J Chem Crystallogr (2015) 45:369–375
DOI 10.1007/s10870-015-0603-1

ORIGINAL PAPER

Synthesis, Crystal Structure and Characterization of a 2D-Hybrid Cobalt Hypophosphite

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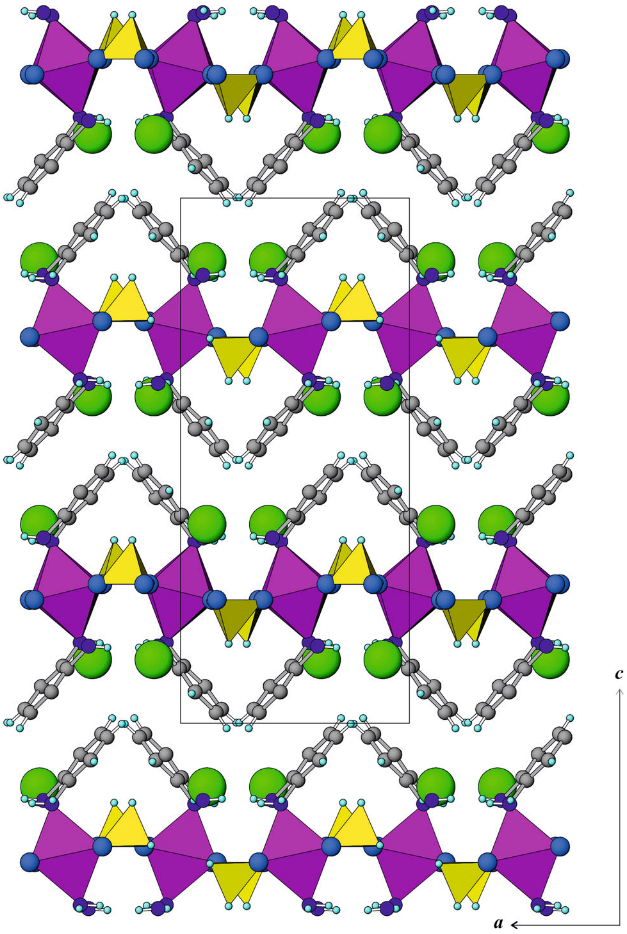
Received: 30 June 2015 / Accepted: 11 July 2015 / Published online: 21 July 2015

Abstract A new two-dimensional inorganic–organic hybrid *ortho*-phenylenediamine cobalt hypophosphite chloride, $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$, has been prepared by slow evaporation from an aqueous solution. It was investigated by means of single-crystal X-ray diffraction, infrared spectroscopy and thermal analysis. The title compound crystallise in orthorhombic space group *Pbcn*, with unit cell parameters at 298(1) K of $a = 9.5538(19)$ Å, $b = 9.1466(18)$ Å, $c = 21.9222(4)$ Å, $V = 1915.7(7)$ Å^3, $Z = 2$. Its structure is characterised by inorganic layers parallel to (001) of alternating CoO_4N_2 octahedra and H_2PO_2 tetrahedra establishing eight-membered ring cavities. This mixed-polyhedral motive is decorated with the *ortho*-phenylenediamine ligands towards the inter-layer region thus forming a cationic organic–inorganic hybrid layer charge compensated by the chlorine anions. Infrared spectroscopy revealed absorption bands corresponding to the *ortho*-phenylenediamine molecule and the hypophosphite anion. The compound was proven to be stable up to 474 K under N_2 atmosphere.

Graphical Abstract A new two-dimensional inorganic–organic hybrid *ortho*-phenylenediamine cobalt hypophosphite chloride, $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$, has been prepared by slow evaporation from an aqueous solution and characterized by means of single-crystal X-ray diffraction, infrared spectroscopy and thermal analysis.



