

Full Length Research Paper

Syntheses and crystal structures of two o-phthalate based transition metal complexes

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We report the synthesis and the crystal structures of two complexes. The two metal complexes; (1) [Zn(bipy)₂(HPht)](HPht)·H₂O and (2) [Cu₂(Pht)₂(Bipy)₂]·4H₂O (where Pht²⁻ = dianion of o-phthalic acid, HPht⁻ = anion of o-phthalic acid, Bipy = 2, 2'-bipyridine) have been synthesized and their crystal structures were determined by elemental analyses, IR and single crystal diffraction analyses. X-ray

diffraction studies show that the complex 1 crystallizes in triclinic system, space group $P\bar{1}$, with lattice parameters $a = 10.0134(4)$, $b = 11.7090(4)$, $c = 14.0979(5)\text{Å}$, $\alpha = 111.0560(10)$, $\beta = 105.9690(10)$, $\gamma = 91.028^\circ(2)$, $V = 1617.27(10)\text{Å}^3$ and $Z = 2$; Complex 2 crystallizes in monoclinic system, space group $P2(1)/n$, with lattice parameters $a = 8.8148(6)$, $b = 12.9931(9)$, $c = 15.7454(11)\text{Å}$, $\beta = 100.131^\circ(2)$, $V = 2954.24\text{Å}^3$ and $Z = 4$.

Key words: 2, 2'-bipyridine, zinc, cupric, crystal structure, potassium biphthalate.

INTRODUCTION

The construction of metal-organic hybrid compounds are of considerable interest and importance in recent years, owing to not only their intriguing structural motifs but also their potential applications in catalysis, medicine, host-guest chemistry and the promising photomaterials, electromaterials and magnetic materials (Leininger et al., 2000; Hagman et al., 1999; Zhang et al., 2002; Feng and Xu, 2001). O-Phthalic acid is a versatile ligand for coordinating to metal ions in various modes, such as monodentate bonding through a carboxylic O atom, bidentate fashion *via* two carboxylic O atoms and triple coordination through its three carboxylic O atoms, and bridging mode with two or four O atoms of its carboxylate groups. The coordination properties thus allow for the preparation of complexes with a large variety of architectures, forming isolated mono-, di- and polynuclear, as well as one-, two- and three-dimensional networks. Mixed ligand complexes with o-Phthalic acid and 2, 2'-bipyridine are investigated extensively recently

and some crystal structures have been determined for Cu²⁺ (Zhang et al., 2000; Hao et al., 2004), Co²⁺ (Baca et al., 2005; Hu et al., 2004), Mn²⁺ (Ma et al., 2004; Yang et al., 2005), Ni²⁺ (Poletti et al., 1900; Xue et al., 1993) and Pb²⁺ (Yu et al., 2008). In this paper, we report the hydrothermal synthesis and structural characterization of two complexes (1) [Zn(bipy)₂(HPht)](HPht)·H₂O and (2) [Cu₂(Pht)₂(bipy)₂]·4H₂O.

MATERIALS AND METHODS

Materials and physical measurements

All reagents were commercially available and used without further purification. C, H and N data were obtained using American PE 2400 II CHNS/O elemental analyzer. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system.

Preparation of complexes 1-2

Synthesis of [Zn(bipy)₂(Pht)](HPht)·H₂O(1)

Zn(SO₄)₂·7H₂O (0.2870 g, 1 mmol), KHphth (Potassium

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Table 1. Crystal data and structure refinement for 1 and 2.

