

Electronic supplement materials for:

New molecular heptanuclear cobalt phosphonates: synthesis, structures and magnetic properties

I. Doroshenko,^{ab} M. Babiak,^{ab} A. Buchholz,^c H. Görls,^c W. Plass,^{c*} J. Pinkas^{ab*}

^a Department of Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, CZ-61137 Brno, Czech Republic.

^b Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5, CZ-62500 Brno, Czech Republic.

^c Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Humboldtstraße 8, 07743 Jena, Germany.

jpinkas@chemi.muni.cz

secr.plass@uni-jena.de

1 Experimental part

1.1 Characterization techniques

IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer with a Bruker Alpha-Platinum ATR system. ICP-OES analyses were done on an ICP-OES spectrometer iCAP 6500 Duo (Thermo, generator 27.12 MHz, amplitude 1.15 kW, plasma gas flow 12 dm³ min⁻¹) emission lines 228.616 and 238.892 nm for Co, 213.618, 214.914 nm for P and 588.995, 589.952 nm for Na were used. Elemental analysis (C, H, and N) was performed on a Flash 2000 CHNS Elemental Analyzer (Thermo Scientific). ESI-MS spectra were measured on an Agilent 6224 Accurate-Mass TOF mass spectrometer (Agilent Technologies, Wilmington, DE, USA) with a dual electrospray ionisation source from a methanol solution. Following parameters were used: nitrogen flow 7 l min⁻¹, gas temperature 325 °C, nebulizer 45 psi, skimmer 65 V, fragmentor 80 V. Solution NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer (400.1 MHz for ¹H and 161.9 MHz for ³¹P). CD₃OD was used as an external lock. The spectra were referenced to the residual proton signal of CHD₂OD (3.33 ppm) while ³¹P spectra were referenced to 85 % H₃PO₄ (0 ppm). Thermogravimetric analysis (TG/DSC) was done on a Netzsch 449C Jupiter apparatus at the temperature range 25–1000 °C with a heating rate of 5 K min⁻¹ under the atmosphere of 90 % of nitrogen and 10 % of synthetic air (70 cm³ min⁻¹). Powder X-ray analysis (PXRD) was performed on a GNR EUROPE XRD 600 diffractometer. Co-K_α radiation ($\lambda = 1.7903 \text{ \AA}$) was used (40 kV, 15 mA). Single crystal X-ray measurements for the compound **1**·nH₂O was carried out on a Nonius KappaCCD diffractometer. The intensity data for compounds **1**·nMeOH and **2** were collected on a Rigaku diffraction system (MicroMax007HF DW rotating anode source with multilayer optic, partial χ axis goniometer, Saturn 724+ HG detector and Cryostream cooling device). The Mo-K_α radiation was used in both cases. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[1, 2, 3] *CrystalClear* (Rigaku 2014) and *CrysAlisPro* (Agilent Technologies 2013) software packages were used for data collection and data reduction of **1**·nMeOH and **2**. The structures were solved using *SHELXT*[5] program and refined (full matrix least-squares refinement on F_o^2) using *SHELXL*[4] program. The hydrogen atoms bonded to the water molecules O4W to O6W (**1**·nH₂O) and to the hydroxy-groups of O1_1 and O1_3 (**1**·nSolv) were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically. Magnetic measurements were performed for ground polycrystalline sample using a Quantum Design MPMS-5 SQUID magnetometer. The magnetic susceptibilities were measured at an applied field of 1000 and 2000 Oe in the temperature range of 2 to 300 K. The magnetization measurements up to 5 T were performed at different temperatures (2–5 K). The collected data were corrected for the diamagnetism of the sample holder as well as the capsula and the diamagnetic contribution of the ligand.

