Chapter 6

1D lead(II) coordination chains with carboxylate containing ligands. A rare example of polyrotaxane 1D→1D interpenetrated coordination polymer

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6.1. Introduction

In recent years different levels of interpenetration have been reported and such assemblies most commonly involve interpenetrated 2D or 3D frameworks, while interpenetrated 1D polymers are rather rare since these polymers require the presence of rings in the chain. [250] In addition a literature survey shows that most of metal-organic framework (MOF) research is focused on complexes comprising transition metals due to their unique structures and potential applications, while MOFs containing main group metals are less explored. Recently, the rapid development of materials science and crystal engineering moved the interest of inorganic chemists towards the investigation of Pb(II) complexes. The attention was dictated also for the presence in this metal of the 6s electron lone pair that drives the coordination sphere towards unusual geometries. In fact the stereochemically active 6s electrons usually give rise to a hemidirected coordination geometry leaving a distinct void or gap in the coordination sphere; on the contrary the lack of this void is indicative of stereochemically inactive 6s lone pair. [251,252] Continuing our interest in the use of lead(II) in the construction of polymeric complexes, [252] we report herein the synthesis, structural determination of two new Pb compounds $[Pb(ind)_2(H_2O)]_n$ (**11**) and $[Pb(dbsf)(bipy)]_n$ (**12**), built by carboxylate containing ligands (Hind = indane-2-carboxylic acid, H_2dbsf = 4,4′-sulfonyldibenzoic acid, and bipy 4,4′-bipyridine).

6.2 Experimental

6.2.1 Materials

Lead acetate trihydrate and o-phenanthroline were purchased from Merck. Iminodiacetic acid and naphthalene-2,6-dicarboxylic acid were purchased from SIGMA-ALDRICH Inc. All the chemicals were used without any further purification.

6.2.2 Physical Measurements

Spectroscopic data were collected as follows: IR spectra for **11-12** were recorded with JASCO FT/IR-6200 using ATR technique in the range of 4000–400 cm^{-1}. Elemental analyses (C,H,N) were performed using a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) were done under nitrogen (flow rate of 20 mL min^{-1}) with TA (SDT Q60) analyzer in the temperature range of 25–800˚C with a heating rate of 10˚C/min.

6.2.3 Synthesis

6.2.3.1 Synthesis of $[Pb(ind)_2(H_2O)]_n$ (11)

$Pb(NO_3)_2$ (0.5 mmol, 0.165605 g) and indane-2,2’-dicarboxylic acid (0.5 mmol, 0.10309 g) were dissolved in 10 mL de-ionized water. To this solution 5 mL aqueous NaOH solution (5M) was added drop wise and the mixture was homogenized by stirring. The solution was transferred in to a Teflon-lined autoclave (23 mL) and heated at 160 °C for four days. After cooling the solution to room temperature, colorless needle shaped crystals were isolated by filtering the supernatant liquid and washed with deionized water and dried in air. Yield: 60%. Elemental analysis calculated for $C_{20}H_{20}O_5Pb$ (547.55): C, 43.87; H, 3.68. Found: C, 43.81; H, 3.63. IR (KBr, cm-1): 561(w), 606(w), 658(w), 677(w), 756(w), 866(s), 956(w), 1018(m), 1086(m), 1164(m), 1294(s), 1410(s), 1553(s), 1630(w), 2105(w), 2851(w), 2941(w), 3450(broad).

