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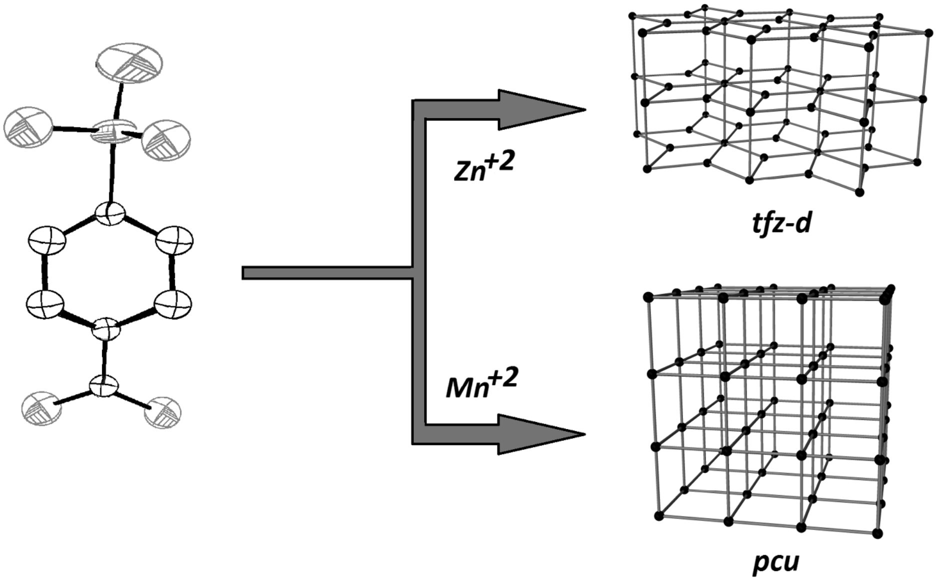
Zn+2
Mn+2
tfz-d
pcu

Preparation and topological properties of two structures with p-sulfobenzoic ligand and Zn^{2+} and Mn^{2+} ions.

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Abstract

There has been recent interest in coordinated polymers due to their structural and topological properties, and the search for efficient synthesis processes to construct these materials exploiting different organic ligands has intensified. In this context, two coordinated polymers (Zn-psb and Mn-psb) consisting of p-sulfobenzoic acid and either Zn^{2+} or Mn^{2+} ions, respectively, were synthesized by crystallization in gel using ethambutol hydrochloride as a new crystallization agent. Both compounds crystallized in the triclinic system and space group P-1 and have similar unit cell volumes with a difference of 2%. Crystal data for Zn-psb: a = 8.080(4) Å, b = 11.385(6) Å, c = 12.282(6) Å, α = 97.402(4)°, β = 106.530(4)°, γ = 110.445(5)°, and Mn-psb: a = 8.055(5) Å, b = 10.152(7) Å, c = 12.541(8) Å, α = 99.084(6)°, β = 95.358(5)°, γ = 106.090(6)°. Despite the structural similarity, two different networks (***tfz-d*** and ***pcu*** for Zn-psb and Mn-psb, respectively) were formed, and their topological properties were explored by reticular chemistry.

Keywords: Polymers, X-ray diffraction, reticular chemistry, topological properties.

Introduction

The literature describes several compounds involving carboxylate ligand and transition metal sites [1-5]. These complexes have received special attention recently due to their potential applications in gas adsorption [6-8], catalysis [9, 10] and magnetic properties [11-13]. In this sense, these materials exhibit many applications with physical chemical properties interesting with the size of cages from 0.9 to 3.4 nm [14, 15]. Certain compounds derived from *o*-, *m*- and *p*-sulfobenzoic acid ligands and metallic ions are described in the literature, such as complexes with cobalt [16, 17], nickel [18, 19], zinc [20, 21], copper [22-25], manganese [26-29] and silver [30, 31]. These compounds are associated in various ways with metal ions connected through carboxylate groups or nitrogen ligands. However, in almost all of the compounds, the sulfonate groups are not coordinated directly to metal sites. Therefore, the coordination chemistry of compounds with sulfonate groups has been discarded because these groups are considered poor ligands [32].

The p-sulfobenzoic acid (psb) may be used as a precursor for different polymers because it exhibits different coordination sites with two different functional groups (carboxylate and sulfonate). The advantage of this ligand over carboxylate is that it allows an additional dimension for building networks and greater flexibility of modes combined with a nearly spherical shape [33]. However, most of these compounds described in the literature display a hydrated metal ion with the sulfonate group working as a non-coordinated ion or a free sulfonate group in the lattice [18, 25, 34-36].

The formation of these compounds may be explained by the Principle of Hard and Soft Acids and Bases (HSAB), where Lewis acids and bases are classified into three categories: hard, soft and borderline. Thus, *"Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases"*[37]. Moreover, according to Klopman, solvation effects are also highly important [38]. Therefore, in aqueous solution, there is a competition between sulfonate groups and water molecules over transition metal ions in the system. The covalent nature of transition metal ions appears to favor the hydration of metal ions over interaction with sulfonate groups. This reduced hardness of the transition metal is responsible for the lack of chemical reactivity in aqueous solution [39, 40].

