot 7.5H_2O$ is similar to that of the Co complex; however, there exist two types of racemic pairs of columns. In the crystal of Λ-[$Co(tn)_3$]$P_3O_9 \cdot 2.5H_2O$, a pair of columns consisting of alternately stacked Λ-[$Co(tn)_3$]$^{3+}$ cations and $P_3O_9{}^{3-}$ anions are linked by hydrogen bonds. Neighboring column pairs are further linked by hydrogen bonds to form a three-dimensional (3-D) sheet structure. The crystal structure of Λ-[$Cr(tn)_3$]$P_3O_9 \cdot 2.5H_2O$ is isomorphous with the Co complex. The circular dichroism (CD) spectra of aqueous solutions of Λ-[$M(tn)_3$]Br_3 (M = Co, Cr) change when $P_3O_9{}^{3-}$ is added, and the changes were explained by ion pair formation through hydrogen bonds.

Introduction

Hydrogen bonding has been the subject of contemporary research interest for nearly a century because of its prevalence and importance in various branches of science.[1] It is operative in determining molecular conformation and molecular aggregation, and in the function of a vast number of chemical systems ranging from inorganic to biological. In crystal structures, the packing of the molecules mainly depends on the symmetry of the lattice and the ensuing intermolecular interactions that drive the molecules to assemble. One of the most decisive steering forces in this context is hydrogen bonding. The utility of hydrogen-bonded motifs in the generation of new materials has been extensively studied. Earlier, we reported the formation of a 2-D homochiral sheet structure created by self-organization of chiral self-complementary cobalt(III) complexes with a tripodal ligand containing three imidazole groups through NH···N hydrogen bonds.[2]

In a previous paper,[3] we reported the crystal structures of *rac*- and Λ-[$Co(en)_3$]$P_3O_9 \cdot 2H_2O$ (en = 1,2-diaminoethane = ethylenediamine; P_3O_9 = cyclotriphosphate(3−)). In the racemic complex, the [$Co(en)_3$]$^{3+}$ cations with either Δ or Λ configuration and $P_3O_9{}^{3-}$ anions were alternately arrayed and connected by multiple hydrogen bonds to form a homochiral columnar structure. Adjacent homochiral columns of different chirality were connected by intercolumn hydrogen bonds through $P_3O_9{}^{3-}$ anions to form a tetrameric cyclic cylindrical structure. In the crystal of the Λ-complex, the adjacent columns of the same chirality (Λ) were connected to form the cyclic cylindrical structure. In both complexes, all six amino groups per [$Co(en)_3$]$^{3+}$ participated in the formation of 12 hydrogen bonds, in which eight hydrogen bonds contributed to the construction of a homochiral column and the remaining four hydrogen bonds contributed to the intercolumn interactions. The CD spectrum of an aqueous solution of Λ-[$Co(en)_3$]$^{3+}$ changed drastically when excess $P_3O_9{}^{3-}$ was added, and this change was explained by ion pair formation through hydrogen bonds.

In this study, the cation–anion assembly between [$M(tn)_3$]$^{3+}$ (M = Co, Cr; tn = 1,3-diaminopropane = trimethylenediamine) and $P_3O_9{}^{3-}$ has been examined. The six-membered tn chelate ring is conformationally labile and can assume several conformations (Scheme 1)[4] and the orientation of N–H group is different in each conformation. Thus, different interactions from those in [$Co(en)_3$]P_3O_9 are expected to be observed. An X-ray diffraction study has revealed that a homochiral columnar structure is formed by multiple NH···O hydrogen bonds between [$M(tn)_3$]$^{3+}$ and $P_3O_9{}^{3-}$. The crystal structures and

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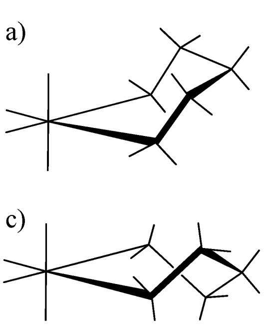
† Electronic supplementary information (ESI) available: CD spectra, X-ray crystal structures and tables of the structural data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00270d



Scheme 1 Conformations of six-membered tn chelate rings (a) chair, (b) boat, and (c) skew-boat.

the nature of the cation–anion interactions in aqueous solutions as studied by CD spectra are reported.

Results and discussion

Synthesis, characterization, and properties

The Cr complexes were prepared in the dark because they are unstable to light exposure. The $[Co(tn)_3]^{3+}$ and $[Cr(tn)_3]^{3+}$ complexes were resolved by fractional crystallization of the diastereomeric salts with 3-nitro-*d*-camphor, $[M(tn)_3]$(3-nitro-*d*-camphor)$_3$ (M = Co or Cr).[5] The Λ-isomer was obtained as the less soluble part. The resolving agent was removed by dissolving Λ-$[M(tn)_3]$(3-nitro-*d*-camphor)$_3$ in 47% HBr, and the bromide, Λ-$[M(tn)_3]Br_3$, was precipitated by the addition of ethanol. Λ-$[M(tn)_3]Br_3$ was allowed to react with $Ag_3P_3O_9$, and after removing precipitated AgBr, slow evaporation of the filtrate gave Λ-$[M(tn)_3]P_3O_9$ as pink (M = Co) or yellow (M = Cr) crystals. The racemic complexes, *rac*-$[M(tn)_3]P_3O_9$, were prepared from $[M(tn)_3]Cl_3$ and $Ag_3P_3O_9$. The IR spectra of *rac*- and Λ-$[M(tn)_3]P_3O_9$ showed characteristic bands attributable to $\nu(PO_2)$ and ν(POP) at 1293–1297 and 978–981 cm^{-1}, respectively.[6] The $[Co(tn)_3]^{3+}$ complex showed the first ($^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h)) and the second ($^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h)) d–d absorption bands at 488 and 351 nm, respectively, while $[Cr(tn)_3]^{3+}$ showed the first ($^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h)) and the second bands ($^4A_{2g} \rightarrow {}^4T_{1g}$ (O_h)) at 464.5 and 354 nm, respectively; the data are in accordance with those reported in the literature.[7]