Keywords $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ · Crystal growth · Crystal structure · Thermal analysis · Infrared spectroscopy

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Introduction

During the last few years, several metal hypophosphite compounds have been reported in the literature, incorporating alkali and alkali earth metals, transition metals and lanthanides [1–7]. This class of materials is widely studied in both chemistry and material science due to their industrial applications as mild reducing agents, reagents in catalytic syntheses and antioxidants [8, 9]. However, in literature only few classes of hybrid hypophosphite materials result form an interaction of transition metals with amine groups, either as ligands or directing structure agents are known [10–12]. In the complex $[Cu_2(H_2PO_2)_2(\mathrm{bipyridine})_2](NO_3)_2$ [10] discrete pairs of $[Cu(H_2PO_2)(\mathrm{bipyridine})]$ subunits are linked by the hypophosphite ligands to form a divalent cation. The complex $[Cu_2(H_2PO_2)_2(\mathrm{phenantroline})_2](NO_3)_2$ [11] adopts a similar structural arrangement to that of $[Cu_2(H_2PO_2)_2(\mathrm{bipyridine})_2](NO_3)_2$ and the copper(II) hypophosphite $[Cu(H_2PO_2)_2(\mathrm{urea})]$ [12]. In the present work we report synthesis, crystal structure, infrared spectra and some thermal properties of a new inorganic–organic hybrid *ortho*-phenylenediamine cobalt hypophosphite chloride $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$.

Experimental

Synthesis

The title compound is synthesized at room temperature by dissolving 410 mg of cobalt chloride (prolabo) in an aqueous solution (6 mL H_2O, 310 mg of H_3PO_2) of hypophosphorous acid (30–32 %; sd Fine-Chem Limited). To the resulting solution 120 mg of *ortho*-phenylenediamine (prolabo) was added under continuous stirring. The mixture was allowed to concentrate at ambient conditions for 3 days and the investigated sample material was filtered off and washed with acetone. $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ crystallizes as pink crystals of prismatic shape with average dimensions 30 × 50 × 60 µm.

Infrared Spectroscopy and Thermal Analysis

Infrared spectrum of the title compound was recorded on a VERTEX 70 FTIR Spectrometer, in the range 4000–400 cm^{-1}, using the ATR Technique.

For characterization of the thermal properties of $Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ 16.96 mg of carefully grinded sample material were loaded to 70 µL Al_2O_3 crucibles covered with an open lid. The measurements were performed on a Mettler-Toledo TGA/SDTA851 thermo balance from 298 to 1373 K with a heating rate of 10 K min^{-1} and N_2 flow of 25 mL min^{-1} as purge gas (Messer 5.0) at the Department of Mineralogy and Crystallography, University of Vienna. Prior to evaluation, data were corrected by blind curves measured before and after the sample measurement. For evaluation the Mettler-Toledo STAR^e software was used.

Table 1 Crystal data, data collection and refinement details for $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$

Crystal data	
Chemical formula	$[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$
Temperature	298(1) K
Formula weight, M_r (g/mol)	563.94
Space group (No.) Z	*Pbcn* (60), 2
a (Å)	9.5538(19)
b (Å)	9.1466(18)
c (Å)	21.922(4)
V (Å^3)	1915.7(7)
F (000), ρ_{calc} (g/cm^3)	972, 1.651
Absorption coefficient, μ (mm^{-1})	1.376
T_{min}/T_{max}	0.922/0.960
Crystal size (mm^3)	0.03 × 0.05 × 0.06
Data collection	
Crystal-detector distance (mm)	35
Frame rotation width (°)	2
Total no. of frames	536
Collection time per frame (s)	250
h, k, l ranges	−13/+ 12, −11/+ 12, ± 30
Absorption correction	Multi-scan
Reflections collected/unique	2568/1758
Observed reflections [$I > 2\ \sigma(I)$]	2568
R_{int}	0.0855
Collection mode, $2\theta_{max}$ (°)	Complete sphere; 60
Refinement	
Extinction coefficient, k^a	0.0003(3)
Refined parameters	138
R-indices [$I > 4\ \sigma(I)$]	$R_1 = 0.0629$ $wR_2 = 0.1113$
R-indices (all data)	$R_1 = 0.1069$ $wR_2 = 0.1225$
Goodness-of-fit, S	1.184
$(\Delta/\sigma)_{max}$	0.001
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e$^-$Å^{-3})	0.537; −1.066
a, b^b	0.0275, 6.2327

[a] $F_c^* = kF_c[1 + 0.001 \times F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

