A trinuclear cobalt(III) phosphate complex with a novel molecular structure: Synthesis and crystal structure of \(\{[\text{Co(en)}_2]_3(\text{PO}_4)(\text{HPO}_4)\}_2(\text{H}_2\text{PO}_4)\text{Cl}_7 \cdot 6\text{H}_2\text{O}\)

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Received 7 March 2006; accepted 4 April 2006
Available online 22 April 2006

Abstract

A novel trinuclear cobalt(III) phosphate complex, \(\{[\text{Co(en)}_2]_3(\text{PO}_4)(\text{HPO}_4)\}_2(\text{H}_2\text{PO}_4)\text{Cl}_7 \cdot 6\text{H}_2\text{O}\), has been synthesized and characterized by single crystal X-ray structure determination and NMR spectroscopy. The compound includes an unprecedented type of discrete cluster with three metal atoms bridged by two phosphate anions. The clusters are associated in chains by strong hydrogen bonds PO_4 \cdot H \cdot \cdot PO_4. The crystal lattice is stabilized by extensive hydrogen bonding.

Keywords: Cobalt(III); Coordination chemistry; Crystal structure; Ethylenediamine; Phosphate; NMR spectroscopy

Transition metal phosphates are a large family of materials [1] with a structural diversity (3D frameworks, 2D sheets, 1D chains) analogous to the better known aluminium phosphates [2]. Many metals have been used to build such materials and plenty of examples can be found for Fe [3], Mo [4], and V [5] among others. In many cases, such materials display a porous nature with potential applications as solid catalysts [1]. The presence of organic ammonium cations balancing the charge of the anionic polymer may influence its formation, acting as templates [6–9]. Co(III), due to its inertness and the possibility of blocking some of its coordination positions with ligands such as ammonia or amines, could be a good candidate for trying to build this kind of structures in a rational way but the only structurally characterized phosphates containing cat-ionic cobaltammines are two compounds without direct Co–phosphate bonds [10,11] or the simple monomeric complex \([\text{Co(en)}_2(\text{PO}_4)]\) [12]. We have studied the interaction of the cation [\(\text{trans}-\text{Co(en)}_2\text{Cl}_2\)]^+ with HPO_4^- in aqueous medium [13] to check whether the simple salt [\(\text{trans}-\text{Co(en)}_2\text{Cl}_2\cdot\text{HPO}_4\)] is obtained or if a linear polymer is generated by substitution of the chloride ions in \(\text{trans}\) position: the observed result was in fact the substitution of chloride by phosphate but, at the same time, a change in the disposition of the amines from \(\text{trans}\) to \(\text{cis}\) takes place and thus an unprecedented discrete trinuclear cluster is obtained instead of a monodimensional polymer. The crystal structure of this compound [14] is described here.

The basic units of the structure are trinuclear clusters formed by three \([\text{cis}-\text{Co(en)}_2]\) subunits linked by two phosphate triple bridges, each phosphate being linked to each cobalt atom of the cluster through one of its oxygen atoms. The coordination sphere of each metal atom is formed by four nitrogen atoms from the two chelating en ligands and two oxygen atoms, one of each phosphate, in an all-\(\text{cis}\) disposition. The punctual symmetry of the cluster is roughly \(D_3\), a view of it being depicted in Fig. 1. Distances around the cobalt atoms are, averaging for all crystallographically different but chemically equivalent atoms, 1.931 Å (Co–O), 1.939 Å (Co–N \(\text{trans}\) to O), and 1.955 Å
(Co–N trans to N); the coordination octahedra are somewhat distorted, the main distortions being the chelating N–Co–N angles (below 86°) and the O–Co–O angles (above 93.5°). Phosphate groups display a slight trigonal distortion, according to the symmetry of the cluster, the bond distance of the P atom to the terminal O-atom being slightly longer than the distance to the coordinated O-atoms (ranges, 1.540–1.561 Å and 1.524–1.540 Å, respectively, for P–Ot and P–Oc) and bond angles being above tetrahedral for Oc–P–Oc and below tetrahedral for Ot–P–Oc. One of the amino groups of each en ligand forms an intracluster hydrogen bond with one of the phosphate oxygens (N–O distances ranging from 2.83 to 3.00 Å), six such H-bonds are present in each cluster (see Fig. 1) contributing to its stability.

To our knowledge, this trinuclear Co(III)–phosphate cluster is unprecedented, although Co₃(HPO₄)₂ subunits can be found as a portion of extended polymeric species [16]. Neither we have found any example for other metal atoms with inorganic phosphates, the only analogous clusters that we have been able to find being two compounds containing Cu(II) [17] or Zn(II) [18] and organic phosphates. On the other hand, many examples of polymeric materials can be found, with the metal atoms coordinated to more than two phosphates, which in our case is avoided by the presence of two ethylenediamine moieties in cis position.

Two crystallographically independent clusters are present in the asymmetric unit, they are chemically equivalent except their chirality, which is opposite. Nevertheless, it has not been possible to determine the absolute structure of the whole crystal in the chiral group P2₁, the refinement having being performed assuming a twin of both enantio-

meric components with equal weight. This may be also interpreted as the coexistence of regions of opposite chirality within the crystal.