Table 1 lists the CD spectral data for Λ-$[M(tn)_3]Br_3$ (M = Co, Cr) and Λ-$[M(tn)_3]P_3O_9$ in water. The data for the bromides are compatible with those reported in the literature.[8,9] The CD intensity of Λ-$[Co(tn)_3]Br_3$ is extremely small compared with that of the five-membered en-ring complex, Λ-$[Co(en)_3]Br_3$.[7] It has been reported that in a series of $[Co(en)_{3-n}(tn)_n]^{3+}$ (n = 0–3), the CD intensity of the first absorption band region decreases as the number of tn chelate rings increases.[7a] Fig. 1 shows the CD spectral changes of Λ-$[Co(tn)_3]Br_3$ (2.5 mM) as a function of the $P_3O_9^{3-}$ concentration. In the absence of $P_3O_9^{3-}$, the complex exhibits a positive and a negative band at 534 and 476 nm, respectively, in the first absorption band region. With an increase in the $P_3O_9^{3-}$ concentration, the strength of the negative CD band increases at the expense of the positive CD band. Similar spectral changes were reported when an oxoanion such as PO_4^{3-} or SO_4^{2-} was added to an aqueous solution of Λ-$[Co(tn)_3]^{3+}$.[10] The changes were ascribed to the stereochemical lability of the tn chelate ring between a chair and a skew-boat conformation in solution (*cf.* Scheme 1).[11] When $P_3O_9^{3-}$, PO_4^{3-}, or SO_4^{2-} was added to an aqueous solution of Λ-$[Co(en)_3]^{3+}$, a similar spectrum change (*i.e.*, an increase of the negative CD band at the expense of the positive band) was observed in the first absorption band region, and the change was attributed to the stabilization of the δ (*lel*) conformation.[3,11] Thus, the δ skew-boat (*lel*) conformation of the tn chelate ring may be stabilized by an increase in the $P_3O_9^{3-}$ concentration.

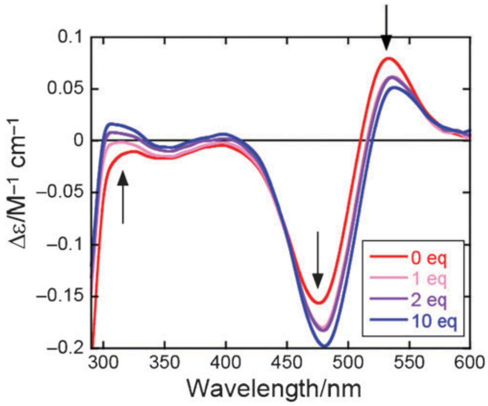


Fig. 1 CD spectral changes of Λ-$[Co(tn)_3]Br_3$ (2.5 mM) as a function of $Na_3P_3O_9$ concentration (0–25 mM).

The CD spectral changes of Λ-$[Cr(tn)_3]Br_3$ as a function of the $P_3O_9^{3-}$ concentration were also studied (Fig. S1, ESI†). Although the strength of the positive CD band at 480 nm decreased with an increase in the $P_3O_9^{3-}$ concentration, a negative CD band did not appear in the shorter wavelength region of the first absorption band region.

X-Ray crystal structures

Structure of *rac*-$[Co(tn)_3]P_3O_9 \cdot 7.3H_2O$. The crystallographic data are summarized in Table 2. This compound crystallized in the monoclinic space group $P2_1/c$ (No. 14) with

Table 1 CD spectral data for Λ-$[M(tn)_3]Br_3$ (M = Co, Cr) and Λ-$[M(tn)_3]P_3O_9$ in water

Complex	λ/nm	$\Delta\varepsilon$/M^{-1} cm^{-1}	Complex	λ/nm	$\Delta\varepsilon$/M^{-1} cm^{-1}
Λ-$[Co(tn)_3]Br_3$	534	0.079	Λ-$[Cr(tn)_3]Br_3$	480	0.392
	476	−0.147		346	0.012
	344	−0.010			
Λ-$[Co(tn)_3]P_3O_9$	538	0.057	Λ-$[Cr(tn)_3]P_3O_9$	480	0.350
	478	−0.176		341	0.015
	349	−0.014		270	0.014
	311	0.0001			

$Z = 4$. The asymmetric unit of the crystal contains three $[Co(tn)_3]^{3+}$ cations, three $P_3O_9^{3-}$ anions, and 22 water molecules. Thus, 12 $[Co(tn)_3]^{3+}$ cations exist in the unit cell. Fig. 2 shows an ORTEP view of *rac*-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$ with selected atom numbering schemes. There are three types of $[Co(tn)_3]^{3+}$, each Co (Co1, Co2, and Co3) being coordinated by three tn chelate rings through two amine nitrogen atoms to form an octahedral Co^{III} complex. The three six-membered tn chelate rings around each Co assume different conformations; they assume the chair (N1–N2) and the skew-boat (N3–N4, N5–N6) conformation around Co1, the chair (N7–N8, N11–N12) and the skew-boat (N9–N10) conformation around Co2, and the chair (N13–N14, N15–N16, N17–N18) conformation around Co3. The relevant coordination bond lengths and bond angles are listed in Table 3. The average Co–N coordinate bond length is 1.986 Å, which is close to the value (1.979 Å) for Λ-$[Co(tn)_3]Cl_3{\cdot}H_2O$.[12] The $P_3O_9^{3-}$ anion is conformationally labile and can assume several forms; for example, in the crystals of *rac*- and Λ-$[Co(en)_3]P_3O_9{\cdot}2H_2O$,[3] the $P_3O_9^{3-}$ anion assumes a boat conformation, while the anion assumes a chair conformation in the crystal of $ErNa_3(P_3O_9)_2{\cdot}9H_2O$.[13] One of the three $P_3O_9^{3-}$ anions in *rac*-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$ assumes a chair conformation (P7–P9), while the other two (P1–P3 and P4–P6) assume a skew-boat conformation (Figs. 2 and 3). The $[Co(tn)_3]^{3+}$ cations and the $P_3O_9^{3-}$ anions are stacked alternately in the order Co1–$P_3O_9^{3-}$–Co2–$P_3O_9^{3-}$–Co3–$P_3O_9^{3-}$–Co1 by linking with multiple NH···O hydrogen bonds to form a columnar structure along the [201] direction (Fig. 3(a)). It is to be noted that each column is homochiral, consisting of only one of the two enantiomers, Δ- and Λ-$[Co(tn)_3]^{3+}$. The neighboring homochiral columns with opposite configurations are linked by six hydrogen bonds, N1···O4, N6···O4, N7···O22, N12···O22, N13···O13, and N18···O13, to construct a racemic pair of columns (Fig. 3(a)). The crystal involves 40 types of NH···O hydrogen bonds, the distances being listed in Table S1, ESI.† In a previous paper,[3] we reported the crystal structure of the analogous en complex, *rac*-$[Co(en)_3]P_3O_9{\cdot}2H_2O$. In the en complex, a similar homochiral columnar structure to the tn complex is formed, and adjacent homochiral columns with different chirality are further connected by intercolumn hydrogen bonds through $P_3O_9^{3-}$ anions to form a tetrameric cyclic cylindrical structure. In the present tn complex, the racemic pairs of columns described above are connected intricately with lattice water molecules by hydrogen bonds to form a 3-D network structure (Fig. 3(b)).