Parameter	1	2
Empirical formula	C ₃₆ H ₂₈ N ₄ O ₉ Zn	C ₃₆ H ₃₂ Cu ₂ N ₄ O ₁₂
Formula weight	725.99	839.74
Temperature(K)	296(2)	296(2)
Wavelength(Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$\bar{1}$ P1	P2(1)/n
<i>a</i> (Å)	11.0134(4)	8.8148(6)
<i>b</i> (Å)	11.7090(4)	12.9931(9)
<i>c</i> (Å)	14.0979(5)	15.7454(11)
α (°)	111.0560(10)	90
β (°)	105.9690(10)	100.131(2)
γ (°)	91.028(2)	90
<i>V</i> (Å ³)	1617.27(10)	1775.2(2)
<i>Z</i>	2	2
<i>D_c</i> (mg/m ³)	1.491	1.571
<i>F</i> (000)	748	860
<i>h</i>	-13 ≤ <i>h</i> ≤ 13	-10 ≤ <i>h</i> ≤ 10
<i>k</i>	-14 ≤ <i>k</i> ≤ 9	-14 ≤ <i>k</i> ≤ 16
<i>l</i>	-13 ≤ <i>l</i> ≤ 17	-19 ≤ <i>l</i> ≤ 15
Completeness	94.3	99.9
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.0645, <i>wR</i> ₂ =0.1873	<i>R</i> ₁ =0.0402, <i>wR</i> ₂ =0.1220
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0725, <i>wR</i> ₂ =0.1970	<i>R</i> ₁ =0.0461, <i>wR</i> ₂ =0.1277
Goodness-of-fit on <i>F</i> ²	1.092	1.112

bipthalate) (0.2040 g, 1 mmol) and 2, 2'-bipyridine (0.1560 g, 1 mmol) were mixed in 10 mL deionized water and 10 mL C₂H₅OH. After stirring half an hour, the mixture was placed in 25 mL Teflon-lined reactor and heated at 130°C in an oven for 3 days, cooled slowly to room temperature and the pale yellow block crystals of the title complex 1 suitable to X-ray diffraction analysis were obtained. C₃₆H₂₈N₄O₉Zn (725.99) Anal. Found: C 59.50, H 3.86, and N 6.61. Calcd: C 59.56, H 3.56, N 6.58. IR data: (KBr pellet, cm⁻¹), 3414(m), 2607(w), 1910(w), 1716(s), 1579(s), 1543(s), 1478(s), 1404(s), 1315(m), 1252(m), 1157(m), 1022(s), 864(m), 773(s), 779(w), 650(m), 575(m).

Synthesis of [Cu₂(Pht)₂(bipy)₂]·4H₂O (2)

The procedure is similar to that of 1, except that Cu(SO₄)₂·5H₂O was used. C₃₆H₃₂Cu₂N₄O₁₂ (839.74) Anal. Found: C 51.46, H 3.84, and N 6.63. Calcd: C 51.44, H 3.81, N 6.67. IR data: (KBr pellet, cm⁻¹), 3448 (m), 3064 (m), 2324 (w), 1604 (s), 1472 (m), 1443 (m), 1376 (s), 1152 (m), 1107 (m), 850 (s), 807 (m), 770 (s), 730 (m), 651(w), 522 (w).

Crystal structure determination

The X-ray single crystal data collections for complex 1 and 2 were performed on a Bruker Smart CCD diffractometer equipped with a graphite monochromator Mo-Kα radiation (λ=0.71073 Å). Multi-scan absorption correction was applied using the SADABS program (Sheldrick, 1996). The structures were solved by direct method using the SHELXS-97 program (Sheldrick, 1997). Refinements on

*F*² were performed using SHELXL-97 (Sheldrick, 1997) by full-matrix least-squares with anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms of Pht²⁻, HPht⁻ and 2, 2'-bipyridine were generated geometrically, while the H atoms of lattice water molecules were located from Fourier difference map and refined subject to an O-H=0.85(1)Å. Part H atoms of lattice water molecule in 2 were not located for high values of temperature factor of O atoms. The crystal data is given in Table 1.

Supplementary material

Crystallographic data for title compounds 1 and 2 were deposited to the Cambridge crystallographic data center with deposition numbers CCDC, 701976 and 615071, respectively.

RESULTS AND DISCUSSION

Spectroscopic properties

The IR spectrum exhibit a medium-intensity and broad band with maxima at 3414 and 3448 cm⁻¹ for 1 and 2 corresponding to the stretching vibration of lattice water molecules. The strong peaks at 1579 to 1543 and 1478 to 1404 cm⁻¹ regions for 1, 1604 and 1472 to 1443 cm⁻¹ for 2, can be attributed to the asymmetric and symmetric stretching vibrations of the coordinated carboxylate