There have been many efforts using different techniques to develop high performance these materials such as crystallization by diffusion [41-42], hydrothermal [43-45] and microwave hydrothermal [46-48] synthesis reactions where different solvents (water, methanol, ethanol, dimethylformamide) can be used to provide interactions between species allowing a good environment for crystallization, however, there is no satisfactory results. The main methodology used in this work was crystallization of crystals in gels for construction of polymers. This technique has been used in the literature for the crystallization of inorganic compounds and crystallization of macromolecules where the agents of crystallization has been frequently used are agarose, polyacrylamide and silica [49, 50].

In this context, we have recently worked with the synthesis of coordination polymers containing sulfonate groups by crystallization in gel using ethambutol hydrochloride as a new crystallization agent to encourage the construction of networks using transition metal ions and sulfonate group ligands.

Experimental section

Synthesis

$[Zn(C_7H_5O_5S)_2(KC_7H_5O_5S)_2].6H_2O$: (Zn-psb)

Two milliliters of ethanolic solution of zinc(II) nitrate hexahydrate (29.8 mg, 1 mmol) was added slowly drop by drop to 5 mL of aqueous solution containing monopotassium salt of 4-sulphobenzoate acid salt (24.2 mg, 1 mmol) and ethambutol hydrochloride (30.0 mg, 1.08 mmol). After approximately 6 months, single crystals were obtained by crystallization into gel. However, only a few crystals were obtained, and a suitable one was used for X-ray diffraction.

$[Mn(C_7H_5O_5S)_2(KC_7H_5O_5S)_2].6H_2O$: (Mn-psb)

The synthesis of Mn-psb was analogous to the synthesis of Zn-psb, except that instead of ethanolic solution of zinc(II) nitrate hexahydrate, the synthesis of Mn-psb used 2 mL of ethanolic solution of manganese(II) nitrate tetrahydrate (29.8 mg, 1.19 mmol). After approximately 6 months, single crystals were obtained by crystallization into gel. Similar to the Zn-psb compound, only a few suitable crystals were obtained and used for X-ray diffraction studies.

Crystallographic determination

X-ray diffraction measurements for both compounds were carried out on an Oxford GEMINI A-Ultra CCD diffractometer with graphite monochromated MoKα (λ = 0.71073 Å) at room temperature. These structures were resolved by direct methods and then refined by full-matrix least square refinement on F^2 using SHELXL-97 [51]. The figures were drawn by the ORTEP-3 for Windows [52], Mercury [53] and TOPOS4.0 [54] programs. Maximum symmetry of embedding for nets was given by the Systre [55] program. Crystallographic data for the compounds were deposited in the Cambridge Crystallographic Data Centre (CCDC) upon request (http://www.ccdc.cam.ac.uk, CCDC deposition numbers 1004574 and 1004580).

Results and discussions

Structural description

The crystallographic data on the compounds are displayed in Table 1. Both compounds crystallize in the triclinic crystal system and space group P-1. The crystal structure of Zn-psb is displayed in Figure 1(a), which shows that the ligand is coordinated to a Zn and K atoms and presents the coordinated and free water molecules. The Zn-O distances are 2.02(2) Å [Zn-O12] and 2.14 (2) Å [Zn-O13] for water molecules and 2.12(2) Å [Zn-O5] for the ligand, whose O5 atom is derived from the sulfonate group. The Zn site adopts a slightly distorted octahedral geometry, and it is still possible to perceive that this atom is coordinated to the sulfonate group of the ligand by coordination mode ***ημk*** [56].

There are two different types of psb ligand in the crystal structure, one that is coordinated to Zn and K atoms and another that interacts only with K ions, but in both cases, the carboxylic group remains in acid form. The Mn-psb compound has the same quantity of water molecules in the crystal structure as the Zn-psb and ligand; however, the interactions are different. The Mn atom forms a slightly distorted octahedral geometry with distance Mn-O11 at 2.17(2) Å of oxygen atoms from water molecules and Mn-O5 and Mn-O8, with distances at 2.21 (3) Å and 2.17 (2) Å, respectively, from oxygen atoms of the sulfonate groups, as shown in Figure 1(b). The distances are similar in both compounds, but there is only one type of psb ligand in the Mn-psb structure with coordination mode ***ημκ*** for whole sulfonate groups.

The coordination between the metal and the oxygen atoms of sulfonate groups can be elucidated by the presence of electrons in the *d* orbitals. The stability results from the increased the number of *d* electrons that decrease with hardness in Lewis acids. Thus, Mn^{2+} ions are considered a hard acid, while Zn^{2+} ions have an intermediate hardness. When considering the effects of electronegativity, polarizability and oxidation state for Lewis bases, the water molecule is classified as a harder base than the sulfonate group. It is known by HSAB that metal-water interactions are more stable than the other bonds considered. However, there is competition among water, psb ligand and ethambutol hydrochloride molecules during the crystallization process.

In very concentrated solutions of ethambutol hydrochloride, the ethambutol molecule may interact with water molecules and chloride ions to bind to soft metal ions such as Zn^{2+}. The addition of crystallization agent should increase the reactivity of metals in aqueous solution with ethambutol-water and chloride-ion interactions and favor metal-sulfonate coordination.

