Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 174 (2003) 116–124
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Divalent transition metal phosphonates with new structure containing hydrogen-bonded layers of phosphonate anions

Jin Yang, Jian-Fang Ma,* Guo-Li Zheng, Li Li, Fang-Fang Li, Yong-Mei Zhang, and Jing-Fu Liu

Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

Received 5 December 2002; received in revised form 20 March 2003; accepted 31 March 2003

Abstract

A series of divalent transition metal phosphonates containing hydrogen-bonded layers of phosphonate anions, namely $[M(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ [M=Co(1), Ni(2), Cu(3)] and $[Cd(phen)_3]\cdot C_6H_5PO_3H\cdot Cl\cdot 7H_2O$ **(4)** have been synthesized, structurally characterized by single-crystal X-ray diffraction method. These compounds all crystallize in the triclinic system, space group P-1. The lattice parameters are $a=12.1646(5)$, $b=12.4155(6)$, $c=15.4117(10)$ Å, $\alpha=78.216(2)$, $\beta=79.735(3)$, $\gamma=77.8380(3)^\circ$, $V=2205.1(2)$ Å^3, $Z=2$ for 1; $a=12.097(2)$, $b=12.606(3)$, $c=15.742(3)$ Å, $\alpha=76.66(3)$, $\beta=80.04(3)$, $\gamma=77.75(3)^\circ$, $V=2263.4(8)$ Å^3, $Z=2$ for 2; $a=12.058(2)$, $b=12.518(3)$, $c=15.781(3)$ Å, $\alpha=77.77(3)$, $\beta=80.02(3)$, $\gamma=77.91(3)^\circ$, $V=2255.5(8)$ Å^3, $Z=2$ for 3 and $a=12.47680(10)$, $b=12.6693(2)$, $c=16.1504(3)$ Å, $\alpha=82.600(1)$, $\beta=71.122(1)$, $\gamma=77.355(1)^\circ$, $V=2352.37(6)$ Å^3, $Z=2$ for 4. All structures are refined by full-matrix least-squares methods [for 1, $R1=0.0602$ using 6458 independent reflections with $I>2\sigma(I)$; for 2, $R1=0.0632$ using 4657 independent reflections with $I>2\sigma(I)$; for 3, $R1=0.0634$ using 6221 independent reflections with $I>2\sigma(I)$; for 4, $R1=0.0400$ using 7930 independent reflections with $I>2\sigma(I)$]. In the crystal structures, the phenylphosphonate anions and water molecules are hydrogen-bonded to form layers, and there exist the cationic species $[M(phen)_3]^{2+}$ between the adjacent layers of anions and water. Luminescence, thermal analysis as well as IR spectroscopic studies are also presented.

Keywords: Metal phosphonates; Crystal structure; IR spectroscopy; Luminescence; Thermal analysis

1. Introduction

The field of metal phosphonate chemistry is expanding at a rapid rate due to the interest in the structural chemistry of their compounds and their potential applications as hosts in intercalation reactions, proton conductors, sorbents, ion exchangers, sensors and catalysts [1–5]. Most of the divalent transition metal phosphonates investigated are layered species where the metal octahedra are bridged by phosphonic acid tetrahedra to form two-dimensional layers [6,7]. Layered phosphonates are found to have structurally and chemically well-defined internal spaces and coordination sites [8], providing relatively easy access to intercalating reagents. The introduction of the second neutral organic ligand into metal phosphonate phases provides a powerful method for synthesis of novel organic–inorganic hybrid materials. Organic components have been used as structure-directing reagents in a wide range of materials including zeolites, mesoporous materials of the MCM-41 class [9]. The study on metal phosphonate containing a second neutral organic ligand is relatively rare [10–12], and we are interested in an attractive approach to the fabrication of new structure. Here we present new materials containing hydrogen-bonded layers of phenylphosphonate anions and water molecules.

2. Experimental

2.1. General procedures

All materials were commercially available and used as received. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. The

*Corresponding author. Fax: +86-431-5684009.
E-mail address: jfma@public.cc.jl.cn (J.-F. Ma).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(03)00185-3

emission spectrum was recorded on a Varian Cary Eclipse spectrometer. TGA was performed using a Perkin-Elmer TG-7 analyzer in nitrogen.

2.2. Syntheses

$[Co(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ **1**: A solution of sodium phenylphosphonate (0.200 g, 1 mmol) in 10 ml of water was added to the solution of $CoCl_2\cdot 6H_2O$ (0.238 g, 1 mmol) in 10 ml of water with constant stirring. The suspension of cobalt phenylphosphonate was obtained. Then *o*-phenanthroline (0.396 g, 2 mmol) was added to the suspension with constant stirring at 80° for 30 min. Orange crystals were obtained by standing the solution at room temperature for several weeks (67% yield based on Co). Calc. for **1**: C, 52.84; H, 5.35; N, 8.81. Found: C, 52.91%; H, 5.17%; N, 8.93%. IR (cm^{-1}, KBr): 3404(vs), 3050(w), 1653(w), 1624(m), 1517(s), 1425(vs), 1132(m), 1103(s), 1063(w), 847(m), 725(vs), 667(w), 590(w).

$[Ni(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ **2**: Crystals of compound **2** were prepared analogously to **1** (72% yield based on Ni). Calc. for **2**: C, 52.85; H, 5.35; N, 8.81. Found: C, 52.94%; H, 5.17%; N, 8.96%. IR (cm^{-1}, KBr): 3493(vs), 3057(w), 1653(w), 1625(m), 1518(s), 1426(vs), 1139(s), 1105(m), 1045(m), 1022(w), 896(m), 869(m), 748(w), 727(vs), 696(m), 644(m), 556(m).

$[Cu(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ **3**: Crystals of compound **3** were prepared analogously to **1** (63% yield based on Cu). Calc. for **3**: C, 52.59; H, 5.32; N, 8.76. Found: C, 52.68%; H, 5.14%; N, 8.89%. IR (cm^{-1}, KBr): 3420(vs), 3053(w), 1650(w), 1518(s), 1508(w), 1427(vs), 1134(m), 1104(w), 1062(w), 849(s), 724(vs), 696(m), 559(v).

$[Cd(phen)_3]\cdot C_6H_5PO_3H\cdot Cl\cdot 7H_2O$ **4**: Crystals of compound **4** were prepared analogously to **1** (58% yield based on Cd). Calc. for **4**: C, 50.02; H, 4.76; N, 8.34. Found: C, 50.21%; H, 4.68%; N, 8.55%. IR (cm^{-1}, KBr): 3432(vs), 3055(w), 1650(w), 2333(vs), 1645(m), 1625(m), 1426(s), 1138(m), 1066(w), 899(w), 851(m), 726(m), 672(w), 556(w).

2.3. X-ray crystallography

The structures of compounds **1**, **2**, **3** and **4** were determined by single-crystal X-ray diffraction. Crystallographic data are shown in Table 1. The data collections were performed on a Rigaku RAXIS-RAPID diffractometer at 293 K, using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) by the ω scan mode. Empirical absorption corrections (multi-scan) were applied in all cases. The structures were solved by direct methods (SHELXS-97) [13] and refined by full-matrix least squares on F^2 (SHELXL-97) [14]. All non-hydrogen atoms were refined anisotropically, and the positions of hydrogen atoms on carbon atoms were calculated theoretically, the hydrogen atoms of water molecules were not located.

Table 1
Crystal data and structure refinement for compounds **1–4**

	1	**2**	**3**	**4**
Formula	$C_{42}H_{51}CoN_6O_{14}P$	$C_{42}H_{51}NiN_6O_{14}P$	$C_{42}H_{51}CuN_6O_{14}P$	$C_{42}H_{48}CdN_6O_{12}P$
Formula weight	953.79	953.57	958.40	1007.68
Crystal size (mm)	$0.44\times0.31\times0.19$	$0.26\times0.31\times0.13$	$0.25\times0.42\times0.13$	$0.23\times0.38\times0.28$
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.1646(5)	12.097(2)	12.058(2)	12.47680(10)
b (Å)	12.4155(6)	12.606(3)	12.518(3)	12.6693(2)
c (Å)	15.4117(10)	15.742(3) (3)	15.781(3)	16.1504(3)
α (deg)	78.216(2)	76.66(3)	77.77(3)	82.6000(10)
β (deg)	79.735(3)	80.04(3)	80.02(3)	71.1220(10)
γ (deg)	77.8380(10)	77.75(3)	77.91(3)	77.3550(10)
V (Å^3)	2205.1(2)	2263.4(8)	2255.5(8)	2352.37(6)
Z	2	2	2	2
Dc ($g\,cm^{-3}$)	1.436	1.399	1.411	1.423
$F(000)$	998	1000	1002	1036
λ (Mo$K\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.500	0.536	0.592	0.620
Temperature (K)	293	293	293	293
Reflections collected	15239	16482	16571	17403
Unique reflections	9734	10130	10242	10692
Observed reflections ($I>2\sigma(I)$)	6458	4657	6221	7930
R_1 ($I>2\sigma(I)$)	0.0602	0.0632	0.0634	0.0400
wR_2 ($I>2\sigma(I)$)	0.1934	0.1843	0.1873	0.1218
Goodness of fit	1.013	0.938	0.981	1.034

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-192807 for **1**, CCDC-192808 for **2**, CCDC-192809 for **3**, and CCDC-192810 for **4**.

