

Crystal structure of Co-Li and Zn-Li complexes derived from a Schiff base ligand bis(2-carboxyphenyl)disulfide

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Abstract: Reactions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ with 2-mercaptobenzoic acid gave new complexes $\{[\text{CoLi}_2\text{C}_{28}\text{H}_{18}\text{O}_9\text{S}_4]\}$ (1) and $\{[\text{Zn}_2\text{Li}_2\text{C}_{56}\text{H}_{32}\text{O}_{16}\text{S}_8] \cdot 3(\text{H}_2\text{O})\}$ (2) in which the 2-mercaptobenzoic acid underwent in situ oxidation to give the bis(2-carboxyphenyl)disulfide ligand. Co(II) and Zn(II) complexes are chemically similar. The only difference lies in the number of crystallization solvent molecules. The two complexes crystallize in the same system with the same space group with very similar cell parameters. In each complex the central 3d metal ion is surrounded by four oxygen atoms, resulting in a O_4 coordination set which is best described as a distorted tetrahedral geometry. In complex (1) one Li(I) is situated in O_4 site and one Li(I) in O_4S site are present. In complex (2), the Li(I) ions are situated in O_4S coordination set. The environment around the five coordinated Li(I) is best described as a distorted trigonal bipyramidal geometry, while the tetracoordinated Li(I) ions are situated in a tetrahedral geometry. The intra-molecular $\text{Co1} \cdots \text{Li1}$ and $\text{Zn1} \cdots \text{Li1}$ separations are 3.750(8) Å and 3.168(4) Å, respectively. In complex 1, intra-molecular hydrogen bonding involving the coordinated water molecule as donor and a carboxylate oxygen atom as acceptor ($\text{O9} \cdots \text{HO9A} \cdots \text{O6}$) is observed in the structure. The packing of the molecules reveals that the sheets of the coordination polymer units are connected through unclassical $\text{C} \cdots \text{H} \cdots \text{S}$ interactions and intermolecular bonding hydrogen involving the coordinated water molecule as donor and a sulfur atom as donor ($\text{O10} \cdots \text{H10B} \cdots \text{S4}$), leading to a three-dimensional supramolecular. In complex 2, the packing of the molecules is ensured by $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{O} \cdots \text{H} \cdots \text{S}$ intermolecular hydrogen bonding resulting in a three-dimensional network.

Keywords: Cobalt, Zinc, Lithium, Disulfide, Tetrahedral, Bipyramidal

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I. Introduction

Chemists are increasingly interested in the design and synthesis of heteropolynuclear complexes of d-block and s-block elements because of the novel structures and magnetic [1,2], catalytic [3,4] and luminescent [5] properties. Organic ligands capable of holding the M^{n+} ion ($n = 2$ or 3) of the d-block and the M^{p+} ion ($p = 1$ or 2) of the s-block, are widely used to establish bridges in order to improve exchanges between metal centers. Alkali ion coordination chemistry has been developed in recent decades aimed at naturally mimicking molecules present in biological media that are responsible for ion selection and transport [6,7]. Complexes with Na^+ ions are the most studied because of their implications in the molecular recognition of biological systems [8,9]. Organic molecules with phenolic or carboxylic oxygen atoms are good candidates for the synthesis of these complexes. One of the strategies to obtain d-s heterometallic compounds relies on the preparation of ligand having pockets of different sizes providing variable environments where different metal ions can bind selectively [10–12]. The oxophilic nature of the s-block ions allows the formation of complexes with various coordination with O-donor and N,O-donor atoms. Sulfide derivatives have also been explored as bridging ligands in coordination chemistry. The bridging nature of this type of ligand depends on the characteristics of the metal and the coordination sites of the ligand [13,14]. Sulfur-containing compounds play an important role in nature. By in situ oxidation, S—S groups are formed. Compounds of R-S-S-R' structure are called symmetrical or unsymmetrical disulfides depending on whether R and R' are the same or different. It is in this context that we report the synthesis of $\text{Co}^{2+}/\text{Li}^+$ and $\text{Zn}^{2+}/\text{Li}^+$ complexes formulated from 2-mercaptobenzoic

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acid which undergoes in situ oxidation to give the bis(2-carboxyphenyl)disulfide ligand. The compounds are obtained by directly mixing the ligand with lithium hydroxide and the cobalt or zinc salt to obtain a heterodinuclear compounds. The crystal structures of the two complexes and physico-chemistry are reported here.