The neutrality of compounds is produced by protonation of all the carboxylate groups present in the structures with average C-OH distances at 1.32(4) Å. The sulfonate groups are deprotonated with similar S-O bond distances, C-S-O angles and O-S-O angles in both compounds, with values of approximately 1.45(2) Å, 106.30(14)° and 112.32(12)°, respectively. The coordination environment of potassium ions is shown in Figure 2, and it has been observed that the K-O interactions are similar in the two structures with average interaction distances of approximately 2.92(2) Å and 2.84(2) Å for Zn-psb and Mn-psb, respectively.

As seen in Figure 3, the K-O interactions in Zn-psb give rise to a 2D network in the ***ac***-plane that extends along the ***b***-axis through Zn octahedral atoms coordinated with a psb ligand, forming a 3D polymeric net. Similarly, Mn-psb forms a 2D network in the ***ab***-plane, and the 2D ladder is formed by K-O interactions and Mn octahedral atoms and extends by bridge ligands to make a 3D polymeric net along the ***c***-axis. As single-crystal X-ray diffraction analysis reveals that although the Zn-psb and Mn-psb structures show distinct environments for metal ion coordination, they have analogous crystallographic relationships, such as space group, unit cell and similar interactions with a difference in unit cell volume of approximately 2%.

Topological description

For rigorous structural analysis, it is important to use topological description as a tool to clearly understand the extent of these compounds. The details of the crystal packing can be studied using the Topos4.0 package [54]. Crystal packing is the result of the sum of different interaction contributions, and in this case, hydrogen bonds have a secondary influence in building the compounds. A topological study of the packing modes of hydrogen bonds is difficult in compounds because the patterns of interactions are dispersed in 3D space. However, the presence of water molecules in the compounds leads to the formation of a complex system of hydrogen bonds. Pertinent parameters, such as the O···O distances for carboxylic, sulfonate and water oxygen atoms are given in Table 2. In both compounds, the distances for classical hydrogen bonding are classified as moderate to weak.

The geometric factors derived from the Voronoi-Dirichlet Polyhedral (VDP) were also considered (Table 2). Figure 4 shows the VDP of certain hydrogen atoms in the Zn-psb and Mn-psb structures. The method considers the whole surroundings of atoms, where the size of the face of the convex polyhedron formed represents the solid angle of the face (Ω) and is a definite percentage of the sum of solid angles of all other faces that can represent different types of interactions, such as hydrogen bonds [Ω(H···A)][57]. These results show that when the distances H···A begin to decrease, the percentage of solid angles increases, and more strong hydrogen bonds are found.

Certainly, their observation is associated directly with a contribution to the construction of the VDP faces. For the Zn-psb compound, the hydrogen bond network extends in 3D space for infinite chains made by interactions of the oxygen atoms of carboxyl groups (O1, O2), water molecules (O11, O12, O13) and sulfonate groups (O4, O10 and O4, O6), as shown in Figure 5. Similar interactions are found in the Mn-psb compound; however, the complex packing of hydrogen bonds among these groups can be explored using graph theory such as graph-set assignments[58]. In particular, Mn-psb possesses hydrogen bond motifs involving oxygen atoms of carboxyl groups (O6), water molecules (O13, O11) and sulfonate groups (O4) that form a highly extensive ring motif specified as $R_4^4(70)$, as illustrated in Figure 6. To build the simplified model for other interactions, a set of atoms associated with the actual connection of the structure was considered, respecting the nature and extent of connections into crystal structures. For example, in the Zn-psb structure, the ligand center includes a vertex 3-connected to another vertex by 8-connected potassium ions, as illustrated in Figure 7.

The structure of Zn-psb consists of a binodal (3,8)-connected system and can be described with a point symbol (4^3) by the vertex formed for the ligand and $(4^6.6^{18}.8^4)$ for the vertex constructed using the potassium ions. This network is deposited in RCSR [59] as a net of type ***tfz-d*** with hexagonal symmetry P6/mmm having two different tiles of transitivity [2222] and signature $3[4^2.6^2]+2[6^3]$, as illustrated by Figure 8(a). Despite the structural similarities of the compounds, a simple modification of the metal ion in the reaction leads to a tendency toward a different network with different topological properties. The Mn-psb structure leads to the formation of a single regular ***pcu*** type network with Pm-3m symmetry where one type of tile is observed in cubic form with transitivity [1111] and signature $[4^6]$, as shown in Figure 8(b). This evidence may be used to predict possible structural modifications that may cause the growth of interpenetrated nets.

The construction of tiles of networks for structures in combination with the VDP method was used to investigate the system cavities in the crystal structures. As shown in **Figure 9**, the systems of cavities in the network described by tiles are blocked for the ligands facing the direction of potential voids with a volume of approximately 279.54 $Å^3$ and 265.17 $Å^3$, respectively, for Zn-psb and Mn-psb.