2 Synthetic procedures

2.1 Ligand

2.1.1 NaH₂SAA.

Salicylaldehyde (6.78 cm³, 64.0 mmol) was added to a boiling and stirred solution of H₂AIPA (2.50 g, 16.0 mmol) and NaOH (0.637 g, 16.0 mmol) in methanol (50 cm³). The color of the solution immediately changed to bright yellow. In several minutes the solution became clear yellow and then it was boiled under reflux for 3 h. An oily mass was obtained after complete evaporation of methanol. Excess salicylaldehyde and residual solvent were removed at 85 °C under vacuum (7.5 10⁻⁴ Torr) during 2 d. 4.040 g of a dry product was obtained. $M_r(\text{C}_{10}\text{H}_{13}\text{NNaO}_4\text{P} \cdot 0.58\text{MeOH}) = 283.94 \text{ g mol}^{-1}$. Yield is 88.9 %.

Elemental analysis (ICP-OES, calc. for C₁₀H₁₃NNaO₄P·0.58MeOH / found): Na 8.09/7.78; P 10.90/11.37 %.

IR (cm⁻¹): ν 2990 vw, 2973 vw, 2870 vw, 1635 s, 1611 vs, 1528 s, 1504 m, 1470 m, 1394 w, 1298 w, 1202 vs, 1188 vs, 1147 s, 1116 s, 1081 s, 1054 m, 1012 m, 923 s, 909 vs, 847 m, 834 m, 765 s, 737 s, 682 m, 610 m, 552 vs, 527 vs, 493 w, 472 m, 441 vs.

¹H NMR (400.1 MHz, CD₃OD, ppm): δ 1.62 (d, J = 13.0 Hz, 6H), 6.68 (m, J = 7.5 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 7.26–7.35 (m, 2H), 8.51 (d, J = 3.05 Hz, 1H).

³¹P NMR (161.9 MHz, CD₃OD, ppm): δ 18.44 (sept, J = 12.1 Hz, 1P).

ESI-MS (+) (APCI): m/z 266.05 [C₁₀H₁₃NO₄PNa + H]⁺, 100 %; 509.12 [C₂₀H₂₇N₂O₈P₂Na + H]⁺, 40 %.

ESI-MS (-): m/z 242.06 [C₁₀H₁₄NO₄P - H]⁻, 40 %; 485.12 [C₂₀H₂₈N₂O₈P₂ - H]⁻, 100 %.

2.1.2 Na₂HSAA.

Into the boiling and stirred suspension of H₂AIPA (2.50 g, 16.0 mmol) and NaOH (1.273 g, 32.0 mmol) in ethanol (50 cm³) salicylaldehyde (3.88 cm³, 32.0 mmol) was added. The suspension immediately became bright yellow. After several minutes a bright yellow precipitate began to form. The formed mixture was boiled and stirred under reflux for 3 h. The yellow precipitate was filtered off, washed by ethanol and dried under vacuum (7.5 10⁻⁴ Torr) at 80 °C for 1 d. 4.136 g of dry Na₂HSAA · 0.5 EtOH · 2 H₂O was isolated M_r (C₁₀H₁₂NNa₂O₄P · 2 H₂O · 0.5 EtOH) = 346.23 g mol⁻¹. Yield 74.0 %. A small part of the obtained ligand was recrystallized from methanol. Transparent yellow needle-like crystals were obtained. Molecular structure was solved from the single crystal X-ray diffraction data.

Elemental analysis (ICP-OES, calc. for C₁₀H₁₂NNa₂O₄P · 2 H₂O · 0.5 EtOH / found): Na 13.28/13.01; P 8.94/9.23 %.

IR (cm⁻¹): ν 2969 w, 2908 w, 2867 w, 1640 s, 1616 m, 1558 vw, 1524 m, 1494 m, 1470 w, 1385 w, 1304 w, 1246 w, 1209 m, 1192 m, 1141 m, 1124 s, 1094 vs, 1050 s, 1019 m, 968 vs, 901 w, 863 vw, 836 w, 768 m, 738 s, 690 m, 612 m, 558 s, 528 s, 497 w, 456 m.