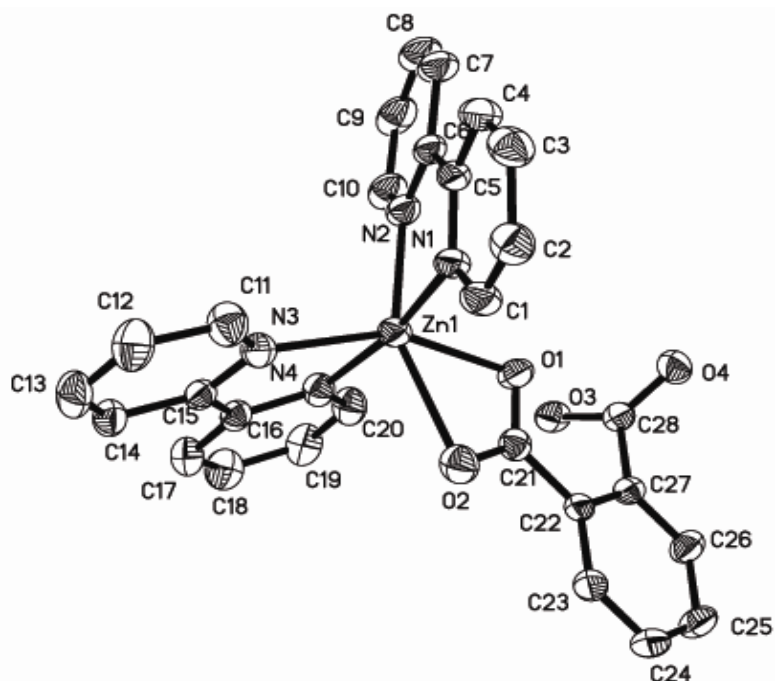


Figure 1. The coordination environment of the Zn(II) ion in 1. All hydrogen atoms are omitted for clarity.

groups of the phthalate ligands, respectively. Absorption band at 1716 cm^{-1} indicates the presence of uncoordinated o-phthalic acid in the complex 1.

Crystal structures

The structure of $[\text{Zn}(\text{bipy})_2(\text{HPht})](\text{HPht}) \cdot \text{H}_2\text{O} (1)$

X-ray diffraction analysis revealed that 1 consists of a mononuclear $[\text{Zn}(\text{bipy})_2(\text{HPht})]^+$ cation, HPht anion and one solvate H_2O molecule, which is different from the structure of a dimer $[(\text{bpy})_2\text{Zn}(\text{Pht})\text{H}(\text{Pht})\text{Zn}(\text{bpy})_2](\text{HPht})(\text{H}_2\text{Pht}) \cdot 2\text{H}_2\text{O}$ (Svetlana et al., 2003), as shown in Figure 1. Zn atom in the mononuclear unit has a distorted octahedral geometry with four nitrogen atoms from two chelating bpy ligands (Zn–N bond distances range from 2.104(3) to 2.149(3) Å) and two oxygen atoms from one chelating carboxylate group of HPht ligand (Zn–O 2.094(3) and 2.336(3) Å) (Table 2). Bond lengths of C(28)–O(3) (1.287(5) Å) are distinctly longer than those of C(28)–O(4) (1.216(5) Å), indicating that the uncoordinated carboxylate groups have not been ionized.

Nevertheless, the bond lengths of C(21)–O(1) and C(21)–O(2) (1.255(5) and 1.246(5) Å) are very close, which shows that the chelating carboxylate group are deprotonated. The observed distortion from octahedral geometry can be caused by small bite angle of the chelating carboxylate group [O(1)–Zn(1)–O(2) bond angle

is $58.66(10)^\circ$]. The other two bite angles N(2)–Zn(1)–N(1), N(4)–Zn(1)–N(3) ($77.71(13)$ and $76.54(13)^\circ$) deviate normal angle for octahedral geometry. The bicyclic rings A: N1/C1/C2/C3/C4/C5 and B: N2/C6/C7/C8/C9/C10, C: N3/C11/C12/C13/C14/C15 and D: N4/C16/C17/C18/C19/C20, are essentially coplanar with corresponding dihedral angles of 8.3° and 1.6° , respectively. The coordinated carboxylate group (C21/O1/O2) is coplanar with the base plane E: C22/C23/C24/C25/C26/C27 with the dihedral angle 8.5° , while the uncoordinated carboxylate group (C28/O3/O4) is non-coplanar with base plane E: C22/C23/C24/C25/C26/C27 with dihedral angle 76.3° . The lattice water and uncoordinated carboxylate O atoms participate to form hydrogen bonds, thus forming three-dimensional network (Figure 2 and Table 3).