II. Materials and method

2.1. Starting materials and instrumentation

2-mercaptobenzoic acid, cobalt chloride hexahydrate, zinc chloride tetrahydrate, and lithium hydroxide hydrate were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm^{-1} region. The molar conductance of 1×10^{-3} M in DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: $\text{Hg}[\text{Co}(\text{SCN})_4]$).

2.2. Synthesis of Cobalt(II)-Lithium(I) complex (1)

2-mercaptobenzoic acid (2.0 mmol, 0.3084 g) was dissolved in 15 mL of methanol and refluxed with a $\text{LiOH} \cdot \text{H}_2\text{O}$ solution (2.0 mmol, 0.083 g) in methanol (5 mL). A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2 mmol, 0.4758 g) in methanol (10 mL) was added to the mixture and refluxed for 2 h. After filtering, the solution was allowed to evaporate. After 4 days blue crystals of **1** were obtained. The crystals were washed with acetone and air dried. The compound was formulated as $([\text{CoLi}_2\text{C}_{28}\text{H}_{18}\text{O}_9\text{S}_4])_n$. Yield: 63 %. Elemental Anal. Found (Calcd.) (%): C, 48.08 (48.10); H, 2.59 (2.57); S, 18.34 (18.31). IR (ν , cm^{-1}): $[\nu(\text{C}=\text{O})$ 1588, 1574, 1539, 1455, 1435, 1393, 1280, 1036, 743, 704; 625, 480. Λ ($\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$): 7. μ_{eff} (MB): 4.88.

2.3. Synthesis of Zinc(II)-Lithium(I) complex (2)

The same procedure was used. $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ (2 mmol, 4167 g) was used instead $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. After 2 days yellow crystals of **2** were obtained. The crystals were washed with acetone and air dried. The compound was formulated as $\{[\text{Zn}_2\text{Li}_2\text{C}_{56}\text{H}_{32}\text{O}_{16}\text{S}_8]\cdot 3(\text{H}_2\text{O})\}_n$. Yield: 68 %. Elemental Anal. Found (Calcd.) (%): C, 47.50(47.48); H, 2.70 (2.72); S, 18.11 (18.09). IR (ν , cm^{-1}): $[\nu(\text{C}=\text{O})$ 1589, 1548, 1443, 1419, 1394, 1281, 1087, 738, 708, 657, 501. Λ ($\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$): 10. μ_{eff} (MB): 0.

2.4. X-ray crystallography

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL* [15]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [16]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using *ORTEP-3* [17].

III. Result and discussions

3.1. General study

In the case of this kind of compounds, the values of the asymmetric and symmetric vibrations of COO are important. FTIR spectra (Fig. 1) of both coordination polymers were compared to infrared data of the 2-mercaptobenzoic acid. The broad band centered at 3086 cm^{-1} in the spectra of the 2-mercaptobenzoic acid is due to the O—H stretching vibration of the —COOH moiety. The band pointed at 2628 cm^{-1} is assignable to the —S—H stretching [18]. Two strong bands pointed at 1677 cm^{-1} and 1664 cm^{-1} are respectively attributed to the asymmetric and symmetric vibrations of COOH group. The band at 706 cm^{-1} is due to the C—S stretching. Upon reaction of 2-mercaptobenzoic acid with lithium hydroxide and $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ ($\text{Mn} = \text{Co}^{2+}$, $x=6$; $\text{M}=\text{Zn}^{2+}$, $x=4$) in methanol, a Co(II) (**1**) and Zn(II) (**2**) complexes were obtained. The band assigned to —S—H stretching in the spectrum of 2-mercaptobenzoic acid disappears, while the bands due to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ shift