Table 3 Relevant coordination bond lengths (Å) and angles (°) with their estimated standard deviations in parentheses for *rac*-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$

Bond length/Å			
Co(1)–N(1)	1.977(3)	Co(1)–N(4)	1.986(3)
Co(1)–N(2)	1.990(3)	Co(1)–N(5)	1.996(3)
Co(1)–N(3)	1.984(3)	Co(1)–N(6)	1.991(3)
Co(2)–N(7)	1.981(3)	Co(2)–N(10)	1.987(3)
Co(2)–N(8)	1.993(3)	Co(2)–N(11)	1.985(3)
Co(2)–N(9)	1.969(3)	Co(2)–N(12)	1.990(3)
Co(3)–N(13)	1.994(3)	Co(3)–N(16)	1.983(3)
Co(3)–N(14)	1.986(3)	Co(3)–N(17)	1.992(3)
Co(3)–N(15)	1.965(3)	Co(3)–N(18)	1.997(3)
	$Co–N_{av}$	1.986 Å	
Bond angle/°			
N(1)–Co(1)–N(2)	90.89(15)	N(7)–Co(2)–N(8)	90.86(14)
N(3)–Co(1)–N(4)	89.52(15)	N(9)–Co(2)–N(10)	94.94(15)
N(5)–Co(1)–N(6)	88.67(14)	N(11)–Co(2)–N(12)	94.73(15)
N(13)–Co(3)–N(14)	91.60(15)		
N(15)–Co(3)–N(16)	91.83(14)		
N(17)–Co(3)–N(18)	94.58(15)		

Structure of *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$. The crystallographic data are summarized in Table 2. This compound crystallized in the triclinic space group $P\bar{1}$ (No. 2) with $Z = 2$. The asymmetric unit of the crystal contains two $[Cr(tn)_3]^{3+}$ cations, two $P_3O_9^{3-}$ anions, and 15 water molecules. Fig. 4 shows an ORTEP view of *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$ with selected atom numbering schemes. Each Cr (Cr1, Cr2) is coordinated by three tn chelate rings through two amine nitrogen atoms to form an octahedral Cr^{III} complex. All three six-membered tn

Table 2 X-Ray crystallographic data for *rac*-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$, *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$, Λ-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$, and Λ-$[Cr(tn)_3]P_3O_9{\cdot}2.5H_2O$

	rac-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$	*rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$	Λ-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$	Λ-$[Cr(tn)_3]P_3O_9{\cdot}2.5H_2O$
Formula	$C_{27}H_{134}Co_3N_{18}O_{49}P_9$	$C_{18}H_{90}Cr_2N_{12}O_{33}P_6$	$C_{18}H_{70}Co_2N_{12}O_{23}P_6$	$C_{18}H_{70}Cr_2N_{12}O_{23}P_6$
Formula weight	1951.01	1292.80	1126.53	1112.65
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a/Å	11.9653(3)	10.5938(3)	10.4652(3)	10.4697(3)
b/Å	28.8024(6)	17.1108(5)	14.9511(4)	14.9840(3)
c/Å	23.1787(5)	17.6112(4)	28.3327(6)	28.6381(6)
α/°	90	116.9937(10)	90	90
β/°	94.9064(9)	99.0448(9)	90	90
γ/°	90	96.3816(14)	90	90
V/Å^3	7958.3(3)	2748.12(13)	4433.12(19)	4492.68(19)
Z	4	2	4	4
$D_{calc.}$/g cm^{-3}	1.628	1.562	1.688	1.645
μ/cm^{-1}	9.077	6.689	10.570	7.883
R_1 [$I > 2.0\sigma(I)$]^a	0.0666	0.0411	0.0283	0.0273
R_W [all data]^b	0.2057	0.1378	0.0417	0.0511
T/K	103	103	93	103
Flack parameter	—	—	0.004(7)	0.012(10)

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

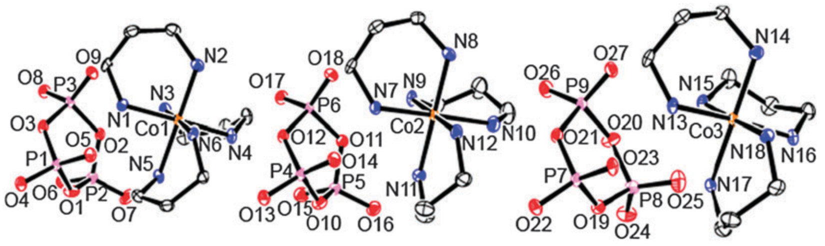


Fig. 2 ORTEP view of *rac*-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$ with selected atom numbering schemes showing the 50% probability ellipsoids. Water molecules and hydrogen atoms are omitted for clarity.