The structure of $[\text{Cu}_2(\text{Pht})_2(\text{bipy})_2] \cdot 4\text{H}_2\text{O} (2)$

X-ray diffraction analysis revealed that the title complex 2 consists of isolated dicarboxylato-bridged dinuclear $[\text{Cu}_2(\text{bipy})_2(\text{pht})_2]$ unit and lattice water molecules, which is different from the structure of a reported o-phthalate-bridged copper(II) chain complex of $\{[\text{Cu}(\text{bipy})(\text{m-phthalate})\text{H}_2\text{O}] \cdot 3.5\text{H}_2\text{O}\}_n$ (Zhang et al., 2000). The molecular structure of the title complex 2 is shown in Figure 3, with all hydrogen atoms and water molecules omitted for clarity. The coordination environment around central copper (II) ion in the structure is slightly distorted

Table 2. Selected bond distances (Å) and bond angles (°) for compounds 1 and 2.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)-O(1)	2.094(3)	Zn(1)-N(1)	2.124(3)
Zn(1)-O(2)	2.336(3)	Zn(1)-N(2)	2.104(3)
Zn(1)-N(3)	2.149(3)	Zn(1)-N(4)	2.134(4)
O(3)-C(28)	1.287(5)	O(4)-C(28)	1.216(5)
O(1)-C(21)	1.255(5)	O(2)-C(21)	1.246(5)
Angle	ω , deg	Angle	ω , deg
O(1)-Zn(1)-N(2)	96.53(12)	O(1)-Zn(1)-N(1)	98.66(12)
N(2)-Zn(1)-N(1)	77.71(13)	O(1)-Zn(1)-N(4)	91.92(12)
N(1)-Zn(1)-N(3)	93.43(13)	N(4)-Zn(1)-N(3)	76.54(13)
O(1)-Zn(1)-O(2)	58.66(10)	N(1)-Zn(1)-O(2)	94.66(12)
N(4)-Zn(1)-O(2)	90.09(13)	N(3)-Zn(1)-O(2)	97.28(12)
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cu(1)-O(1)	2.4080(19)	Cu(1)-O(1)#1	1.9446(18)
Cu(1)-O(4)#1	1.903(2)	Cu(1)-N(1)	1.993(2)
Cu(1)-N(2)	1.980(2)		
Angle	ω , deg	Angle	ω , deg
O(4)#1-Cu(1)-O(1)#1	91.63(9)	O(1)#1-Cu(1)-N(2)	94.63(9)
O(4)#1-Cu(1)-N(1)	92.27(10)	N(2)-Cu(1)-N(1)	81.38(10)
O(4)#1-Cu(1)-O(1)	94.51(9)	O(1)#1-Cu(1)-O(1)	76.56(8)
N(2)-Cu(1)-O(1)	89.63(9)		

