

Correlation between Solution and the Solid State: The pH Dependent Composition in the Ternary System [Co(H₂O)₆]²⁺ or [Ni(H₂O)₆]²⁺/Piperazine/Phosphate

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 60th Birthday

Abstract. The protolytic equilibria of piperazine (C₄H₁₀N₂) and phosphate have been investigated in the presence of cobalt or nickel chloride or nitrate by potentiometric titrations between pH 2 and 8. Potentiometric titrations suggest the presence of [M²⁺(H₂O)₅(C₄H₁₁N₂⁺)]³⁺ and [M²⁺(H₂O)₅(C₄H₁₀N₂)²⁺] in solution with stability constants logK of 3.1 and 3.8 for M = Co and 3.1 and 3.6 for M = Ni, respectively. Crystallization experiments were then conducted at selected pH values to isolate desired species from the known solution composition. Crystallization afforded [M(H₂O)₆]²⁺(C₄H₁₂N₂²⁺)(HPO₄²⁻)₂ at pH 3.5 and 6.2 (M = Co,

Ni), and Co₃(PO₄)₂·8H₂O at pH 10.5. No crystals with the dihydrogenphosphate anion or a metal-bound piperazine ligand could be isolated under the reaction conditions. The solid-state assembly in the isomorphous structures of [M(H₂O)₆](C₄H₁₂N₂)(HPO₄)₂ with M = Co and Ni is based on an extended hydrogen bonded network between the three ionic building blocks.

Keywords: Piperazine; Crystal engineering; Hydrogen bonding; Potentiometric titration; Phosphates

Korrelation zwischen Lösung und Festkörper: Die pH-abhängige Zusammensetzung im ternären System [Co(H₂O)₆]²⁺ oder [Ni(H₂O)₆]²⁺/Piperazin/Phosphat

Inhaltsübersicht. Das Protolysegleichgewicht von Piperazin (C₄H₁₀N₂) und Phosphat wurde in Gegenwart von Cobalt- oder Nickelchlorid oder -nitrat durch potentiometrische Titration zwischen pH 2 und 8 untersucht. Die potentiometrischen Titrations weisen auf die Spezies [M²⁺(H₂O)₅(C₄H₁₁N₂⁺)]³⁺ und [M²⁺(H₂O)₅(C₄H₁₀N₂)²⁺] in Lösung hin, mit den Stabilitätskonstanten logK 3.1 und 3.8 für M = Co und 3.1 und 3.6 für M = Ni. Es wurden sodann Kristallisationsexperimente bei ausgewählten pH-Werten durchgeführt, um gewünschte Spezies ausgehend

von der bekannten Lösungszusammensetzung zu isolieren. Die Kristallisationen lieferten [M(H₂O)₆]²⁺(C₄H₁₂N₂²⁺)(HPO₄²⁻)₂ bei pH 3.5 und 6.2 (M = Co, Ni), und Co₃(PO₄)₂·8H₂O bei pH 10.5. Es konnten unter den Reaktionsbedingungen keine Kristalle mit dem Dihydrogenphosphat-Anion oder mit Metall-koordiniertem Piperazin isoliert werden. Die Festkörperanordnung in den isomorphen Strukturen von [M(H₂O)₆](C₄H₁₂N₂)(HPO₄)₂ mit M = Co und Ni basiert auf einem ausgedehnten Wasserstoffbrücken-Netzwerk zwischen den drei ionischen Baugruppen.

Introduction

Crystallization and crystal structure design are of great importance in inorganic coordination chemistry but are often highly unpredictable and incompletely understood. Recent interest in crystal growth indicates the need for a greater understanding of crystallization processes [1]. Major inter-

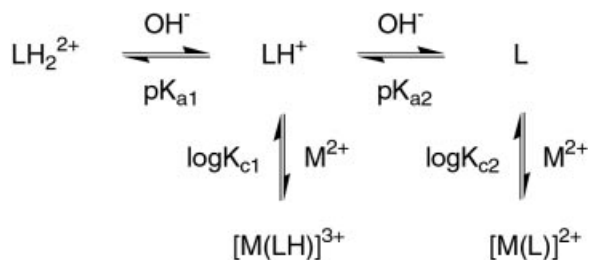
actions relevant to (inorganic) crystal structure design are covalent metal-ligand interactions, hydrogen bonding [2, 3, 4, 5] and even π -stacking or C–H $\cdots\pi$ interactions [5, 6, 7]. One technique for the characterization of solution species is electrospray ionization mass spectrometry (ESI-MS) [5, 8, 9]. When protonated ligands are used as building blocks, the species distribution and the competition for the ligand between the metal and the proton can be investigated by potentiometric titration, to gain insight in the solution composition for the crystallization.

