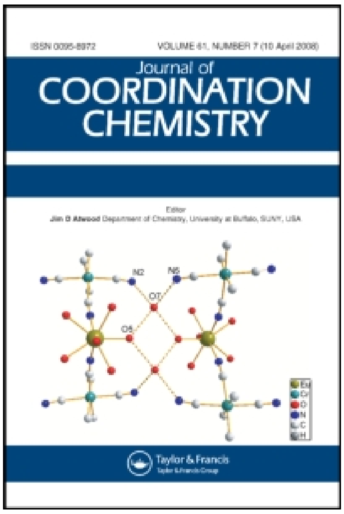

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Syntheses, crystal structures and thermoanalyses of alkaline earth metal complexes derived from dinitropyridone

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Syntheses, crystal structures and thermoanalyses of alkaline earth metal complexes derived from dinitropyridone

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Six new alkaline-earth metal compounds derived from dinitropyridone ligands (3,5-dinitropyrid-2-one, 2HDNP; 3,5-dinitropyrid-4-one, 4HDNP and 3,5-dinitropyrid-4-one-*N*-hydroxide, 4HDNPO) were synthesized and characterized by elemental analysis, FT-IR and partly by powder XRD, TG-DSC and X-ray single-crystal diffraction analysis. The structural determination revealed that one molecule of both magnesium salts ($Mg(2DNP)_2 \cdot 8H_2O$, (**1**), and $Mg(4DNP)_2 \cdot 6H_2O$ (**4**)) comprise one cation $[Mg(H_2O)_6]^{2+}$ and two anions displaying centro-symmetry with the Mg atom located at the center. Two anions (and crystalline water molecules) are joined by hydrogen bonds. The barium salt $Ba(4DNP)_2 \cdot 4H_2O$ (**5**), is a centro-symmetric dimer with each Ba(II) being coordinated by one monodentate ligand anion, two bidentate ligand anions (different coordination pattern) and five water molecules. Another barium salt, $Ba(4DNPO)_2 \cdot 6H_2O$ (**6**), is a coordination polymer, the ten-coordinate (BaO_{10}) barium environment comprising four water molecules, a pair of 4DNPOs *via* the pyridine-*N*-oxide oxygen, and one 4DNPOs from an adjacent metal atom offering chelating nitro group oxygen, bridging adjacent bariums. Abundant intermolecular hydrogen bonds link the molecules of each complex into multi-dimensional chains. The X-ray powder diffraction analysis confirmed the phase homogeneity of the polycrystalline samples. The TG-DSC results revealed that $Mg(2DNP)_2 \cdot 8H_2O$ and $Ba(4DNP)_2 \cdot 6H_2O$ each has three main weight-loss stages. The first step is the loss of all water molecules and the last step is the loss of the nitro groups and/or decomposition of the pyridine rings with the release of heat.

Keywords: Alkaline-earth metal complex; Dinitropyridone; Crystal structure; Powder XRD; Thermoanalysis

1. Introduction

Attention has focused on interactions of common alkali-metal and alkaline-earth-metal cations with biorelevant ligands since these metals are abundant in biological systems [1]. Recent work has contributed to a better understanding of the action of these cations on a molecular level, although many details remain unexplored [1–5].

A variety of substituted dinitropyridone compounds are used as herbicidal chemicals to control the growth of undesired plants or as important intermediates

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for oxidative dyestuffs, medicines or agrochemicals [6a, b]. Also, some dinitropyridone derivatives have nonlinear optics [6c]. A few dinitropyridone derivatives and their metal complexes have higher explosion temperatures and lower sensitivity and are therefore used as energetic catalysts for solid propellants in order to adjust and improve their trajectory properties [6d–6g]. In general, a pyridone has two tautomeric forms: pyridone and hydroxylpyridine. An investigation of the molecular structures of metal complexes derived from pyridone compounds will, therefore, help to understand which form they employ in coordination to metal atoms. To gain insight into coordination modes of heavy alkali and alkaline-earth metal cations towards dinitropyridone compounds, we have synthesized and characterized a number of alkali and alkaline earth metal compounds derived from *ortho* or *para* 3,5-dinitropyridone(–*N*–hydroxide) ligands [7]. The preparation, molecular structures and thermal analyses of a few alkaline earth metal analogs are reported in the present paper.

2. Experimental

2.1. *Physical measurements*

3,5-dinitropyrid-2-one, 3,5-dinitropyrid-4-one and 3,5-dinitro-4-pyridone-N-hydroxide were synthesized following methods previously described with slight modifications [6e, 8]. Alkaline earth metal hydroxides were of analytical reagent grade and used directly without further purification. All experiments were carried out in doubly-distilled water. Infrared spectra were recorded as KBr pellets on a Nicolet 170SX FT-IR spectrometer. Elemental analysis (C, H, N) was determined with a German Vario EL III instrument. Powder XRD was performed on a Rigaku D/MAX2550VB3 +/PC diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å). The DCS and TG-DTG measurement were done with a Thermoanalyzer Systems Q1000DSC+LNCS+FACS Q600SDT of TA company.

2.2. *Complex syntheses*

All complexes were readily prepared by neutralization of a dinitropyridone with the corresponding alkaline-earth metal hydroxide in aqueous solution. The products are highly soluble in water, so single-crystal growth was only successfully accomplished under empirically modified conditions in some cases.

Mg(2DNP)$_2$ · H$_2$O (1). Yield: 85.1%. $F_w = 536.63\,\mathrm{g\,mol^{-1}}$, Anal. Calcd for $C_{10}H_{20}N_6O_{18}Mg$: C, 22.38; H, 3.76; N, 15.66%. Found: C, 22.44; H, 3.64; N, 15.23%. IR(KBr, cm^{-1}): 3429, vs, (O–H); 1598, s, (C=O); 1539, s, $_{\mathrm{asym}}$(N–H); 1334, s, $_{\mathrm{sym}}$(N–O).