Conclusion

In spite of the similarities between structural parameters of the compounds Zn-psb and Mn-psb, it was observed the modification of the metal in the synthesis process leads to the construction of two different networks (***tdz-d*** and ***pcu***, respectively) with divergent topological properties that the system of cavities found are blocked by the presence of the psb ligand in both compounds. The coordination of the sulfonate group with transition metal is usually measured as weakly interacting making an *aqua* complex. However, when the crystallization in gel method was employed, a major interaction between the transition metal and sulfonate group was observed that may be explained by the fact that the presence of ethambutol hydrochloride provides a lower affinity of metal with water molecules, preventing the formation of *aqua* ligands and giving greater accessibility of the sulfonate group to metal. However the results are satisfactory for obtaining polymeric crystal structures involving the sulfonate group and transition metals with similar structures and different topological proprieties. It has been observed that the use of ethambutol hydrochloride as a new crystallization gel increases the crystallization time of small molecules, demonstrated by the low yields of these materials. Other crystallization agents with densities higher than that of water, such as glycerin and ethylene glycol, have been tried in our research group to increase the yields of these crystals. However, they reduce sedimentation and nucleation, proving an obstacle to the formation of precipitate or crystals from the solution. Future efforts should be directed toward the advancement of methods to produce crystals using sulfonate groups and transition metal ions.

Acknowledgements

This research used resources of the Coordination of Improvement of Higher Education Personnel (CAPES), the Foundation for Research Support of Minas Gerais (FAPEMIG) and the National Council for Scientific and Technological Development (CNPq). The authors thank the Crystallography Laboratory (LabCri - UFMG) for providing facilities for the measurement of X-ray diffraction.

Table 1 - Crystallographic data for Zn-psb and Mn-psb.

Compound	***Zn-psb***	***Mn-psb***
Empirical formula	$ZnC_{28}H_{32}K_2O_{26}S_4$	$MnC_{28}H_{32}K_2O_{26}S_4$
Formula weight/ $(g.mol^{-1})$	1056.35	1045.92
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
$T(K)$	293(2)	293(2)
$a(Å)$	8.080(4)	8.055(5)
$b(Å)$	11.385(6)	10.152(7)
$c(Å)$	12.282(6)	12.541(8)
$\alpha(\circ)$	97.402(4)	99.084(6)
$\beta(\circ)$	106.530(4)	95.358(5)
$\gamma(\circ)$	110.445(4)	106.090(6)
$V(Å^3)$	981.61(9)	962.78(11)
Z	1	1
$MoK\alpha(cm^{-1})$	0.71073	0.71073
$D\ (g.cm^{-3})$	1.787	1.804
$R(F_o)$ [a]	0.0441	0.0484
$R_w(F_o^2)$ [b]	0.0903	0.0862
S	1.136	1.079

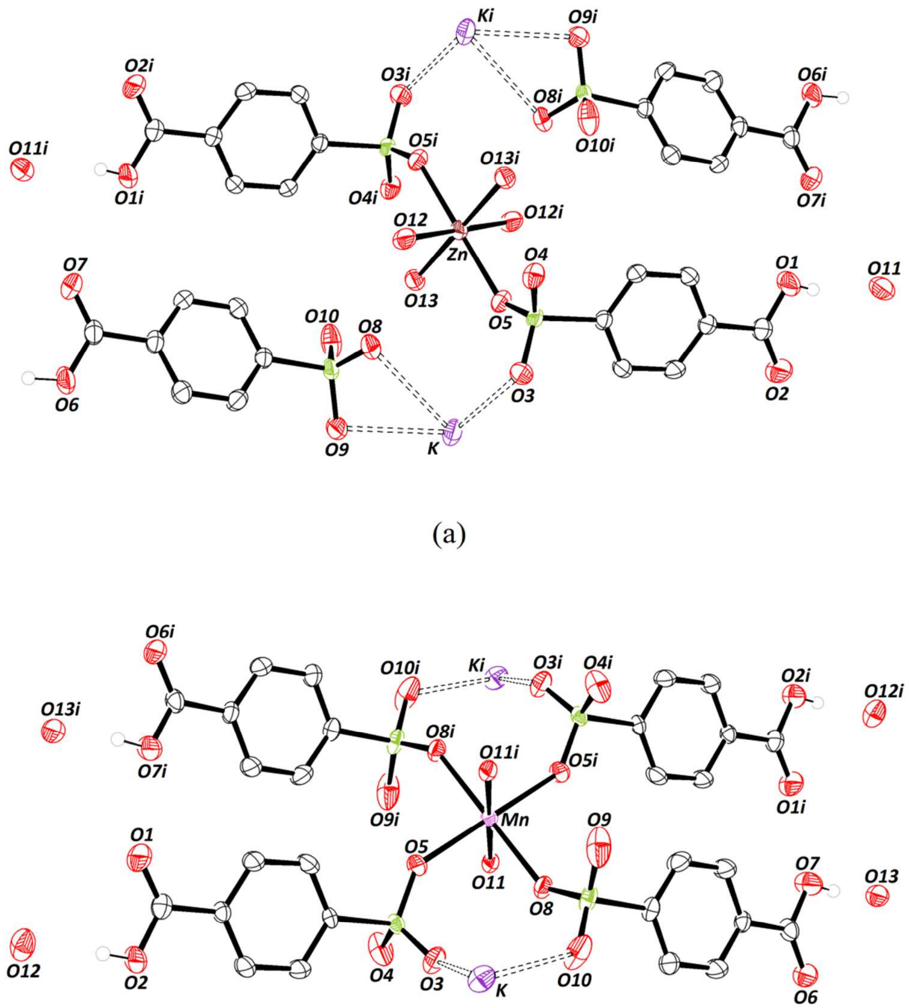
[a] $R(F_o) = \sum\left||F_o| - |F_c|\right| / \sum|F_o|$