strongly to low frequencies in the spectrum of the complexes. The stretching vibrations centered at about 1588 cm^{-1} for (1) and 1589 cm^{-1} (2) are assigned to the asymmetric mode of the acetate groups, and those at about 1435 cm^{-1} (1) and 1443 cm^{-1} (2), to the symmetric mode. $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ is a criterion to distinguish the possible coordination modes of the acetate moiety according to Deacon and Philips[19], when the $\Delta\nu$ (164 cm^{-1}) of ionic acetate was taken as reference. Increasing of $\Delta\nu$ is indicative of monodentate bonding acetate group, while decreasing of $\Delta\nu$ is indicative of bidentate chelating acetate group. For bidentate bridging mode of acetate group, $\Delta\nu$ remains similar to free anion $\Delta\nu$ value. The $\Delta\nu$ values of 153 cm^{-1} and 146 cm^{-1} are indicative of bidentate bridging acetate groups in both complexes [20]. Some peaks belonging to aromatic C=C stretching vibrations are also observed at about 1450–1350 cm^{-1} [21]. At *ca.*1280 cm^{-1} there are peaks corresponding to C–O stretching vibrations. In both spectrum of (1) and (2), bands pointed at *ca.* 705 cm^{-1} and 500 cm^{-1} are attributed respectively to C–S and to -S–S- vibrations[22]. Vibrations pointed in the range 750-735 cm^{-1} can be assigned to ortho-disubstituted aromatic rings (743 cm^{-1} (1) and 738 cm^{-1} (2)). The molar conductivities measured in DMF solutions were respectively 7 and 10 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ indicating that the complexes are neutral electrolyte[23]. For both complexes the diamagnetic Li(I) ion does not contribute to magnetic moment. Magnetic moment value at room temperature for complex 1 of 4.88 μ_{B} is in consistency with the presence of three unpaired electron and is close proximity of the spin only value of 4.80 μ_{B} expected for one d^7 cobalt(II) ion in tetrahedral environment[24,25]. This fact, clearly shows the absence of exchange interactions between metallic centers. For the paramagnetic complex 2, the zinc(II) ion has d^{10} configuration showing absence of unpaired electron.

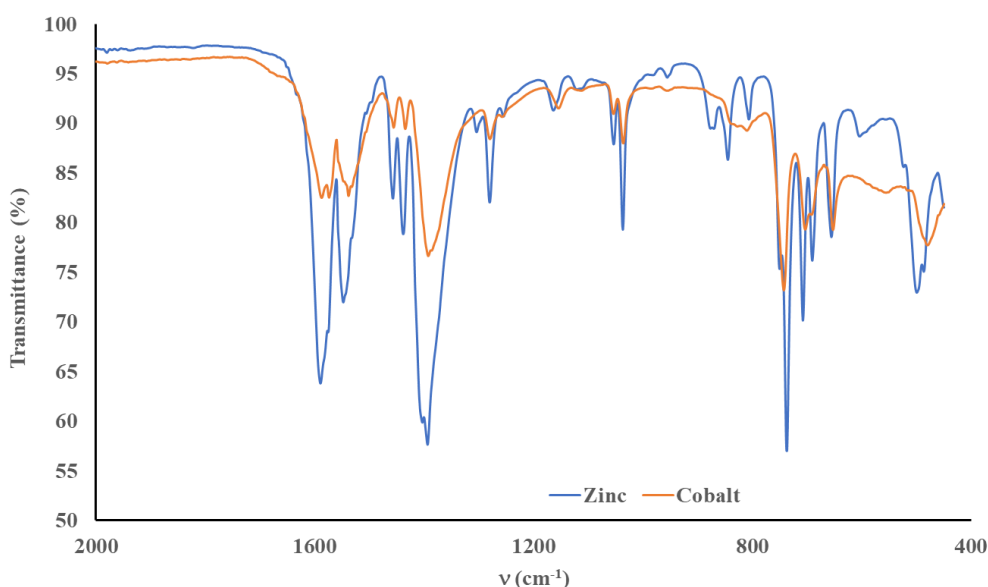


Fig.1. Infrared spectra of complexes 1 and 2.

Table 1. Crystal data and details of the structure determination for complex.

Chemical formula	[CoLi ₂ C ₂₈ H ₁₈ O ₈ S ₄]	{[Zn ₂ Li ₂ C ₅₆ H ₃₂ O ₁₆ S ₈]}·3(H ₂ O)}
M_r	699.53	1415.96
Crystal system	Trigonal	Trigonal
Space group	<i>R</i> -3	<i>R</i> -3
Temperature (K)	293	102
a (Å)	46.189 (4)	46.1728 (10)
c (Å)	8.8514 (5)	8.7782 (2)
V (Å ³)	16354 (2)	16207.2 (8)
Z	9	9
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.75	0.96

Crystal size (mm)	0.27 × 0.1 × 0.08	0.31 × 0.12 × 0.09
Diffractometer	XtaLAB AFC12 (RINC): Kappa single	XtaLAB AFC12 (RINC): Kappa single
Absorption correction	Multi-scan	Gaussian
T_{\min} , T_{\max}	0.805, 1.000	0.641, 1.000
No. of measured reflections	49454	36744
No. of independent reflections	8679	9675
No. of observed [$I \geq 2\sigma(I)$] reflections	5171	7865
R_{int}	0.124	0.034
$R[F^2 > 2\sigma(F^2)]$	0.070	0.045
$wR(F^2)$	0.227	0.159
S	1.01	0.76
No. of reflections	8679	9675
No. of parameters	415	428
No. of restraints	2	0
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ ($e \text{ \AA}^{-3}$)	1.16, -1.09	1.27, -0.92