Ca(2DNP)$_2$ · H$_2$O (2). Yield: 68.6%. $F_w = 426.27\,\mathrm{g\,mol^{-1}}$, Anal. Calcd for $C_{10}H_6N_6O_{11}Ca$: C, 28.18; H, 1.42; N, 19.72%. Found: C, 28.21; H, 1.46; N, 19.77%. IR(KBr, cm^{-1}): 3478, vs, (O–H); 1602, s, (C=O); 1539, s, $_{\mathrm{asym}}$(N–H); 1339, s, $_{\mathrm{sym}}$(N–O).

$Sr(2DNP)_2 \cdot 2H_2O$ (3). Yield: 68.4%. $F_w = 491.82\,g\,mol^{-1}$, Anal. Calcd for $C_{10}H_8N_6O_{12}Sr$: C, 24.42; H, 1.64; N, 17.09%. Found: C, 24.29; H, 1.66; N, 17.37%. IR(KBr, cm^{-1}): 3481, vs, (O–H); 1608, s, (C=O); 1536, s, $_{asym}$(N–H); 1351, s, $_{sym}$(N–O).

$Mg(4DNP)_2 \cdot 6H_2O$ (4). Yield: 66.4%. $F_w = 500.60\,g\,mol^{-1}$, Anal. Calcd for $C_{10}H_{16}N_6O_{16}Mg$: C, 23.22; H, 3.99; N, 16.79%. Found: C, 23.46; H, 3.86; N, 16.68%. IR(KBr, cm^{-1}): 3571, vs, (O–H); 1649, s, (C=O); 1550, s, $_{asym}$(N–H); 1355, s, $_{sym}$(N–O).

$Ba(4DNP)_2 \cdot 4H_2O$ (5). Yield: 72.35%. $F_w = 1191.22\,g\,mol^{-1}$, Anal. Calcd for $C_{20}H_{28}Ba_2N_{12}O_{30}$: C, 20.17; H, 2.37; N, 14.11%. Found: C, 20.19; H, 2.33; N, 14.22%. IR(KBr, cm^{-1}): 3395, vs, (O–H); 1645, s, (C=O); 1545, s, $_{asym}$(N—H); 1355, s, $_{sym}$(N–O).

$Ba(4DNPO)_2 \cdot 6H_2O$ (6). Yield: 62.62%. $F_w = 645.63\,g\,mol^{-1}$, Anal. Calcd for $C_{10}H_{16}N_6O_{18}Ba$: C, 18.60; H, 2.50; N, 13.02%. Found: C, 18.89; H, 2.23; N, 13.22%. IR(KBr, cm^{-1}): 3391, vs, (O–H); 1665, s, (C=O); 1543, s, $_{asym}$(N–H); 1350, s, $_{sym}$(N–O); 1275, s, (N_{py}–O).

2.3. *Single crystal X-ray diffraction analysis*

The determination of the unit cell and the data collection for **1**, **4**, **5** and **6** were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω–2θ scan technique. The structures were solved by direct methods using SHELXS-97 [9] and refined against F^2 by full matrix least-squares using SHELXL-97 [9]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of water were positioned by difference Fourier maps and refined using a riding model with restraints and the thermal parameters set equal to $1.5U_{eq}$ of the parent oxygen atoms. A summary of the crystal data, experimental details and refinement results are listed in table 1. Selected bond lengths and angles of **1**, **4**, **5** and **6** are listed in table 2 and table 3, respectively. Intermolecular hydrogen bonds of all compounds are summarized in table 4.

3. Results and discussion

3.1. *Description of crystal structures of the complexes*

The molecular structure and atom labeling of **1** are shown in figure 1; the packing of the molecule in the crystal lattice is illustrated in figure 2. The structural analysis revealed a centro-symmetric molecule with Mg located at the center of symmetry. Six oxygen atoms of six water molecules coordinate with Mg to form $[Mg(H_2O)_6]^{2+}$. Two 2DNP anions and two crystalline water molecules are obtained by hydrogen bonds.

As shown in table 2, the distances between Mg to O6–O8 are 2.0697(11), 2.0451(11) and 2.047(11) Å and the bond angles of O7–Mg–O6, O8–Mg–O6 and O7–Mg–O8 are 89.39(5), 89.40(5) and 88.49(5)°, respectively. Therefore, the octahedron formed by the Mg and the six oxygen atoms of water is slightly deformed. In this respect,

Table 1. Crystallographic data for **1**, **4**, **5** and **6**.

	1	**4**	**5**	**6**
Empirical formula	$C_{10}H_{20}N_6O_{18}Mg$	$C_{10}H_{16}N_6O_{16}Mg$	$C_{20}H_{28}Ba_2N_{12}O_{30}$	$C_{10}H_{16}N_6O_{18}Ba$
Crystal size (mm^3)	0.41 × 0.35 × 0.28	0.48 × 0.25 × 0.23	0.45 × 0.43 × 0.37	0.44 × 0.36 × 0.15
Molecular mass	536.63	500.60	1191.22	645.63
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/n$	Fdd2
a (Å)	7.1859(11)	7.477(2)	6.6707(8)	24.143(3)
b (Å)	7.6277(11)	13.190(3)	13.6140(16)	26.133(3)
c (Å)	11.0183(16)	9.880(3)	21.401(3)	6.5855(7)
α (°)	74.795(2)	90.00	90.00	90.00
β (°)	96.8340	98.101(3)	92.0300(10)	90.00
γ (°)	70.996(2)	90.00	90.00	90.00
Volume (Å^3)	550.08(14)	964.5(4)	1942.4(4)	4154.9(8)
Z	1	2	2	8
Temperature (K)	291(2)	298(2)	291(2)	293(2)
Calculated density (g cm^{-3})	1.620	1.724	2.037	2.064
$F(000)$	278	516	1168	2544
Reflections collected	4105	4895	14523	5451
Independent reflections	2039	1692	4386	1907
Data/restraints/parameters	2039/12/193	1692/0/151	2603/18/289	1907/1/159
Goodness-of-fit on F^2	1.092	1.003	1.063	1.087
Final R indices $[I>2\sigma(I)]$	$R_1=0.0316$, $wR_2=0.0827$	$R_1=0.0378$, $wR_2=0.0968$	$R_1=0.0204$, $wR_2=0.0511$	$R_1=0.0123$, $wR_2=0.0309$
R indices (all data)	$R_1=0.0354$, $wR_2=0.0862$	$R_1=0.0511$, $wR_2=0.1116$	$R_1=0.0223$, $wR_2=0.0522$	$R_1=0.0127$, $wR_2=0.0312$