¹H NMR (400.1 MHz, CD₃OD, ppm): δ 1.20 (t, J = 7.0 Hz, -CH₃ of EtOH), 1.64 (d, J = 11.3 Hz, 6H), 3.63 (q, J = 7.0 Hz, -CH₂- of EtOH), 6.48–6.52 (m, 1H), 6.68 (d, J = 8.5 Hz, 1H), 7.24–7.29 (m, 2H), 8.49 (d, J = 2.1 Hz, 1H).

³¹P NMR (161.9 MHz, CD₃OD, ppm): δ 16.03–16.29 (sept, J = 12.1 Hz, 1P).

ESI-MS (+): m/z 288.10 [C₁₀H₁₂NO₄PNa₂ + H]⁺, 100 %; 310.10 [C₁₀H₁₁NO₄PNa₃ + H]⁺, 30 %.

ESI-MS (-): m/z 242.2 [C₁₀H₁₄NO₄P - H]⁻, 100 %.

2.2 Complexes

2.2.1 [Co₇(SAA)₂(HSAA)₄] · nH₂O (1 · nH₂O).

A solution of NaH₂SAA · 0.58 MeOH (0.283 g, 1.00 mmol) in methanol (15 cm³) was added to a solution of CoCl₂ · 6 H₂O (0.118 g, 0.500 mmol) in methanol (15 cm³). A dark violet clear solution was formed. After several days, due to the hydrolysis of NaH₂SAA, white spherulites of H₂AIPA · nSolv (0.057 g) (confirmed by IR spectroscopy and ICP-OES analysis) were formed. Subsequently, dark violet crystals of **1** grew on the spherulites within several weeks. We were not able to quantitatively separate the crystals of complex **1** from spherulites but several of them were suitable for the single crystal X-ray diffraction experiment.

IR (cm⁻¹): ν 3159 m, 2983 m, 1628 s, 1604 vs, 1539 m, 1470 m, 1446 s, 1394 m, 1380 m, 1349 w, 1325 w, 1270 w, 1250 w, 1215 w, 1171 m, 1143 vs, 1098 vs, 1054 vs, 1040 vs, 971 vs, 902 s, 851 m, 803 w, 761 vs, 706 vs, 631 vs, 582 s, 545 s, 455 s.