Potentiometric titration [10, 11] is the measurement of the change in electrostatic potential of the electrode relative to a reference electrode. The pH is then calculated from calibration data. When investigating metal/ligand speciations, this usually involves the addition of hydroxide to the fully protonated ligand in the presence of the metal of interest. Deprotonations of the ligand are measured by acidity

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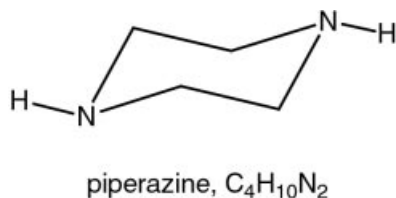
constants (K_a or pK_a values). The metal-ligand interactions are quantified through complex stability constants, as K_c or $\log K_c$ values. The piperazine and phosphate ligands of interest here contain more than one proton, so several acid and complex stability constants must be taken into account. Successive deprotonations of the ligand lead to processes such as those shown in Scheme 1.



Scheme 1 Sequence of deprotonation and coordination, with relevant constants.

The variation of pH with added hydroxide yields information on the thermodynamic equilibria, in solution, of species such as those shown above. While acid/base reactions are generally fast, metal-ligand exchanges can be very slow. Direct titration methods are only suitable for reasonably labile metal species, in order to be completed in a reasonable time-frame. Estimated formation constants for the proposed species are refined mathematically to obtain values that best fit the experimental data. These constants can then be combined to form speciation plots, which show the distribution of the species with pH.

Piperazine (1,4-diazacyclohexane, $\text{C}_4\text{H}_{10}\text{N}_2$) is both a good hydrogen-bond acceptor and metal-complexing ligand which makes it an interesting building block for coordination and supramolecular chemistry. Piperazine can be protonated to give two types of salts either with a mono- or dication, $(\text{C}_4\text{H}_{11}\text{N}_2)^+$ or $(\text{C}_4\text{H}_{12}\text{N}_2)^{2+}$, respectively. A cobalt methylpiperazinium phosphate of formula $[(\text{C}_5\text{H}_{14}\text{N}_2)][\text{Co}(\text{HPO}_4)_2]$ and with a linear chain structure was recently reported within the family of open-framework transition-metal phosphates [12]. Open-framework (transition-)metal phosphates are a promising novel class of compounds with a stable porous structure and catalytic, zeolite-type behavior [13]. Organic amines or quaternary ammonium cations are used as templates to achieve the porosity of the metal phosphates [14]. A sizable number of porous metal-phosphate based compounds have been reported and applied as a catalyst, molecular sieves or ion-exchange materials [15,16,17,18,19,20].



Our investigations into controlled, reliable syntheses of open-framework transition-metal phosphates led to a study

of the solution behaviour of the building blocks as a function of the pH value. A determination of the species distribution over the pH range in aqueous solution should provide for a crystallization of the desired building blocks with the pH variable. We correlate here a solution investigation on the ternary system $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ /piperazine/phosphate by potentiometric titration to the results of crystallization experiments at selected pH values.

Results and Discussion

The potentiometric titrations were carried out at the 1:1:1 M:piperazine:phosphate ratio, where $\text{M} = \text{Co}^{\text{II}}$ and Ni^{II} . Variation of the metal:ligand ratio was not expected to yield extra information, and was not attempted. As part of initial investigation, the ligands piperazine and phosphate were titrated separately to verify both ligand purity and the literature values for the acidity constants. The results of the individual titrations confirmed the literature values (see Fig. 1) [21] or the accuracy of our experimental setup, respectively. As piperazine and phosphate show only hydrogen-bonding interactions, titrating a mixture of both confirms the individual literature values again. The species distribution plot for the binary system piperazine/phosphate (Fig. 1) is a superposition of the individual species distributions (not shown here).

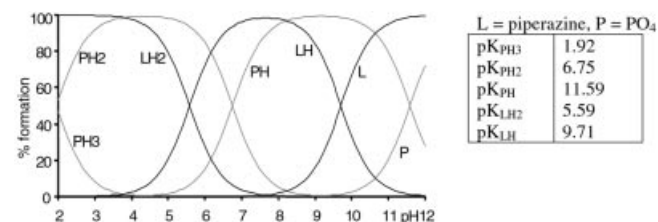


Fig. 1 Species distribution for piperazine/phosphate in the range pH 2–12. pK values are given at the right hand side. L = piperazine, P = PO_4 .