3.2. Description of the structures

Compounds **1** and **2** were obtained by mixing methanolic solution of Cobalt(II) chloride or Zinc(II) chloride with methanol solution of 2-mercapto-benzoic acid and lithium hydroxide. After the reaction, gradual evaporation of the filtered solutions yields crystals of **1** and **2** suitable for X-ray diffraction. During formation of **1** and **2**, the 2-mercapto-benzoic acid molecule is oxidized to form bis(2-carboxyphenyl)disulfide.

3.1.1. Description of the structure of **1**

Compound **1** which is formulated as $\{[\text{CoLi}_2\text{C}_{28}\text{H}_{16}\text{O}_9\text{S}_4]\}$ crystallizes in the trigonal crystal system with R-3 space group. In the asymmetric unit, two bis(2-carboxyphenyl)disulfide ligand, one cobalt(II) two Li(I) and two water molecule are present. Fig.2 depicts the perspective view of the coordination polymer complex. Selected bond lengths and angles are listed in Table 2, and the hydrogen bonding parameters are listed in Table 3.

The coordination polyhedron of the cobalt(II) ion (**1**) is constructed by four oxygen atoms of acetate moieties from four different ligand molecules, resulting in a tetracoordinated Co(II) ion. The polyhedron around the Li1 is constructed by three oxygen atoms of acetate moieties from three different ligand molecules, one sulfur atom and one oxygen atom from another ligand molecule resulting in a pentacoordinated Li(I) ion. The polyhedron around the Li2 is constructed by two oxygen atoms of acetate moieties from two different ligand molecules and two oxygen atoms from coordinated water molecules resulting in a tetracoordinated Li(I) ion.

The geometry around the tetracoordinated Co1 and the tetracoordinated Li2 cations are determined using the distortion index or the tetragonality parameter [26] which is stated as follows $\tau_4 = (360 - \beta - \alpha) / 141$ (β and α are the two largest angles around the central atom). $\tau_4 = 0$ designates a perfect square planar geometry and $\tau_4 = 1$ gives a perfect tetrahedron. The value of $\tau_4 = 0.8550$ is indicative of a distorted tetrahedron geometry around Co1 (Fig.2), while the value of $\tau_4 = 0.6830$ is indicative of a distorted tetrahedron geometry around Li2. In fact, the bond angle values around Co1 and Li2 are in the range $[81.7(9)^\circ - 136.5(16)^\circ]$ and are severely deviated from the ideal value of $109^\circ 28'$ for a perfect tetrahedron geometry. The geometry around the pentacoordinated Li1 cation is determined using the Addison parameter [27] which is stated as follows $\tau = (\beta - \alpha) / 60$ where β and α are the largest values of the bond angles around the central atom. The coordination geometry around a pentacoordinated metal center can be discussed: $\tau = 0$ describes a perfect square pyramidal while $\tau = 1$ describes a perfect trigonal bipyramidal geometry. The τ value of 0.76 indicates that the coordination polyhedron around the Li1 is best described as a trigonal bipyramidal geometry. However, the modified index suggested by Konno et al. [28] $\chi = (\beta + \gamma + \delta - 2\alpha) / 180$ which takes into account the other angles (β and α are the largest angles, γ and δ are the other angles around the metal centers without the donor atoms defining β); $\chi = 0$ described a perfect square-based pyramid and $\chi = 1$ describes a perfect trigonal bipyramid) is more efficient. The χ value of 0.8278 for Li1 described the environment as a distorted trigonal

bipyramid around the Li(I). The basal plane is occupied by three oxygen atoms (O2, O4, O6) from three carboxylate moieties with the sum of the angles subtended by these atoms of 323.2°. The apical positions are occupied by one oxygen atom from acetate group and one sulfur atom with angle O8—Li1—S1ⁱ (155.5(4)°) severely deviated from the ideal value of 180°.

The oxygen atoms of the acetate groups are strongly linked to the cobalt (II) ion as shown by the short distance values of Co1—O which are in the range 1.925(4) Å—1.988(3) Å. These values are in accordance with those reported for similar complexes in which the acetate group acts in bidentate bridging mode [29].