[b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$

Table 2 Bond distances (Å) and angles (°) for $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$

Co–O2	2.053(3) × 2		
Co–O1	2.123(3) × 2	C6–C1	1.382(6)
Co–N1	2.196(4) × 2	C6–C5	1.387(6)
		C3–C2	1.378(6)
P–O2	1.488(3)	C3–C4	1.382(6)
P–O1	1.507(3)	C4–C5	1.384(6)
		C1–C2	1.390(5)
N1–C1	1.422(5)		
N2–C2	1.465(5)	O2–P–O1	114.26(19)
		P–O1–Co	140.30(18)
O2–Co–O2	97.9(2)	P–O2–Co	153.3(2)
O2–Co–O1	91.34(12)	C1–N1–Co	120.8(3)
O2–Co–O1	170.66(13)		
O2–Co–O1	91.34(12)	C6–C1–C2	118.2(4)
O1–Co–O1	79.42(16)	C3–C2–C1	121.9(4)
O2–Co–N1	86.05(13)	C2–C3–C4	119.2(4)
O2–Co–N1	91.33(14)	C3–C4–C5	119.9(4)
O1–Co–N1	90.41(13)	C4–C5–C6	120.3(4)
O1–Co–N1	92.65(12)	C1–C6–C5	120.5(4)
O2–Co–N1	91.33(14)	C6–C1–N1	121.5(3)
O2–Co–N1	86.05(13)	C2–C1–N1	120.3(4)
O1–Co–N1	92.65(12)	C3–C2–N2	120.1(4)
O1–Co–N1	90.41(13)	C1–C2–N2	118.0(4)
N1–Co–N1	176.02(19)		

Hydrogen bond geometry

Donor (D)	H-atom	Acceptor(A)	D–H	H···A	D–H···A	D···A
N1	H11	Cl	0.843	2.56(5)	164(5)	3.384
N1	H12	Cl	0.82(5)	2.61(5)	163(4)	3.418(4)
N2	H21	Cl	0.84(5)	2.33(5)	166(5)	3.153(5)
N2	H22	Cl	0.84(5)	2.35(5)	175(4)	3.162(4)

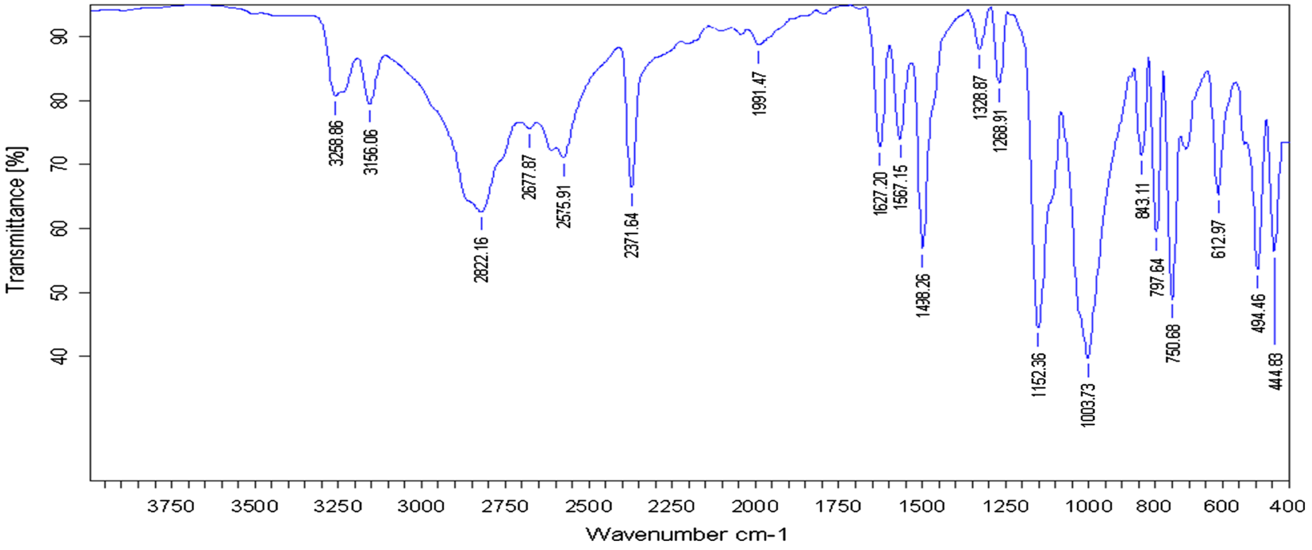

Fig. 1 IR absorption spectrum of $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$