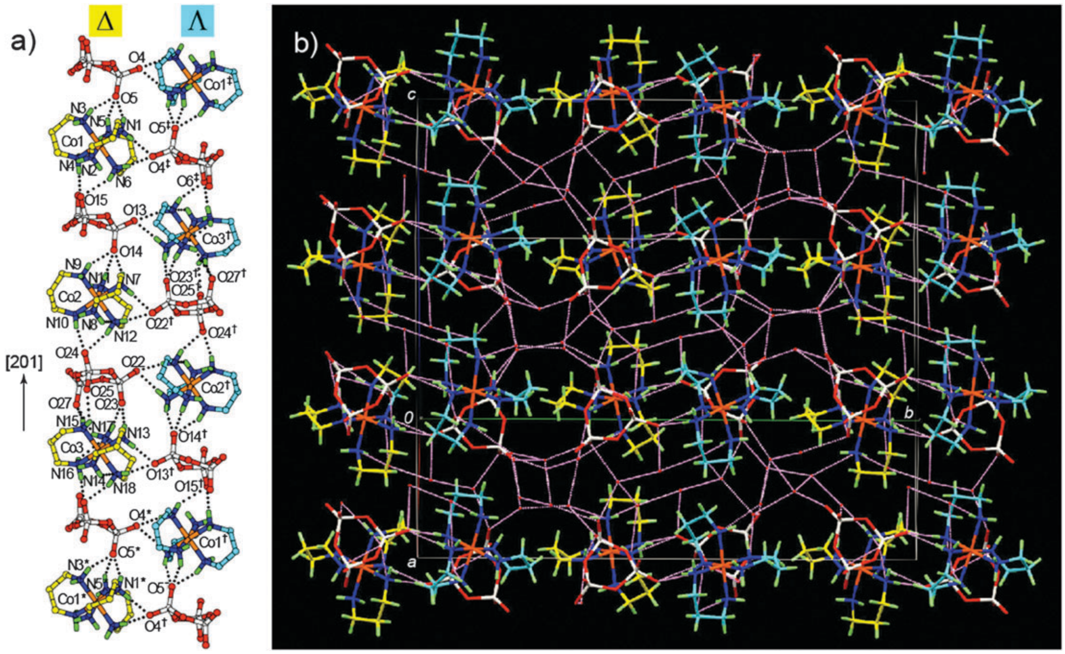


Fig. 3 X-Ray crystal structure of *rac*-$[Co(tn)_3]P_3O_9{\cdot}7.3H_2O$. (a) Racemic pair columnar structure constructed by two columns with Δ- and Λ-$[Co(tn)_3]^{3+}$. The alternately stacked $[Co(tn)_3]^{3+}$ cations and the $P_3O_9{}^{3-}$ anions are linked by NH···O hydrogen bonds. (b) Top view of the crystal structure, showing a racemic pair of columns constructed by intercolumn hydrogen bonds to form a 3-D structure. Color code; Co: orange, N: blue, O: red, P: white, H: pale green. Yellow and light blue show the carbon atoms of the Δ- and Λ-enantiomers, respectively. Symmetry operators, *: $x + 2, y, z + 1$; †: $2 - x, -y, 1 - z$; ‡: $-x, -y, -z$.

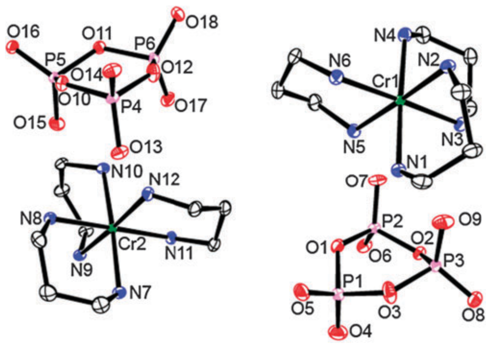


Fig. 4 ORTEP view of *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$ with selected atom numbering schemes showing the 50% probability ellipsoids. Water molecules and hydrogen atoms are omitted for clarity.

chelate rings around Cr1 assume a chair conformation, while chair (N7–N8, N11–N12) and skew-boat (N9–N10) conformations are involved around Cr2. The relevant coordination bond lengths and bond angles are listed in Table 4. The average Cr–N coordinate bond length is 2.092 Å, which is larger than in the analogous Co complex (1.986 Å) by about 0.1 Å. The difference is in accord with the difference in the ionic radius between Cr^{3+} (6-coord, 0.76 Å) and Co^{3+} (6-coord, low spin, 0.67 Å).[14] One $P_3O_9{}^{3-}$ anion (P4–P6) assumes a chair conformation; the other one (P1–P3) assumes a skew-boat conformation. Five amine NH groups of Cr1 are linked to the oxygen atoms of the skew-boat $P_3O_9{}^{3-}$ anion by NH···O hydrogen bonds, and the cations and anions are stacked alternately to form a columnar structure along the *a*-axis (Fig. 5(a)). Furthermore, a column involving complexes with a single configuration (Δ, for example) is linked to the neighboring column involving the complexes with the opposite configuration (Λ, for example) by two types of hydrogen bonds, N2H···O8 and N3H···O8, to construct a racemic pair of columns (Fig. 5(a)). Similarly, five amine NH groups of Cr2 are linked to the oxygen atoms of the $P_3O_9{}^{3-}$ anion with the chair conformation by NH···O hydrogen bonds. Two columns consisting of Δ-Cr2 and Λ-Cr2 are linked by hydrogen bonds, N8···O16 and N9···O16, to form a racemic pair of

Table 4 Relevant coordination bond lengths (Å) and angles (°) with their estimated standard deviations in parentheses for *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$

