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A new luminous end-to-end thiocyanato bridged heptacoordinated coordination polymer of lead(II) containing a tetradentate Schiff base

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ABSTRACT

A new end-to-end thiocyanato bridged coordination polymer [Pb(enbzpy)($\mu_{1,3}$-NCS)(NCS)]$_n$ (**1**) has been synthesized using a one-pot reaction of Pb(OAc)$_2$.3H$_2$O, tetradentate Schiff base *N,N* -(bis(pyridine-2-yl)benzylidene)ethane-1,2-diamine (enbzpy) and NH$_4$NCS in MeOH solution at room temperature. Single crystal X-ray diffraction measurement reveals that each lead(II) adopts a pentagonal bipyramidal geometry with a PbN$_6$S chromophore coordinated through four N atoms of enbzpy, two $\mu_{1,3}$-bridged N and S atoms and one terminal N atom of thiocyanates. In crystalline state, **1** forms a 2D honeycomb like (6^3) topology through S···S interaction and the layers stack through face-to-face π···π interaction giving rise to a 3D network. At room temperature DMF solution of **1** displays a high-energy intraligand ^{1}(π-π*) fluorescence.

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A vast majority of current work centers around the use of molecular building components to isolate inorganic–organic hybrid [1,2] functional materials [3–7] of different shapes and sizes [8] through control and manipulation of metal ligand covalent bonds [9,10] with malleable coordination spheres and multiple lateral non-covalent forces [11–15] like hydrogen bondings and C-H···π, π···π, S···S, Se···Se, etc. interactions. One-pot synthesis [16] using metal ion templates, organic spacers and inorganic/organic terminals/bridges in varied molar ratios may lead to different molecular and crystalline architectures with tunable target properties. Recently, we are interested [17–19] in the construction of different coordination polymers and polymer based supramolecular entities through variation of ligand backbones and metal ion coordination environments; in this regard, Schiff base spacers and pseudohalide terminals/bridges have been remarkable. Schiff bases [20] are useful ligands because of their ease of preparation, structural variety, varied denticities and subtle steric and/or electronic effects. Ambidentate thiocyanate [21] may act as terminal and bridging ligands, and in terminal mode often participates in hydrogen bondings [22], S···S interactions [23–25] that influence crystalline architectures. The present work stems from our interest to build new molecular and crystalline aggregates of lead(II), a heavy p-block metal ion that has intrinsic features owing to the presence of stereochemically active 6 s^2 electrons [26–29]. In the present work we have examined the coordination behaviour of a tetradentate Schiff base, N,N -(bis(pyridin-2-yl)benzylidene)ethane-1,2-diamine (enbzpy) towards lead(II) in combination with thiocyanate, that remains unexplored to date. Successfully, we have synthesized and X-ray crystallographically characterized one luminous end-to-end thiocyanate bridged heptacoordinated neutral 1D coordination polymer of the type [Pb(enbzpy)($\mu_{1,3}$-NCS)(NCS)]$_n$ (**1**) through a one-pot reaction of lead(II) acetate trihydrates, enbzpy and NH$_4$NCS in a 1:1:2 molar ratio in methanolic solution [30]. Compound **1** assembles into a 2D honeycomb like (6^3) topology through S···S interaction and the successive 2D sheets are stacked via π···π interaction affording a 3D supramolecular architecture. This luminous compound is an example of a unique heptacoordinated thiocyanato bridged coordination polymer of lead(II) which has very scarce literature [31,32] Scheme 1.