3. Results and discussion

3.1. Crystal structures

Selected bond distances and angles for **1**−**4** are listed in Table 2. Atomic coordinates, isotropic thermal parameters and anisotropic thermal parameters are listed in Tables 3 and 4, respectively. **1**, **2** and **3** show similar structure, each of them consists of cationic species $[M(\text{phen})_3]^{2+}$, in which metal anion is six-coordinated by six nitrogen atoms from three *o*-phenanthroline ligands (Fig. 1). Since $-PO_3^{2-}$ is a strong ligand for divalent transition metal, in the reported structure of divalent metal phenylphosphonate, $-PO_3^{2-}$ group is directly bonded to metal cation to form polymeric structure [6]. However, in compounds **1**, **2** and **3**, owing to the strong chelating role of *o*-phenanthroline towards the metal cation (II), the phenylphosphonate anion was segregated from the central metal cation (II). Generally, metal phosphonates possess layered solid state structures, where the octahedrally coordinated metal cation is within the polymeric layer and the organic moiety directed into the interlamellar space [15–18]. The structures of **1**, **2** and **3** are not layered in traditional case, but are better described as consisting of hydrogen-bonded layers of phenylphosphonate anions and water molecules with $[M(\text{phen})_3]^{2+}$ cations locating between the adjacent layers as presented in Fig. 2. Within the layer of phenylphosphonate anions and water molecules, there are rows of anions with the orientations of $-PO_3^{2-}$ groups alternating up and down, as shown in Fig. 3. There are some lattice water molecules which are hydrogen-bonded to phenylphosphonate anions to result in an interesting two-dimensional hydrogen-bonding network (Fig. 3). The hydrogen bonds in this study have been considered with liberal distance cut-off criteria of $2.5 < O\cdots O < 3.0$ Å. In compound **1**, the dihedral angle between the benzene ring (C1–C6) of phenylphosphonate anion and *o*-phenanthroline (C201–C212) is 11.4°; and the distance between them is about 3.6 Å. There may exist weak $\pi-\pi$ stacking interaction between them.

Compound **4** consists of $[Cd(phen)_3]^{2+}$ cations and two kinds of un-coordinating anions: Cl^- and $-PO_3H^-$ (Fig. 4). The *M*–N average distance is much longer than those observed in compounds **1**, **2** and **3**. Compound **4** shows a similar structure to **1**, but the hydrogen-bonded layers of **4** are composed of Cl^-, $-PO_3H^-$ and water molecules. The phenyl ring (C1–C6) of phenylphosphonate anion and *o*-phenanthroline (C301–C312) planes are almost parallel with a dihedral angle of 4.9° and the distance between them is about 3.7 Å. There may also exist weak $\pi-\pi$ stacking interaction between them.

Table 2
Selected bond lengths (Å) and angles (deg) for compounds **1–4**

$[Co(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ **1**			
N(1)–Co(1)	2.158(3)	N(2)–Co(1)	2.118(3)
N(3)–Co(1)	2.112(3)	N(4)–Co(1)	2.146(3)
N(5)–Co(1)	2.150(3)	N(6)–Co(1)	2.126(3)
N(3)–Co(1)–N(2)	98.26(11)	N(3)–Co(1)–N(6)	93.97(12)
N(2)–Co(1)–N(6)	164.49(11)	N(3)–Co(1)–N(4)	78.07(12)
N(2)–Co(1)–N(4)	96.50(11)	N(6)–Co(1)–N(4)	95.33(12)
N(3)–Co(1)–N(5)	168.02(11)	N(2)–Co(1)–N(5)	91.15(11)
N(6)–Co(1)–N(5)	78.12(12)	N(4)–Co(1)–N(5)	93.57(11)
N(3)–Co(1)–N(1)	94.22(11)	N(2)–Co(1)–N(1)	77.96(11)
N(6)–Co(1)–N(1)	91.71(11)	N(4)–Co(1)–N(1)	169.88(11)
N(5)–Co(1)–N(1)	94.99(10)		
$[Ni(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ **2**			
N(1)–Ni(1)	2.110(3)	N(2)–Ni(1)	2.085(4)
N(3)–Ni(1)	2.083(4)	N(4)–Ni(1)	2.098(4)
N(5)–Ni(1)	2.098(4)	N(6)–Ni(1)	2.085(4)
N(3)–Ni(1)–N(2)	94.99(14)	N(3)–Ni(1)–N(6)	93.79(15)
N(2)–Ni(1)–N(6)	168.23(14)	N(3)–Ni(1)–N(5)	170.31(14)
N(2)–Ni(1)–N(5)	92.44(14)	N(6)–Ni(1)–N(5)	79.77(15)
N(3)–Ni(1)–N(4)	9.87(15)	N(2)–Ni(1)–N(4)	94.50(14)
N(6)–Ni(1)–N(4)	94.75(14)	N(5)–Ni(1)–N(4)	93.36(14)
N(3)–Ni(1)–N(1)	93.83(15)	N(2)–Ni(1)–N(1)	79.23(14)
N(6)–Ni(1)–N(1)	92.39(14)	N(5)–Ni(1)–N(1)	93.67(13)
N(4)–Ni(1)–N(1)	170.77(14)		
$[Cu(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ **3**			
N(1)–Cu(1)	2.272(3)	N(2)–Cu(1)	2.082(3)
N(3)–Cu(1)	2.051(3)	N(4)–Cu(1)	2.252(3)
N(5)–Cu(1)	2.074(3)	N(6)–Cu(1)	2.089(3)
N(3)–Cu(1)–N(5)	168.69(12)	N(3)–Cu(1)–N(2)	95.10(12)
N(5)–Cu(1)–N(2)	92.86(12)	N(3)–Cu(1)–N(6)	93.76(13)
N(5)–Cu(1)–N(6)	80.19(13)	N(2)–Cu(1)–N(6)	165.34(11)
N(3)–Cu(1)–N(4)	77.96(12)	N(5)–Cu(1)–N(4)	93.20(12)
N(2)–Cu(1)–N(4)	96.41(12)	N(6)–Cu(1)–N(4)	96.86(12)
N(3)–Cu(1)–N(1)	95.63(12)	N(5)–Cu(1)–N(1)	93.99(11)
N(2)–Cu(1)–N(1)	76.91(11)	N(6)–Cu(1)–N(1)	90.62(11)
N(4)–Cu(1)–N(1)	170.42(12)		
$[Cd(phen)_3]\cdot C_6H_5PO_3H\cdot Cl\cdot 7H_2O$ **4**			
N(1)–Cd(1)	2.366(3)	N(2)–Cd(1)	2.340(3)
N(3)–Cd(1)	2.372(3)	N(4)–Cd(1)	2.395(3)
N(5)–Cd(1)	2.337(3)	N(6)–Cd(1)	2.361(3)
N(5)–Cd(1)–N(2)	99.03(9)	N(5)–Cd(1)–N(6)	71.92(9)
N(2)–Cd(1)–N(6)	112.99(10)	N(5)–Cd(1)–N(1)	160.51(10)
N(2)–Cd(1)–N(1)	71.82(9)	N(6)–Cd(1)–N(1)	95.39(9)
N(5)–Cd(1)–N(3)	97.07(10)	N(2)–Cd(1)–N(3)	90.26(9)
N(6)–Cd(1)–N(3)	155.26(10)	N(1)–Cd(1)–N(3)	100.08(9)
N(5)–Cd(1)–N(4)	103.41(10)	N(2)–Cd(1)–N(4)	152.19(10)
N(6)–Cd(1)–N(4)	89.69(9)	N(1)–Cd(1)–N(4)	90.95(9)
N(3)–Cd(1)–N(4)	70.97(9)		

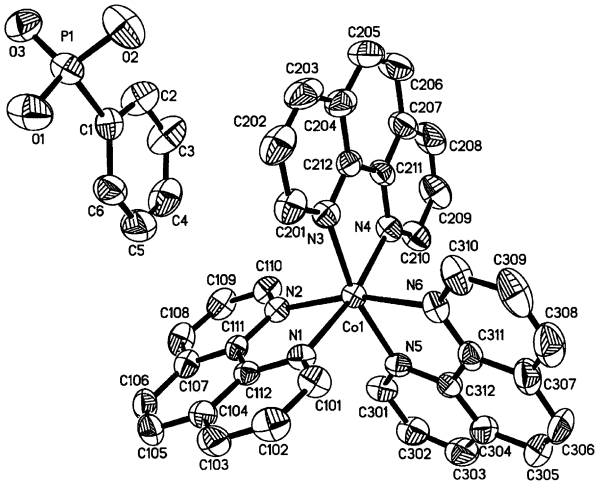

Fig. 1. Asymmetric unit of **1** (the water molecules and hydrogen atoms are omitted for clarity). Atoms are shown as 50% probability ellipsoids.