Titration on the binary metal/phosphate system was completed to determine the effect of the metal on the phosphate ligand components, before titration of the ternary metal/piperazine/phosphate system.

Both the Co and Ni/phosphate titrations found the presence of a $\text{M}(\text{HPO}_4)$, with $\log K_c = 2.21(13)$ and $2.11(23)$ respectively, compared with literature values [21] of $\log K_c = 2.18$ and 2.10 (Co, Ni). This confirms the validity of our potentiometric procedure. Inclusion of literature values for $\log K_c[\text{M}(\text{PO}_4)]$ in our model demonstrated that this species would only form after the onset of hydroxide precipitation. Still, the speciation plots for the ternary system to be discussed below (Fig. 2 and 3) show that less than 5% of the metal forms as $\text{M}(\text{HPO}_4)$ at maximum concentration. Thus, it is unreasonable to clearly see a $\text{M}(\text{H}_2\text{PO}_4)$ or $\text{M}(\text{H}_3\text{PO}_4)$ species.

Results from the titrations of the ternary metal/piperazine/phosphate systems are shown in Fig. 2 and 3. The cal-

culations for both Co and Ni indicated the presence of an MLH species (L = piperazine) that represents a significant percentage formation. This would not be an unreasonable species to form, given the affinity of the metals to nitrogen donors. Although the ML complex does not appear to be significantly more stable than the MLH complex, it is in the region of the speciations where hydroxide is developing as a competing ligand at these low ligand concentrations. It is anticipated, however, that the ML complex will be more stable in the more concentrated crystallization solutions. The stability constants for the complexes present in a metal/piperazine/phosphate solution are found in good agreement between cobalt and nickel.

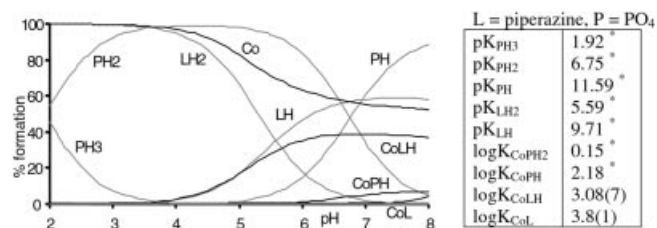


Fig. 2 Species distribution for the ternary cobalt/piperazine/phosphate system in the range pH 2–8. pK values are given at the right hand side. L = piperazine, P = PO₄. * indicates literature values [21] held constant.

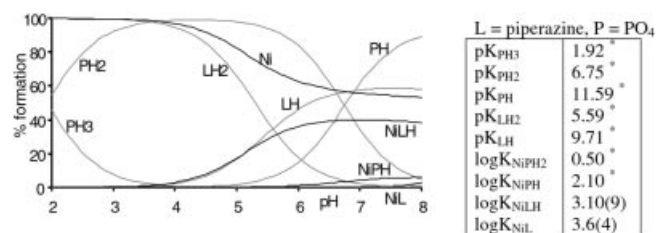


Fig. 3 Species distribution for the ternary nickel/piperazine/phosphate system in the range pH 2–8. pK values are given at the right hand side. L = piperazine, P = PO₄. * literature values [21] held constant.

Crystallization experiments were carried out from solutions containing a 1:1:1 M:piperazine:phosphate ratio and with a pH starting at 3.5, 6.2, and 10.5. Crystallization was induced by cooling (at pH = 3.5) or slow solvent evaporation at room temperature. When the crystals were collected the pH of the remaining solution was found to have dropped to 3.1, 5.6, and 10.0, respectively. The crystals grown at pH 3.5 and 6.2 were of identical composition and contained the HPO₄²⁻ anion. Crystal from pH 10.5 contained the PO₄³⁻ anion. The removal of HPO₄²⁻ or PO₄³⁻, respectively, from the H₃PO₄/H₂PO₄⁻/HPO₄²⁻/PO₄³⁻ equilibrium shifts the equilibrium with the release of protons (thus the drop of pH) from H₃PO₄ and H₂PO₄⁻.