Bond length/Å			
Cr(1)–N(1)	2.099(2)	Cr(1)–N(4)	2.091(2)
Cr(1)–N(2)	2.094(2)	Cr(1)–N(5)	2.092(2)
Cr(1)–N(3)	2.086(2)	Cr(1)–N(6)	2.092(2)
Cr(2)–N(7)	2.091(2)	Cr(2)–N(10)	2.099(2)
Cr(2)–N(8)	2.085(2)	Cr(2)–N(11)	2.093(2)
Cr(2)–N(9)	2.103(2)	Cr(2)–N(12)	2.076(2)
	$Cr–N_{av}$	2.092 Å	
Bond angle/°			
N(1)–Cr(1)–N(2)	93.43(9)	N(7)–Cr(2)–N(8)	90.18(9)
N(3)–Cr(1)–N(4)	89.44(9)	N(9)–Cr(2)–N(10)	86.59(9)
N(5)–Cr(1)–N(6)	87.38(10)	N(11)–Cr(2)–N(12)	90.13(10)

columns. Thus, there are two types of racemic pairs of columns in *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$, and the crystal structure is different from that of the analogous cobalt(III) complex. These two types of racemic pairs of columns are situated along the [011] direction. Fig. 5(b) gives the top view of the columns, showing that the columns involving the same absolute configurations are arrayed vertically, and the columns with opposite configurations are positioned alternately in the horizontal direction. Water molecules intricately link the racemic pairs to construct a 3-D structure. The distances of 26 types of NH···O hydrogen bonds in the crystal are listed in Table S2, ESI.†

Structure of Λ-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$. The crystallographic data are summarized in Table 2. This compound crystallized in the acentrosymmetric orthorhombic space group $P2_12_12_1$ (No. 19) with $Z = 4$. The asymmetric unit of the crystal contains two $[Co(tn)_3]^{3+}$ cations, two $P_3O_9{}^{3-}$ anions, and five water molecules. The absolute configuration around Co was confirmed to be Λ by the Flack parameter (0.004(7)).[15] Fig. 6 shows an ORTEP view of Λ-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$ with selected atom numbering schemes. There are two types of $[Co(tn)_3]^{3+}$ (Co1, Co2), and both complexes have the same tn conformations, two chair and one skew-boat conformations. One $P_3O_9{}^{3-}$ anion (P4–P6) assumes a chair conformation, while the other (P1–P3) assumes a skew-boat conformation. The relevant coordination bond lengths and bond angles are listed in Table S3, ESI.† The average Co–N coordinate bond length, 1.987 Å, is almost the same (1.986 Å) as for the racemic complex.

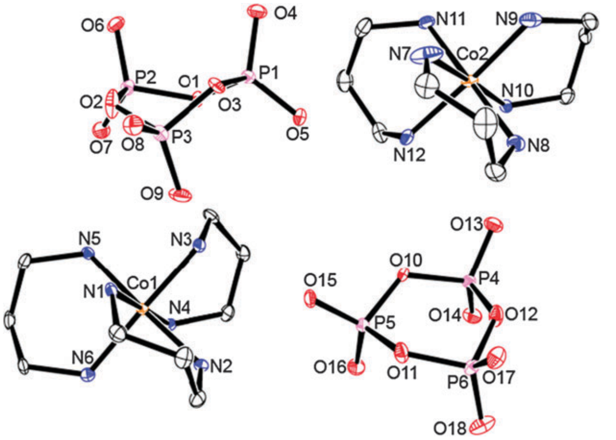


Fig. 6 ORTEP view of Λ-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$ with selected atom numbering schemes showing the 50% probability ellipsoids. Water molecules and hydrogen atoms are omitted for clarity.

Fig. 7 shows the packing diagram of the crystal. Six NH groups of Co1 are hydrogen bonded to the O atoms of the $P_3O_9{}^{3-}$ anions with the skew-boat conformation. Alternately stacked $[Co(tn)_3]^{3+}$ cations and $P_3O_9{}^{3-}$ anions form a columnar structure along the *a*-axis. Similarly, six NH groups of Co2 are linked by multiple NH···O hydrogen bonds to the O atoms of a $P_3O_9{}^{3-}$ anion with the chair conformation to construct a column along the *a*-axis. These two neighboring columns are linked further by hydrogen bonds (N2···O15, N3···O15,

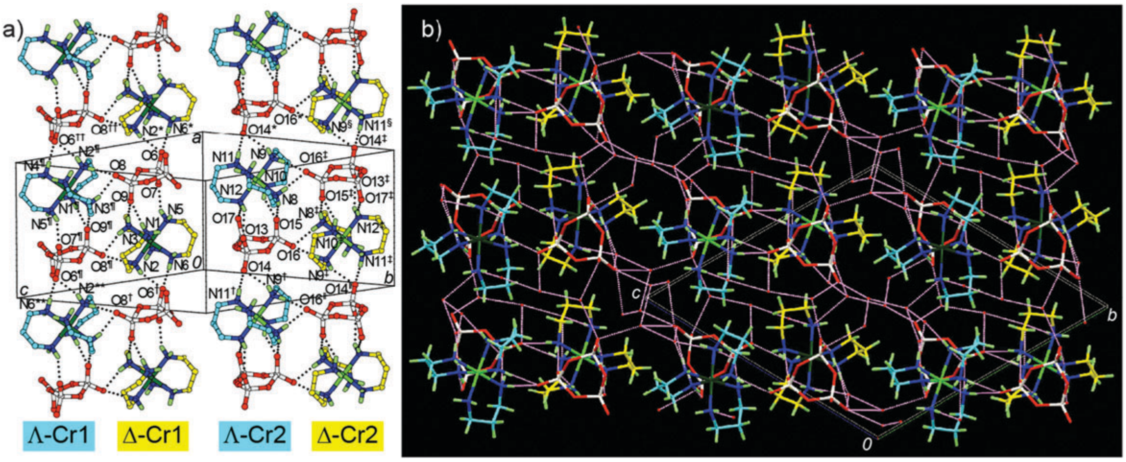


Fig. 5 X-Ray crystal structure of *rac*-$[Cr(tn)_3]P_3O_9{\cdot}7.5H_2O$. (a) Two types of racemic pair columnar structures. Each column is constructed by alternate stacking of the hydrogen-bonded $[Cr(tn)_3]^{3+}$ cations and the $P_3O_9{}^{3-}$ anions, and the two columns involving the $[Cr(tn)_3]^{3+}$ cations with opposite configurations (Δ, Λ) are linked by hydrogen bonds to form a racemic pair of columns. (b) Top view of the structure showing that the columns involving the same absolute configurations are arrayed vertically. Water molecules intricately link the racemic pairs to construct a 3-D structure. Color code; Cr1: dark green, Cr2: light green, N: blue, O: red, P: white, H: pale green. Yellow and light blue show the carbon atoms of the Δ- and Λ-enantiomers, respectively. Symmetry operators, *: $x + 1, y, z$; †: $x - 1, y, z$; ‡: $1 - x, 1 - y, -z$; §: $2 - x, 1 - y, -z$; ‖: $-x, 1 - y, -z$; ¶: $1 - x, -y, 1 - z$; **: $2 - x, -y, 1 - z$; ††: $-x, -y, 1 - z$.