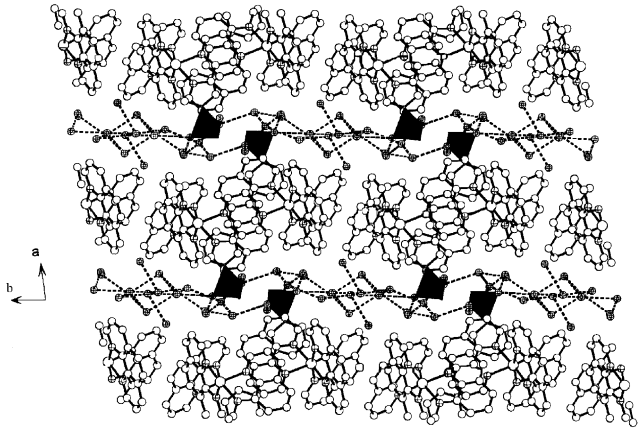

Fig. 2. $[M(\text{phen})_3]^{2+}$ cations located between the adjacent layers of phenylphosphonate anions and water molecules in compound **1**.

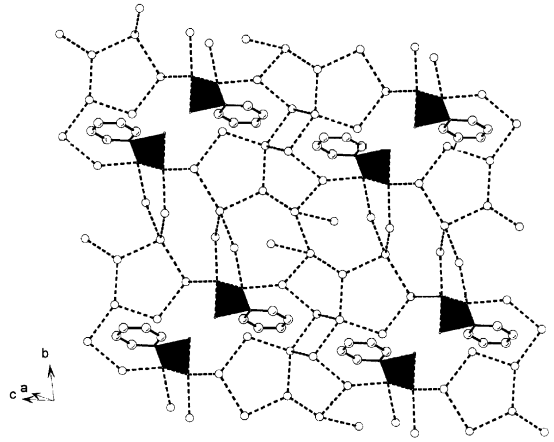

Fig. 3. Two-dimensional network constructed by hydrogen bonds in compound **1**.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **1**–**4**: U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
[Co(phen)$_3$] · C$_6$H$_5$PO$_3$ · 11H$_2$O **1**				
C(1)	6773(3)	3670(3)	6300(3)	38(1)
C(2)	7520(4)	4007(4)	5547(3)	54(1)
C(3)	8565(4)	4215(5)	5614(3)	62(1)
C(4)	8890(4)	4084(4)	6453(4)	62(1)
C(5)	8160(5)	3785(5)	7200(4)	68(1)
C(6)	7092(4)	3590(4)	7128(3)	54(1)
C(101)	7778(3)	6830(4)	9140(2)	40(1)
C(102)	7389(3)	6142(4)	9913(3)	48(1)
C(103)	7958(4)	5066(4)	10117(3)	46(1)
C(104)	8909(3)	4674(3)	9539(2)	38(1)
C(105)	9581(4)	3580(3)	9709(3)	48(1)
C(106)	10507(4)	3243(3)	9129(3)	47(1)
C(107)	10832(3)	3955(3)	8324(3)	38(1)
C(108)	11763(3)	3640(4)	7688(3)	48(1)
C(109)	12026(3)	4388(4)	6931(3)	47(1)
C(110)	11352(3)	5437(3)	6804(3)	39(1)
C(111)	10200(3)	5036(3)	8137(2)	29(1)
C(112)	9232(3)	5402(3)	8764(2)	30(1)
C(201)	7278(3)	6643(4)	6893(3)	47(1)
C(202)	6497(4)	6603(4)	6339(4)	59(1)
C(203)	6645(4)	7056(4)	5475(4)	62(1)
C(204)	7597(4)	7561(4)	5116(3)	50(1)
C(205)	7842(5)	8046(5)	4192(3)	68(1)
C(206)	8792(6)	8475(5)	3885(3)	71(2)
C(207)	9593(4)	8468(4)	4459(3)	52(1)
C(208)	10630(5)	8882(4)	4170(3)	65(1)
C(209)	11336(4)	8856(4)	4765(3)	60(1)
C(210)	11006(3)	8440(4)	5671(3)	46(1)
C(211)	9366(3)	8035(3)	5367(2)	37(1)
C(212)	8354(3)	7556(3)	5702(2)	37(1)
C(301)	11652(3)	7527(4)	7992(2)	42(1)
C(302)	12332(4)	8002(4)	8389(3)	52(1)
C(303)	11886(4)	8960(4)	8707(3)	59(1)
C(304)	10740(4)	9480(4)	8622(3)	49(1)
C(305)	10227(6)	10466(4)	8935(4)	70(2)
C(306)	9141(6)	10928(4)	8828(3)	71(2)
C(307)	8483(4)	10431(4)	8389(3)	56(1)
C(308)	7350(5)	10877(4)	8247(4)	67(1)
C(309)	6823(4)	10382(4)	7779(4)	68(2)
C(310)	7397(3)	9405(4)	7461(3)	51(1)
C(311)	8987(3)	9441(3)	8069(2)	38(1)
C(312)	10135(3)	8947(3)	8201(2)	35(1)
N(1)	8678(2)	6481(3)	8568(2)	31(1)
N(2)	10451(2)	5770(2)	7379(2)	30(1)
N(3)	8199(3)	7111(3)	6582(2)	37(1)
N(4)	10060(3)	8026(3)	5967(2)	36(1)
N(5)	10586(2)	7978(3)	7892(2)	32(1)
N(6)	8446(3)	8928(3)	7609(2)	37(1)
O(1)	4834(3)	2957(3)	7085(2)	64(1)
O(2)	4724(2)	4498(3)	5771(2)	62(1)
O(3)	5671(3)	2548(3)	5539(2)	53(1)
OW1	13022(2)	10993(2)	9568(1)	32(1)
OW2	6292(3)	8809(3)	2463(2)	65(1)
OW3	5306(4)	8023(4)	8277(3)	100(1)
OW4	4466(4)	9290(4)	6692(3)	98(1)
OW5	5056(5)	5840(4)	8767(3)	106(2)
OW6	13876(3)	5475(4)	7562(4)	107(2)
OW7	13583(3)	7445(5)	6244(3)	115(2)
OW8	5040(10)	8991(8)	9743(5)	234(4)

Table 3 (*continued*)