[b] $R_w(F_o^2) = [\sum_w(F_o^2 - F_c^2)^2 / \sum_w F_o^2]^{1/2}$

Table 2 – Parameters for hydrogen bonds for Zn-psb and Mn-psb structures.

D	H	A	D-H	H···A	D···A	D-H···A	Ω(A)/Å^2	Ω(H···A)/%
				Zn-psb				
O1	H1C	O11^{i}	0.6900	1.9500	2.625(4)	168.00	23.94	22.18
O6	H6C	O4^{ii}	0.8600	2.1700	2.948(3)	150.00	29.11	16.80
O11	H11B	O13	0.8400	2.1300	2.880(3)	150.00	19.81	18.98
O12	H12A	O2^{iii}	0.8500	1.8800	2.727(3)	170.00	34.43	23.50
O12	H12B	O8	0.8100	1.9600	2.744(3)	162.00	36.02	18.78
O13	H13A	O4^{iv}	0.8400	2.1300	2.879(3)	149.00	29.11	15.80
O13	H13B	O10	0.8400	1.9000	2.733(4)	171.00	33.86	23.00
				Mn-psb				
O2	H2C	O12	0.7900	1.8600	2.650(4)	176.00	22.36	23.57
O7	H7C	O13^{v}	0.8300	1.8000	2.618(3)	167.00	21.61	20.96
O11	H11A	O4^{vi}	0.8300	2.0100	2.784(4)	155.00	31.09	19.17
O11	H11B	O6^{vii}	0.8300	1.9000	2.732(4)	179.00	33.49	21.53
O12	H12A	O10^{viii}	0.8400	2.3100	3.130(5)	166.00	34.50	15.04
O12	H12B	O11^{ix}	0.8100	2.1100	2.887(4)	160.00	19.44	15.12
O13	H13A	O8^{vii}	0.8400	2.1200	2.942(4)	168.00	31.56	17.81
O13	H13B	O4^{x}	0.8300	2.2600	2.973(4)	145.00	31.19	15.68

*Symmetry code: **i**(-1-x,-y,-1-z); **ii**(1-x,1-y,1-z); **iii**(1+x,y,1+z); **iv**(-x,-y,-z), **v**(2-x,1-y,2-z); **vi**(1+x,y,z); **vii**(x,y,-1+z), **viii**(-1+x,y,-1+x), **ix**(-1+x,y,-1+x), **x**(1-x,1-y,1-z).*



(a)

(b)

Figure 1 – Crystal structures of (a) Zn-psb and (b) Mn-psb. Symmetry code: *i(-x,-y,-z)*. Thermal ellipsoids at 50% probability.

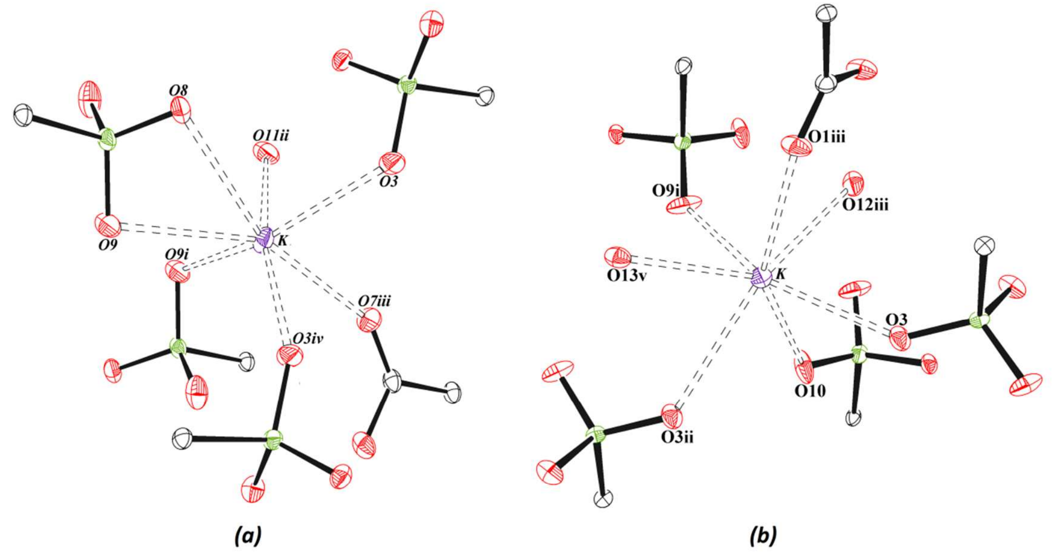


Figure 2 – Coordination environment of potassium ion for a) Zn-psb and b) Mn-psb. Symmetry code: *: **i**(-x+1, -y+1, -z), **ii**(-x-1, -y, -z-1), **iii**(x-1, -y+1, -z), **iv**(-x, -y+1, -z) for Zn-psb and **i**(-x+2, -y, -z+2), **ii** (-x+1, -y, -z+2), **iii** (-x+1, -y, -z+1), **v** (x-1, y-1,z-1) for Mn-psb*. Thermal ellipsoids at 25% probability.