3 Figures SI:

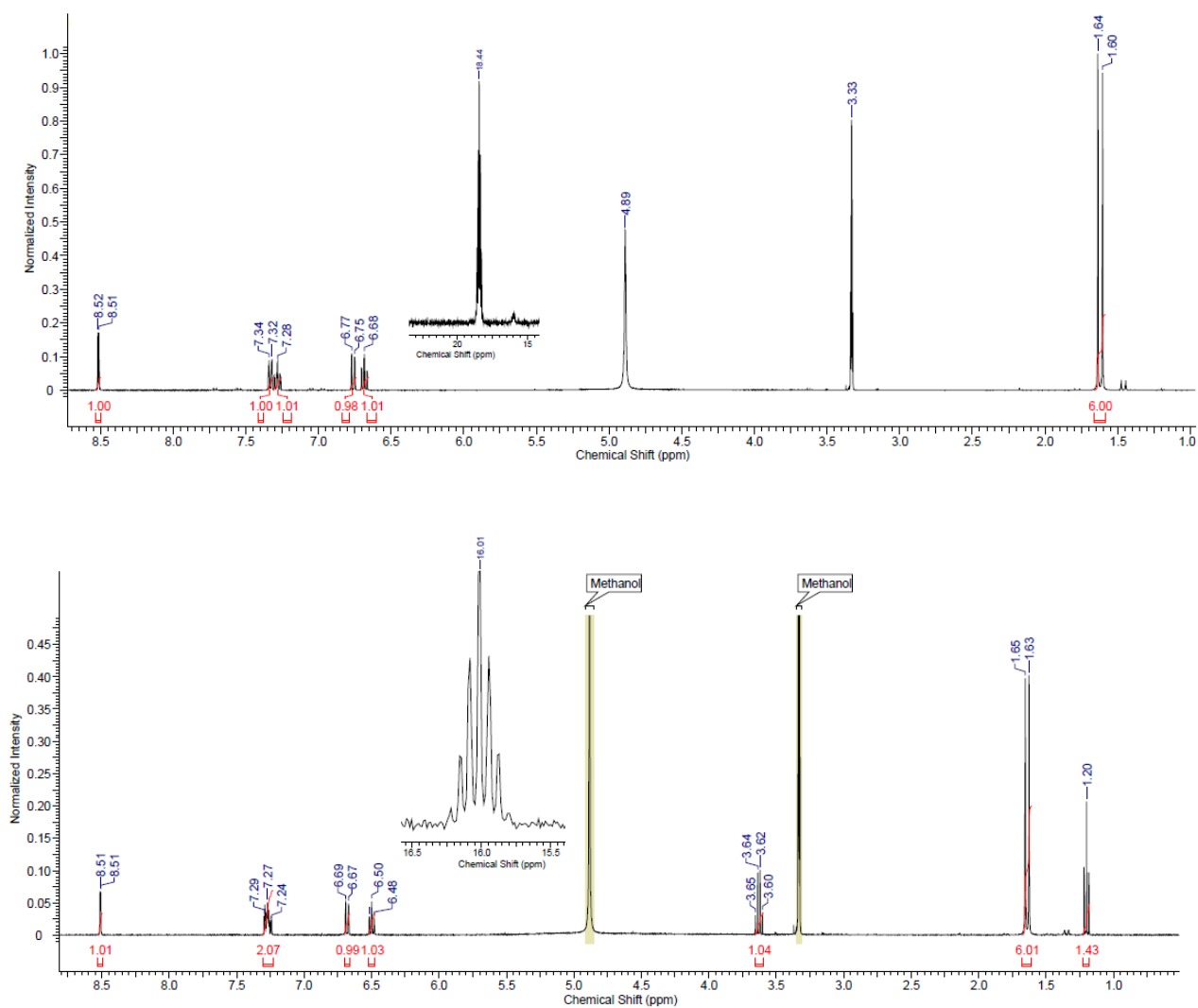


Figure S1: ^1H NMR and ^{31}P NMR (insets) spectra of $\text{NaH}_2\text{SAA} \cdot 0.58\text{MeOH}$ (top) and $\text{Na}_2\text{HSAA} \cdot 0.5\text{EtOH} \cdot 2\text{H}_2\text{O}$ (bottom).