Table 3 IR band assignment for $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$

Wavenumber (cm^{-1})	Assignment
3258, 3156	NH_2 stretching
1627, 1567	NH_2 bending
1328, 1268	C–N stretching
2371	PH_2 stretching
1152, 797	PH_2 bending
1003	PO_2 stretching
444, 495	PO_2 bending
2822, 2677, 2575	C–H stretching
1498	C=C stretching

X-ray Diffractometry and Crystal Structure Solution

A single crystal of $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ was studied on a Bruker X8 Kappa APEX II CCD diffractometer, equipped with a monocapillary optics collimator and graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at the Department of Mineralogy and Crystallography, University of Vienna. Single-crystal X-ray diffraction data were collected at ambient conditions, integrated and corrected for Lorentz and polarization factors and absorption corrected by scaling of partial multiscans. The intensity data were processed with the Bruker-Nonius programme suite SAINT-Plus. [13]. An orthorhombic unit cell with a primitive Bravais type and space-group symmetry *Pbcn* were derived from the extinction rules and intensity statistics, both confirmed by the consecutive structure refinement. The crystal structure was solved by direct methods and refined with SHELXL-97 [14] and WinGX [15]. Anisotropic displacement parameters were allowed to vary for all non-hydrogen atoms. All H atoms were located in a difference Fourier map and with exception of the H atoms of the phenylene group, their isotropic displacement parameters as well as the coordinates were allowed to vary. The hydrogen atoms (H3-6) bonded to the phenylene C atoms (C3-6) were located at geometrically calculated positions and refined using the riding model [C–H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C)$.

Relevant information on crystal data, data collection, and refinements are compiled in Table 1. Details of the