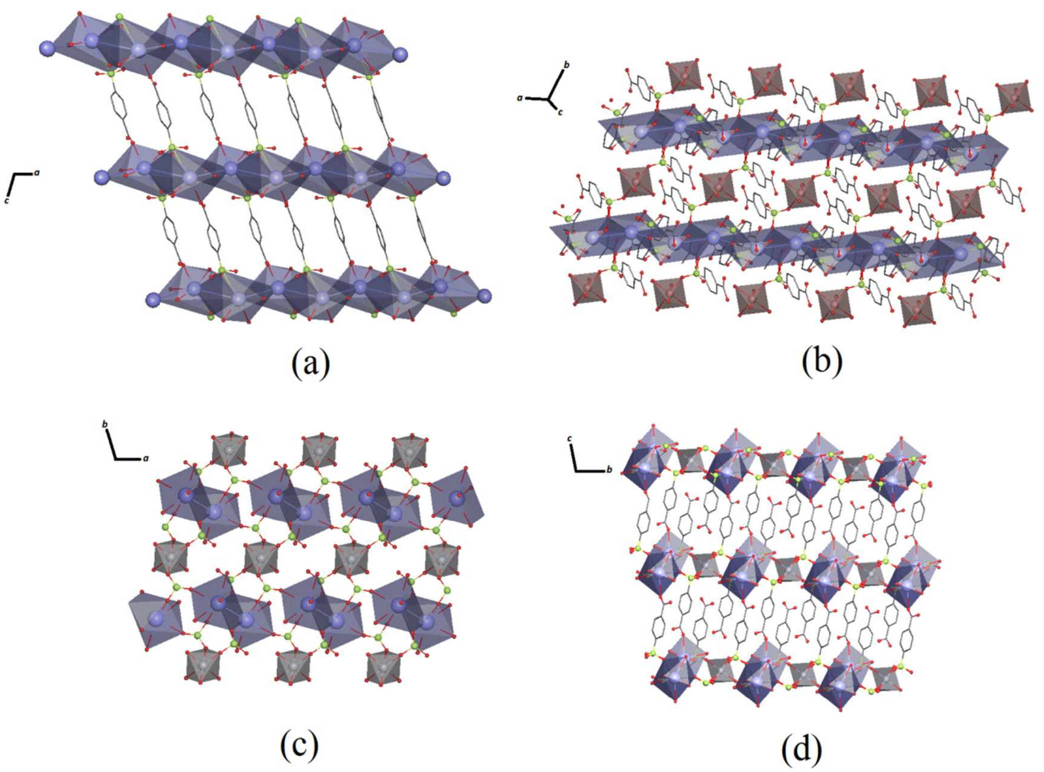


Figure 3 - *(a)* Extension of Zn-psb structure along the *ac*-plane and *(b)* along the ***b***-axis. *(c)* Extension of Mn-psb structure along the ***ab***-plane and *(d)* along the ***bc***-plane. Color code: C: gray, O: red, S: green, K: lilac, Mn: light gray, Zn: brown.

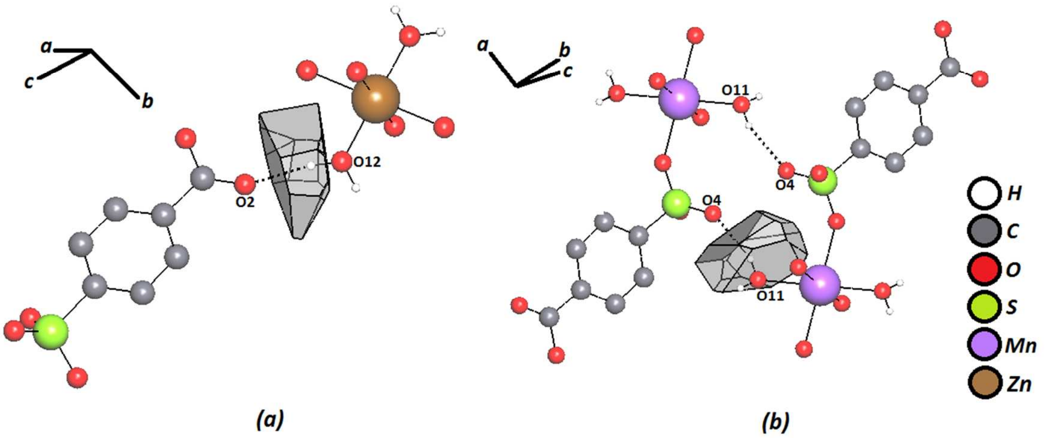


Figure 4 - Voronoi-Dirichlet polyhedron of a hydrogen atom for a) Zn-psb and b) Mn-psb. Hydrogen bonds are shown by dash-and-dot lines.