	x	y	z	U(eq)
OW9	6033(4)	10339(4)	5510(3)	96(1)
OW10	6214(4)	3748(5)	9557(4)	116(2)
OW11	4920(3)	2643(4)	8846(2)	83(1)
P(1)	5418(1)	3370(1)	6168(1)	39(1)
Co(1)	9402(1)	7371(1)	7315(1)	29(1)
[Ni(phen)$_3$] · C$_6$H$_5$PO$_3$ · 11H$_2$O **2**				
C(1)	6773(4)	3709(4)	6277(4)	60(1)
C(2)	7557(5)	4010(5)	5558(4)	81(2)
C(3)	8609(5)	4212(6)	5639(5)	96(2)
C(4)	8863(6)	4090(5)	6481(6)	98(2)
C(5)	8062(7)	3832(6)	7218(5)	97(2)
C(6)	7046(6)	3640(5)	7093(4)	79(2)
C(101)	7862(4)	6898(4)	9132(3)	53(1)
C(102)	7454(5)	6208(5)	9901(3)	61(1)
C(103)	7984(5)	5144(5)	10075(3)	64(2)
C(104)	8899(4)	4744(4)	9495(3)	47(1)
C(105)	9529(5)	3631(4)	9629(4)	69(2)
C(106)	10419(5)	3289(4)	9073(4)	63(1)
C(107)	10764(4)	4022(4)	8276(3)	51(1)
C(108)	11676(4)	3709(4)	7657(4)	61(1)
C(109)	11935(4)	4470(5)	6916(4)	65(2)
C(110)	11300(4)	5537(4)	6809(3)	51(1)
C(111)	10153(4)	5126(3)	8115(3)	39(1)
C(112)	9238(4)	5481(3)	8740(3)	38(1)
C(201)	7315(4)	6692(4)	6955(4)	62(1)
C(202)	6545(5)	6632(5)	6399(5)	83(2)
C(203)	6714(6)	7042(6)	5531(5)	88(2)
C(204)	7669(5)	7524(5)	5189(4)	70(2)
C(205)	7966(8)	7958(6)	4266(5)	104(3)
C(206)	8925(8)	8384(6)	3963(4)	100(3)
C(207)	9679(6)	8444(5)	4540(3)	72(2)
C(208)	10689(7)	8875(5)	4271(4)	88(2)
C(209)	11360(6)	8901(5)	4866(4)	82(2)
C(210)	11019(4)	8513(4)	5772(3)	62(1)
C(211)	9412(5)	8043(4)	5453(3)	53(1)
C(212)	8407(4)	7564(4)	5772(3)	52(1)
C(301)	11637(4)	7527(4)	8029(3)	52(1)
C(302)	12308(5)	7976(5)	8439(4)	69(2)
C(303)	11869(6)	8919(5)	8724(4)	76(2)
C(304)	10728(5)	9449(4)	8611(3)	62(1)
C(305)	10181(7)	10441(5)	8899(4)	87(2)
C(306)	9118(7)	10913(5)	8776(4)	89(2)
C(307)	8495(5)	10414(4)	8330(3)	64(2)
C(308)	7372(6)	10866(5)	8169(4)	87(2)
C(309)	6814(5)	10363(5)	7715(4)	79(2)
C(310)	7408(5)	9394(4)	7427(3)	63(1)
C(311)	8983(4)	9453(4)	8037(3)	46(1)
C(312)	10127(4)	8943(4)	8195(3)	46(1)
N(1)	8723(3)	6553(3)	8561(2)	40(1)
N(2)	10433(3)	5872(3)	7375(2)	40(1)
N(3)	8220(3)	7151(3)	6651(2)	47(1)
N(4)	10076(3)	8088(3)	6054(2)	47(1)
N(5)	10578(3)	7986(3)	7909(2)	41(1)
N(6)	8451(3)	8942(3)	7582(2)	44(1)
O(1)	4913(5)	2808(5)	6937(4)	170(3)
O(2)	4667(4)	4557(5)	5915(4)	147(2)
O(3)	5621(7)	2543(7)	5570(5)	94(2)
O(3′)	5505(10)	3532(12)	5082(8)	101(4)
OW1	13010(2)	10988(2)	9519(2)	31(1)
OW2	6422(4)	8787(4)	2504(3)	115(2)
OW3	5314(4)	7844(5)	8356(4)	139(2)
OW4	4408(6)	9240(5)	6827(5)	196(3)
OW5	5136(5)	5632(6)	8911(4)	159(2)

Table 3 (*continued*)

	x	y	z	U(eq)
OW6	13803(5)	5400(6)	7761(5)	181(3)
OW7	13565(5)	7380(11)	6289(5)	322(8)
OW8	4688(7)	8725(6)	9837(5)	201(3)
OW9	5832(6)	10471(6)	5594(4)	188(3)
OW10	6435(7)	3254(7)	9502(4)	198(3)
OW11	4650(9)	2768(8)	8639(7)	276(5)
P(1)	5411(1)	3464(2)	6122(1)	87(1)
Ni(1)	9412(1)	7433(1)	7345(1)	38(1)
[Cu(phen)$_3$] · C$_6$H$_5$PO$_3$ · 11H$_2$O **3**				
C(1)	6792(3)	3679(3)	6250(3)	59(1)
C(2)	7553(4)	3990(5)	5530(3)	81(1)
C(3)	8615(4)	4184(5)	5631(4)	94(2)
C(4)	8905(5)	4037(5)	6453(5)	99(2)
C(5)	8133(5)	3762(5)	7168(4)	99(2)
C(6)	7084(5)	3578(4)	7059(3)	83(1)
C(101)	7771(4)	6830(4)	9204(3)	64(1)
C(102)	7398(4)	6099(5)	9972(3)	79(1)
C(103)	7962(4)	5045(4)	10129(3)	69(1)
C(104)	8893(3)	4678(3)	9533(2)	57(1)
C(105)	9564(4)	3578(4)	9660(3)	75(1)
C(106)	10471(4)	3258(4)	9080(3)	69(1)
C(107)	10780(3)	4000(3)	8294(3)	56(1)
C(108)	11695(4)	3709(4)	7656(3)	71(1)
C(109)	11925(4)	4455(4)	6929(3)	72(1)
C(110)	11270(3)	5506(4)	6835(3)	61(1)
C(111)	10136(3)	5091(3)	8148(2)	45(1)
C(112)	9201(3)	5436(3)	8778(2)	45(1)
C(201)	7388(4)	6674(4)	6902(3)	70(1)
C(202)	6609(4)	6585(5)	6385(5)	92(2)
C(203)	6726(5)	7019(5)	5541(5)	98(2)
C(204)	7674(5)	7524(4)	5172(3)	79(1)
C(205)	7888(7)	7985(6)	4269(4)	120(3)
C(206)	8848(8)	8427(6)	3936(4)	120(3)
C(207)	9680(5)	8476(4)	4494(3)	86(2)
C(208)	10683(7)	8925(5)	4199(4)	113(2)
C(209)	11398(6)	8935(5)	4765(4)	105(2)
C(210)	11106(4)	8509(4)	5651(3)	80(1)
C(211)	9448(4)	8055(3)	5390(2)	61(1)
C(212)	8454(3)	7565(3)	5731(2)	57(1)
C(301)	11618(4)	7568(4)	7997(3)	63(1)
C(302)	12283(4)	8030(5)	8396(3)	81(1)
C(303)	11837(5)	8945(5)	8703(3)	87(2)
C(304)	10680(5)	9461(4)	8615(3)	72(1)
C(305)	10155(6)	10448(5)	8909(4)	99(2)
C(306)	9045(8)	10900(5)	8814(4)	110(2)
C(307)	8399(5)	10391(4)	8369(3)	72(1)
C(308)	7262(6)	10813(4)	8221(4)	95(2)
C(309)	6734(5)	10299(4)	7763(4)	90(2)
C(310)	7338(4)	9352(4)	7461(3)	70(1)
C(311)	8929(4)	9441(3)	8055(2)	53(1)
C(312)	10082(3)	8951(3)	8197(2)	54(1)
N(1)	8642(3)	6495(3)	8624(2)	50(1)
N(2)	10397(2)	5833(2)	7412(2)	47(1)
N(3)	8286(3)	7141(3)	6600(2)	52(1)
N(4)	10159(3)	8087(3)	5958(2)	59(1)
N(5)	10550(3)	7995(3)	7894(2)	50(1)
N(6)	8404(3)	8918(3)	7596(2)	54(1)
O(1)	4886(4)	2831(5)	6936(4)	161(2)
O(2)	4674(3)	4532(4)	5885(4)	143(2)
O(3)	5634(5)	2527(5)	5511(4)	84(2)
O(3′)	5561(10)	3496(13)	5035(9)	134(4)
OW1	13076(2)	10975(2)	9485(1)	41(1)
OW2	6402(3)	8818(3)	2528(3)	107(1)

Table 3 (*continued*)