The Li1 and Li2 are bridged by two carboxylate oxygen atoms from different carboxylate moieties, resulting in a Li₂O₂ unit with Li1...Li2 distance of 2.80 (2) Å. The Li—O_{acetate} bridge is asymmetric as revealed by Li1—O2 = 1.964 (7) Å, Li2—O2 = 2.23 (3) Å, Li1—O8 = 1.920 (9) Å and Li2—O8 = 2.17 (2) Å. The Li—O_{acetate} distances are longer than those reported for lithium acetate complexes [30]. The Li—O_{water} distances are in the range reported for similar complex [31]. The bridge angle values, Li1—O2—Li2 = 83.0 (6)° and Li1—O8—Li2 = 85.6 (7)°, are in accordance with those found for a carboxylate lithium complex [32].

The intra-molecular Co1...Li1 separation is 3.750(8) Å. Intra-molecular hydrogen bonding involving the coordinated water molecule as donor and an oxygen carboxylate atom as acceptor (O9—H9a...O6) (Table 3), which close in *S*(6), stabilized the structure. The packing of the molecules reveals that the sheets of the coordination polymer units are connected through unclassical C—H...S interactions (Table 3) leading to a three-dimensional supramolecular (Fig.3).

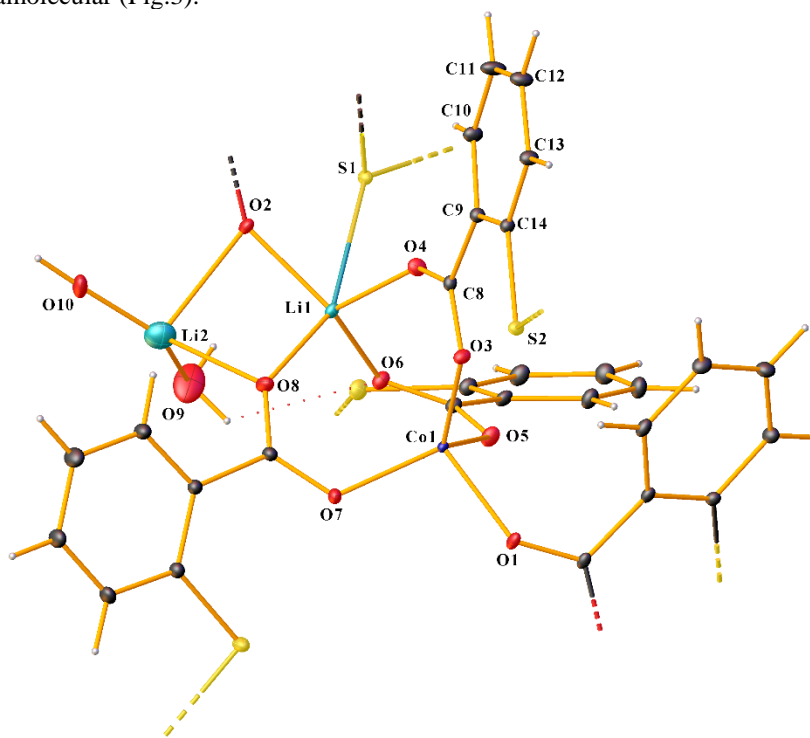


Fig.2. The molecular structure of (1), showing 30% probability displacement ellipsoids and the atom numbering scheme.

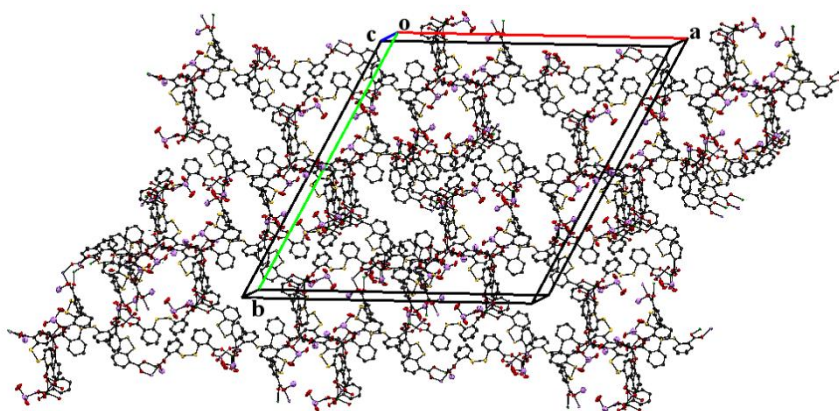


Fig.3. Packing diagram of (1) viewed along the *ab* plane.