Crystals grown at pH 3.5 and 6.2 had the composition $[\text{M}(\text{H}_2\text{O})_6](\text{C}_4\text{H}_{12}\text{N}_2)(\text{HPO}_4)_2$ (M = Co **1**, Ni **2**) as elucidated by single-crystal X-ray structure determinations. Both

the cobalt and nickel compound are isostructural. The asymmetric unit of the cobalt salt **1** is depicted in Fig 4, as an example. A section of the crystal structure of **1** is shown in Fig. 5. Both structures consist of a hydrogen-bonded framework between the hexaaquametal complexes, the piperazinium dication and the two hydrogenphosphate anions. All protic hydrogen atoms are occupied in hydrogen bonding.

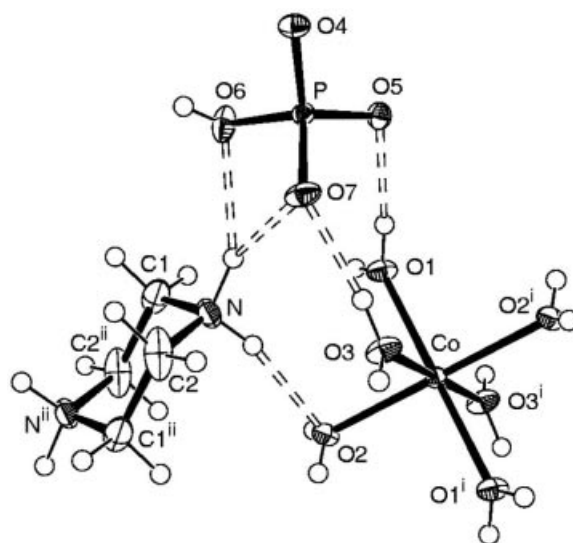


Fig. 4 ORTEP [31] drawing of the asymmetric unit of compound **1**, illustrating also some of the hydrogen bonding. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii, symmetry code: i = -x, -y, -z; ii = -x, 1-y, -z.

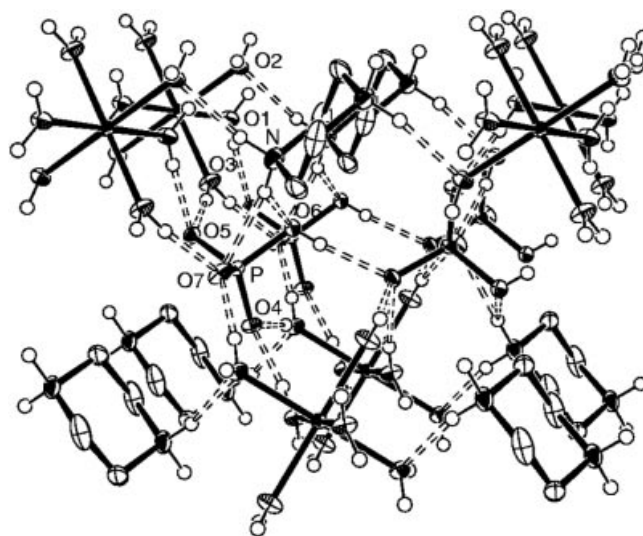


Fig. 5 Section of the extended crystal structure of compound **1** with the three-dimensional hydrogen bonding network; view approximately along *a*. Hydrogen atoms on carbon have been omitted for clarity.

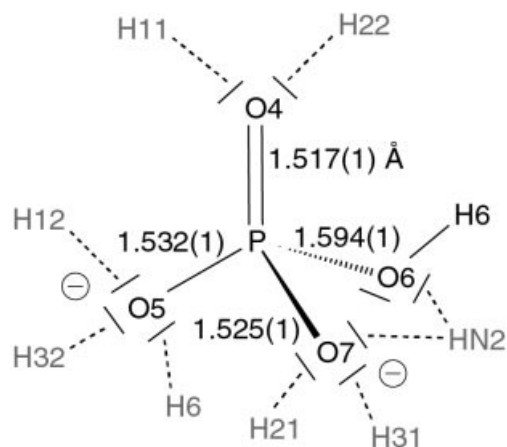
Details of the hydrogen-bonding network are given in Table 1. We just note that the terminal phosphate oxygen atoms are different in their hydrogen accepting character. Atom O5 and O7 each accept three hydrogen bonds, whereas O4 accepts only two. Together with the slight P–O bond length variation, we can assign the mesomeric formula from the solid-state structure of **1** and **2** as in Scheme 2 to the HPO_4^{2-} anion. This assignment is based on the often observed 'lone pair directionality' for hydrogen bonding [22].