The air- and moisture-insensitive compound is insoluble in methanol, ethanol, dichloromethane, acetonitrile but soluble in dimethylformamide and dimethylsulphoxide. In IR spectrum of **1** three strong peaks at 2073, 2047, 2024 cm^{-1} are observed assignable to ν_{as}(CN) stretching vibrations of the thiocyanate ligands [33]. Three bands corresponding to ν(CS) stretching frequency appear at 766, 749, 701 cm^{-1}. The position and number of signals strongly suggests mutual *cis* alignment and terminal as well as N- and S-coordinated bridging behaviour of the bound thiocyanates [33]. X-ray study [34] corroborates this hypothesis and defines the molecular structure and crystalline architecture. The stretching vibrations ν(C=N) plus ν(C=C) of the Schiff base are observed at 1630 and 1580 cm^{-1}, and 1621 and 1584 cm^{-1} for free and in metal bound states, respectively.

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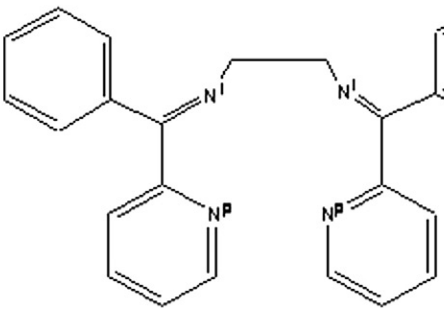

Scheme 1. (N^p, N^i, N^i, N^p) donor set in enbzpy.

Single crystal X-ray diffraction study of **1** reveals that the crystal lattice consists of [Pb(enbzpy)($\mu_{1,3}$-NCS)(NCS)]$_n$ unit. An ORTEP diagram with atom numbering scheme is shown in Fig. 1. The coordination polyhedra around each lead(II) center is best described as a distorted pentagonal bipyramid (pbp) with a PbN_6S chromophore. The distortion from ideal pbp geometry is due to the asymmetric nature of the bound enbzpy and the deviation of the refine angles formed at each metal center. The coordination includes tetradentate Schiff base, enbzpy, ligated by two N^p atoms (N1, N5), two N^i atoms (N2, N4), two end-to-end ($\mu_{1,3}$-) bridged nitrogen and sulphur atoms (N3*, S2; symmetry code: *1-x, 1/2 + y, 1/2-z) and one terminal N (N6) of thiocyanates. The equatorial plane of the pentagon consists of one bridging thiocyanate nitrogen (N3*), and N1, N2, N4, N5 atoms of enbzpy, the axial positions are occupied by terminal N6 and bridging S2 of two thiocyanates. The degrees of distortion from an ideal pbp geometry are reflected in the *equatorial* [60.58(17)-85.3(2)°] and the *axial* 154.0(2)° angles. Each lead(II) center deviates 0.434 Å from the mean plane towards S2. Five equatorial nitrogens, N1, N2, N3, N4 and N5 also show considerable deviation (N1 0.096 Å, N2 0.093 Å, N3 0.064 Å, N4 0.025 Å and N5 0.036 Å) from the mean plane. The ethylenic part (N2-C26-C25-N4) of the Schiff base is to some extent puckered. The intrachain Pb···Pb separation across the single $\mu_{1,3}$-NCS bridge is 7.414 Å.

The 1D covalent chains in **1** are associated into a 2D honeycomb like (6^3) topology (Fig. 2) arising from S···S [S(4)···S(4)** separation: 3.473(6) Å, symmetry code: **2-x, 2-y, -z; which is lower [35] than the sum of the van der Waals radii (4.06 Å) of S atoms] interaction between two S [S(4)] atoms of terminal thiocyanates along *a*-axis. The successive 2D sheets pack alongside each other to give a 3D network (Fig. 3) through face-to-face π···π interaction [Ring(1)-Ring(1): Cg(1)-Cg(1)*** separation: 3.864(5) Å, vertical displacement of Cg: 3.578 Å; dihedral angle 0.0°; symmetry code: ***1-x, 2-y, -z; Cg(1) = N(1)-C(1)-C(2)-C(3)-C(4)-C(5)] propagating along *c*-axis due to the availability of pyridyl π interaction sites which align optimally to facilitate the π···π stacking between the sheets.