	x	y	z	U(eq)
OW3	5303(4)	7792(5)	8314(4)	151(2)
OW4	4480(6)	9195(5)	6815(4)	175(2)
OW5	5146(6)	5608(6)	8889(4)	192(3)
OW6	13843(5)	5447(6)	7696(5)	182(3)
OW7	13610(5)	7356(9)	6296(4)	249(5)
OW8	4735(6)	8713(6)	9767(5)	191(3)
OW9	5836(6)	10403(6)	5543(5)	193(3)
OW10	6341(6)	3268(6)	9542(4)	181(2)
OW11	4685(8)	2786(7)	8594(6)	254(4)
P(1)	5419(1)	3417(1)	6096(1)	83(1)
Cu(1)	9411(1)	7421(1)	7331(1)	43(1)
[Cd(phen)]$_3$·C$_6$H$_5$PO$_3$H·Cl·7H$_2$O **4**				
C(1)	−776(3)	1694(3)	1326(3)	52(1)
C(2)	−752(5)	2066(4)	2076(4)	85(1)
C(3)	−588(6)	3129(5)	2083(5)	116(2)
C(4)	−390(6)	3786(5)	1308(6)	115(2)
C(5)	−421(5)	3419(4)	572(5)	100(2)
C(6)	−618(4)	2387(3)	572(3)	74(1)
C(101)	3099(3)	6496(3)	2883(2)	51(1)
C(102)	3502(4)	7156(3)	3276(3)	64(1)
C(103)	4369(4)	6718(3)	3627(3)	67(1)
C(104)	4841(3)	5615(3)	3575(2)	56(1)
C(105)	5773(4)	5104(4)	3915(3)	78(1)
C(106)	6231(4)	4041(5)	3830(3)	79(1)
C(107)	5790(3)	3374(3)	3411(2)	57(1)
C(108)	6249(4)	2271(4)	3294(3)	75(1)
C(109)	5803(4)	1702(3)	2884(3)	73(1)
C(110)	4866(3)	2214(3)	2576(3)	58(1)
C(111)	4865(3)	3836(3)	3084(2)	42(1)
C(112)	4390(3)	4987(3)	3164(2)	41(1)
C(201)	1823(4)	2658(3)	4032(3)	58(1)
C(202)	1041(4)	2306(3)	4812(3)	71(1)
C(203)	−40(4)	2908(3)	5079(3)	67(1)
C(204)	−350(3)	3867(3)	4591(2)	50(1)
C(205)	−1452(3)	4558(3)	4874(3)	60(1)
C(206)	−1724(3)	5485(3)	4400(3)	61(1)
C(207)	−915(3)	5774(3)	3579(2)	50(1)
C(208)	−1174(4)	6706(3)	3054(3)	67(1)
C(209)	−388(4)	6936(3)	2291(3)	71(1)
C(210)	684(3)	6241(3)	2041(3)	56(1)
C(211)	182(3)	5110(2)	3284(2)	40(1)
C(212)	477(3)	4141(2)	3821(2)	39(1)
C(301)	2515(4)	1961(3)	1579(3)	64(1)
C(302)	2380(4)	1305(3)	985(4)	80(1)
C(303)	2478(4)	1688(3)	149(4)	74(1)
C(304)	2742(3)	2710(3)	−140(3)	58(1)
C(305)	2820(4)	3171(4)	−1004(3)	74(1)
C(306)	3057(4)	4186(4)	−1261(3)	73(1)
C(307)	3234(3)	4826(3)	−662(2)	54(1)
C(308)	3484(4)	5878(3)	−890(3)	65(1)
C(309)	3689(4)	6425(3)	−301(3)	63(1)
C(310)	3630(3)	5931(3)	536(2)	51(1)
C(311)	3173(3)	4385(2)	202(2)	42(1)
C(312)	2892(3)	3322(2)	484(2)	44(1)
N(1)	3518(2)	5441(2)	2820(2)	42(1)
N(2)	4414(2)	3255(2)	2678(2)	44(1)
N(3)	1555(2)	3538(2)	3546(2)	45(1)
N(4)	973(2)	5353(2)	2516(2)	43(1)
N(5)	2769(3)	2942(2)	1321(2)	47(1)
N(6)	3359(2)	4952(2)	786(2)	42(1)
O(1)	−1633(3)	−73(2)	2183(2)	65(1)
O(2)	−1542(2)	334(2)	591(2)	53(1)
O(3)	284(2)	−361(2)	985(2)	56(1)

Table 3 (*continued*)

	x	y	z	U(eq)
OW1	4010(3)	8268(3)	1011(2)	81(1)
OW2	−3914(3)	941(2)	672(2)	68(1)
OW3	4900(3)	−542(2)	1885(2)	72(1)
OW4	−1406(4)	64(5)	3814(3)	141(2)
OW5	2979(3)	186(2)	3298(2)	83(1)
OW6	1691(3)	−1529(3)	1936(3)	103(1)
OW7	977(4)	−662(4)	3594(3)	135(2)
OW8	−3631(3)	173(3)	5170(3)	96(1)
OW9	−3301(3)	−1320(2)	2569(2)	67(1)
P(1)	−947(1)	316(1)	1299(1)	46(1)
Cd(1)	2830(1)	4195(1)	2241(1)	40(1)
Cl(1)	−4025(1)	−1963(1)	4628(1)	69(1)

3.2. Luminescence

Among the four complexes, compound **4** shows luminescent property. The emission spectrum exhibits two peaks at 365 and 382 nm upon photoexcitation at 320 nm. These emission bands may be attributed to *o*-phenanthroline $\pi^* \rightarrow \pi$ transition. Compound **4** may be a potential luminescent material.

3.3. FT-IR spectra

In the IR spectra, all compounds show absorption bands at 3404–3493 cm^{-1}, corresponding to the presence of water. The C–H stretching modes for the phenyl rings are relatively weak and are observed at about 3055 cm^{-1}. The multiple bands in the region of 900–1150 cm^{-1} are phosphonate P–O vibrations [19,20]. A series of characteristic peaks in the 1425–1520 cm^{-1} range are attributed to *o*-phenanthroline molecules [21].

3.4. Thermal analysis

In order to characterize more fully these compounds in terms of thermal stability, the thermal behavior of compound **3** was studied using TGA (Fig. 5). Compound **3** was heated from 35°C to 800°C in N_2. When the crystals were removed from the mother liquor, they immediately lost part of the water molecules. TGA was performed after part of their water molecules had evaporated. A weight loss corresponding to the remaining water was observed over the wide temperature range 35–120°C. From 195°C to 700°C, the anhydrous compound decomposes with stepwise loss of the organic portion. However, it is difficult to determine these weight losses accurately as these processes are overlapped with the weight losses due to the dissociation of the organic fractions.

In summary, the divalent transition metal phenylphosphonate complexes with *o*-phenanthroline ligand

Table 4
Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1–4**

	U11	U22	U33	U23	U13	U12
[Co(phen)$_3$] · C$_6$H$_5$PO$_3$ · 11H$_2$O **1**						
C(1)	34(2)	34(2)	43(2)	−7(2)	−1(2)	−3(2)
C(2)	41(2)	78(3)	49(2)	−24(2)	7(2)	−20(2)
C(3)	39(2)	88(4)	67(3)	−35(3)	15(2)	−28(2)
C(4)	39(2)	64(3)	92(4)	−22(3)	−14(3)	−16(2)
C(5)	75(3)	71(3)	65(3)	3(3)	−30(3)	−28(3)
C(6)	62(3)	61(3)	41(2)	6(2)	−13(2)	−27(2)
C(101)	30(2)	47(2)	39(2)	−9(2)	3(2)	−3(2)
C(102)	37(2)	64(3)	41(2)	−13(2)	9(2)	−12(2)
C(103)	49(2)	55(3)	33(2)	−3(2)	4(2)	−21(2)
C(104)	38(2)	45(2)	36(2)	−2(2)	−5(2)	−21(2)
C(105)	59(3)	39(2)	47(2)	5(2)	−11(2)	−20(2)
C(106)	54(3)	30(2)	59(3)	−3(2)	−17(2)	−7(2)
C(107)	30(2)	35(2)	50(2)	−12(2)	−9(2)	−4(2)
C(108)	33(2)	37(2)	71(3)	−20(2)	−5(2)	5(2)
C(109)	32(2)	51(3)	60(3)	−25(2)	4(2)	−3(2)
C(110)	31(2)	48(2)	38(2)	−15(2)	6(2)	−8(2)
C(111)	24(2)	29(2)	36(2)	−9(1)	−5(1)	−5(1)
C(112)	28(2)	36(2)	30(2)	−6(1)	−5(1)	−10(2)
C(201)	30(2)	53(2)	63(3)	−13(2)	−6(2)	−16(2)
C(202)	35(2)	61(3)	91(4)	−29(3)	−15(2)	−10(2)
C(203)	48(3)	66(3)	83(4)	−31(3)	−37(3)	7(2)
C(204)	48(2)	49(3)	57(3)	−20(2)	−24(2)	5(2)
C(205)	84(4)	67(3)	58(3)	−15(2)	−39(3)	1(3)
C(206)	106(5)	64(3)	40(2)	−6(2)	−28(3)	4(3)
C(207)	69(3)	45(2)	35(2)	−3(2)	−11(2)	1(2)
C(208)	88(4)	59(3)	34(2)	7(2)	6(2)	−13(3)
C(209)	57(3)	63(3)	49(3)	8(2)	10(2)	−16(2)
C(210)	37(2)	50(2)	45(2)	5(2)	−1(2)	−12(2)
C(211)	42(2)	32(2)	33(2)	−2(1)	−6(2)	3(2)
C(212)	37(2)	32(2)	42(2)	−9(2)	−12(2)	0(2)
C(301)	31(2)	57(3)	36(2)	−3(2)	−5(2)	−14(2)
C(302)	42(2)	66(3)	52(2)	−3(2)	−13(2)	−23(2)
C(303)	66(3)	68(3)	54(3)	−1(2)	−22(2)	−35(3)
C(304)	65(3)	44(2)	41(2)	−5(2)	−9(2)	−20(2)
C(305)	109(5)	44(3)	69(3)	−15(2)	−33(3)	−18(3)
C(306)	123(5)	37(3)	55(3)	−23(2)	−6(3)	−9(3)
C(307)	76(3)	35(2)	45(2)	−5(2)	8(2)	1(2)
C(308)	75(3)	43(3)	70(3)	−9(2)	7(3)	4(2)
C(309)	44(2)	49(3)	86(4)	7(3)	6(3)	16(2)
C(310)	34(2)	43(2)	66(3)	3(2)	−2(2)	−3(2)
C(311)	47(2)	30(2)	32(2)	−1(1)	4(2)	−7(2)
C(312)	42(2)	34(2)	29(2)	−3(1)	−2(2)	−11(2)
N(1)	25(1)	38(2)	29(1)	−9(1)	0(1)	−4(1)
N(2)	24(1)	35(2)	32(1)	−9(1)	1(1)	−6(1)
N(3)	31(2)	39(2)	40(2)	−8(1)	−7(1)	−4(1)
N(4)	32(2)	37(2)	36(2)	−2(1)	−3(1)	−7(1)
N(5)	29(1)	39(2)	27(1)	−4(1)	−1(1)	−8(1)
N(6)	30(2)	34(2)	42(2)	−1(1)	2(1)	−4(1)
O(1)	49(2)	101(3)	41(2)	7(2)	1(1)	−33(2)
O(2)	32(2)	65(2)	72(2)	9(2)	−1(2)	5(1)
O(3)	46(2)	64(2)	55(2)	−14(2)	−12(1)	−15(2)
OW1	46(1)	23(1)	23(1)	−4(1)	10(1)	−7(1)
OW2	57(2)	63(2)	71(2)	0(2)	−15(2)	−8(2)
OW3	69(3)	110(4)	117(4)	−12(3)	−4(3)	−26(3)
OW4	98(3)	79(3)	115(4)	−34(3)	12(3)	−18(2)
OW5	135(4)	109(4)	80(3)	−16(3)	−20(3)	−32(3)
OW6	50(2)	130(4)	163(5)	−92(4)	−3(3)	−9(2)
OW7	57(2)	217(6)	71(3)	−39(3)	−1(2)	−15(3)
OW8	322(12)	209(9)	136(6)	−36(6)	−12(7)	18(8)
OW9	98(3)	80(3)	114(3)	−29(3)	−7(3)	−20(2)
OW10	105(4)	144(5)	112(4)	−19(3)	−27(3)	−45(3)
OW11	80(3)	103(3)	63(2)	−27(2)	15(2)	−18(2)