Table 1 Hydrogen bonds /Å, ° in compound **1** and **2**

1				
D–H...A	D–H	H...A	D...A	D–H...A
O1–H11...O4 ^a	0.86(3)	1.83(3)	2.698(2)	177(3)
O1–H12...O5	0.82(3)	1.94(3)	2.747(2)	172(3)
O2–H21...O7 ^a	0.83(3)	1.87(3)	2.689(2)	171(2)
O2–H22...O4 ^b	0.67(3)	1.97(3)	2.643(2)	174(3)
O3–H31...O7	0.85(3)	1.83(3)	2.682(2)	173(3)
O3–H32...O5 ^c	0.89(3)	1.85(3)	2.730(2)	174(2)
O6–H6...O5 ^d	0.75(3)	1.86(3)	2.607(2)	174(3)
N–HN1...O2	0.91(3)	2.00(3)	2.886(2)	166(2)
N–HN1...O1	0.91(3)	2.58(2)	3.100(2)	117(2)
N–HN2...O6	1.01(3)	2.15(3)	3.006(2)	142(3)
N–HN2...O7	1.01(3)	2.11(3)	2.998(2)	145(3)

2				
D–H...A	D–H	H...A	D...A	D–H...A
O1–H11...O4 ^a	0.84(3)	1.86(3)	2.699(2)	177(2)
O1–H12...O5	0.82(2)	1.95(2)	2.757(2)	170(2)
O2–H21...O7 ^a	0.83(2)	1.86(2)	2.690(2)	172(2)
O2–H22...O4 ^b	0.71(3)	1.94(3)	2.647(2)	176(3)
O3–H31...O7	0.82(3)	1.87(3)	2.687(2)	175(3)
O3–H32...O5 ^c	0.83(3)	1.91(3)	2.737(2)	177(2)
O6–H6...O5 ^d	0.77(3)	1.83(3)	2.598(2)	175(3)
N–HN1...O2	0.89(2)	1.99(2)	2.877(2)	170(2)
N–HN1...O1	0.89(2)	2.61(2)	3.102(2)	116(1)
N–HN2...O6	0.92(3)	2.19(3)	2.987(2)	144(2)
N–HN2...O7	0.92(3)	2.19(3)	2.990(2)	145(2)

D = Donor, A = acceptor. Symmetry transformations: a = x, 0.5–y, 0.5+z; b = 1+x, 0.5–y, 0.5+z; c = 1+x, y, z; d = –1–x, 0.5+y, –0.5–z



Scheme 2 Hydrogen bonding situation around HPO_4^{2-} with assignment of the mesomeric structure based on the 'lone pair directionality' and bond length variation.

Further bond distances and angles between non-hydrogen atoms are unremarkable and selected values are listed in Table 2. A related amine phosphate structure has been reported recently, which consists of a polymeric one-dimensional methylpiperazinium cobalt hydrogenphosphate of formula $[\text{C}_5\text{H}_{12}\text{N}_2]^{2+}[\text{Co}(\text{HPO}_4)_2]^{2-}$. There, the tetrahedrally coordinated cobalt atoms are bridged by two phosphate anions. The linear chains are held together by hydrogen bond interactions involving the hydrogen atoms of the amine and the framework oxygen atoms [12].

Table 2 Selected bonds lengths/Å and angles/° in compounds **1** and **2**

	1 (M = Co)	2 (M = Ni)
M–O1	2.0797(12)	2.0441(11)
M–O2	2.0984(13)	2.0695(11)
M–O3	2.0869(12)	2.0570(11)
P–O4	1.5174(12)	1.5195(11)
P–O5	1.5316(12)	1.5334(10)
P–O6	1.5939(13)	1.5948(12)
P–O7	1.5254(13)	1.5259(11)
O1–M–O2	85.66(5)	86.15(5)
O1–M–O3	88.58(5)	88.57(5)
O2–M–O3	89.51(5)	89.00(5)
O1–M–O2 ⁱ	94.34(5)	93.85(5)
O1–M–O3 ⁱ	91.42(5)	91.43(5)
O2–M–O3 ⁱ	90.49(5)	91.00(5)

Symmetry transformation: i = –x, –y, –z

There is clearly a mismatch between the solution composition and the crystallization results in the acidic pH regime. Figure 1–3 demonstrated that the major phosphate species between pH 2 and 6.5 is H_2PO_4^- . The hydrogenphosphate anion, HPO_4^{2-} found as the counteranion in the precipitated crystals reaches only about 30 % of the phosphate anions at pH = 6.5. Further attempts to grow a crystal with a dihydrogenphosphate species have led to the growth of crystals at pH 1 which appear different from those obtained at pH = 3.5 but could not to be characterized by single-crystal X-ray studies (no diffraction).