To examine thermal stability, thermogravimetric and differential thermal analyses (TG-DTA) were made between 40 and 900 °C in the static atmosphere of nitrogen. Compound **1** is stable up to 229 °C, and the TG curve (Fig. S1) indicates that the weight loss (obs.: 42.66%; calcd.: 54.73%) between 229 and 585 °C corresponds to the departure of the Schiff base (enbzpy) with an exothermic effect at 266 °C and two thiocyanate groups (obs.: 21.79%, calcd.: 16.24%) in the range 585–674 °C followed by another exothermic peak with a maximum at 626 °C.

Faint yellow DMF solutions of the free ligand (enbzpy) and the compound **1** show strong absorption band at 273 nm presumably due to ligand based transition [36,37]. Excitation at 273 nm, the free Schiff base containing the pyridine moieties exhibits emission at 378 nm with lower intensity value, whereas the compound **1** shows greater intensity at ~378 nm presumably due to the increase in conformational rigidity of the ligand upon coordination [38]. In each

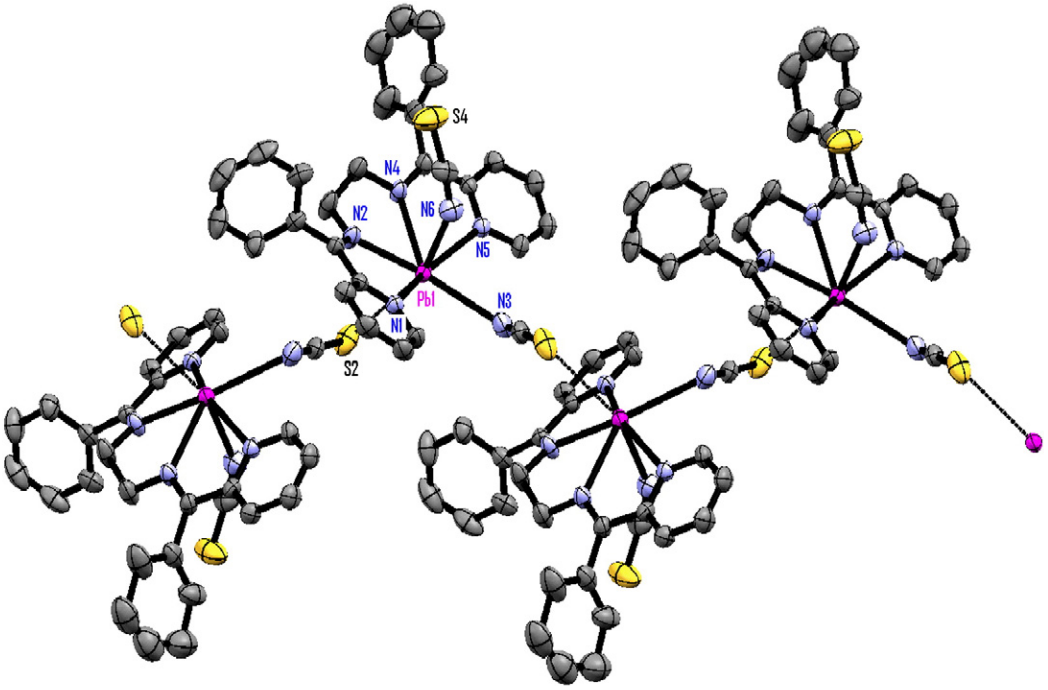

Fig. 1. An ORTEP view of a segmented 1D zig-zag chain structure in **1** with atom labeling scheme and 30% thermal ellipsoid probability for all non-hydrogen atoms. Selected bond distances (Å) Pb(1)-S(2) 3.192(3), Pb(1)-N(1) 2.642(6), Pb(1)-N(2) 2.527(6), Pb(1)-N(4) 2.642(6), Pb(1)-N(5) 2.754(6), Pb(1)-N(6) 2.416(8), Pb(1)-N(3)* 2.835(8), and bond angles (°) N(1)-Pb(1)-N(2) 62.97(18), N(2)-Pb(1)-N(4) 65.68(18), N(4)-Pb(1)-N(5) 60.58(17), N(5)-Pb(1)-N(3)* 80.15(19), N(1)-Pb(1)-N(3)* 85.3(2), S(2)-Pb(1)-N(6) 154.0 (2); *1-x, 1/2 + y, 1/2-z.