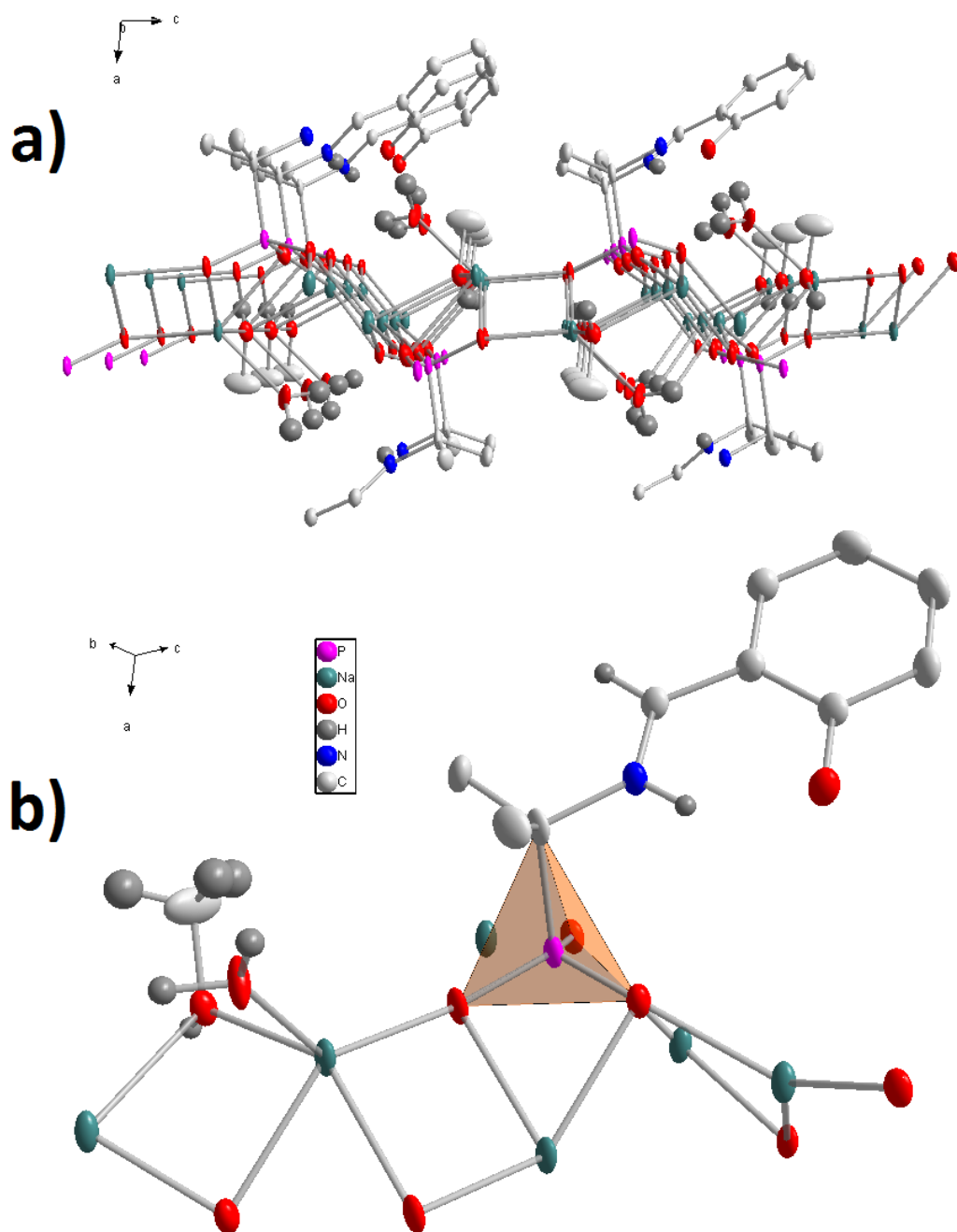


Figure S2: Crystal structure of $\text{Na}_2\text{HSAA} \cdot \text{MeOH} \cdot \text{H}_2\text{O}$ recrystallized from methanol. Projection of layer (a), and a single molecular unit with the neighboring atoms (b). Oxygen (red), phosphorus (pink), nitrogen (dark blue), hydrogen (dark grey), carbon (grey), sodium (green). All the hydrogen atoms except water and methanol molecules, imino-, methylen-hydrogens were omitted for the sake of clarity (b). Phosphorus polyhedron is depicted for the sake of clarity (b). Thermal ellipsoids are drawn at the 50 % probability level.