Table 2. Selected geometric parameters (Å, °) for (**1**).

Co1—O3	1.948 (3)	S1—S2 ⁱ	2.0403 (17)
Co1—O1	1.988 (3)	S1—C7 ⁱⁱ	1.784 (5)
Co1—O7	1.948 (3)	S2—C14	1.796 (5)
Co1—O5	1.925 (4)	S3—S4 ⁱⁱⁱ	2.042 (2)
Li1—S1	3.029 (8)	S3—C21	1.790 (6)
Li1—O2	1.964 (7)	S4—C28	1.788 (5)
Li1—O4	1.920 (9)	O2—Li2	2.23 (3)
Li1—O8	1.920 (9)	O8—Li2	2.17 (2)
Li1—O6	1.957 (8)		
O3—Co1—O1	107.70 (15)	O8—Li1—S1	155.5 (4)
O7—Co1—O3	110.69 (16)	O8—Li1—O2	95.5 (4)
O7—Co1—O1	99.16 (14)	O8—Li1—O6	104.5 (4)
O5—Co1—O3	117.22 (17)	O6—Li1—S1	81.8 (3)
O5—Co1—O1	95.39 (14)	O6—Li1—O2	127.2 (4)
O5—Co1—O7	122.22 (17)	O8—Li2—O2	81.7 (9)
O2—Li1—S1	63.2 (2)	O9—Li2—O2	96.2 (13)
O4—Li1—S1	90.7 (3)	O9—Li2—O8	97.8 (11)
O4—Li1—O2	108.8 (4)	O10—Li2—O2	98.3 (12)
O4—Li1—O8	108.6 (4)	O10—Li2—O8	124.7 (13)
O4—Li1—O6	109.9 (4)	O10—Li2—O9	136.5 (16)

Symmetry codes: (i) $x-y+2/3, x+1/3, -z+4/3$; (ii) $x, y, z-1$; (iii) $-x+y+1/3, -x+5/3, z-1/3$.

Table 3. Hydrogen-bond geometry (Å, °) for (**1**)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots S2 ⁱ	0.93	2.62	3.161 (5)	117.8
C27—H27 \cdots S3 ⁱⁱ	0.93	2.72	3.186 (7)	112.3
O9—H9A \cdots O6	0.87	2.60	3.136 (18)	120.9
O10—H10B \cdots S4 ⁱⁱⁱ	0.90 (2)	2.61 (13)	3.267 (9)	131 (13)

Symmetry codes: (i) $x-y+2/3, x+1/3, -z+7/3$; (ii) $-y+5/3, x-y+4/3, z+1/3$; (iii) $x, y, z-1$.

3.1.2. Description of the structure of **2**

Compound **2** which is formulated as $\{[Zn_2Li_2C_{56}H_{32}O_{16}S_8]\cdot 3(HO_2)\}$ crystallizes in the trigonal crystal system with R-3 space group. In the asymmetric unit, four bis(2-carboxyphenyl)disulfide ligand, two zinc(II), two lithium(I) and three water molecules are present. Fig.4 depicts the perspective view of the coordination polymer complex. Selected bond lengths and angles are listed in Table 4 and the hydrogen bonding parameters are listed in Table 5.

The geometry around the tetracoordinated Zn(II) cation (**2**) is tetrahedral (Fig. 3) as found for Co(II) in complex (**1**) with τ_4 value of 0.8698. The O—Zn1—O angle values in the range $[95.77(9)^\circ - 120.29(10)^\circ]$ are severely deviated from the ideal value of $109^\circ 28'$ for a perfect tetrahedron geometry. The oxygen atoms of the acetate groups are strongly linked to the zinc (II) atom as shown by the short distance values of Zn1—O which are in the range $1.935(2) \text{ \AA} - 1.981(2) \text{ \AA}$. As observed in complex (**1**), the Zn1—O distances are comparable to values reported for similar zinc(II) complexes with acetate group acting in bidentate bridging fashion[33]. The pentacoordinated Li1 cation is surrounded by four carboxylate oxygen atoms from different ligand molecules and one sulfur atom from a sulfanyl moiety. According to the Addison index[27], the τ value of 0.5543 for Li1 is