6.2.3.2 Synthesis of [Pb(dbsf)(bipy)]$_n$ (12)

10 ml of methanolic solution containing 4,4’ bipyridine (0.5 mmol, 0.07809 g) was added drop wise to an aqueous solution (20 mL) of $Pb(OAc)_2.3H_2O$ (1 mmol, 0.37933 g) with constant stirring. After half an hour 10 mL DMF-H_2O solution of 4,4’-sulfonyldibenzoic acid (1 mmol, 0.3063 g) was added to the mixture that was homogenized by stirring. The solution was transferred into a Teflon-lined autoclave (23 mL) and heated at 160 °C for 4 days.The resulting solution was cooled to room temperature and filtered. Colorless block shaped single crystals were obtained from the solution after 3 days at room temperature. The crystals were isolated by decanting the supernatant liquid and washed with deionized water-ethanol mixture and dried in air. Yield: 55%. Elemental analysis calculated for $C_{19}H_{12}NO_6PbS$ (589.55): C, 38.70; H, 2.05; N, 2.37. Found: C, 38.62; H, 2.02; N, 2.34. IR (KBr, cm-1): 540(m), 577(s), 616(s), 695(m), 725(w), 744(w), 778(m), 809(s), 856(s), 870(w), 1009(s), 1068(m), 1097(m), 1130(m), 1160(s), 1222(m), 1295(w), 1322(w), 1378(broad), 1484(m), 1555(broad), 1600(m), 1644(w), 1780(w), 1832(m), 1957(m).

6.3 X-ray Crystallography

Diffraction data for compounds **11** and **12** were collected on a four-circle Xcalibur Sapphire 3 diffractometer ($\lambda = 0.71073$ Å) equipped with CCD. Measurements were done at 293(2) K for **11** and at 120(2) K for **12**. Cell refinement, indexing and scaling of the data set were carried out using CrysAlisPro program. [191]The structures were solved by using OLEX2 program [193] and subsequent Fourier analyses [137]and refined by the full-matrix least-squares method based on F^2 with all observed reflections. [137] The Flack parameter in **12** was refined to 0.522(18) meaning that the crystal consists of a racemic mixture of two enantiomers. The contribution of H atoms at calculated position was introduced in the final cycles of refinement. Molecular graphics were done using the Diamond program. [140] **11**: $C_{20}H_{20}O_5Pb$, M = 547.55, monoclinic, space group $P\ 2_1$, a = 8.4925(2), b = 7.14780(19), c = 15.5621(5) Å, β = 101.524(3)°, V = 925.61(5) Å^3, Z = 2, D_c = 1.965 g/cm^3, μ(Mo-Kα) = 9.141 mm^{-1}, F(000) = 524, θ max = 27.50°. Final $R1$ = 0.0327, $wR2$ = 0.0663, S = 1.089 for 237 parameters and 4207 unique reflections [R(int) = 0.0429], of which 3888 with $I > 2\sigma(I)$, max positive and negative peaks in ΔF map 1.022, –1.012 e. Å^{-3}.

12: $C_{19}H_{12}NO_6PbS$, M = 589.55, triclinic, space group P **-**1, a = 7.8214(2), b = 10.3016(4), c = 12.0331(5) Å, α = 110.123(4), β = 94.436(3), γ =104.783(3)°, V = 865.54(6) Å^3, Z = 2, D_c = 2.262 g/cm^3, μ(Mo-Kα) = 9.907 mm^{-1}, F(000) = 558, θ max = 26.00°. Final $R1$ = 0.0295, $wR2$ = 0.0586, S = 1.039 for 253 parameters and 3406 unique reflections [R(int) = 0.0572], of which 3080 with $I > 2\sigma(I)$, max positive and negative peaks in ΔF map 1.741, –0.997 e. Å^{-3}.

6.4 Results and Discussion

6.4.1 Crystal structure of 11

The X-ray crystallographic analysis of compound **11**, of formulation $[Pb(ind)_2(H_2O)]n$, revealed for this a 1-D chain-like coordination polymer. The lead atom is chelated by two indan-2-carboxylato groups and by two oxygen's, which come from symmetry related different ind ligands.

The coordination sphere is completed by a water molecule (Fig. 6.1). In the PbO_7 chromophore the Pb−O (carboxylate) bond distances range from 2.503 (13) to 2.662 (13) Å, while the $Pb-OH_2$ bond is slightly longer of 2.745 (7) Å. The coordination sphere around Pb shows an evident void [the largest bond angles are O(3)-Pb-O(1w) = 150.2 (4)°, O(4)-Pb-O(2'') = 143.2(4)°] with all the Pb−O bonds distributed in a hemisphere. The structural consequence is a hemidirected coordination geometry of the Pb center due to the presence of the stereo chemical active 6s lone pair electrons. In the coordination sphere the chelating carboxylate groups form a dihedral angle of 88.5°.