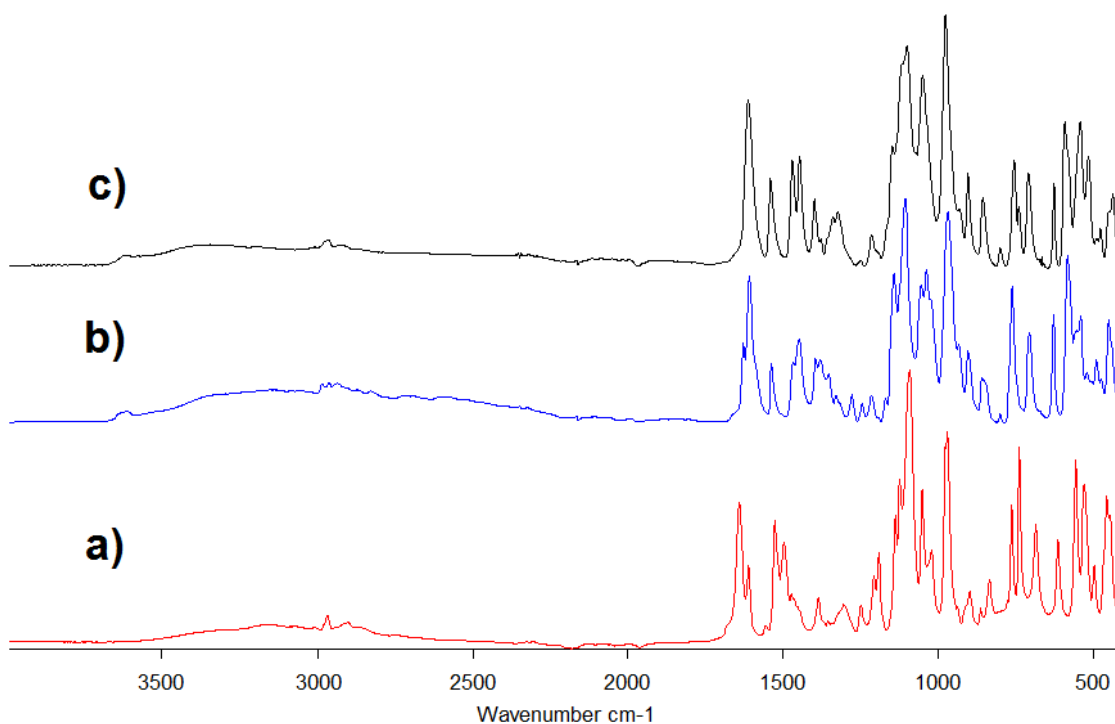


Figure S3: The comparison of IR spectra of Na₂HSAA (a) and complexes [Co₇(SAA)₂(HSAA)₄] (**1**) (b), [Co₇(SAA)₂(NaSAA)₄] (**2**) (c).

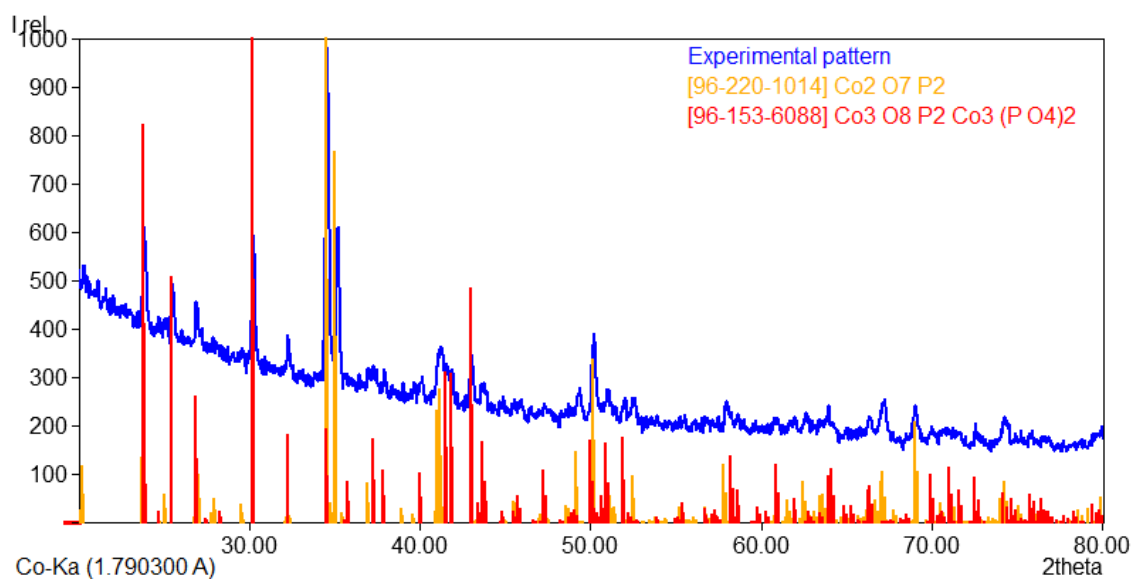


Figure S4: X-ray powder diffractogram of a sample of **2** calcined at 1000 °C compared with the calculated patterns for Co₃(PO₄)₂ (COD: 96-153-6088) and Co₂P₂O₇ (COD: 96-220-1014).