Table 4 (*continued*)

	U11	U22	U33	U23	U13	U12
P(1)	28(1)	48(1)	37(1)	0(1)	−1(1)	−7(1)
Co(1)	23(1)	32(1)	29(1)	−4(1)	−2(1)	−5(1)
[Ni(phen)$_3$] · C$_6$H$_5$PO$_3$ · 11H$_2$O **2**						
C(1)	47(3)	61(3)	68(3)	−9(3)	−12(3)	−1(3)
C(2)	59(4)	118(5)	77(4)	−40(4)	−7(3)	−16(4)
C(3)	55(4)	137(6)	110(5)	−54(5)	9(4)	−35(4)
C(4)	78(5)	83(5)	152(7)	−46(5)	−57(5)	−2(4)
C(5)	104(6)	102(5)	90(5)	2(4)	−43(5)	−31(5)
C(6)	85(5)	83(4)	70(4)	2(3)	−24(3)	−26(4)
C(101)	47(3)	54(3)	53(3)	−11(2)	0(2)	−4(2)
C(102)	61(4)	71(4)	49(3)	−11(3)	12(3)	−21(3)
C(103)	73(4)	65(4)	50(3)	7(3)	1(3)	−30(3)
C(104)	51(3)	43(3)	48(3)	0(2)	−6(2)	−16(2)
C(105)	85(4)	58(4)	60(3)	9(3)	−9(3)	−28(3)
C(106)	72(4)	38(3)	76(4)	0(3)	−22(3)	−4(3)
C(107)	49(3)	41(3)	66(3)	−10(2)	−20(3)	−8(2)
C(108)	46(3)	48(3)	89(4)	−23(3)	−11(3)	5(2)
C(109)	41(3)	71(4)	86(4)	−39(3)	5(3)	−1(3)
C(110)	42(3)	57(3)	54(3)	−14(2)	2(2)	−9(2)
C(111)	34(2)	38(2)	49(3)	−9(2)	−14(2)	−8(2)
C(112)	37(3)	36(2)	43(2)	−6(2)	−11(2)	−11(2)
C(201)	45(3)	65(4)	84(4)	−25(3)	−13(3)	−12(3)
C(202)	48(4)	87(5)	131(6)	−48(4)	−28(4)	−11(3)
C(203)	67(5)	96(5)	116(6)	−47(5)	−48(4)	6(4)
C(204)	78(4)	66(4)	74(4)	−30(3)	−42(3)	12(3)
C(205)	151(8)	94(6)	73(5)	−26(4)	−66(5)	18(5)
C(206)	153(8)	94(5)	45(3)	−7(3)	−38(5)	9(5)
C(207)	99(5)	60(4)	44(3)	−4(3)	−9(3)	8(3)
C(208)	125(7)	70(4)	46(3)	7(3)	11(4)	−7(4)
C(209)	80(5)	72(4)	69(4)	10(3)	17(4)	−9(3)
C(210)	54(3)	58(3)	61(3)	6(3)	6(3)	−13(3)
C(211)	67(4)	42(3)	44(3)	−5(2)	−14(3)	4(2)
C(212)	56(3)	47(3)	54(3)	−15(2)	−19(3)	4(2)
C(301)	43(3)	62(3)	49(3)	−1(2)	−9(2)	−14(3)
C(302)	57(4)	80(4)	77(4)	0(3)	−29(3)	−31(3)
C(303)	89(5)	75(4)	80(4)	−4(3)	−33(3)	−46(4)
C(304)	89(4)	51(3)	58(3)	−5(3)	−27(3)	−26(3)
C(305)	121(6)	67(4)	86(4)	−21(3)	−40(4)	−23(4)
C(306)	143(7)	55(4)	81(4)	−33(3)	−24(4)	−12(4)
C(307)	79(4)	43(3)	62(3)	−4(3)	−7(3)	−2(3)
C(308)	112(6)	51(4)	85(4)	−19(3)	10(4)	3(4)
C(309)	62(4)	56(4)	99(5)	−5(3)	−10(3)	20(3)
C(310)	55(4)	53(3)	72(4)	0(3)	−12(3)	−2(3)
C(311)	58(3)	35(2)	43(2)	−3(2)	−2(2)	−11(2)
C(312)	55(3)	41(3)	43(2)	0(2)	−13(2)	−17(2)
N(1)	36(2)	43(2)	38(2)	−8(2)	0(2)	−8(2)
N(2)	34(2)	41(2)	43(2)	−7(2)	−8(2)	−6(2)
N(3)	38(2)	51(2)	53(2)	−14(2)	−10(2)	−4(2)
N(4)	46(2)	44(2)	47(2)	−3(2)	−6(2)	−6(2)
N(5)	37(2)	45(2)	40(2)	−3(2)	−8(2)	−11(2)
N(6)	35(2)	40(2)	50(2)	0(2)	−5(2)	−1(2)
O(1)	98(4)	177(6)	204(6)	93(5)	−52(4)	−76(4)
O(2)	52(3)	132(5)	208(6)	60(4)	−29(3)	0(3)
O(3)	95(6)	99(6)	103(6)	−18(5)	−38(5)	−32(5)
O(3′)	95(9)	133(11)	105(9)	−47(8)	−40(7)	−36(8)
OW1	39(2)	20(1)	38(1)	−16(1)	−12(1)	1(1)
OW2	101(4)	104(4)	123(4)	1(3)	−26(3)	−1(3)
OW3	84(4)	162(5)	170(5)	−40(4)	−12(4)	−20(4)
OW4	191(7)	115(5)	224(7)	−23(5)	87(6)	−4(4)
OW5	165(6)	182(6)	150(5)	−56(4)	−39(4)	−38(5)
OW6	87(4)	222(7)	266(8)	−131(6)	−26(5)	−6(4)
OW7	60(4)	760(20)	138(6)	−115(9)	−3(4)	−46(8)
OW8	214(8)	161(6)	228(8)	−68(6)	−68(6)	28(6)

Table 4 (*continued*)