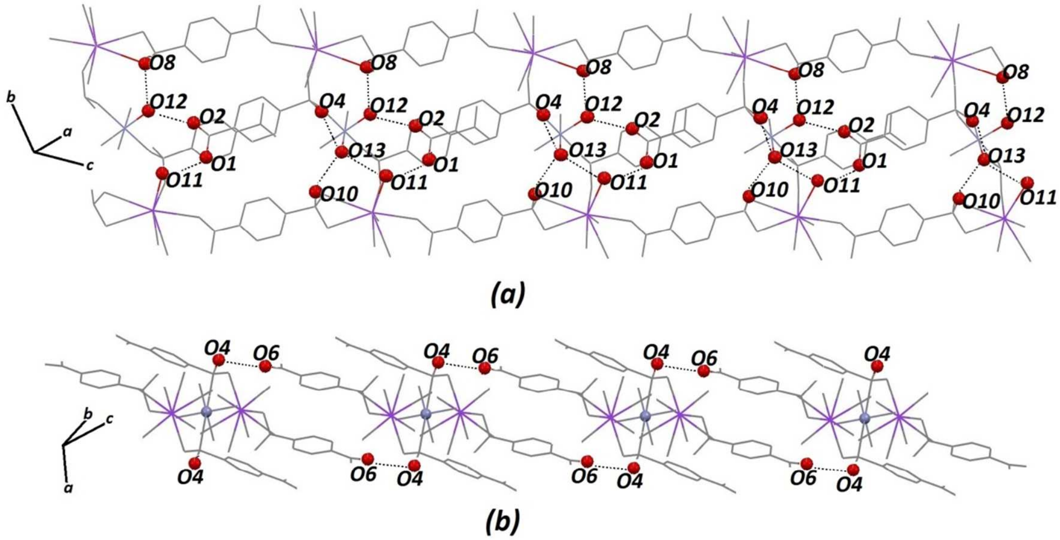


Figure 5 - Extensions of hydrogen bond network in 3D space for Zn-psb structure. Some atoms are not shown for clarity.

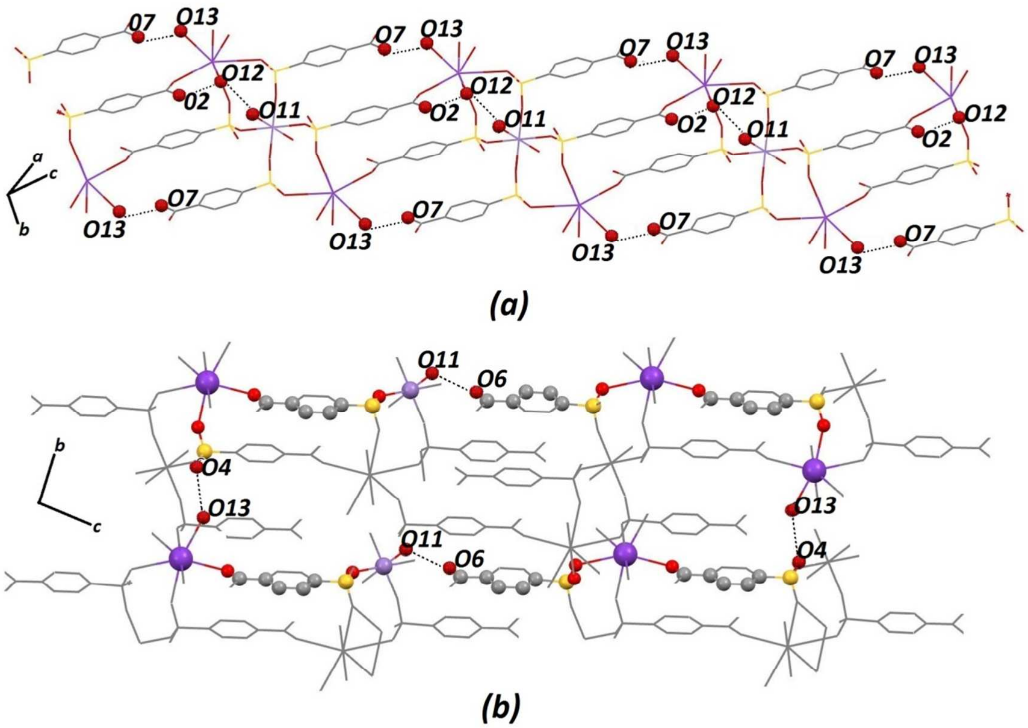


Figure 6 – For Mn-psb structure, (a) extension of hydrogen bond network in 3D space and (b) graph-set for hydrogen bond motif selected. Some atoms are not shown for clarity.