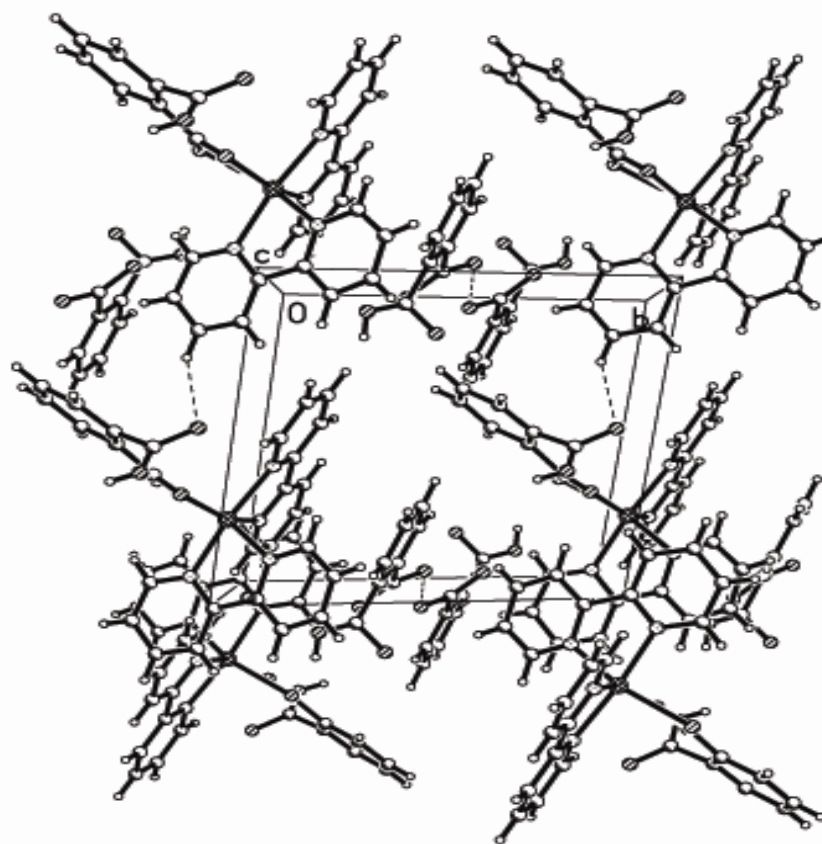
**Figure 2.** Crystal packing view of 1 along the c axis.

Table 3. Hydrogen bonds for 1.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4)...O(9)#1	0.82	2.27	2.838(6)	126.8
O(9)-H(9B)...O(7)#2	0.852(10)	1.86(5)	2.572(7)	140(8)
O(9)-H(9B)...O(8)#2	0.852(10)	2.58(3)	3.362(11)	153(5)

Symmetry transformations used to generate equivalent atoms: #1 x, y, z-1, #2 -x,-y+1,-z+1.

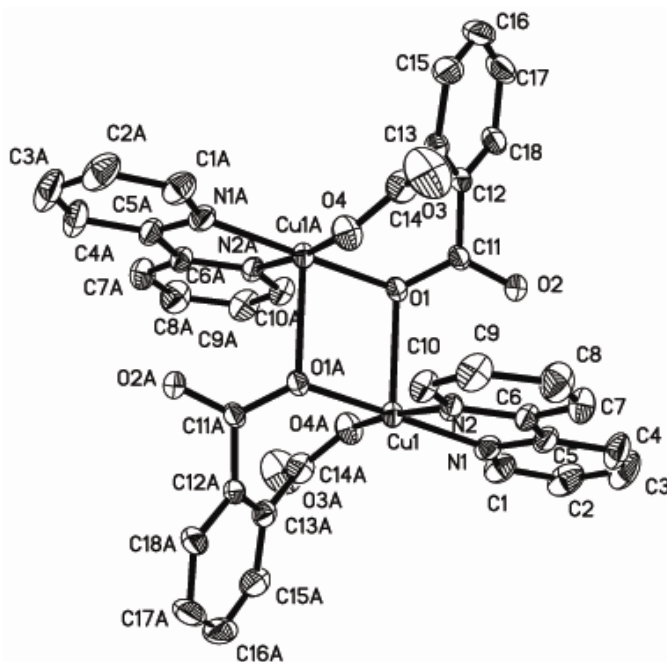


Figure 3. The coordination environment of the Cu(II) ion in 2. All hydrogen atoms are omitted for clarity.

square pyramid. The Cu^{2+} is located 0.0314 \AA above the average plane defined by oxygens N1, N2, O1A and O4A, which deviate from such average plane 0.0016 \AA above (N1), 0.0131 \AA above (N2), 0.0031 \AA above (O1A) and 0.0137 \AA above (O4A). In the equatorial plane, the Cu^{2+} is coordinated by two nitrogen atoms [N(1) and N(2)] from one chelate 2, 2'-bipyridine molecule with the bond distances of [$\text{Cu}(1)\text{-N}(1) = 1.993(2) \text{ \AA}$, $\text{Cu}(1)\text{-N}(2) = 1.980(2) \text{ \AA}$] and two oxygen atoms [O(1A) and O(4A)] from one bridging carboxylate group of Phth^{2-} with the bond distances of [$\text{Cu}(1)\text{-O}(1\text{A}) = 1.9446(18) \text{ \AA}$, $\text{Cu}(1)\text{-O}(4\text{A}) = 1.903(2) \text{ \AA}$].