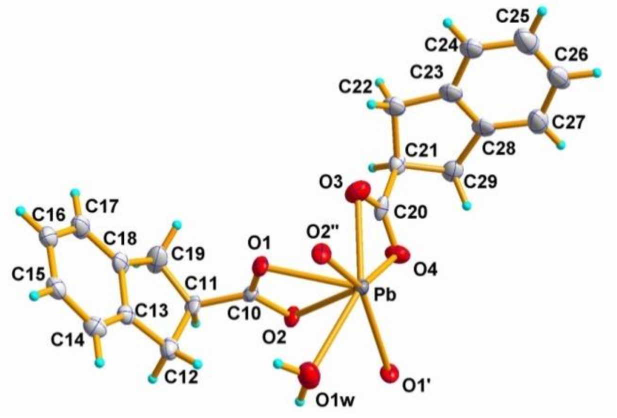

Fig. 6.1 ORTEP drawing (50% probability level) of the crystallographic independent unit in complex **11**.Coordination bond distances (Å): Pb-N(1) 2.556(4), Pb-O(3')2.689(4), Pb-O(1) 2.596(4),Pb-O(4') 2.334(4), Pb-O(2) 2.342(3).

Of the two crystallographic independent carboxylate groups, one is chelating (O3/O4), while the other (O1/O2) acts as chelating-bridging (μ-η^1:η^2:η^1) connecting three Pb atoms giving rise to a 1D polymer elongated along axis *b* (Fig. 6.2). The intermetallic distance is of 4.291(1) and a Pb…Pb…Pb angle of 112.79(1)°. It is worth noting that the chain is reinforced by intramolecular H-bonds between O1w and caboxylate group O3/O4 (O1w…O3 = 3.14(3) Å, O1w-H1a…O3 = 164°; O1w…O4 = 2.60(2) Å, O1w-H1b…O4 = 175°), and the second interaction appears to be rather strong. The crystal packing shows discrete coordination polymers and no significant π-π interaction is detected among the chains.

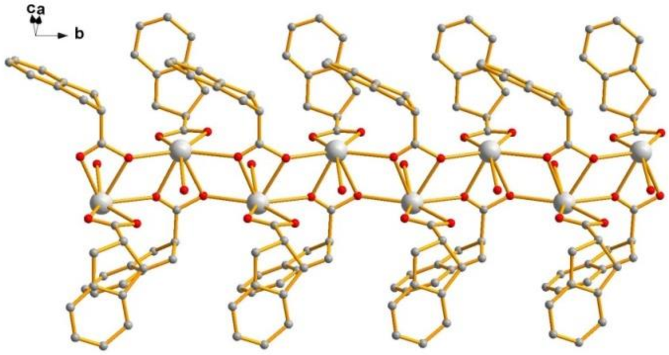

Fig .6.2 The 1D coordination polymer in compound **11**.

6.4.2 Crystal structure of 12

The crystallographic independent unit of compound **12**, $[Pb(dbsf)(bipy)]_n$, comprises a Pb atom beside one dbsf anion and a bipy ligand. Fig. 3 shows the coordination sphere around the metal and a selection of bond lengths and angles is reported in Table 6.2 (INCLUDE TABLE IN TEXT). The lead(II) atom is penta coordinated, being double chelated by the carboxylic groups from symmetry related dbsf anions and further bound by a bipy nitrogen donor. The hemidirected coordination geometry is evident from Fig. 6.3 and 6.4 where a distinct void around the metal sphere is evident.

Each carboxylate group chelates the metal in an asymmetrical fashion with one Pb-O bond distance shorter (Pb-O(2) = 2.342(3), Pb-O(4') = 2.334(4) Å), with respect to the other (Pb-O(1) = 2.596(4), Pb-O(3') = 2.689(4) Å), assuming the primary coordination sphere of Pb(II) atom limited to a Pb-O distance of 2.80-2.90 Å.[142] The bipy ligands, connecting adjacent $Pb_2(dbsf)_2$ rings (Pb-N(1) = 2.556(4) Å), give rise to a 1D polymer having a staircase arrangement (Fig. 6.4). In the chain the metals are separated by 13.501 and 12.133 Å through the sdba e bipy ligands, respectively, while the dimensions of the $Pb_2(dbsf)_2$ ring, defined by the Pb-S distances, are of 8.837 and 8.794 Å.