the complex is similar to magnesium(II) picrate undecahydrate and magnesium(II) 4-nitrophenoxide octahydrate [10]. Because the two 2DNP anions are centrosymmetrical around the Mg, they are parallel. The bond length of carbonyl (C=O) is 1.2569(17) Å, longer than that in the free ligand (1.223(3) Å). Moreover, the 3,5-dinitro-2-pyridone anion displays hydrogen-bond interactions with waters of the octahedral array (for example: O6 ··· O1B = 2.8720(16) and O6 ··· O2B = 3.0318(17) Å) and also to lattice water molecules O9(O1D ··· O9 = 2.8060(16) and O2A ··· O9 = 2.9163(17) Å). The anion planes lie completely normal to b, stacked in head-to-head disposition, spacing b (7.6277(11) Å). The molecular structure of **4** is similar to **1**. Again, one molecule of $[Mg(H_2O)_6]^{2+}$ and two ligand anions 4DNP are linked by hydrogen bonds, but **4** contains no lattice water molecules. One unit cell of **4** contains two molecules and the 4DNP anion planes lie completely normal to a, spacing a (7.477(2) Å).

The crystal structure of $Ba(4DNP)_2 \cdot 4H_2O$, (**5**), together with the atomic numbering scheme, is shown in figure 3. The complex is binuclear with a crystallographic inversion center located between two barium ions. Each Ba(II) is ten-coordinate comprising one unidentate anion *via* the pyridine ring nitrogen atom, two bidentate/chelate anions *via* nitro oxygen and/or 4-pyridonato oxygen atoms as well as five waters. It is different in coordination mode from the $Ba(2DNP)_2 \cdot 4H_2O$ [7b] analog due to the different position of the carbonyl group on the pyridine ring. The Ba–O bond distances lie between 2.7–3.3 Å, in the range reported for comparable barium complexes [11a, b]; the Ba(1)–N(1) distance is 2.9302(18) Å. The two barium atoms are bridged by two oxygen atoms from two nitro groups to form a Ba_2O_2 motif which makes an approximately regular parallelogram, with Ba–O distances of 3.2722(17) Å

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **4**.

Mg(2DNP) · 8H_2O (**1**)				Mg(4DNP) · 6H_2O (**4**)			
Mg(1)–O(7)	2.0451(11)	Mg(1)–O(8)	2.047(11)	Mg(1)–O(7)	2.0759(15)	Mg(1)–O(8)	2.0601(17)
Mg(1)–O(6)	2.0697(11)	O(1)–C(5)	1.2569(17)	Mg(1)–O(6)	2.0292(16)	O(1)–C(3)	1.239(3)
O(7)–Mg(1)–O(8)	88.49(5)	O(7)–Mg(1)–O(6)	88.68(5)	O(7)–Mg(1)–O(8)	88.80(7)	O(7)–Mg(1)–O(6)	88.46(7)
O(7)–Mg(1)–O(6)A	89.39(5)	O(7)–Mg(1)–O(8)A	91.51(5)	O(7)–Mg(1)–O(6)A	91.54(7)	O(7)–Mg(1)–O(8)A	91.20(7)
O(8)–Mg(1)–O(6)	89.40(5)	O(8)–Mg(1)–O(6)A	90.61(5)	O(8)–Mg(1)–O(6)	91.53(7)	O(8)–Mg(1)–O(6)A	88.47(7)

Transformations of the asymmetric unit for Mg complexes: Mg(2DNP) · 8H_2O (**1**) A $x+1/2$, $-y+3/2$, $z+1/2$; Mg(4DNP) · 6H_2O (**4**) A $-x$, $-y+2$, $-z$.

Table 3. Selected bond lengths (Å) and angles (°) for **5** and **6**.