	U11	U22	U33	U23	U13	U12
OW9	159(6)	231(8)	153(6)	−24(5)	−1(5)	−19(6)
OW10	244(8)	226(8)	139(5)	−11(5)	−44(6)	−86(7)
OW11	283(11)	259(10)	277(10)	−135(9)	130(9)	−78(8)
P(1)	47(1)	121(2)	89(1)	−11(1)	−13(1)	−15(1)
Ni(1)	35(1)	39(1)	39(1)	−5(1)	−5(1)	−7(1)
[Cu(phen)$_3$] · C$_6$H$_5$PO$_3$ · 11H$_2$O **3**						
C(1)	49(2)	61(3)	66(2)	−11(2)	−13(2)	−2(2)
C(2)	60(3)	111(4)	77(3)	−34(3)	−5(2)	−16(3)
C(3)	60(3)	124(5)	111(4)	−50(4)	7(3)	−30(3)
C(4)	76(4)	87(4)	154(6)	−41(4)	−51(4)	−7(3)
C(5)	111(5)	105(5)	93(4)	2(3)	−49(4)	−40(4)
C(6)	83(3)	93(4)	73(3)	2(3)	−21(3)	−25(3)
C(101)	52(2)	67(3)	71(3)	−19(2)	−6(2)	−1(2)
C(102)	66(3)	104(4)	70(3)	−28(3)	13(2)	−26(3)
C(103)	71(3)	70(3)	64(3)	−1(2)	1(2)	−27(2)
C(104)	60(2)	56(2)	57(2)	−2(2)	−9(2)	−23(2)
C(105)	93(4)	58(3)	74(3)	10(2)	−22(3)	−31(3)
C(106)	79(3)	43(2)	85(3)	−2(2)	−24(3)	−10(2)
C(107)	55(2)	45(2)	74(2)	−15(2)	−25(2)	−5(2)
C(108)	50(2)	59(3)	104(3)	−30(2)	−15(2)	5(2)
C(109)	50(2)	85(3)	82(3)	−32(3)	5(2)	−8(2)
C(110)	53(2)	67(3)	63(2)	−19(2)	3(2)	−12(2)
C(111)	43(2)	44(2)	53(2)	−9(2)	−14(2)	−10(2)
C(112)	43(2)	46(2)	49(2)	−6(1)	−13(1)	−13(2)
C(201)	50(2)	72(3)	93(3)	−26(2)	−13(2)	−8(2)
C(202)	57(3)	94(4)	143(5)	−51(4)	−28(3)	−12(3)
C(203)	73(3)	109(5)	132(5)	−59(4)	−57(3)	11(3)
C(204)	86(3)	77(3)	82(3)	−37(2)	−46(3)	17(3)
C(205)	165(7)	115(5)	85(4)	−34(4)	−76(5)	30(5)
C(206)	195(8)	99(5)	53(3)	−6(3)	−48(4)	18(5)
C(207)	122(5)	66(3)	53(2)	−3(2)	−8(3)	8(3)
C(208)	145(6)	87(4)	70(4)	14(3)	26(4)	1(4)
C(209)	98(5)	79(4)	105(5)	10(3)	33(4)	−10(3)
C(210)	64(3)	63(3)	98(3)	5(2)	0(2)	−8(2)
C(211)	77(3)	46(2)	51(2)	−6(2)	−16(2)	8(2)
C(212)	61(2)	52(2)	58(2)	−18(2)	−26(2)	12(2)
C(301)	50(2)	79(3)	62(2)	−5(2)	−7(2)	−21(2)
C(302)	64(3)	93(4)	90(3)	−1(3)	−23(2)	−30(3)
C(303)	100(4)	93(4)	88(3)	−5(3)	−35(3)	−54(3)
C(304)	100(4)	60(3)	66(3)	−11(2)	−22(2)	−29(3)
C(305)	137(6)	71(4)	103(4)	−21(3)	−48(4)	−24(4)
C(306)	195(8)	57(3)	89(4)	−31(3)	−35(4)	−16(4)
C(307)	99(4)	47(2)	64(3)	−4(2)	−10(2)	−5(2)
C(308)	109(5)	61(3)	92(4)	−13(3)	9(3)	12(3)
C(309)	72(3)	68(3)	111(4)	−7(3)	−11(3)	19(3)
C(310)	55(3)	68(3)	79(3)	1(2)	−16(2)	−2(2)
C(311)	67(2)	42(2)	46(2)	−2(2)	−2(2)	−11(2)
C(312)	66(2)	47(2)	48(2)	1(2)	−11(2)	−19(2)
N(1)	47(2)	52(2)	52(2)	−11(1)	−8(1)	−6(1)
N(2)	44(2)	49(2)	48(2)	−6(1)	−9(1)	−9(1)
N(3)	47(2)	54(2)	57(2)	−17(1)	−11(1)	−5(1)
N(4)	59(2)	51(2)	62(2)	0(2)	−15(2)	−4(2)
N(5)	49(2)	51(2)	47(2)	−4(1)	−7(1)	−10(1)
N(6)	52(2)	51(2)	55(2)	−3(1)	−7(1)	−10(2)
O(1)	103(3)	173(5)	184(5)	78(4)	−39(3)	−72(3)
O(2)	56(2)	134(4)	196(5)	58(3)	−24(3)	−5(2)
O(3)	78(4)	84(4)	100(4)	−19(3)	−32(3)	−20(3)
O(3′)	101(8)	184(13)	159(11)	−78(10)	−55(8)	−44(9)
OW1	50(1)	31(1)	46(1)	−14(1)	−13(1)	−4(1)
OW2	96(3)	100(3)	117(3)	−3(2)	−29(2)	−7(2)
OW3	98(3)	189(5)	168(5)	−47(4)	−13(3)	−20(3)
OW4	178(6)	119(4)	207(6)	−36(4)	20(5)	−14(4)

Table 4 (*continued*)

	U11	U22	U33	U23	U13	U12
OW5	226(7)	201(7)	171(5)	−43(5)	−56(5)	−57(6)
OW6	107(4)	204(6)	257(7)	−104(5)	−30(4)	−13(4)
OW7	79(3)	514(15)	146(5)	−85(7)	−10(3)	−21(6)
OW8	182(6)	160(5)	229(7)	−57(5)	−49(5)	14(5)
OW9	182(6)	194(6)	191(6)	−54(5)	0(5)	−9(5)
OW10	206(6)	204(6)	154(5)	−27(4)	−41(4)	−77(5)
OW11	241(9)	269(9)	254(8)	−125(7)	108(7)	−90(7)
P(1)	50(1)	114(1)	83(1)	−16(1)	−13(1)	−14(1)
Cu(1)	38(1)	44(1)	46(1)	−7(1)	−9(1)	−6(1)
[Cd(phen)$_3$] · C$_6$H$_5$PO$_3$H · Cl · 7H$_2$O **4**						
C(1)	40(2)	54(2)	62(2)	−13(2)	−15(2)	−6(2)
C(2)	87(4)	97(3)	86(3)	−22(3)	−28(3)	−34(3)
C(3)	117(5)	109(5)	145(6)	−65(5)	−41(5)	−31(4)
C(4)	99(5)	64(3)	191(8)	−25(4)	−48(5)	−18(3)
C(5)	105(4)	60(3)	139(5)	14(3)	−44(4)	−28(3)
C(6)	77(3)	57(2)	90(3)	1(2)	−31(3)	−15(2)
C(101)	61(2)	36(2)	56(2)	−3(1)	−19(2)	−6(2)
C(102)	84(3)	40(2)	73(3)	−10(2)	−22(2)	−17(2)
C(103)	82(3)	63(2)	68(3)	−16(2)	−25(2)	−30(2)
C(104)	56(2)	68(2)	51(2)	−9(2)	−19(2)	−18(2)
C(105)	74(3)	100(4)	79(3)	−17(3)	−44(3)	−15(3)
C(106)	60(3)	115(4)	72(3)	−5(3)	−41(2)	−9(3)
C(107)	46(2)	68(2)	47(2)	3(2)	−14(2)	3(2)
C(108)	53(3)	85(3)	71(3)	11(2)	−20(2)	14(2)
C(109)	69(3)	50(2)	79(3)	−2(2)	−15(2)	17(2)
C(110)	54(2)	40(2)	68(2)	−5(2)	−11(2)	4(2)
C(111)	38(2)	47(2)	36(2)	2(1)	−9(1)	−4(1)
C(112)	42(2)	46(2)	34(2)	0(1)	−10(1)	−11(1)
C(201)	59(2)	43(2)	60(2)	4(2)	−11(2)	0(2)
C(202)	75(3)	54(2)	67(3)	22(2)	−13(2)	−6(2)
C(203)	66(3)	69(2)	55(2)	11(2)	−5(2)	−20(2)
C(204)	49(2)	52(2)	48(2)	−2(2)	−14(2)	−12(2)
C(205)	47(2)	75(3)	54(2)	−5(2)	−8(2)	−14(2)
C(206)	38(2)	73(2)	70(3)	−18(2)	−15(2)	−2(2)
C(207)	42(2)	52(2)	60(2)	−7(2)	−20(2)	−5(2)
C(208)	47(2)	59(2)	89(3)	−4(2)	−26(2)	11(2)
C(209)	66(3)	52(2)	87(3)	15(2)	−32(3)	5(2)
C(210)	52(2)	50(2)	62(2)	11(2)	−19(2)	−6(2)
C(211)	40(2)	37(1)	50(2)	−8(1)	−20(2)	−6(1)
C(212)	40(2)	37(1)	42(2)	−6(1)	−13(1)	−8(1)
C(301)	77(3)	36(2)	84(3)	4(2)	−31(2)	−18(2)
C(302)	81(3)	38(2)	128(5)	−17(2)	−35(3)	−16(2)
C(303)	80(3)	51(2)	104(4)	−33(2)	−38(3)	−6(2)
C(304)	51(2)	57(2)	69(3)	−28(2)	−19(2)	−4(2)
C(305)	71(3)	90(3)	67(3)	−40(2)	−23(2)	−4(2)
C(306)	76(3)	97(3)	46(2)	−14(2)	−16(2)	−13(3)
C(307)	48(2)	66(2)	42(2)	−10(2)	−5(2)	−9(2)
C(308)	65(3)	73(2)	45(2)	11(2)	−5(2)	−19(2)
C(309)	67(3)	51(2)	62(2)	8(2)	−4(2)	−20(2)
C(310)	59(2)	42(2)	50(2)	0(2)	−11(2)	−17(2)
C(311)	37(2)	44(2)	41(2)	−7(1)	−8(1)	−5(1)
C(312)	40(2)	41(2)	52(2)	−15(1)	−15(2)	−2(1)
N(1)	48(2)	35(1)	43(2)	−3(1)	−14(1)	−6(1)
N(2)	39(2)	37(1)	47(2)	−3(1)	−9(1)	1(1)
N(3)	49(2)	35(1)	47(2)	2(1)	−15(1)	−5(1)
N(4)	41(2)	39(1)	49(2)	2(1)	−16(1)	−4(1)
N(5)	51(2)	34(1)	59(2)	−4(1)	−20(2)	−9(1)
N(6)	48(2)	36(1)	42(2)	−2(1)	−9(1)	−11(1)
O(1)	65(2)	74(2)	51(2)	5(1)	−10(1)	−17(1)
O(2)	47(1)	59(1)	59(2)	−6(1)	−24(1)	−11(1)
O(3)	48(2)	58(1)	56(2)	−4(1)	−20(1)	4(1)
OW1	99(3)	75(2)	85(2)	6(2)	−46(2)	−24(2)