Attempts to grow crystals with the unprotonated piperazine ligand (and perhaps a phosphate anion PO_4^{3-}) were carried out in the basic region. At pH = 10.5 crystals could be obtained which analyzed as $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ [23] by X-ray powder diffraction [24] (and elemental analysis). In summary, it is evident that the solid-state composition is primarily influenced by the solubility and not by the solution composition.

Experimental

Deionized water was used as the solvent. In the potentiometric titrations analytical grade K_2HPO_4 and piperazine were used as supplied by Merck and Acros, respectively. KCl, KOH, HCl and potassium hydrogen phthalate (KHP, primary standard) were of high purity and used as received from Riedel-de-Haën, Roth, J. T. Baker and Aldrich, respectively. A cobalt salt solution was formed from analytical grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ from Merck. A nickel solution was made with a high purity spectroscopy standard of the dichloride

salt from Fluka. The separate synthesis of H₂piperazinium hydrogenphosphate (see below) facilitated the equimolar reaction with the transition metal.

Metal and hydrogen concentrations of the metal stock solutions were established by weighing the appropriate amount of stock solution (densities determined experimentally) and titrating at various concentrations. Concentration and purity of piperazine and phosphate ligands in solution were assessed by potentiometric titration (see below) of ligand alone. As for metal and ligand titrations, all measurements were triplicate, and completed prior to further investigations. This stage also verified the ligand stability constants (as $\log\beta$ values) found in literature [21]. Initially the total amount (n /mmol) of ligand was verified by calculation using $\log\beta$ values from literature and refining both n_{H} and n_{L} . The new amounts were averaged and the data was re-calculated, this time holding n_{H} and n_{L} constant and refining the $\log\beta$ values. A significant deviation from the literature values ($> \pm 0.04$) prompted further investigation into the ligand before use.

IR spectra were carried out using a Bruker Optic IFS 25 spectrometer as KBr disks. Elemental analysis were done on a VarioEL from Elementaranalysensysteme GmbH. NMR spectra were recorded on a Bruker Avance DPX200 spectrometer (200.1 MHz for ¹H) with calibration against the solvent signal (D₂O 4.87 ppm). X-ray powder diffractograms were collected on a STOE STADIP using Mo-K α radiation, a Ge-monochromator in Debye-Scherrer arrangement and with the samples in glass capillaries on a rotating probe head. A Mettler-Toledo pH meter MP220 was used for pH measurements. The instrument was calibrated using using pH 4.01, 7.00 and 9.00 buffers from Merck.

Potentiometric Titrations

All titrations were carried out with a Metrohm 716DMS Titrimo (1 mL burette) using a Metrohm combined glass electrode with internal Ag/AgCl reference. Titration solutions were held at 25.0 (± 0.1) °C under a positive pressure of argon, to exclude air from the apparatus. The electrode was monitored using pH 4.01, 7.00 and 9.00 buffers from Merck. Calibration was done by titration against a strong acid (HCl) before and after each measurement, in order to calculate E° and $\text{p}K_{\text{w}}$ values. A significant deviation of these values from the normal range (± 1.5 mV; 0.01 within 13.77–13.85) indicates instability of the electrode and these titrations results were not used. KOH concentration was confirmed by titrating pre-dried potassium hydrogen phthalate 5 times.

0.1 mol/L KOH was used in all titrations, with 0.1 mol/L KCl as the inert electrolyte. Titration solutions were generally 50 mL, containing approximately 1 mmol/L ligand and 1 mmol/L metal. Piperazinium phosphate solutions were acidified with HCl (where relevant). 100 increments of the titrant were added slowly (0.030 mL/4min) with constant stirring. Titrations were repeated until at least 3 comparable titration curves were obtained.