indicative of a distorted trigonal pyramidal geometry around the Li(I) cation. The modified index suggested by Konno *et al.*[28], which is more efficient (χ value of 0.6822) confirms the previously predicted geometry around Li1. The basal plane is occupied by three carboxylate oxygen atoms with angle values deviating severely from the ideal value of 120° ($O4-Li1-O6 = 108.5(2)^\circ$, $O7-Li1-O6 = 108.1(2)^\circ$ and $O4-Li1-O7 = 126.3(3)^\circ$). The value of the sum of the subtended angles in the equatorial plane is 342.9° rather than the ideal value of 360° for a perfect trigonal bipyramidal geometry. The apical positions are occupied by one carboxylate oxygen atom and one sulfur atom with angle value of $159.7(2)^\circ$ [$O2-Li1-S4$] far from the ideal value of 180° . The bond lengths of $Li1-O$ in the range $1.891(5) \text{ \AA} - 1.979(5) \text{ \AA}$ are shorter than the distance value of $Li1-S4$ [$3.020(5) \text{ \AA}$]. In fact, the hard character of the carboxylate oxygen atoms and the soft character of the sulfur atom of the sulfanyl moiety can explain the strongly difference between $Li1-O$ and $Li1-S$ distances.

The $S-S$ distance $2.0448(11) \text{ \AA}$ and $2.0420(9) \text{ \AA}$, the $C-S$ distances which fall in the range [$1.781(3) \text{ \AA} - 1.794(3) \text{ \AA}$] and the $C-S-S$ angle [$104.25(9)^\circ - 105.11(9)^\circ$] are comparable to the values reported for complex derived from the sulfane bis(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane[35]. The dihedral angles between the phenyl rings linked by the disulfide bridges are respectively $71.61(2)^\circ$ for $C2/C7-S1-S2-C9/C21$ and $85.17(2)^\circ$ for $C16/C21-S3-S4-C23/C28$.

The structure of the compound **2** present intermolecular hydrogen bonding of type $O-H \cdots O$ involving free water molecules: $O11-H11B \cdots O10A$ and $O10A-H10D \cdots O11$. Numerous intra-molecular hydrogen bonding involving $C-H$ as donor and sulfur atoms as acceptor ($C-H \cdots S$) (Table 5), stabilized the structure. The packing of the molecules reveals that the sheets of the coordination polymer units are connected through intermolecular hydrogen bonding involving water molecules as donor and carboxylate oxygen atoms as acceptor (*ie.* $O10-H10C \cdots O7^i$; $i = x-y+2/3, x+1/3$) and water molecule as donor and sulfur atom as acceptor ($O10A-H10A \cdots S2^{iii}$; $iii = -x+1, -y+1, -z+1$) (Table 5) leading to a three-dimensional supramolecular (Fig.5). The structure is consolidated by the presence of intermolecular hydrogen bonding type of $C-H \cdots O$.

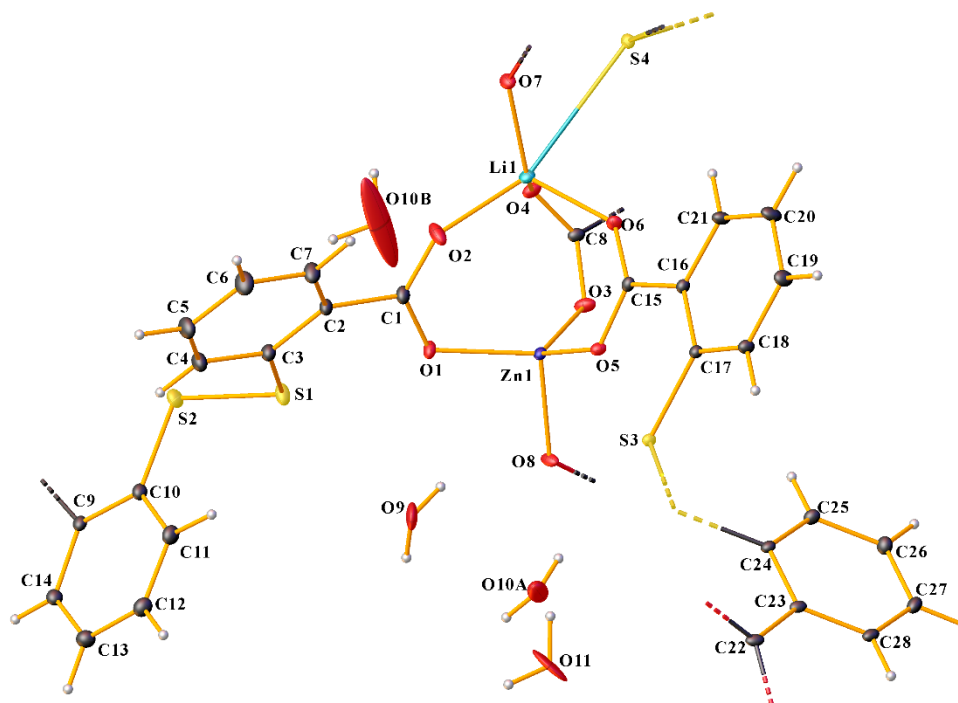


Fig.4. The molecular structure of (**2**), showing 30% probability displacement ellipsoids and the atom numbering scheme.