$Ba(4DNP)_2 \cdot 4H_2O$ (**5**)				$Ba(4DNPO)_2 \cdot 6H_2O$ (**6**)			
Ba(1)–O(7)	3.2722(17)	Ba(1)–O(7)A	3.0798(16)	Ba(1)–O(1)	2.7590(16)	Ba(1)–O(5)	3.0690(16)
Ba(1)–O(11)	2.8114(17)	Ba(1)–O(12)	2.8989(18)	Ba(1)–O(6)	2.9895(18)	Ba(1)–O(7)	2.7967(16)
Ba(1)–O(15)	2.8398(17)	Ba(1)–N(1)	2.9302(18)	Ba(1)–O(8)	2.8215(16)	O(2)–C(3)	1.244(3)
Ba(1)–O(6)	3.1019(17)	Ba(1)–O(8)A	2.7204(16)	N(1)–O(1)	1.355(2)		
Ba(1)–O(13)	2.7568(18)	Ba(1)–O(14)	2.8244(17)				
O(3)–C(3)	1.249(2)	O(8)–C(8)	1.247(2)				
O(8)–Ba(1)–O(13)	74.25(6)	O(8)–Ba(1)–O(11)	69.96(5)	O(1)–Ba(1)–O(1)A	66.54(6)	O(1)–Ba(1)–O(7)	74.49(5)
O(13)–Ba(1)–O(11)	143.17(6)	O(8)A–Ba(1)–O(14)	144.41(5)	O(1)–Ba(1)–O(7)A	140.93(5)	O(7)–Ba(1)–O(7)A	144.57(8)
O(13)–Ba(1)–O(14)	70.89(6)	O(11)–Ba(1)–O(14)	142.15(5)	O(1)–Ba(1)–O(8)A	128.20(4)	O(7)–Ba(1)–O(8)	81.12(5)
O(8)A–Ba(1)–O(15)	93.55(5)	O(13)–Ba(1)–O(15)	68.37(5)	O(7)–Ba(1)–O(8)A	69.65(5)	O(1)–Ba(1)–O(8)	139.55(4)
O(11)–Ba(1)–O(15)	121.71(5)	O(14)–Ba(1)–O(15)	80.31(5)	O(8)–Ba(1)–O(8)A	68.84(6)	O(1)–Ba(1)–O(6)B	86.02(6)
O(8)A–Ba(1)–O(12)	57.50(5)	O(13)–Ba(1)–O(12)	83.13(6)	O(1)–Ba(1)–O(6)C	66.50(5)	O(7)–Ba(1)–O(6)B	109.04(5)
O(11)–Ba(1)–O(12)	70.63(5)	O(14)–Ba(1)–O(12)	110.55(6)	O(7)A–Ba(1)–O(6)B	81.03(6)	O(8)A–Ba(1)–O(6)B	140.49(6)
O(15)–Ba(1)–O(12)	144.56(5)	O(8)A–Ba(1)–N(1)	123.34(5)	O(8)–Ba(1)–O(6)B	71.96(6)	O(6)B–Ba(1)–O(6)C	147.49(11)
O(13)–Ba(1)–N(1)	117.80(5)	O(11)–Ba(1)–N(1)	76.76(5)	O(1)–Ba(1)–O(5)B	77.71(8)	O(7)–Ba(1)–O(5)B	68.31(5)
O(14)–Ba(1)–N(1)	69.41(5)	O(15)–Ba(1)–N(1)	143.11(5)	O(8)–Ba(1)–O(5)B	63.33(9)	O(5)B–Ba(1)–O(6)B	40.82(5)
O(12)–Ba(1)–N(1)	68.85(5)	O(8)A–Ba(1)–O(7)A	54.78(4)	O(5)B–Ba(1)–O(6)C	137.94(6)	O(1)–Ba(1)–O(5)C	99.78(8)
O(13)–Ba(1)–O(7)A	103.67	O(11)–Ba(1)–O(7)A	61.73(5)	O(7)–Ba(1)–O(5)C	112.66(5)	O(8)–Ba(1)–O(5)C	119.43(9)
O(14)–Ba(1)–O(7)A	141.86(5)	O(15)–Ba(1)–O(7)A	63.39(5)	O(6)B–Ba(1)–O(5)C	137.94(6)	O(5)B–Ba(1)–O(5)C	177.06(17)
O(12)–Ba(1)–O(7)A	106.00(5)	N(1)–Ba(1)–O(7)A	136.53(5)				
O(8)A–Ba(1)–O(6)	146.03(5)	O(13)–Ba(1)–O(6)	133.45(6)				
O(11)–Ba(1)–O(6)	83.07(5)	O(14)–Ba(1)–O(6)	68.51(5)				
O(15)–Ba(1)–O(6)	83.16(5)	O(12)–Ba(1)–O(6)	132.27(5)				
N(1)–Ba(1)–O(6)	66.69(5)	O(7)A–Ba(1)–O(6)	94.63(4)				
O(8)A–Ba(1)–O(7)	108.59(4)	O(13)–Ba(1)–O(7)	135.80(5)				
O(11)–Ba(1)–O(7)	66.47(5)	O(14)–Ba(1)–O(7)	101.31(5)				
O(15)–Ba(1)–O(7)	67.44(4)	O(12)–Ba(1)–O(7)	136.97(5)				
N(1)–Ba(1)–O(7)	97.75(5)	O(7)A–Ba(1)–O(7)	55.37(5)				
O(6)–Ba(1)–O(7)	39.25(4)						

Transformations of the asymmetric unit for Ba complexes: $Ba(4DNP)_2 \cdot 4H_2O$ (**5**) A $-x+1$, $-y+1$, $-z$; $Ba(4DNPO)_2 \cdot 6H_2O$ (**6**) A $-x+1/2$, $-y+1/2$, z; B $x-1/4$, $-y+1/4$, $z-1/4$; C $-x+3/4$, $y+1/4$, $z-1/4$.

Table 4. Hydrogen bonds and angles.