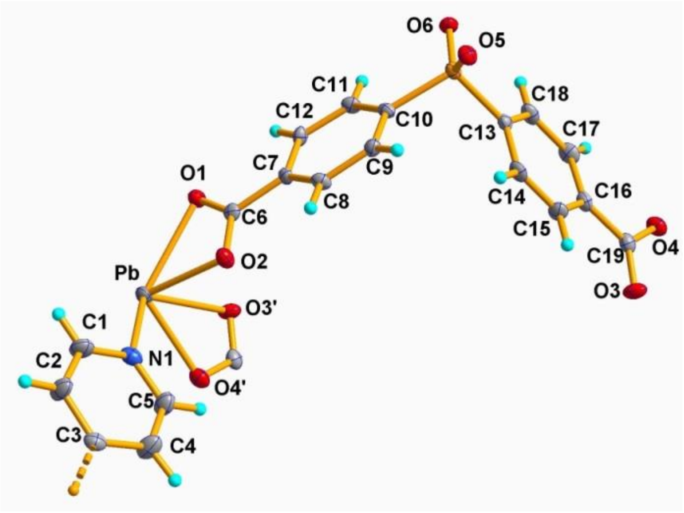

Fig. 6.3 ORTEP drawing (50% probability level) of the crystallographic independent unit in complex **12** with indication of the coordination sphere around Pb atom (primed atoms at 1-x, 2-y, 1-z).

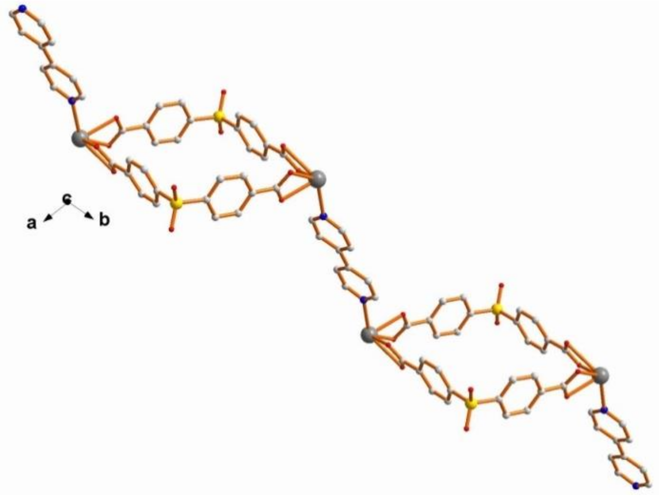

Fig. 6.4 A single 1D polymeric chain in **12** built by centrosymmetrical [$Pb_2(dbsf)_2$] units connected by bipy spacers.

The coordination values here reported are in agreement with those measured in Pb(dbsf) compounds with alkaline or alkaline earth metals reported a few years ago. [253]

The 4,4'-dicarboxybiphenyl sulfone (H_2dbsf) is a typical example of semi-rigid V-shaped dicarboxylate ligand showing different coordination modes and examples of $M_2(dbsf)_2$ or

$M_4(dbsf)_2$ units are not unusual [M = Cd,[254] Cu,[255] Zn,[256]and Ni[257]]. However, in the present complex the dbsf anion presents a bischelating ($\eta^4\mu$) coordination that, at our knowledge, was detected only in compound [Cd(dbsf)(L)] (L= *N*,*N′*-di(4-pyridyl) adipoamide).[258] The dimensions of the $Pb_2(dbsf)_2$ ring connected by the bipy ligands facilitate the interpenetration of a second chain resulting in a 1D-1D polycatenated structure (Fig. 6.5). The supramolecular arrangement is reinforced by π-π interactions between the phenyl C (13-18) and the pyridine ring (centroid-to-centroid distance of 3.782(3) Å, angle of 12.4(3)°).