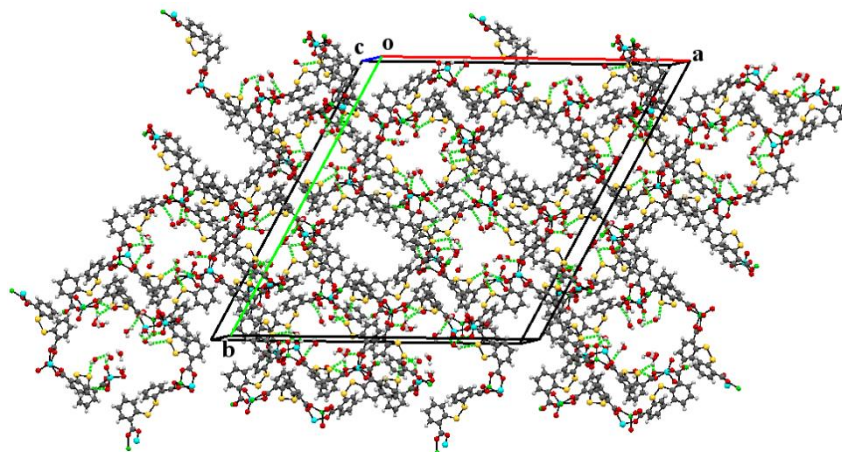

Fig.5. Packing diagram of (2) viewed along the *ab* plane.

Table 4. Selected geometric parameters (Å, °) for (2).

Zn1—O5	1.9426 (19)	S4—Li ⁱ	3.020 (5)
Zn1—O8	1.981 (2)	S4—C24	1.790 (3)
Zn1—O1	1.954 (2)	O6—Li1	1.891 (5)
Zn1—O3	1.935 (2)	O7—Li1	1.943 (5)
S2—S1	2.0448 (11)	O2—Li1	1.940 (5)
S2—C10	1.794 (3)	Li1—O4	1.979 (5)
S3—S4	2.0420 (9)	S1—C3	1.781 (3)
S3—C17	1.791 (3)		
O5—Zn1—O8	106.53 (9)	O6—Li1—O2	108.0 (3)
O5—Zn1—O1	112.91 (9)	O6—Li1—O4	108.5 (2)
O1—Zn1—O8	99.53 (9)	O7—Li1—S4 ⁱⁱ	62.39 (14)
O3—Zn1—O5	117.04 (9)	O7—Li1—O4	126.3 (3)
O3—Zn1—O8	95.77 (9)	O2—Li1—S4 ⁱⁱ	159.7 (2)
O3—Zn1—O1	120.29 (10)	O2—Li1—O7	99.4 (2)
O6—Li1—S4 ⁱⁱ	87.38 (18)	O2—Li1—O4	104.9 (2)
O6—Li1—O7	108.1 (2)	O4—Li1—S4 ⁱⁱ	81.60 (17)

 Symmetry codes: (i) $x-y+2/3, x+1/3, -z+4/3$; (ii) $y-1/3, -x+y+1/3, -z+4/3$.

Table 5. Hydrogen-bond geometry (Å, °) for (2).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...S2	0.95	2.72	3.184(4)	111.0
C11—H11...S1	0.95	2.70	3.205(4)	113.9
C18—H18...S4	0.95	2.56	3.117(3)	117.7
C18—H18...O6 ⁱ	0.95	2.49	3.340(3)	148.6
C25—H25...S3	0.95	2.60	3.148(3)	117.3
C28—H28...O5 ⁱⁱ	0.95	2.50	3.206(3)	131.2
O9—H9A...O7 ⁱ	0.87	2.39	2.917(6)	119.1
O9—H9A...O8 ⁱⁱ	0.87	2.56	2.847(6)	100.1
O11—H11B...O10A	0.87	2.40	2.78(3)	106.8

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