Complex	Atoms	Distance (Å)	Angles (°)	Atoms	Distance (Å)	Angles (°)
Mg(2DNP) $\cdot$ 8H_2O (**1**)	O(7), H(3W)$\cdots$O(9)	2.8483(17), 2.020(9)	173.8(18)	O(6), H(2W)$\cdots$O(1)	2.8830(16), 2.051(10)	173.6(18)
	O(9), H(8W)$\cdots$O(2^{i})	2.9163(17), 2.127(13)	158(2)	O(6), H(1W)$\cdots$O(1^{ii})	2.8720(16), 2.086(12)	158(2)
	O(6), H(1W)$\cdots$O(2^{ii})	3.0318(17), 2.471(18)	173.6(18)	O(7), H(4W)$\cdots$N(1^{iii})	2.7974(16), 1.965(10)	175.0(18)
	O(9), H(7W)$\cdots$O(1^{iv})	2.8060(16), 1.994(12)	163(2)	O(8), H(5W)$\cdots$O(4^{v})	2.9351(17), 2.42(2)	120.6(17)
Mg(4DNP) $\cdot$ 6H_2O (**4**)	O(6), H(6W)$\cdots$O(1)	2.690(2), 1.91	151.9	O(6), H(6W)$\cdots$O(2)	2.882(2), 2.28	128.3
	O(6), H(7W)$\cdots$O(3^{ii})	3.014(3), 2.29	142.6	O(6), H(7W)$\cdots$O(5^{iii})	3.008(3), 2.38	130.7
	O(7), H(8W)$\cdots$O(1)	2.862(2), 2.29	148.9	O(7), H(8W)$\cdots$O(5)	2.965(3), 2.29	136.8
	O(7), H(9W)$\cdots$O(2^{iv})	2.947(2), 2.12	162.7	O(8), H(10W)$\cdots$N(1^{v})	2.757(3), 1.92	169.1
	O(8), H(11W)$\cdots$O(4^{vi})	3.145(3), 2.43	142.8	O(8), H(11W)$\cdots$N(1^{vii})	3.161(3), 2.58	126.3
Ba(4DNP)$_2$ $\cdot$ 4H_2O (**5**)	O(15), H(10W)$\cdots$O(3^{ii})	2.787(2), 2.05	149.73	O(15), H(9W)$\cdots$O(2^{ii})	2.975(2), 2.38	128.14
	O(15), H(9W)$\cdots$O(11^{i})	2.951(2), 2.21	148.02	O(14), H(8W)$\cdots$N(4^{iii})	2.932(2), 2.10	175.86
	O(14), H(7W)$\cdots$O(12^{iv})	2.983(3), 2.23	153.61	O(13), H(6W)$\cdots$O(9^{v})	3.092(3), 2.27	175.08
	O(13), H(5W)$\cdots$O(4^{ii})	3.045(3), 2.38	138.53	O(13), H(5W)$\cdots$O(3^{ii})	2.871(2), 2.15	147.46
	O(12), H(4W)$\cdots$O(9^{i})	3.058(3), 2.39	135.10	O(12), H(4W)$\cdots$O(8^{i})	2.707(2), 2.11	125.94
	O(12), H(3W)$\cdots$N(3^{vi})	3.490(2), 2.70	155.58	O(12), H(3W)$\cdots$O(5^{vi})	3.118(2), 2.51	129.34
	O(12), H(3W)$\cdots$O(4^{vi})	3.039(2), 2.20	169.52	O(11), H(2W)$\cdots$O(15^{vii})	2.833(2), 2.05	158.83
Ba(4DNPO)$_2$ $\cdot$ 6H_2O (**6**)	O(7), H(1W)$\cdots$O(2^{i})	3.121(2), 2.34	158.8	O(8), H(3W)$\cdots$O(1^{iii})	2.745(2), 1.91	178.6
	O(7), H(2W)$\cdots$O(9^{ii})	2.812(3), 2.04	155.2	O(8), H(4W)$\cdots$O(3^{iv})	3.086(2), 2.28	165.0
	O(8), H(3W)$\cdots$N(1^{iii})	3.439(2), 2.68	152.6	O(9), H(6W)$\cdots$O(2)	3.021(2), 2.21	166.4
	O(9), H(5W)$\cdots$O(8^{v})	2.856(2), 2.03	175.3			

Transformations of the asymmetric unit for four complexes:

Mg(2DNP) $\cdot$ 8H_2O (**1**) (i) $-x, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x, y+1, z$; (v) $-x+1, -y+1, -z$.

Mg(4DNP) $\cdot$ 6H_2O (**4**) (i) $-x, -y+2, -z$; (ii) $x, -y+5/2, z-1/2$; (iii) $-x, y+1/2, -z+1/2$; (iv) $-x, y-1/2, -z+1/2$; (v) $-x+1, -y+2, -z+1$; (vi) $x, -y+3/2, z-1/2$; (vii) $x, y, z-1$.

Ba(4DNP)$_2$ $\cdot$ 4H_2O (**5**) (i) $-x+1, -y+1, -z$; (ii) $x-1/2, -y+1/2, z-1/2$; (iii) $-x+1/2, y-1/2, -z+1/2$; (iv) $x-1, y, z$; (v) $x, y-1, z$; (vi) $-x+3/2, y-1/2, -z+1/2$; (vii) $x+1, y, z$; (viii) $-x+3/2, y+1/2, -z+1/2$.

Ba(4DNPO)$_2$ $\cdot$ 6H_2O (**6**) (i) $-x+1, -y+1/2, z-1/2$; (ii) $x-1/4, -y+1/4, z-1/4$; (iii) $-x+1/2, -y+1/2, z-1$; (iv) $-x+3/4, y-1/4, z-3/4$; (v) $x+1/2, y, z+1/2$.

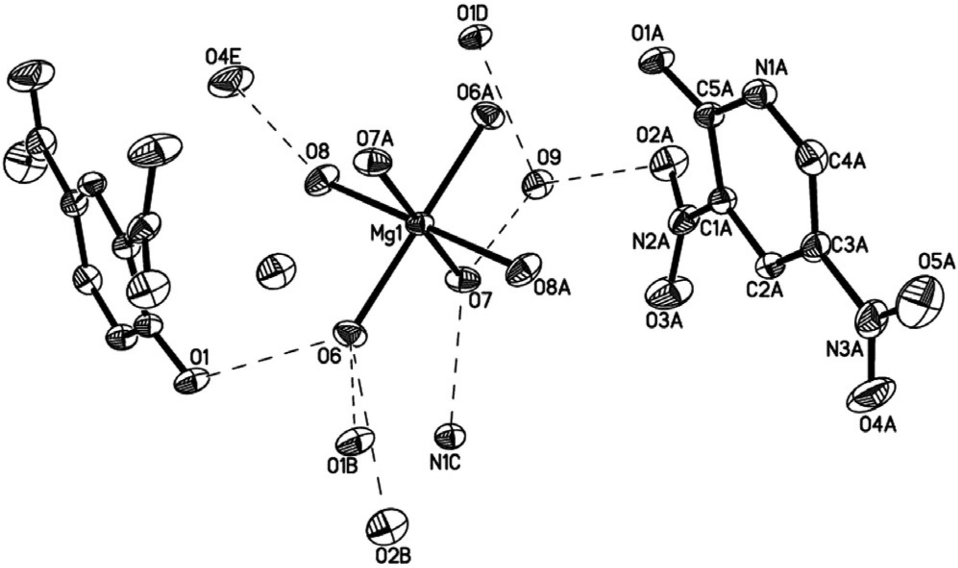

Figure 1. The molecular structure and atom labeling of $Mg(2DNP)_2 \cdot 8H_2O$ (**1**), emphasizing the intra- and intermolecular hydrogen bonds.