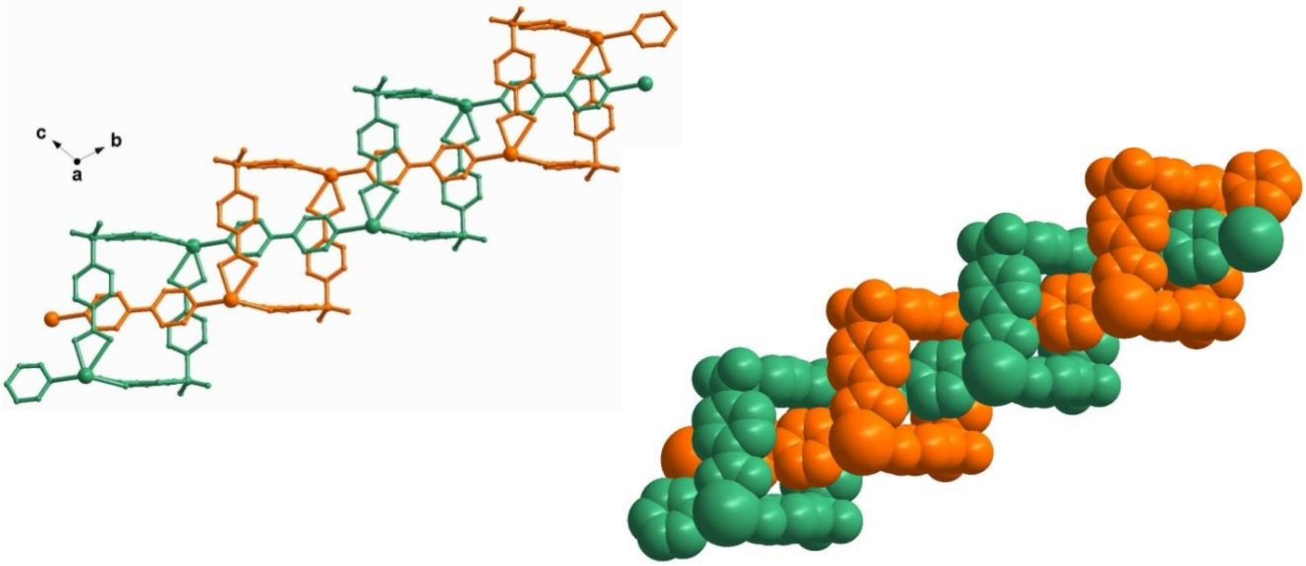

Fig. 6.5 The interpenetrated 1D coordination polymer in compound **12** as ball and stick and space-filling representation

Possible 1D-1D interpenetrated polymer topologies, those of type A and B of Fig. 6 were indicated some years ago as possible arrangements [259] and a recently reported silver complex with a ligand containing four allyloxy phenyl substituents [260] gave rise to an interpenetration of topology type B (Fig. 6.6). Other metallosupramolecular assemblies of mutually interpenetrated 1D polymers were reported with Pt[261] and Rh,[262] mediated by H-bond interactions and with Zn [263] showing Br...Br interactions.

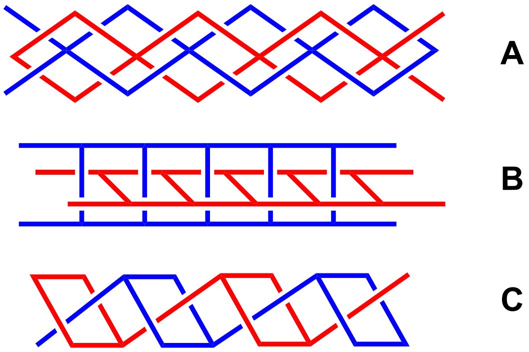

Fig. 6. 6 Schematic representation of possible self-interpenetrating 1D-1D polymers.