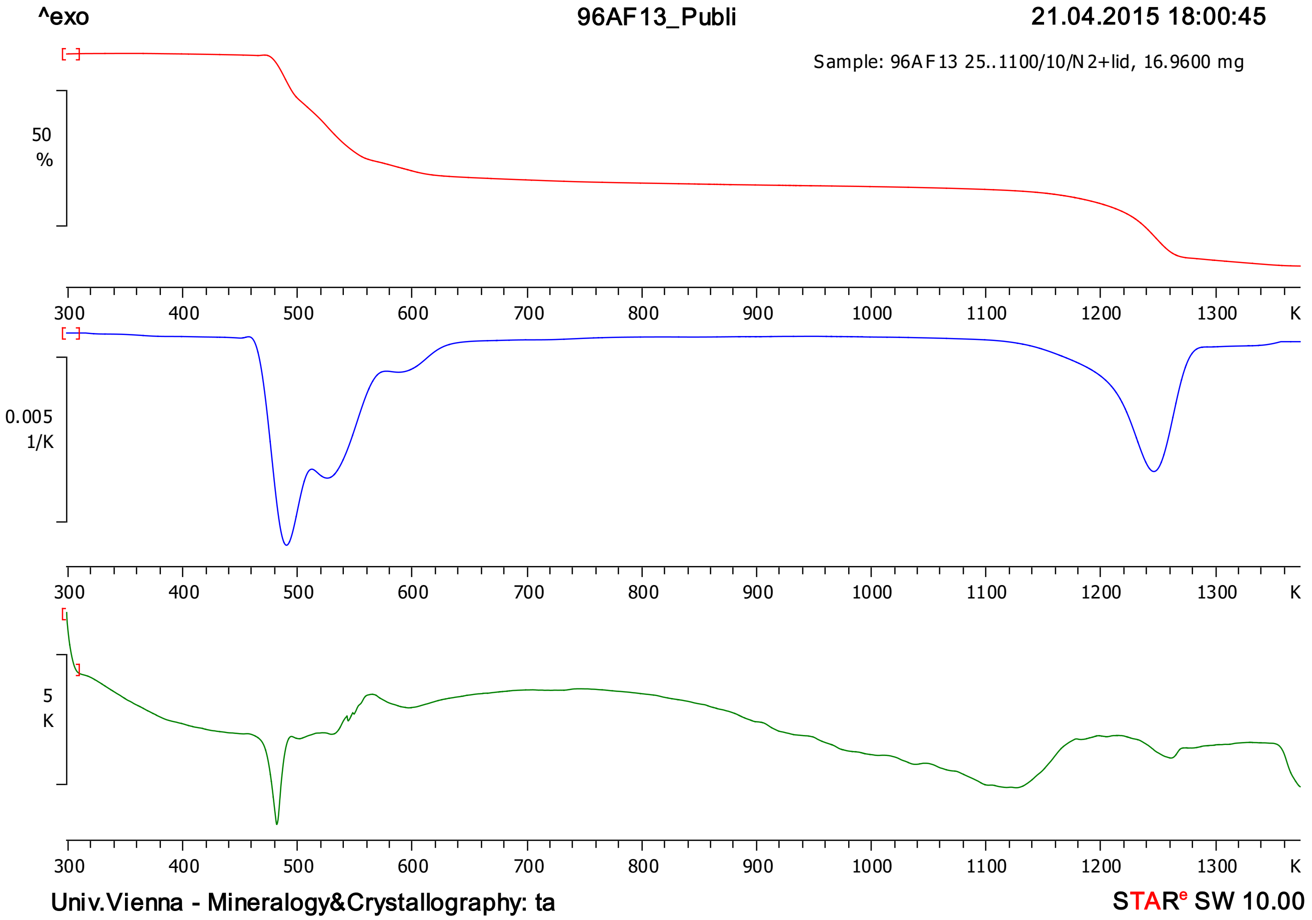

Fig. 2 Thermal analysis of $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ with TG (*red*), DTG (*blue*) and SDTA (*green*) signals from top to bottom, respectively (Color figure online)