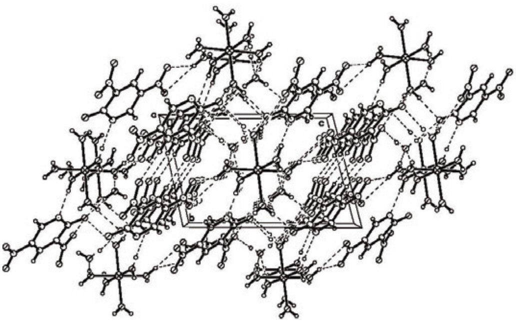

Figure 2. Packing diagram of **1**, projected down *a*.

(Ba(1)–O(7)) and 3.0798(16) Å (Ba(1)–O(7)A). The free and coordinated carbonyl (C=O) distances are almost equal (1.249(2) Å for the free one and 1.247(2) Å for the coordinated one), indicative of delocalization of charge and quinoid structure existing in the compound. There exist several intermolecular hydrogen bonds due to coordinated water, extending the dimeric molecules into a three-dimensional network. The hydrogen bond distances are in the range 2.707(2) to 3.490(2) Å and the detailed data are listed in table 4.

As shown in figures 4 and 5, $Ba(4DNPO)_2 \cdot 6H_2O$ (**6**) is a two-dimensional coordination polymer, generated in space group Fdd2, one-half of the formula unit comprising the asymmetric unit. Successive bariums are linked by a nitro group on the pyridine ring of one 4DNPO anion by the O, O′-chelate ring, so that each

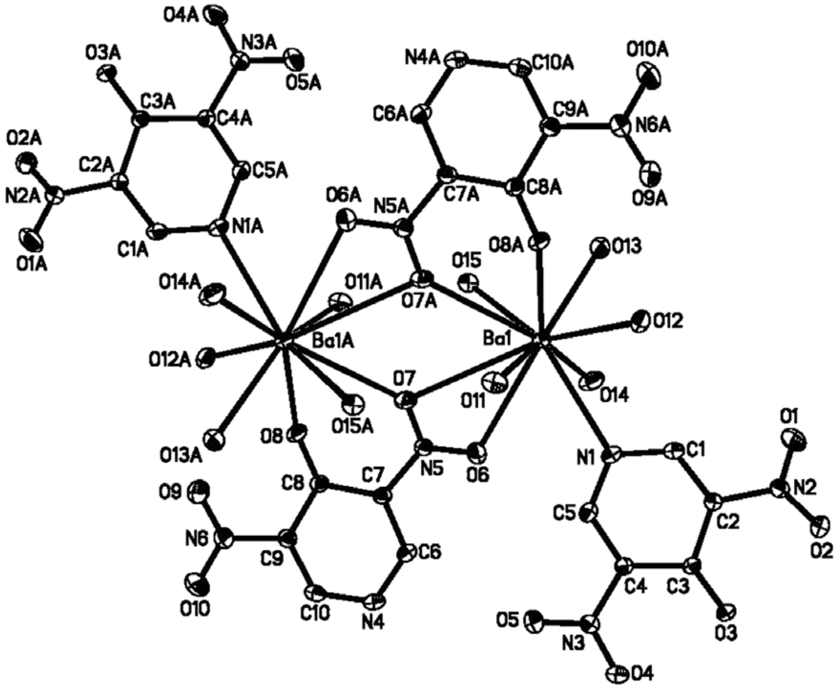

Figure 3. Crystal structure of $Ba(4DNP)_2 \cdot 4H_2O$ (**5**).

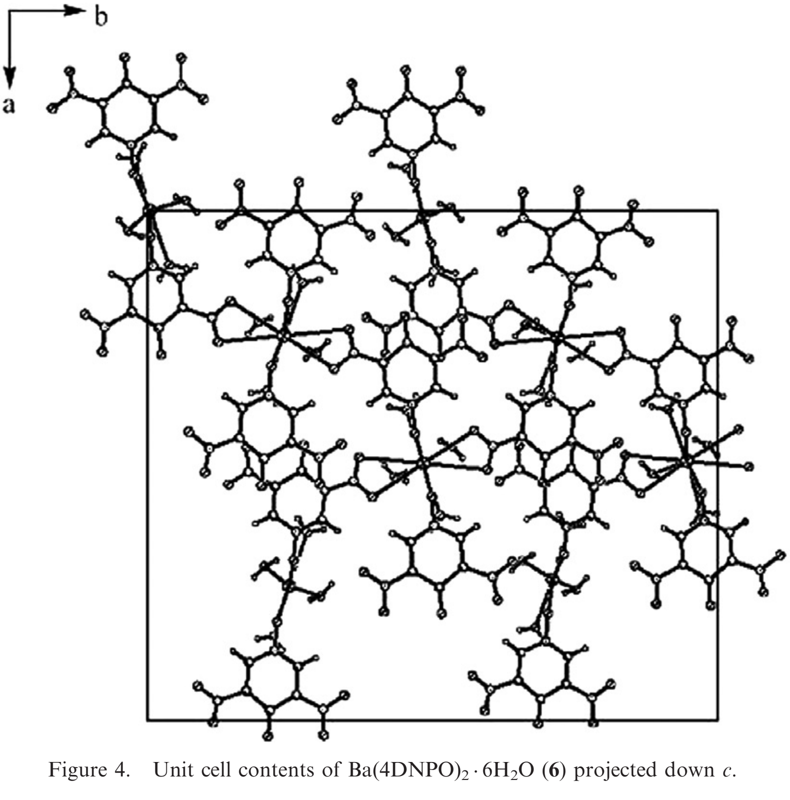

Figure 4. Unit cell contents of $Ba(4DNPO)_2 \cdot 6H_2O$ (**6**) projected down *c*.