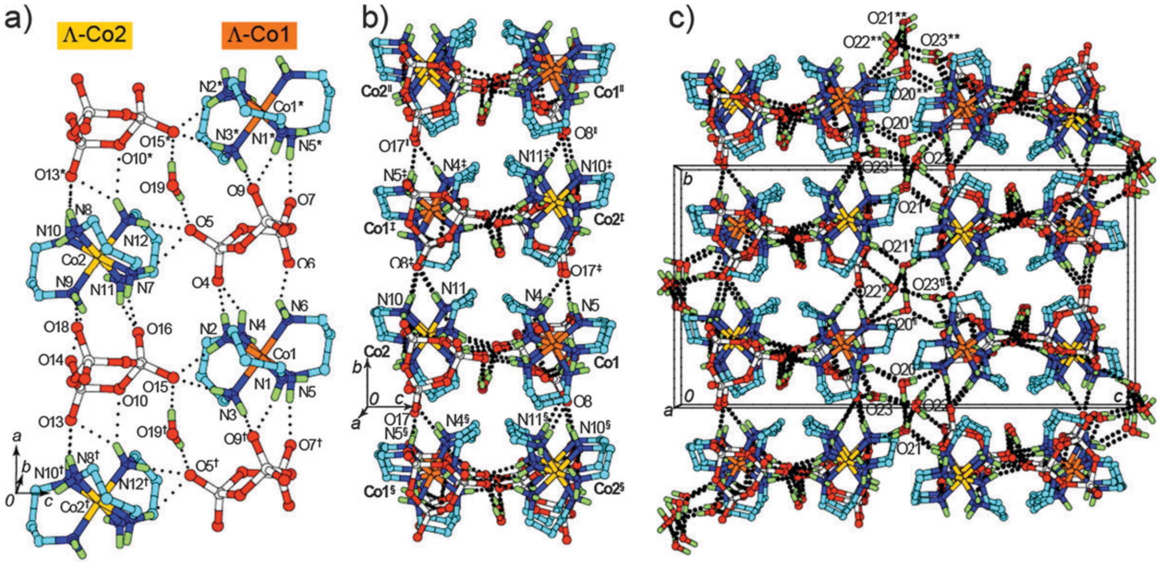


Fig. 7 X-Ray crystal structure of *Λ*-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$. (a) Column pair structure along the *a*-axis, which was constructed by multiple hydrogen bonds between the alternately stacked $[Co(tn)_3]^{3+}$ cations and $P_3O_9{}^{3-}$ anions, and the neighboring columns are further linked by hydrogen bonds. (b) 2-D sheet structure viewed down the *a*-axis. (c) Top view of the crystal structure, showing the intercylinder hydrogen bonds. Color code; Co1: orange, Co2: yellow, N: blue, O: red, P: white, C: light blue, H: pale green. Symmetry operators, *: $x + 1, y, z$; †: $x - 1, y, z$; ‡: $1 - x, 1/2 + y, 1/2 - z$; §: $2 - x, -1/2 + y, 1/2 - z$; ‖: $x, y + 1, z$; ¶: $1/2 + x, 1/2 - y, 1 - z$; **: $1/2 + x, 3/2 - y, 1 - z$.

N7···O5, N12···O5) to form a column pair. A water molecule (O19) serves to stabilize this structure by hydrogen bonds with two $P_3O_9{}^{3-}$ anions (O19···O5, O19···O15) (Fig. 7(a)). Neighboring column pairs along the *b*-axis are linked by four types of hydrogen bonds (N4···O17, N5···O17, N10···O8, N11···O8) to form a 2-D sheet structure in the *ab*-plane (Fig. 7(b)). The 2-D sheets are further linked by hydrogen bonds with water molecules to form a 3-D structure. Fig. 7(c) shows that the two types of complex cations are arrayed in pairs, Co1, Co1, Co2, Co2, Co1, Co1,... along the *c*-axis. There are 25 types of NH···O hydrogen bonds in the crystal, the distances being listed in Table S4, ESI.† The crystal structure is different from that of the corresponding en complex. In the crystal of *Λ*-$[Co(en)_3]P_3O_9{\cdot}2H_2O$, columns constructed by alternate linking of $[Co(en)_3]^{3+}$ cations and $P_3O_9{}^{3-}$ anions are further connected to form a tetrameric cyclic cylindrical structure.[3]

Structure of *Λ*-$[Cr(tn)_3]P_3O_9{\cdot}2.5H_2O$. The crystallographic data are summarized in Table 2. The crystal structure was isomorphous with that of *Λ*-$[Co(tn)_3]P_3O_9{\cdot}2.5H_2O$. The absolute configuration around Cr as determined by the Flack parameter[15] (0.012(10)) was *Λ*, as expected. An ORTEP view and the crystal structure are shown in Fig. S2 and S3, respectively, and the relevant coordination bond lengths and bond angles are listed in Table S5 (ESI†). The average Cr–N coordinate bond length (2.088 Å) is almost the same as for the racemic complex (2.092 Å). There are 25 types of NH···O hydrogen bonds in the crystal, the distances being listed in Table S6, ESI.†

Conclusion

The most striking feature of the crystal structure of *rac*-$[M^{III}(tn)_3]P_3O_9{\cdot}nH_2O$ (M = Co, Cr) is the formation of a columnar structure involving only one of the two possible enantiomers (*Δ*, *Λ*) of the complex cations. The homochiral column is formed by alternate linking of the $[Co(tn)_3]^{3+}$ cations with the same absolute configuration (*Δ* or *Λ*) and the $P_3O_9{}^{3-}$ anions. The components are connected by multiple NH···O hydrogen bonds whereby chiral recognition is achieved. Adjacent homochiral columns with opposite chirality are connected by intercolumn hydrogen bonds to form a racemic pair of columns, and thus conglomerate crystallization did not take place. Although the conformations (chair and skew-boat) of the six-membered tn chelate rings and the $P_3O_9{}^{3-}$ anions are different among the complexes, it is to be noted that all of the complexes have a similar columnar structure consisting of the $[M(tn)_3]^{3+}$ cations and the $P_3O_9{}^{3-}$ anions.