The apical water molecule is coordinated at a longer distance [$\text{Cu}(1)\text{-O}(1) = 2.4080(19) \text{ \AA}$] for the Jahn-Teller effect (Figure 3 and Table 2). Herein the two Phth^{2-} anion acted as a tridentate ligand bridging two Cu atoms and forms an isolated dinuclear unit. The observed distortion from square pyramid geometry can be caused by small bite angle of the chelating 2, 2'-bipyridine ligand [N(1)-Cu(1)-N(2) bond angle is $81.38(10)^\circ$] and other bond angles O-Cu(1)-N [vary from $89.63(9)$ to $94.63(9)^\circ$]. The

bicyclic rings A: N1/C1/C2/C3/C4/C5 and B: N2/C6/C7/C8/C9/C10 of bipy ligand are essentially coplanar with corresponding dihedral angles of 2.1° . The coordinated carboxylate groups (C11/O1/O2) and (C14/O3/O4) is non-coplanar with the base plane C: C12/C13/C14/C15/C16/C17 with the dihedral angle 59.2 and 48.4° , respectively, while the two coordinated carboxylate groups are almost orthogonal with the dihedral angle 84.3° . The lattice water and carboxylate O atoms participate to form hydrogen bonds, thus forming three-dimensional network (Figure 4).

Conclusion

In summary, assembling hybrid ligands of Phth, Bipy and H_2O with Cu^{2+} and Zn^{2+} , the complexes 1 and 2 have been synthesized by hydrothermal process. The complex 1 is a mononuclear molecule, while the 2 is a dimer with the two Phth^{2-} anion acted as a tridentate ligand bridging two Cu atoms to form an isolated binuclear unit.

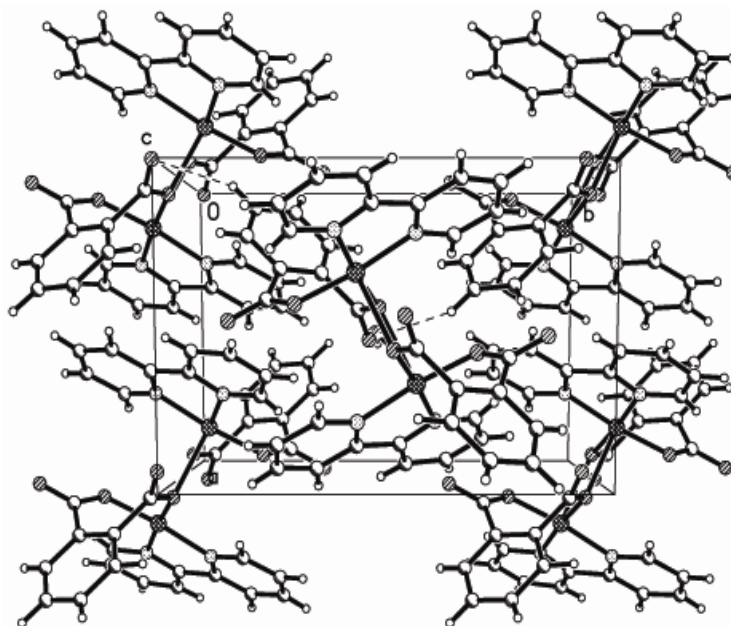


Figure 4. Crystal packing view of 2 along the c axis.