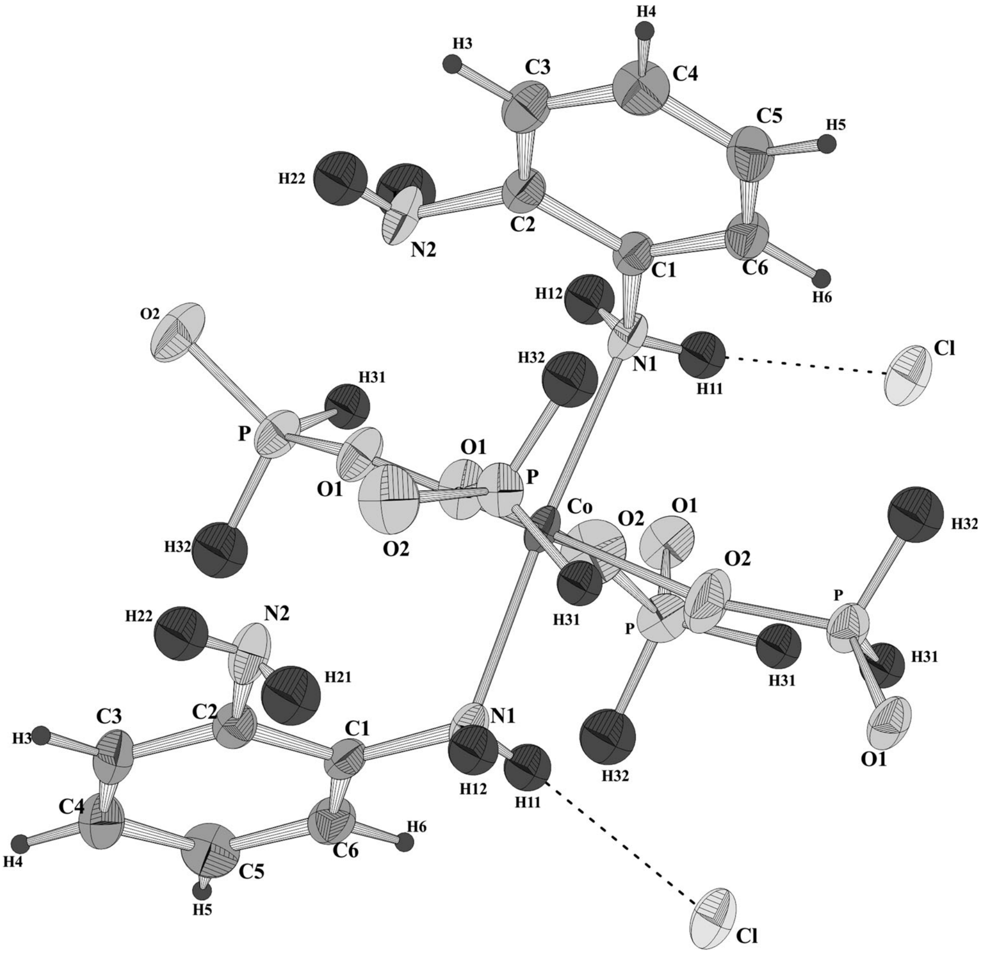

Fig. 3 Displacement ellipsoid plot (50 % probability) of $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$, showing the atomic numbering scheme and coordination around the Co atom

structure refinements (anisotropic displacement parameters, a complete list of distances and angles, *F*o/*F*c-list) may be obtained from Cambridge Crystallographic Datacenter, 12 Union Road, Cambridge, CB2 1EZ, United Kingdom, on quoting the registry number CCDC 1409376, the name of the author and this journal. Selected bond lengths and angles are presented in Table 2. All drawings were plotted using ATOMS [16].

Results and Discussion

Spectroscopy

The infrared spectrum of $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ (Fig. 1) shows bands corresponding to the vibrations of the *ortho*-phenylenediamine molecule and the hypophosphite anion. Table 3 reports the band assignments for the IR spectrum. The characteristic band at 2371 cm^{-1} is assignable to the P–H stretching vibration. The bands at 1152 and 797 cm^{-1} are due to the bending vibration of the PH_2 group. The vibrational bands, which appear at 1003, 495 and 444 cm^{-1}, are assigned to the vibrations for PO_2 group. The presence of *ortho*-phenylenediamine molecule is signalled with absorption bands in the range of 3258–3156 and 1627–1567 cm^{-1} that are due to the stretching and bending vibration of the NH_2 group, respectively. The bands at 1328 and 1268 cm^{-1} are assigned to the C–N stretching vibration. The bands observed at 2822, 2677 and 2575 cm^{-1} corresponding to the C–H stretching vibration and the band that appears at 1498 cm^{-1} is due to the ring stretching vibration.

Thermal Analysis

The results of the thermal analyses, themogravimetry (TG) with first derivative (DTG) and difference thermal signal (SDTA) are plotted in Fig. 2. The TG analysis of $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ shows two steps of weight loss in a total of −77.6 wt% in the measured temperature range. The first weight loss of −45.1 wt% (onset: 474 K, endset: 615 K) correspond to the decomposition of the *ortho*-pheneledіamine molecule (calculated: −45.6 wt%). As one can expect the disintegration of the organic content follows