Data was collected using Vesuv Datalogger [25], stored in Vesuv Database [25] and manipulated using Microsoft Excel. Calibration information was calculated using the program Titkurve [26]. Speciation plots were compiled using the program SPEX [27]. Raw data (U /mV versus Vol_{OH} /mL) obtained from titrations were imported into the program HYPERQUAD [28] for calculation of stability constants in the form of concentration quotients ($\log\beta$ values, as defined previously). Values calculated using HYPERQUAD for the piperazine phosphate system were confirmed using BEST [29]. All stability constants quoted from experimental results are averages from HYPERQUAD; the errors in parentheses are the deviation in

the averages. pH is defined as $-\log[\text{H}^+]$ and $\text{p}K_{\text{w}}$ was taken as the average of the calibration values. Ligand constants (obtained from the literature [21] and verified as described above) were held constant for calculations involving metal and ligand. Metal and ligand concentrations were verified as above and held constant for the calculations.

The onset of hydroxide precipitation is usually visible in titration curves before becoming apparent in the vessel. Data immediately before and all after precipitation were eliminated from calculations. $\log\beta$ values for metal hydroxide species (from literature [21] and established from own metal titrations) were included in initial calculations to verify whether they would still influence the calculations. Points were eliminated until concentrations of metal hydroxide species were too low to influence the results. Refinement of a heterogeneous system is not possible at this stage. Speciation models were estimated using literature values and chemical knowledge. Constants were then refined by least squared regression minimizing the deviation between model and experimental results.

H₂piperazinium hydrogenphosphate monohydrate, (C₄H₁₂N₂)(HPO₄)·H₂O. Piperazine (5.16 g, 60 mmol) was dissolved in 10 mL of water. To this solution, H₃PO₄ (5 mL, 85 wt%, $d = 1.70$ g/mL, 73.75 mmol) was added dropwise with vigorous stirring. The mixture was heated at 110 °C for 20 h and allowed to crystallize at room temperature. Piperazinium phosphate is obtained as a monohydrate. Yield 8.50 g, 70 %.

Calc. for C₄H₁₅N₂O₅P (202.15): C 23.77, H 7.48, N 13.86. Found C 23.03, H 7.88, N 13.08 %.

¹H NMR (D₂O): δ 3.19 (s, CH₂). IR (major peaks only): 3250 (ν N–H), 1455 (ν P=O), 1630 (ν C–N), 975 (ν P–O) cm^{-1} .

Crystallization at pH = 3.5

Hexaaquanickel(II)-H₂piperazinium-bis(hydrogenphosphate) (2). Ni(NO₃)₂·6H₂O (0.290 g, 1.0 mmol) was dissolved in 12.5 mL of water, the pH was adjusted to 3.5 using 1 M HCl. Piperazinium phosphate (0.202 g, 1.0 mmol) was dissolved in 12.5 mL of water, the pH of the solution was adjusted to 3.5 using 1 M HCl. The two solutions were then mixed together and the resulting mixture was refrigerated at 2 °C. After 7 days light green crystals were obtained. The crystals were collected by filtration and dried in air. Yield 130 mg, 59 % (based on phosphate). The supernatant solution had a pH of 3.1. Single-crystal X-ray diffraction showed the crystals to have the composition [Ni(H₂O)₆]²⁺(C₄H₁₂N₂)²⁺(HPO₄)₂²⁻ identical to the crystals obtained at pH = 6.2. The crystal structure had been solved and fully refined from the collected data set.

Crystallization at pH = 6.2

Hexaaquacobalt(II)-H₂piperazinium-bis(hydrogenphosphate) (1). Co(NO₃)₂·6H₂O (0.291 g, 1.0 mmol) and (C₄H₁₂N₂)(HPO₄)·H₂O (0.202 g, 1.0 mmol) were dissolved in 25 mL of water. The pH of the resulting solution was 6.2. The mixture was stirred at room temperature for 6 h. After 3 days of slow evaporation at room temperature pink crystals had developed. The narrowed solution had a pH of 5.6. The crystals were collected by filtration and dried in air. Yield 210 mg, 94 % (based on phosphate).

Calc. for C₄H₂₆CoN₂O₁₄P₂ (447.14): C 10.74, H 5.86, N 6.27. Found C 11.24, H 5.63, N 6.40 %.

IR (major peaks only): 3500 (br, ν OH), 3037 (ν N–H), 1463 (ν P=O), 956 (ν P–O) cm^{-1} .