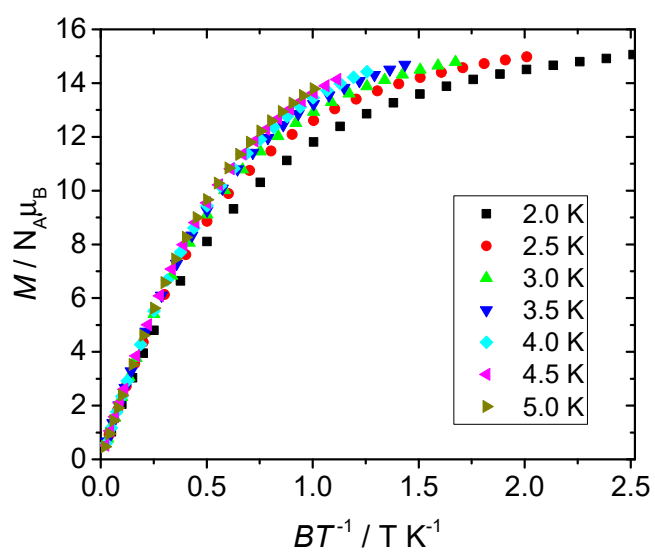
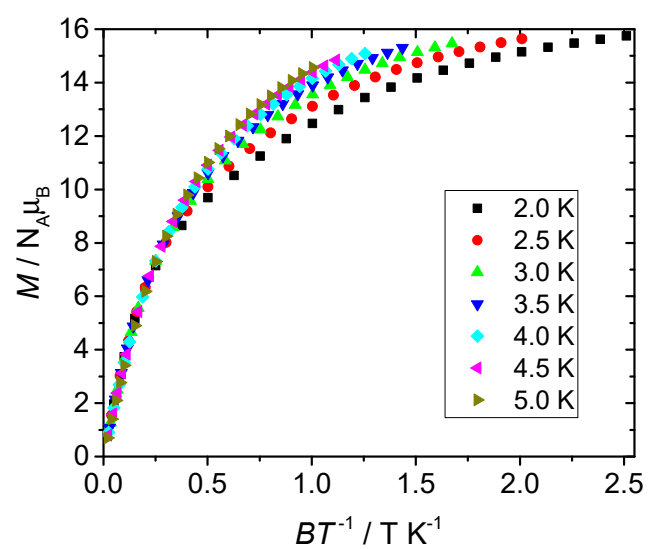


Figure S5: Magnetization M vs. B/T plots at different temperatures for complexes **2** (top) and **3** (bottom).

References

- [1] R Hooft and BV Nonius. Collect data collection and processing user interface. *Collect: Data collection software, Nonius BV, Delft*, 1998.
- [2] Zbyszek Otwinowski and Wladek Minor. Processing of x-ray diffraction data collected in oscillation mode. *Methods Enzymol.*, 276:307–326, 1997.
- [3] George M Sheldrick. Sadabs-bruker nonius scaling and absorption correction, v 2.10. *Bruker AXS Inc., Madison, Wisconsin, USA*, 2003.
- [4] George M Sheldrick. Crystal structure refinement with shelxl. *Acta Crystallogr. Sect. C: Struct. Chem.*, 71(1):3–8, 2015.
- [5] George M Sheldrick. Shelxt–integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A: Found. Adv.*, 71(1):3–8, 2015.