Table 4 (*continued*)

	U11	U22	U33	U23	U13	U12
OW2	71(2)	62(2)	73(2)	3(1)	−28(2)	−10(1)
OW3	72(2)	82(2)	71(2)	3(2)	−27(2)	−27(2)
OW4	139(4)	188(5)	83(3)	23(3)	−44(3)	−3(3)
OW5	93(2)	65(2)	85(2)	−5(2)	−28(2)	−4(2)
OW6	89(3)	87(2)	139(3)	41(2)	−63(2)	−16(2)
OW7	100(3)	161(4)	140(4)	12(3)	−38(3)	−26(3)
OW8	87(3)	97(2)	113(3)	−15(2)	−48(2)	−5(2)
OW9	70(2)	64(2)	70(2)	−2(1)	−27(2)	−9(1)
P(1)	44(1)	48(1)	44(1)	−2(1)	−13(1)	−7(1)
Cd(1)	43(1)	34(1)	43(1)	−2(1)	−14(1)	−6(1)
Cl(1)	68(1)	70(1)	66(1)	−14(1)	−17(1)	−6(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2 U_{11} + \cdots + 2hka^*b^* U_{12}]$.

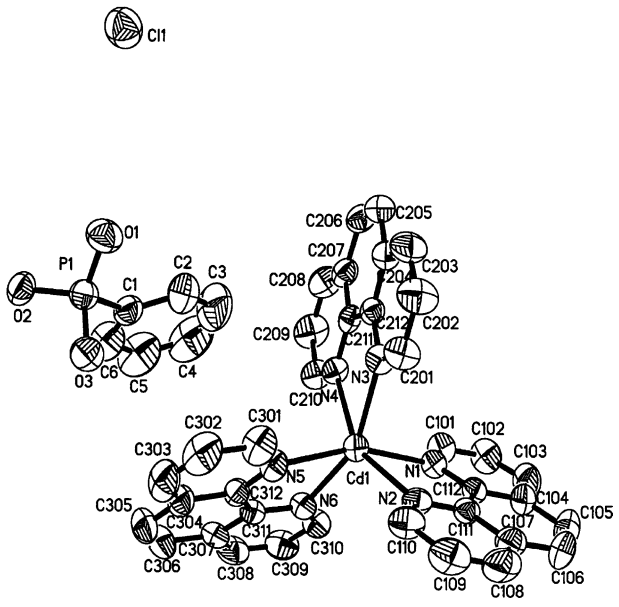

Fig. 4. Asymmetric unit of **4** (the water molecules and hydrogen atoms are omitted for clarity). Atoms are shown as 50% probability ellipsoids.

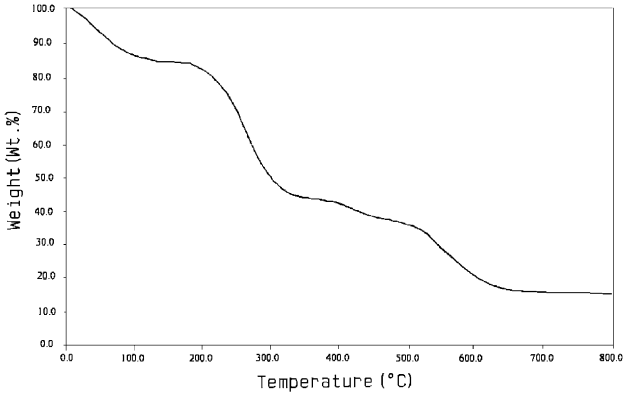

Fig. 5. TGA curve for $[Cu(phen)_3]\cdot C_6H_5PO_3\cdot 11H_2O$ in N_2.

display new remarkable structure containing hydrogen-bonded layers of anions and water molecules. The introduction of *o*-phenanthroline into the divalent transition metal phosphonates in the present work not only displays the function of tailoring the microstructure of layered metal phosphonate, but also provides the methods to extend the knowledge of the chemistry of layered metal phosphonates by introducing organic amine ligand.

Acknowledgments

We thank the Fok Ying Tung Education Foundation and the Ministry of Education of China for Support.

References

[1] J.D. Wang, A. Clearfield, G.Z. Peng, Mater. Chem. Phys. 35 (1993) 208–216.
[2] B.Z. Wan, R.G. Anthony, G.Z. Peng, A. Cleafield, J. Catal. 101 (1986) 19–27.
[3] H. Byrd, A. Cleafield, D.M. Poojary, K.P. Reis, M.E. Thompson, Chem. Mater. 8 (1996) 2239–2246.
[4] D. Deniaud, B. Schollorn, D. Mansuy, J. Rouxel, P. Battioni, B. Bujoli, Chem. Mater. 7 (1995) 995–1000.
[5] G. Alberti, M. Casciola, R. Palombari, Solid State Ion. 61 (1993) 241–244.
[6] A. Clearfield, Curr. Opin. Solid State Mater. Sci. 1 (1996) 268–278.
[7] G. Cao, H. Hong, T.E. Mallouk, Acc. Chem. Res. 25 (1992) 420–427.
[8] G. Cao, T.E. Mallouk, Inorg. Chem. 30 (1991) 1434–1438.
[9] P.J. Zapf, R.C. Haushalter, J. Zubieta, Chem. Commun. (1997) 321–322 and references therein.
[10] J. Morizzi, M. Hobday, C. Rix, J. Mater. Chem. 11 (2001) 794–798.
[11] R.C. Finn, J. Zubieta, Inorg. Chem. 40 (2001) 2466–2467.
[12] R.C. Finn, R.S. Rarig Jr, J. Zubieta, Inorg. Chem. 41 (2002) 2109–2123.
[13] G.M. Sheldrick, Program for crystal structure solution, University of Gottingen, 1997.
[14] G.M. Sheldrick, Program for crystal structure refinement, University of Gottingen, 1997.
[15] G. Cao, H. Lee, V.M. Lynch, T.E. Mallouk, Inorg. Chem. 27 (1988) 2781–2785.
[16] D.M. Poojary, B. Zhang, A. Cabeza, M.A.G. Aranda, S. Bruque, A. Clearfield, J. Mater. Chem. 6 (1996) 639–644.
[17] G. Cao, V.M. Lynch, L.N. Yacullo, Chem. Mater. 5 (1993) 1000–1006.
[18] Y.P. Zhang, A. Clearfield, Inorg. Chem. 31 (1992) 2821–2826.
[19] A. Cabeza, X.Q. Yang, C.V.K. Sharma, M.A.G. Aranda, S. Bruque, A. Clearfield, Inorg. Chem. 41 (2002) 2325–2333.
[20] H.S. Martinez-Tapia, A. Cabeza, S. Bruque, P. Pertierra, S. Garcia-Granda, M.A.G. Abranda, J. Solid State Chem. 151 (2000) 122–129.
[21] Y.G. Li, E.B. Wang, H. Zhang, G.Y. Luan, C.W. Hu, N.H. Hu, H.Q. Jia, J. Solid State Chem. 163 (2002) 10–16.