Experimental section

General

All reagents and solvents used in the syntheses were of reagent grade, and they were used without further purification. $Na_3P_3O_9{\cdot}H_2O$,[3] $Ag_3P_3O_9{\cdot}H_2O$,[16] $[Co(tn)_3]Cl_3$,[17] and $[Cr(tn)_3]Cl_3{\cdot}4H_2O$[7b] were prepared by the literature procedures.

Synthesis of the complexes

***rac*-$[Co(tn)_3]P_3O_9{\cdot}7.5H_2O$.** $[Co(tn)_3]Cl_3$ (0.196 g, 0.5 mmol) in 5 mL of water was added to a suspension of $Ag_3P_3O_9{\cdot}H_2O$ (0.282 g, 0.5 mmol) in 5 mL of water, and the mixture was stirred in the dark for 3 h. After removing AgCl by filtration with the aid of Celite, the filtrate was evaporated slowly at room temperature to give orange crystals. They were collected by filtration and recrystallized from water. Yield: 0.179 g (55%). Found: C, 16.58; H, 6.49; N, 12.75%.

$C_9H_{45}CoN_6O_{16.5}P_3$ requires C, 16.55; H, 6.94; N, 12.86%. IR (KBr disk, ν_{max}/cm^{-1}): 1583, δ(N–H, amine); 1294, ν(PO_2, $P_3O_9{}^{3-}$); 980, ν(POP, $P_3O_9{}^{3-}$).

Λ-[Co(tn)$_3$](3-nitro-*d*-camphor)$_3$·0.5H$_2$O. (This diastereomeric salt was prepared by a slight modification of the procedure of Rancke-Madsen and Woldbye.)[5] An aqueous solution (3 mL) of sodium 3-nitro-*d*-camphor (0.658 g, 3.0 mmol) was mixed with *rac*-[Co(tn)$_3$]Cl$_3$·4H$_2$O (0.919 g, 2.0 mmol) in water (2 mL). The mixture was evaporated slowly at room temperature to yield orange plates, which were collected by filtration, washed with water, and dried in air. Yield: 0.22 g (13%). Found: C, 53.37; H, 8.23; N, 14.30%. $C_{39}H_{73}CoN_9O_{9.5}$ requires C, 53.29; H, 8.37; N, 14.34%. IR (KBr disk, ν_{max}/cm^{-1}): 1595, δ(N–H, amine); 1671, $\nu_{C=O}$(3-nitro-*d*-camphor); 1453, $\nu_{N=O}$(3-nitro-*d*-camphor).

Λ-[Co(tn)$_3$]Br$_3$·H$_2$O. Λ-[Co(tn)$_3$](3-nitro-*d*-camphor)$_3$·0.5H$_2$O (0.206 g, 0.23 mmol) in 47% HBr (2 mL) was slowly added to ethanol (50 mL) to give a pink precipitate, which was collected by filtration, washed with ethanol, and air-dried. Yield: 0.113 g (90%). Found: C, 19.85; H, 5.63; N, 15.12%. $C_9H_{32}Br_3CoN_6O$ requires C, 20.05; H, 5.98; N, 15.59%. IR (KBr disk, ν_{max}/cm^{-1}): 1583, δ(N–H, amine).

Λ-[Co(tn)$_3$]P$_3$O$_9$·2.5H$_2$O. An aqueous solution (4 mL) of Λ-[Co(tn)$_3$]Br$_3$·H$_2$O (0.053 g, 0.098 mmol) was mixed with a suspension of Ag$_3$P$_3$O$_9$·H$_2$O (0.055 g, 0.098 mmol) in 5 mL of water, and the mixture was stirred vigorously in the dark. After removing AgBr by filtration with the aid of Celite, the filtrate was evaporated slowly at room temperature to give pink rods. They were collected by filtration and recrystallized from water. Yield: 0.045 g (82%). Found: C, 19.22; H, 6.03; N, 14.81%. $C_9H_{32}Br_3CoN_6O$ requires C, 19.19; H, 6.26; N, 14.92%. IR (KBr, ν_{max}/cm^{-1}): 1584, δ(N–H, amine); 1294, ν(PO_2, $P_3O_9{}^{3-}$); 978, ν(POP, $P_3O_9{}^{3-}$).

***rac*-[Cr(tn)$_3$]P$_3$O$_9$·7.5H$_2$O.** This complex was prepared in the dark by the same method as for the analogous Co^{III} complex except that [Cr(tn)$_3$]Cl$_3$·4H$_2$O was used instead of [Co(tn)$_3$]Cl$_3$. Yield: 80%. Found: C, 17.05; H, 6.52; N, 13.14%. $C_9H_{45}CrN_6O_{16.5}P_3$ requires C, 16.72; H, 7.02; N, 13.00%. IR (KBr disk, ν_{max}/cm^{-1}) 1589, δ(N–H, amine); 1297, ν(PO_2, $P_3O_9{}^{3-}$); 978, ν(POP, $P_3O_9{}^{3-}$).

Λ-[Cr(tn)$_3$](3-nitro-*d*-camphor)$_3$·0.5H$_2$O. This diastereomer was prepared in the dark by a method similar to that for the cobalt complex. The crude material was recrystallized from water to yield yellow crystals. Found: C, 53.71; H, 8.33; N, 14.45%. $C_{39}H_{73}CrN_9O_{9.5}$ requires C, 53.71; H, 8.44; N, 14.46%. IR (KBr disk, ν_{max}/cm^{-1}): 1589, δ(N–H, amine); 1671, $\nu_{C=O}$(3-nitro-*d*-camphor); 1452, $\nu_{N=O}$(3-nitro-*d*-camphor).