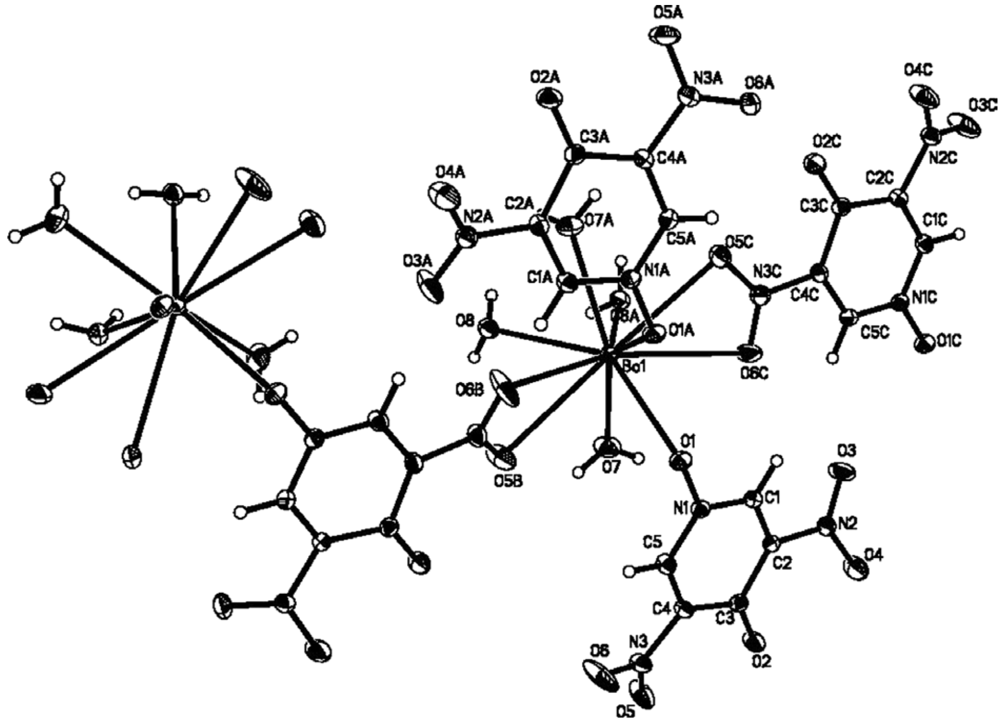

Figure 5. A view of **6**.

ligand is tridentate. The ten-coordinate environment of the metal has four unidentate water molecules (the average Ba(1)–O_w = 2.8091(16) Å) and four ligand anions, two of which bond through the 4-pyridone-*N*-hydroxylato oxygens (Ba(1)–O(1) = 2.7590(16) Å) and the other two through a chelating nitro oxygen (Ba(1)–O_{nitro} = 3.0293(16) Å). With the presence of coordinated and lattice water, intermolecular hydrogen bonds are formed, extending the two-dimensional polymer into a three-dimensional network. The hydrogen bond distances are in the range 2.745(2)–3.439(2) Å and the O–H $\cdots$ O(N) angles in the range 152.6–178.6°. Detailed hydrogen bond data are listed in table 4.

3.2. *Infrared spectra*

The strong and broad adsorption peaks between 3600 and 3200 cm^{-1} for all six complexes are characteristic of OH groups in coordinated water molecules. The peaks between 1645 and 1598 cm^{-1} are attributed to stretching of coordinated carbonyl groups of the ligand anions in comparison with those in corresponding free ligands (1666, 1660 and 1664 cm^{-1}, respectively). The N_{py}–O stretching vibration of the pyridine-*N*-oxide ring in (**6**) (1275 cm^{-1}) shifts to lower wave-number compared with that in the free ligand (1288 cm^{-1}), showing coordination of the Ba(II) ion with the O atom of the pyridine *N*-oxide moiety leading to decrease in the stretching frequency of the N_{py}–O bond. The IR data are consistent with the single crystal structural analysis.

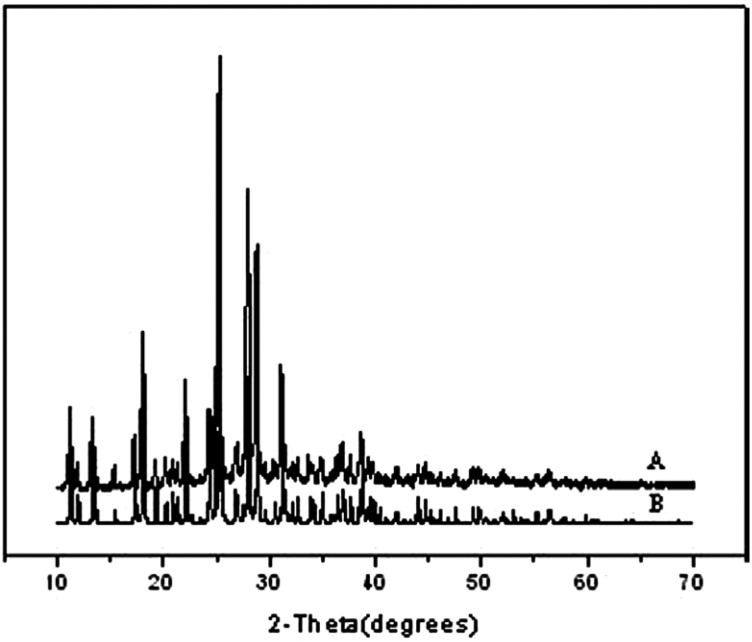

Figure 6. PXRD profiles measured for the bulk sample of $Mg(4DNP)_2 \cdot 6H_2O$ (**4**) (**A**) and calculated from the single-crystal structure of **4** (**B**).