Hexaaquanickel(II)-H₂piperazinium-bis(hydrogenphosphate) (2). Ni(NO₃)₂·6H₂O (0.290 g, 1.0 mmol) and (C₄H₁₂N₂)(HPO₄)·H₂O (0.202 g, 1.0 mmol) were dissolved in 25 mL of water. The pH of

Table 3 Crystal data for compounds **1** and **2**

	1	2
Formula	C ₄ H ₂₆ CoN ₂ O ₁₄ P ₂	C ₄ H ₂₆ N ₂ NiO ₁₄ P ₂
<i>M</i>	447.14	446.92
Crystal size/mm	0.5 x 0.5 x 0.5	0.5 x 0.5 x 0.5
Crystal description	block	block
<i>T</i> /K	205(2)	205(2)
θ range/°	2.65–28.26	2.66–28.29
<i>h</i> ; <i>k</i> ; <i>l</i> range	–8, 8; –5, 12; –16, 16	–8, 8; –12, 11; –13, 17
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	6.3046(5)	6.2954(5)
<i>b</i> /Å	9.5916(8)	9.5690(7)
<i>c</i> /Å	12.8135(11)	12.7617(9)
β /°	92.714(2)	92.580(1)
<i>V</i> /Å ³	773.98(11)	767.99(10)
<i>Z</i>	2	2
<i>D</i> /g cm ^{–3}	1.919	1.933
<i>F</i> (000)	466	468
μ /cm ^{–1}	1.392	1.549
Absorption correction	SADABS [32]	SADABS [32]
Max/min transmission	1.000/0.862	1.000/0.822
Measured reflections	4567	4571
Unique reflections (<i>R</i> _{int})	1811 (0.016)	1805 (0.014)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1603	1700
Parameters refined	158	159
Max/min $\Delta\rho$ /e Å ^{–3} a)	0.259/–0.556	0.354/–0.338
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] b)	0.0243/0.0672	0.0207/0.0574
<i>R</i> 1/ <i>wR</i> 2 (all data) b)	0.0279/0.0691	0.0220/0.0580
Goodness-of-fit on <i>F</i> ² c)	1.061	1.071
Weighting scheme <i>w</i> ; <i>a/b</i> d)	0.0424/0.2226	0.0314/0.4445

a) Largest difference peak and hole – b) $R1 = [\Sigma(|F_o| - |F_c|)] / \Sigma F_o$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$ – c) Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ – d) $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$.

the resulting solution was 6.2. The mixture was stirred at room temperature for 6 h. After 3 days of slow evaporation at room temperature light green crystals had developed. The narrowed solution had a pH of 5.5. The crystals were collected by filtration and dried in air. Yield 180 mg, 81 % (based on phosphate).

Calc. for C₄H₂₆N₂NiO₁₄P₂ (446.92): C 10.75, H 5.86, N 6.27. Found C 11.75, H 5.93, N 6.24%.

IR (major peaks only): 3500 (br, νOH), 3055 (νN–H), 1460 (νP=O), 960 (νP–O).

Crystallization at pH = 10.5

Cobaltphosphate octahydrate, Co₃(PO₄)₂·8H₂O. Co(NO₃)₂·6H₂O (0.291 g, 1.0 mmol) was dissolved in 12.5 mL of water, the pH was adjusted to 10.5 using 1 M NaOH. (C₄H₁₂N₂)(HPO₄)·H₂O (0.202 g, 1.0 mmol) was dissolved in 12.5 mL of water, the pH of the solution was adjusted to 10.5 using 1 M NaOH. The two solutions were then mixed together and the resulting mixture was stirred at room temperature for 6 h. After 1 day of slow evaporation at room temperature pink microcrystals were obtained. The narrowed solution had a pH of 10.0. The crystals were collected by filtration and dried in air. Yield 160 mg, 95 % (based on cobalt). X-ray powder diffraction showed the crystals to have the composition Co₃(PO₄)₂·8H₂O.

Calc. for H₁₆Co₃O₁₆P₂ (510.78) C 0.00, H 3.16, N 0.00. Found C 0.00, H 3.31, N 0.00 %.

Structure determinations

Data were collected by the ω -scan method with Mo-*K* α radiation ($\lambda = 0.71073$) and the use of a graphite monochromator on a Bruker AXS CCD diffractometer at a temperature of 205(2) K. Structure solution was done by direct methods (SHELXS-97 [30]);

refinement was done by full-matrix least squares on *F*² using SHELXL-97 [30]. All non-hydrogen atoms were found and refined anisotropically. Hydrogen atoms were found and refined isotropically. Crystal data are given in Table 3. Graphics were obtained with ORTEP3 for Windows [31]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-187994 (**1**) and -187995 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).

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