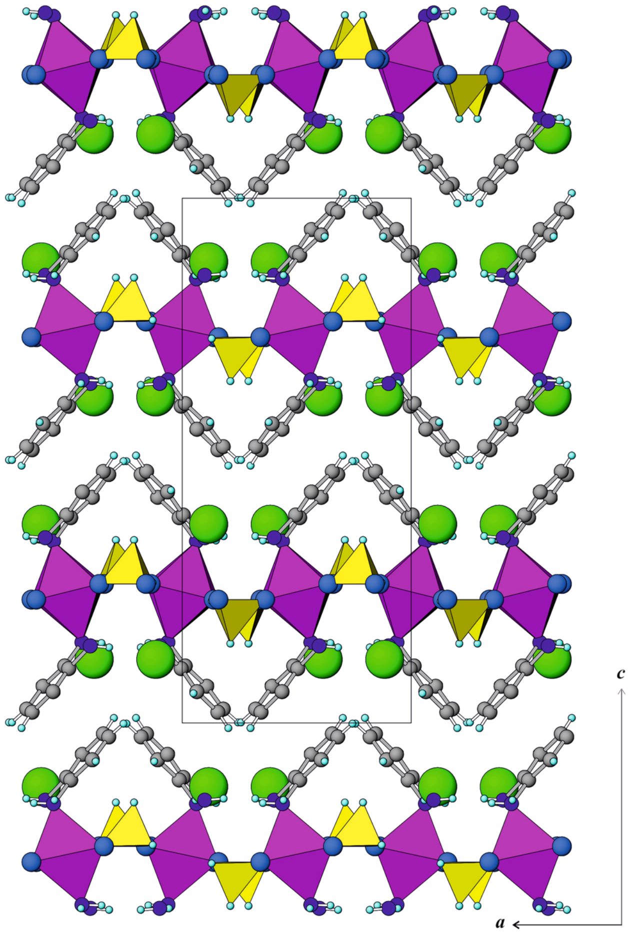

Fig. 4 View of the crystal structure $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ along the *b* axis, showing the inorganic layers parallel (001) and the parallel (102) oriented *ortho*-phenylenediamine groups. The *pink* and *yellow* polyhedral represent CoO_4N_2 octahedra and H_2PO_2 tetrahedra, respectively, *green* spheres the chlorine anions (Color figure online)

a discontinuous, three-step process. According to the DTG and SDTA data this pyrolytic reaction is characterized by two endothermic and one exothermic signal. The weight loss of −32.5 wt% in the range of 1100–1300 K can be attributed to the final degradation of the 2D inorganic framework and the elimination of the chlorine content, which leads to the release of phosphine PH_3 and hydrogen chloride HCl, respectively (calculated: −30.1 wt%). In the SDTA curve this thermal decomposition is documented a predominantly exothermal reaction.

Description of Crystal Structure

The asymmetric unit of the $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ is composed of an CoO_4N_2 octahedron, one H_2PO_2 pseudo-tetrahedron, Cl^- ions and one *ortho*-phenylenediamine ligand (Fig. 3). Co atom lies on the special position and adopt .2. point-symmetry. It is octahedrally coordinated to four oxygens from four hypophosphite groups forming its base, and two nitrogen atoms at its apices from the two *ortho*-phenylenediamine molecules. The Co–O (or N) bond lengths vary from 2.053(3) to 2.196(4) Å, and the average <Co–O (N)> bond length is 2.124 Å. The Co–N distance is 2.196(4) Å, with an N1–Co–N1 angle of 176.02(19)°. These distance and angle are similar to those found in $[Co(OH)(py)_3][Co(py)_2[HPO_2(OH)_3]$ [17] for the two symmetrically distinct Co atoms. The Co–O2 and Co–O1 distances are 2.053(3) and 2.123(3) Å, respectively. The square planar arrangement around the Co atom is slightly distorted, with O1–Co–O2 angles of 170.66(13)° (Table 2). According to the formula $\Delta_{oct} = 1/6\ \Sigma[(d_i\text{-}d_m)/d_m]^2$ [18, 19] the bond-length distortions for the Co atom amount 4.532×10^{-3} and indicate only moderate distortions. These results relate well with the values compiled by Wildner [20] for CoO_6 octahedra in reliable determined crystal structures, who found 672 Co–O bond lengths between 1.959 and 2.517 Å. The average <Co–O> bond lengths for 112 polyhedra are in the range of 2.054–2.182 Å; the overall mean value is 2.112 Å.