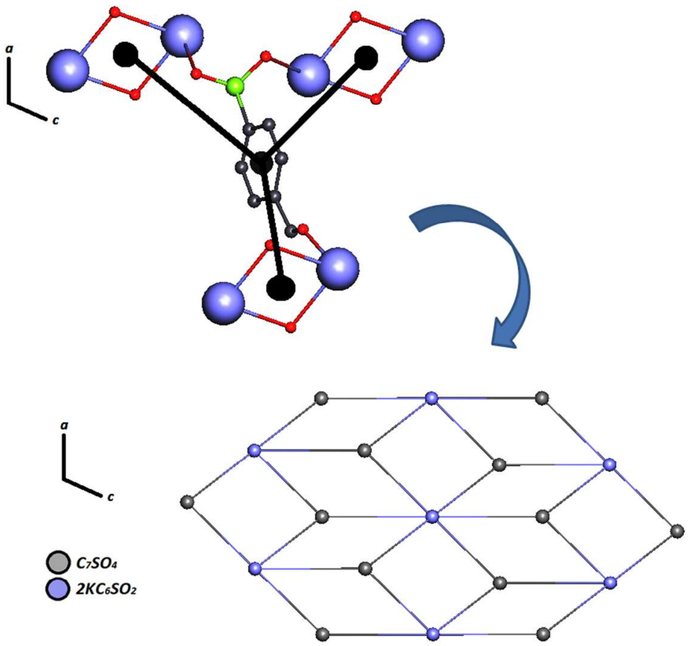
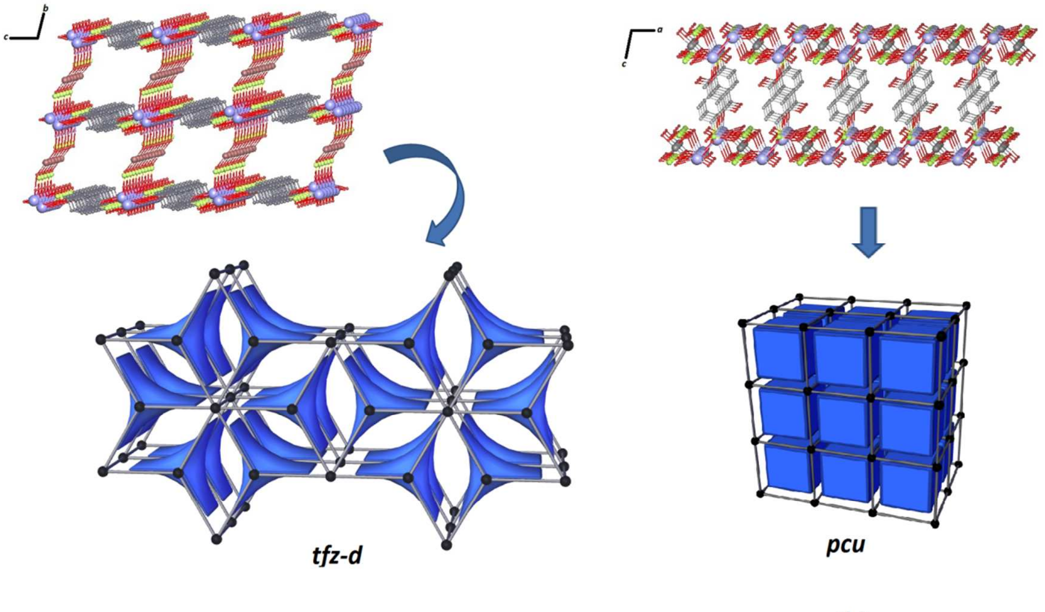
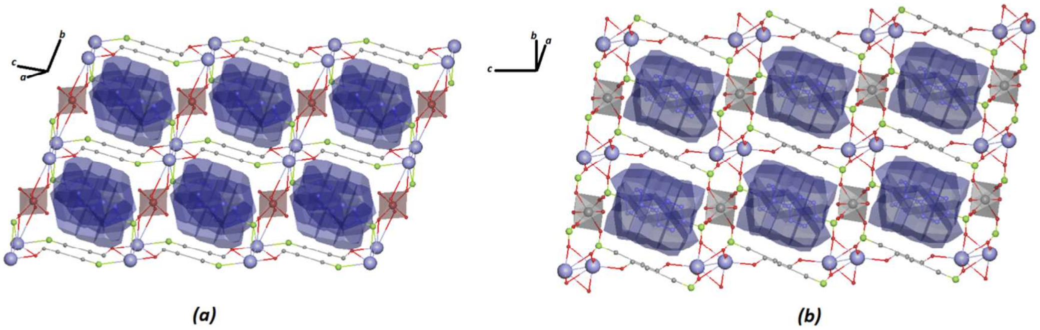


Figure 7 - Simplified model of Zn-psb for building a binodal (3,6)-coordinated ladder along ***ac***-plane.



(a) (b)

Figure 8 – (a) Part of ***tfz-d*** net with P6/mmm symmetry derived from Zn-psb structure. One of the [6^3] tiles for the net is shown in blue. (b) Regular ***pcu*** net derived from Mn-psb structure. The symmetry of the tiling is Pm-3m, which has one type of tile displayed in blue.



(a) *(b)*

Figure 9 - VDP fragments of the crystal structures of (a) Zn-psb and (b) Mn-psb.

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