The fourth oxygen atom of the phosphate, pointing out-wards the cluster is quite close to another analogous oxygen atom of another cluster: the distance is below 2.5 Å, typical of a very strong hydrogen bond involving an acidic proton. Hence, we have one of the phosphates as a true “phosphate” whereas the other is a “monohydrogenphosphate”. P–O(external) distances are virtually identical for all phosphates in the clusters, indicating that we have a dynamic situation with the proton identically shared between the two linked oxygens. The clusters are then linearly arranged along the c axis as follow, alternating clusters of opposed chirality:

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\text{O–PO}_3^+\text{[Co(en)₂]₃PO}_4^–\text{O–H...O–PO}_3^–\text{[Co(en)₂]₃PO}_3^–\text{O–H...O–PO}_3^–\text{[Co(en)₂]₃PO}_3^–
\]

According to this, the average formulation for each cluster is \(\text{[Co(en)₂]₃[PO₄]}(\text{HPO₄})\)\(^{4+}\). The charge of every two clusters is balanced by seven chloride anions and one dihydrogenphosphate ion (H₂PO₄)\(^-\). The presence of two H atoms in this non-coordinated species is required for electrical neutrality and supported by the P–O distances (two are appreciably shorter than the other two, values 1.480(4), 1.485(4), 1.575(5), and 1.589(4) Å); the two O-atoms with the longest distances form fairly strong H-bonds towards water molecules (O–H–O distances 2.646(6) and 2.606(7) Å). Six interstitial water molecules complete the asymmetric unit, therefore the formulation for the full compound is \(\text{[Co(en)₂]₃[PO₄]}(\text{HPO₄})\)\(^{4+}\)\(\text{Cl}_7\cdot6\text{H₂O}\). The co-existence of the three kind of phosphate anions in the same crystal is noteworthy: it is not a unprecedented feature[19] but, to our knowledge, it has not been described for any cobalt compound. An extensive hydrogen bond network is present stabilizing the lattice. Apart from the mentioned intracluster N–OH-bonds, those between the coordinated phosphates and those from the dihydrogen phosphate to water molecules, there are H-bonds from en molecules to water molecules and to phosphate oxygens of neighboring clusters (distances N–O from 2.8 to 3.0 Å), from en molecules to chloride ions (distances N–Cl from 3.15 to 3.45 Å) and from water molecules to phosphate oxygens and other water molecules (distances O–O from 2.74 to 2.80 Å).

The \(^{31}\text{P} \text{NMR} \) spectrum of the compound in D₂O as solvent displays an intense signal at 1.20 ppm and a weaker one at 11.85 ppm. They may be assigned, respectively, to the phosphate species inside the clusters, which are supposed to stand in solution, and to ionic H₃PO₄. The signals overlap so they cannot be separately integrated, the first one should be four times larger than the second one.

TG and DSC diagrams of the compound show dehydration as broad and asymmetric steps starting around 120 and finishing around 200 °C (endothermic peak at 162 °C). The associated weight loss is 6.1% (theoretical, 5.66%) and the dehydration enthalpy is 50.9 kJ/mol of
water. The DSC diagram displays an intense endothermal peak at 250 °C attributable to the melting of the anhydrous compound, which is immediately followed by the pyrolytic decomposition, which continues in several overlapped steps ending around 800 °C.

A novel cobalt(III) complex with phosphate species was unexpectedly obtained from the reaction of [(trans-Co(en)₂Cl₂)]⁺ with monohydrogenphosphate followed by slow evaporation in aqueous medium. The generated [(cis-Co(en)₂]³⁺ unit seems to direct the formation of a trinuclear cluster.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.04.001.

References

[13] Synthesis of the title compound: an aqueous solution of 1 g (0.003 mol) of [(trans-Co(en)₂Cl₂)]Cl in 25 ml water was added to an stoichiometric amount of disodium hydrogen phosphate dissolved in minimum amount of water. The mixture, when allowed to evaporate at room temperature for one day, gave violet colored crystals suitable for single crystal X-ray structure determination which were collected by drawing off the mother liquor and air-dried (yield, 0.7 g, 70% based on [(trans-Co(en)₂Cl₂)]Cl). The complex is soluble in water, ethanol and DMSO but insoluble in acetone. The complex salt decomposes at 190 °C. The elemental analysis is consistent with the composition [(Co(en)₂]3[PO₄][HPO₄]Cl] · 6 H₂O. Found: C, 15.2; N, 17.7; H, 5.9. Calculated for C₂₄H₁₁₂Cl₇Co₆N₂₄O₂₆P₅: C, 15.1; N, 17.6; H, 5.9. The complex is soluble in water and stable in air. M.p. > 200 °C. FT IR (KBr pellets): ν(PO₃⁻) 650, ν(H₂PO₃⁻) 560, δNH₂ 1574 cm⁻¹ which are comparable with literature values. Electronic spectrum (in H₂O): λmax 603, 304 and 247 nm corresponding to d–d transitions typical for octahedral low spin cobalt(III) salts.
[14] Crystal data for the title compound: C₂₄H₁₁₂Cl₇Co₆N₂₄O₂₆P₅, Mᵣ = 1909.96, monoclinic, space group P2₁, a = 12.8349(9) Å, b = 18.7451(13) Å, c = 16.0020(11) Å, β = 109.230(1)°, V = 3635.1(4) Å³, Z = 2, Dc = 1.745 Mg/m³, μ = 1.789 mm⁻¹, R (for reflections with I > 2σ(I)) = 0.0406, wR² (for all data) = 0.0975. Data were collected at room temperature for a crystal with dimensions 0.45 × 0.20 × 0.14 mm in a Bruker SMART APEX CCD system with MoKα radiation. 14874 independent reflections were used for structure solution and refinement in P2₁ by means of the SHELX-97 package [15]. Non-hydrogen atoms were refined anisotropically. H-atoms of ethylenediamine were introduced in ideal positions whereas those linked to O-atoms were not included in the model. Absolute structure could not be determined, the structure being refined as a twin of both enantiomers with equal contributions. Complete crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 298942) and may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.