3.3. *X-ray powder diffraction*

The powder XRD profiles of **4** (figure 6) indicate that the diffraction peaks of the polycrystalline sample are in good agreement with the results simulated on the basis of single-crystal structure, proving the phase purity of the powder product. The differences of diffraction intensity may originate from the preferred orientations of the sample.

3.4. *Thermal analysis*

The thermal behaviors of **1** and **5** were investigated. There are three peaks (82, 241 and 385°C) on the DTG curve of **1** (figure 7), indicating three stages of decomposition. The first stage shows a weight loss (26.2% mass loss) from *ca.* 70 to 207°C, in agreement with theoretical mass loss of 27.1%, corresponding to the dehydration of six coordinated and two lattice waters. At the second stage there is *ca.* 10% mass loss; after the third stage the mass of the residue, 7.19%, agrees with the expectation for MgO (7.45%). The corresponding DSC curve, as shown in figure 8, shows two endothermic peaks (80 and 139°C) and one exothermic peak (398°C), corresponding to two dehydration steps and one decomposition step of the nitro groups and pyridone ring.

The TG-DTG curves of (**5**) also showed three main weight-loss steps, similar to **1**. The first step is loss of 11.92%, in agreement with the theoretical value for loss of four waters (12.1%). Correspondingly, the DSC curve shows two endothermic peaks

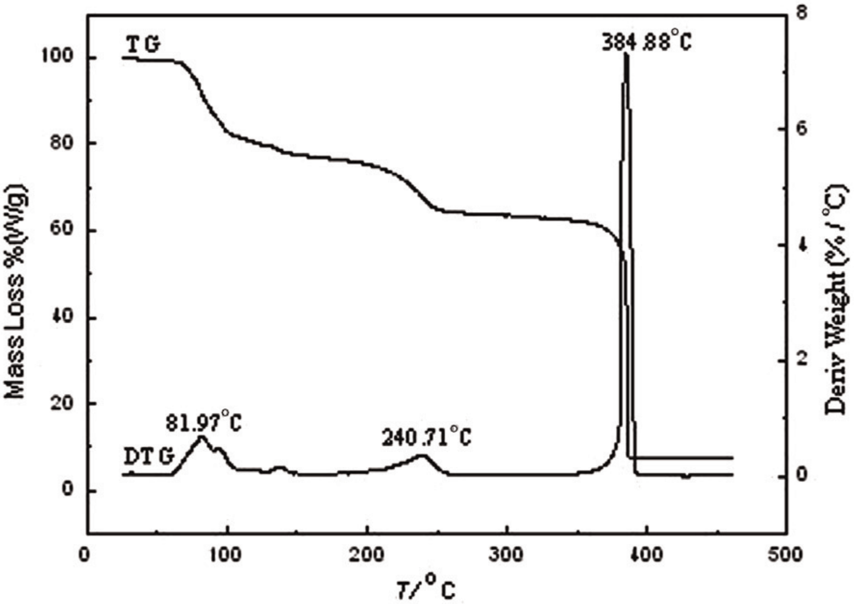

Figure 7. The TG-DTG curves of **1**.

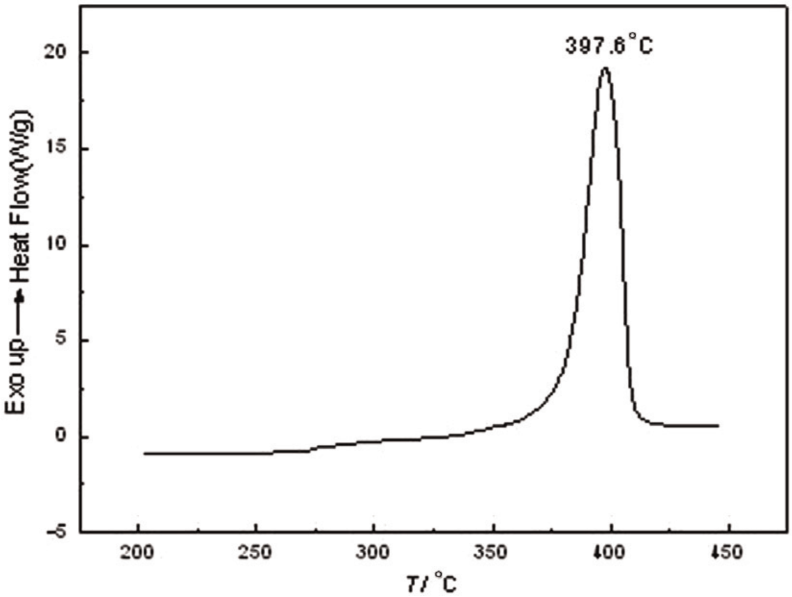

Figure 8. The DSC curves of **1**.

at 57 and 128°C. The second step is weight loss of 10%; after the third step the mass of the residue (26.7%) is consistent with BaO (25.8%). Correspondingly, its DSC curve shows an exothermic peak at 377°C, due to the decomposition of the pyridone ring and/or nitro groups.

4. Conclusion

Six new alkaline-earth metal compounds derived from dinitropyridone, *i.e* 3,5-dinitro-2(4)-pyridone(–*N*–hydroxide) have been synthesized and characterized. The crystal structure analyses showed that both magnesium compounds are ionic salts with each Mg(II) ion coordinated by six waters and the ligand as counter ion. One barium complex is binuclear with a crystallographic inversion center and the other barium complex is a two-dimensional coordination polymer. The thermoanalyses showed that $Mg(2DNP)_2 \cdot 8H_2O$ and $Ba(4DNP)_2 \cdot 6H_2O$ have three main weight-loss stages. For **1**, the first step is the loss of water molecules, the second loss of nitro groups and finally decomposition of the framework of the pyridone ring. As for **5**, similar thermal behavior is encountered, but the second mass-loss step cannot be ascribed.

Supplementary material

CCDC-657227 (**1**), CCDC-657229 (**4**), CCDC-657228 (**5**) and CCDC-654259 (**6**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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