6.4.3 TGA study

Thermogravimetric analysis of **11** was carried in the temperature range of 30-800 °C under flowing N_2 atmosphere at a heating rate of 10 °C min^{-1}. The TG profile of **11** (Fig. 6.7) revealed the thermal instability of the complex. Dehydration occurs in the temperature range of 66–90^0C with a mass decrease of ca. 3.00% (calc. 3.28%), indicating the loss of the coordinated water molecules. On further heating the complete decomposition of the complex takes place in the temperature range 90-350°C to form lead oxide as rest mass of 40.05% (Calc., 40.76%). Complex **12** proved to be thermally stable up to 245 ^{0}C (TG profile shown in Fig. 6.8). On further heating the complex **12** decomposed in a single step under the temperature range 245-502^0C where complete decomposition of the complex takes place to form lead oxide as rest mass of 37.16% (Calc., 37.85%)

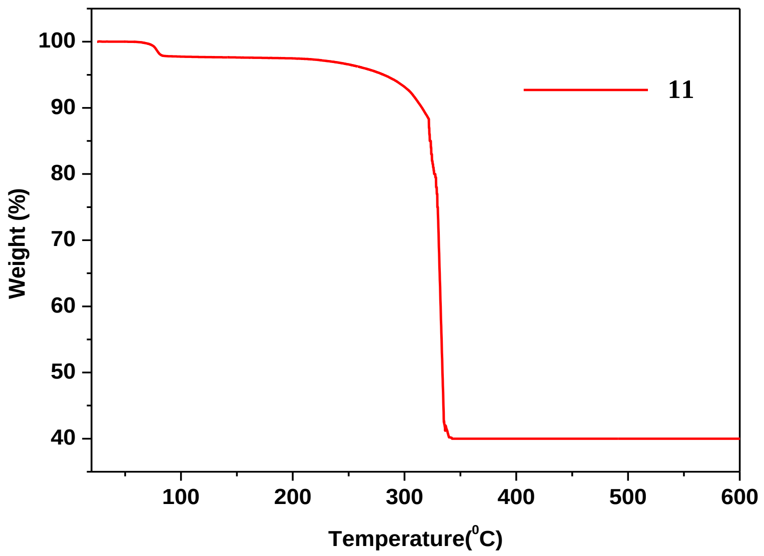

Fig. 6.7 TG analysis of **11**in the temperature ranges 25-600°C with a heating rate of 10°C/min under N_2 atmosphere.

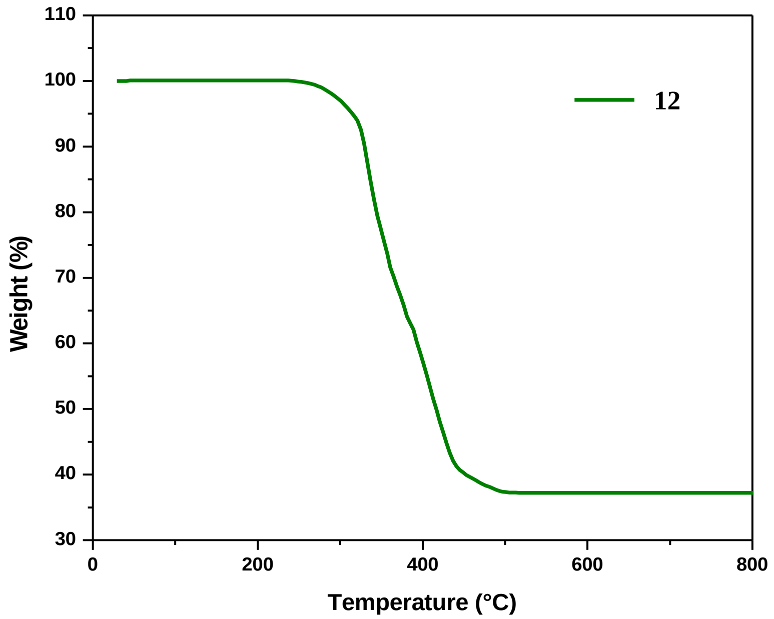

Fig. 6.8 TG analysis of **12**in the temperature range 0-800°C with a heating rate of 10°C/min under N_2 atmosphere.