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REFERENCES

- Baca SG, Filippova IG, Ambrus C, Gdaniec M, Simonov YA, Gerbeleu N, Gherco OA, Decu-rins S (2005). From Mono- and Dinuclear to Polynuclear Cobalt(II) and Cobalt(III) Coordination Compounds Based on *o*-Phthalic Acid and 2,2'-Bipyridine: Synthesis, Crystal Structures and Properties. *Eur. J. Inorg. Chem.*, 15: 3118-3130.
- Feng SH, Xu RR (2001). *New Materials in Hydrothermal Synthesis*. *Acc. Chem. Res.*, 34(3): 239-247.
- Hagrman PJ, Hagrman D, Zubieta J (1999). Organic-Inorganic Hybrid Materials: From "Simple" Coordination Polymers to Organodiamine Templated Molybdenum Oxides. *Angew. Chem. Int. Ed.*, 38(18): 2638-2684.
- Hao N, Li YG, Wang EB, Shen EH, Hu CW, Xu L (2004). Hydrothermal synthesis and crystal structure of an infinite 1D ladderlike metal-organic compound: $[\text{Cu}_2(\text{btec})(2,2'\text{-bipy})_2]_\infty$ (btec=1,2,4,5-benzenetetracarboxylate). *J. Mol. Struct.*, 697(1-3): 1-8.
- Hu ML, Ye MD, Xiao HP, Yuan JX (2004). Crystal structure of bis[triaqua(2,2-bipyridine)cobalt(II)] 1,2,4,5-benzenetetracarboxylate dihydrate, $[\text{Co}_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_6(\text{C}_{10}\text{H}_2\text{O}_8)] \cdot 2\text{H}_2\text{O}$. *Z. Kristallogr.*, 219: 19-20.
- Leininger S, Olenyuk B, Stang PJ (2000). Self-Assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals. *Chem. Rev.*, 100(3): 853-908.
- Ma CB, Wang WG, Zhang XF, Chen CN, Liu QT, Zhu HP, Liao DZ, Li LC (2004). Molecular, One and Two-Dimensional Systems Built from Manganese(II) and Phthalate/Diimine Ligands: Syntheses, Crystal Structures and Magnetic Properties. *Eur. J. Inorg. Chem.*, 17: 3522-3532.
- Poleti D, Karanovic L, Prelesnik BV(1900). Structure of triaqua[1,2-benzenedicarboxylato(2-(2,2'-bipyridine)nickel(II) monohydrate. *Acta. Cryst. Sect. C(Cr.Str.Comm.)*, 46: 2465-2467.
- Sheldrick GM (1996). SADABS, Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Göttingen.
- Sheldrick GM (1997). SHELXL 97, Program for Crystal Structure Refinement. University of Göttingen, Göttingen.
- Sheldrick GM (1997). SHELXS 97, Program for Crystal Structure Solution. University of Göttingen, Göttingen.
- Svetlana GB, Yurii AS, Maria G, Nicolae G, Irina GF, Grigore T (2003). Synthesis and structural characterisation of unprecedented dinuclear zinc(II) complex with H-bonded bridging phthalate ions. *Inorg. Chem. Comm.*, 6: 685-689.
- Xue FC, Jiang ZH, Liao DZ, Ma SL, Yan SP, Wang GL, Yao XK, Wang RJ (1993). Novel structure of nickel(II) complex $\text{Ni}(\text{phth})(\text{bpy})(\text{H}_2\text{O})_3$ (phth²⁻ = the dianion of phthalic acid; BPY = 2,2'-bipyridine). *Polyhedron*, 12(23): 2787-2789.
- Yang JM, Zhou ZH, Zhang H, Wan HL, Lu SJ (2005). Temperature effect on the conversions of phthalato and maleato manganese(II) complexes with diamine ligands. *Inorg. Chim. Acta.*, 358(6): 1841-1849.
- Yu LC, Liu SL, Liang EX, Wen CL (2008). A 1D coordination polymer $\{\text{Pb}[\text{C}_6\text{H}_4(\text{COO})_2] \cdot [\text{phen}]\}_n$ with strong blue fluorescent emission. *J. Coord. Chem.*, 61(5): 810-815.
- Zhang XM, Tong ML, Chen XM (2002). Hydroxylation of N-Heterocycle Ligands Observed in Two Unusual Mixed-Valence Cu^I/Cu^{II} Complexes. *Angew. Chem. Int. d.*, 41(6): 1029-1031.
- Zhang Y, Li J, Su Q, Wang Q, Wu X (2000). Synthesis, structure and spectroscopic properties of an *o*-phthalate-bridged copper (II) chain complex. *J. Mol. Struct.*, 516(2-3): 231-236.
- Zhang Y, Li J, Su Q, Wang Q, Wu X (2000). Synthesis, structure and spectroscopic properties of an *o*-phthalate-bridged copper (II) chain complex. *J. Mol. Struct.*, 516: 231-236.