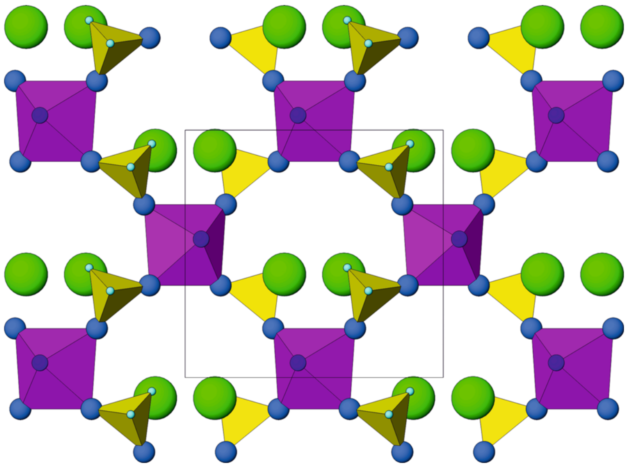

Fig. 5 Neutral layer in $[Co(H_2PO_2)(C_{12}N_4H_{16})]Cl_2$ viewed along [001] direction. The *pink* and *yellow* polyhedral represent CoO_4N_2 and H_2PO_2 polyhedra, respectively. The *dark blue* and *grey circles* represent the N and C, atoms, respectively, and the *green circles* represent the Cl atom (Color figure online)

The phosphorus atom have site symmetry 1 and share two oxygen atoms with adjacent Co atoms and two further ligands being terminal P–H bonds, which are confirmed with a band at 2731 cm^{-1} in the infrared spectrum. The P–O bond distances are in the range from 1.488(3) to 1.507(3) Å (Table 2), with O1–P–O2 angle of 114.26(19) °, and P–H31/H32 bond distances of 1.30(4) and 1.39(4) Å, respectively. These stereochemical findings are very close to that in $[Cu_2(H_2PO_2)_2(C_{10}H_8N_2)_2](NO_3)_2$ [10], $[Cu_2(H_2PO_2)_2(C_{12}H_8N_2)_2](NO_3)_2$ [11] and the different polymorphs of $Cu(H_2PO_2)_2$ [5], $Fe(H_2PO_2)_3$ [6], $(C_6H_5NH_3)[ZnCl(HPO_3)]$ [21] and $Zn_2(HPO_3)_2 0.5(C_{10}H_{28}N_4)$ [22].

The CoO_4N_2 and H_2PO_2 polyhedra are linked to each other via the O1/2 oxygen atoms, establishing a two dimensional network formed by 8-membered rings (Fig. 5). The *ortho*-phenylenediamine groups coordinate to Co atom and spread away from the sheet into the inter-layer region almost parallel (102) (Fig. 4) leading to a cationic organic–inorganic hybrid layer, which is charge compensated by chloride anions. This framework motive of an inorganic layer sandwiched by organic ligands is comparable to the crystal structure of $Zn(C_8H_{17}NH_2)(HPO_3)$ wherein the ZnO_3N and HPO_3 polyhedra connect each other to form a sheet-type network with 4.8^2 membered rings and the neutral tert-octylamine molecules coordinate to Zn atoms as ligand groups [23].

Conclusion

The 2D-hybrid Cobalt Hypophosphite with *ortho*-phenylenediamine as a ligand has been synthesized by slow evaporation at the room temperature. Its framework is build up of CoO_4N_2 and H_2PO_2 polyhedra which are linked to each other via their vertex oxygen atoms, establishing a two dimensional inorganic network formed by 8-membered rings. The *ortho*-phenylenediamine groups are coordinated to Co atom, leading to a cationic organic–inorganic hybrid layer, which is charge compensated by chloride anions. TG analysis shows that at 475 K, *ortho*-phenylenediamine groups are decomposed under nitrogen atmosphere. According to the DTG and SDTA this decomposition is characterized by two endothermic and one exothermic signal. In the range of 1100–1300 K, the 2D inorganic framework decomposes and the chlorine content is eliminated.

Supporting Information

Supplementary tables of the crystal structures and refinements, notably the full list of bond lengths and angles, and the anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. CCDC 1409376. Copies of this information may be obtained free of charge from deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

Acknowledgments The authors from Morocco would like to acknowledge the support and technical assistance of Interface Regional University Center (University Sidi Mohammed Ben Abdellah, Fez), and National Center for Scientific and Technical Research (CNRST-Rabat). T. Đorđević acknowledges financial support of the Austrian Science Foundation (FWF) (Grant No. V203-N19). The authors are thankful to Prof. Dr. Gerald Giester for assisting during the single-crystal X-ray measurement.

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