Λ-[Cr(tn)$_3$]Br$_3$·H$_2$O. Λ-[Cr(tn)$_3$](3-nitro-*d*-camphor)·0.5H$_2$O (0.515 g, 0.6 mmol) in 47% HBr (2 mL) was slowly added to ethanol (100 mL) to give a yellow precipitate, which was collected by filtration, washed with ethanol, and air-dried. Yield: 0.297 g (93%). Found: C, 20.53; H, 5.60; N, 15.44%. $C_9H_{32}Br_3CoN_6O$ requires C, 20.32; H, 6.06; N, 15.79%. IR (KBr disk, ν_{max}/cm^{-1}): 1577, δ(N–H, amine).

Λ-[Cr(tn)$_3$]P$_3$O$_9$·2.5H$_2$O. This complex was prepared in the dark by the same method as for the analogous Co^{III} complex except that Λ-[Cr(tn)$_3$]Br$_3$·H$_2$O was used instead of Λ-[Co(tn)$_3$]Br$_3$·H$_2$O. Yield: 67%. Found: C, 19.41; H, 6.04; N, 14.99%. $C_9H_{35}CrN_6O_{11.5}P_3$ requires C, 19.43; H, 6.34; N, 15.11%. IR (KBr disk, ν_{max}/cm^{-1}): 1577, δ(N–H, amine); 1293, ν(PO_2, $P_3O_9{}^{3-}$); 981, ν(POP, $P_3O_9{}^{3-}$).

Physical measurements

UV-Vis spectra were recorded using a JASCO Ubest-550 spectrophotometer. Infrared spectra were measured using a JASCO FT/IR-550 spectrophotometer. CD spectra were recorded using a JASCO J-720 spectropolarimeter.

X-Ray crystallography

Single crystals were mounted on a glass fiber and coated with epoxy resin. The X-ray data were collected using a Rigaku RAXIS RAPID II imaging plate area detector employing graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were determined by direct methods (SIR2004)[18] and expanded using Fourier techniques[19] and successive Fourier difference methods with refinement of full matrix least squares on F^2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculations using the riding model. All calculations were performed using the *Crystal Structure* 3.8 *software package*.[20]

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (Nos. 16205010, 17350028, and 20550064) from the Ministry of Education, Science, Sports, and Culture of Japan.

References

1 (*a*) W. M. Latimer and W. H. Rodebush, *J. Am. Chem. Soc.*, 1920, **42**, 1419–1433; (*b*) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960; (*c*) T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76; (*d*) G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565–573.

2 (*a*) I. Katsuki, Y. Motoda, Y. Sunatsuki, N. Matsumoto, T. Nakashima and M. Kojima, *J. Am. Chem. Soc.*, 2002, **124**, 629–640; (*b*) H. Nakamura, Y. Sunatsuki, M. Kojima and N. Matsumoto, *Inorg. Chem.*, 2007, **46**, 8170–8181; (*c*) H. Nakamura, M. Fujii, Y. Sunatsuki, M. Kojima and N. Matsumoto, *Eur. J. Inorg. Chem.*, 2008, 1258–1267.

3 T. Nakashima, J. Mishiro, M. Ito, G. Kura, Y. Ikuta, N. Matsumoto, K. Nakajima and M. Kojima, *Inorg. Chem.*, 2003, **42**, 2323–2330.

4 For example: (*a*) A. von Zelewsky, *Stereochemistry of Coordination Compounds*, John Wiley & Sons, Chichester, England, 1996; (*b*) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 2387–2397; (*c*) H. Takazawa, S. Ohba, Y. Saito, H. Ichida and K. Rasmussen, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 2354–2357; (*d*) M. Brorson, F. Galsbøl, K. Simonsen, L. K. Skov and I. Søtofte, *Acta Chem. Scand.*, 1998, **52**, 1017–1023; (*e*) M. R. Sundberg, J. K. Koskimies, J. Matikainen and H. Tylli, *Inorg. Chim. Acta*, 1998, **268**, 21–30.

5 M. Rancke-Madsen and F. Woldbye, *Acta Chem. Scand.*, 1972, **26**, 3405–3412.

6 S. Belaaouad, A. Charaf, K. El Kababi and M. Radid, *J. Alloys Compd.*, 2009, **468**, 270–274.

7 (*a*) M. Kojima, H. Yamada, H. Ogino and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2325–2330; (*b*) E. Pedersen, *Acta Chem. Scand.*, 1970, **24**, 3362–3372.

8 (*a*) M. Fujita, Y. Yoshikawa and H. Yamatera, *J. Chem. Soc., Chem. Commun.*, 1975, 941–942; (*b*) R. R. Judkins and D. J. Royer, *Inorg. Chem.*, 1974, **13**, 945–950.

9 S. Kaizaki, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1100–1109.

10 P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 433–437.

11 M. Kojima, M. Fujita and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 898–906.

12 R. Nagao, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1973, **29**, 2438–2443.

13 H. Assaaoudi, M. Ijjaali, A. Ennaciri, I. S. Butler and J. A. Kozinski, *J. Chem. Crystallogr.*, 2007, **37**, 601–608.

14 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1969, **25**, 925–946.

15 (*a*) H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.*, 2000, **33**, 1143–1148; (*b*) H. D. Flack and G. Bernardinelli, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1999, **55**, 908–915.

16 A. Durif, *Crystal Chemistry of Condensed Phosphates*, Plenum, New York, 1995.

17 J. C. Bailar, Jr. and J. B. Work, *J. Am. Chem. Soc.*, 1946, **68**, 232–235.

18 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381–388.

19 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, A. de R. Gelder, R. Israel and J. M. M. Smits, *DIRDIF99: The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

20 *CrystalStructure 3.8; Crystal Structure Analysis Package*, Rigaku and Rigaku/MSC, The Woodlands, TX, USA, 2001–2007.