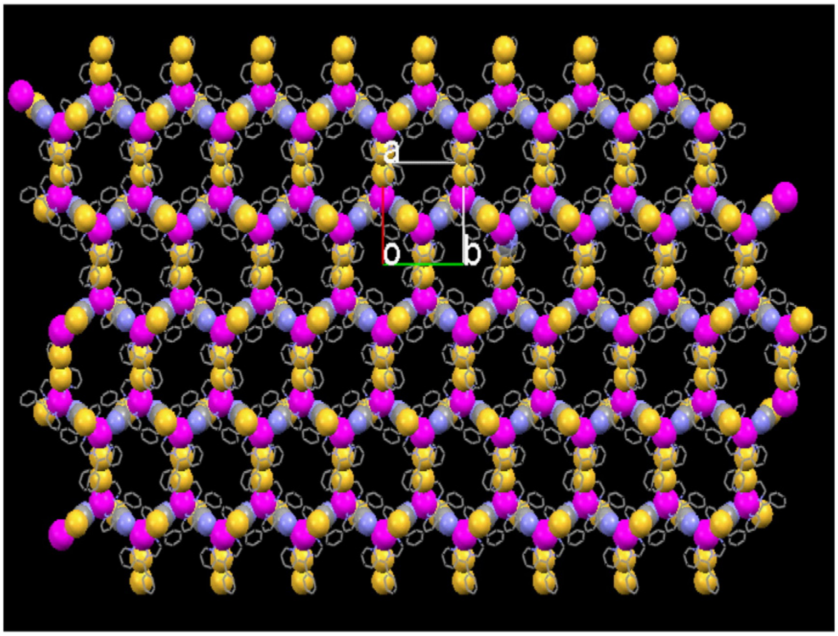

Fig. 2. A view of 2D honeycomb like (6^3) topology in **1** formed through S···S interactions along *a*-axis.

case the luminescence may be attributed to the intraligand $^1(\pi\text{-}\pi^*)$ transition (Fig. 4a). The lead(II) salt and ammonium thiocyanate are not luminescent. To observe the formation of the polynuclear compound, fluorescence behaviour of the Schiff base was studied as a function of lead(II) using a solution concentration of enbzpy and NH_4NCS in the 1:2 molar ratio. The plot of fluorescence intensity as a function of concentration of the metal ion (Table S1) shows that the intensity increases linearly with the concentration of lead(II) $[(0.1\text{-}0.2)\times10^{-6}$ M] up to a mole ratio of 1:1 ligand mixture (enbzpy 0.197×10^{-6} M plus NH_4NCS 0.421×10^{-6} M) and lead(II) ion (0.23784×10^{-6} M); after that it remains constant (Fig. 4b). Use of similar concentration of solid compound **1** and the concentration of lead(II), ammonium thiocyanate and enbzpy according to polynuclear formula gives their almost same intensity value in separate experiments. This shows the polynuclear compound formation is very facile in reaction condition as expected from labile non-transition lead(II) ion.

In summary, we report an interesting crystal structure and luminous behaviour of a heptacoordinated coordination polymer of lead (II) containing thiocyanate and a tetradentate Schiff base in which a 2D honeycomb like (6^3) topology through S···S interaction has been accomplished through deliberate choice of building units. In addition, weak π···π interaction among two closest pyridine rings of enbzpy plays an important role for stacking these 2D sheets into a 3D network structure. This indicates that the complex **1** can be effectively used as a potential scaffold for the design of supramolecular

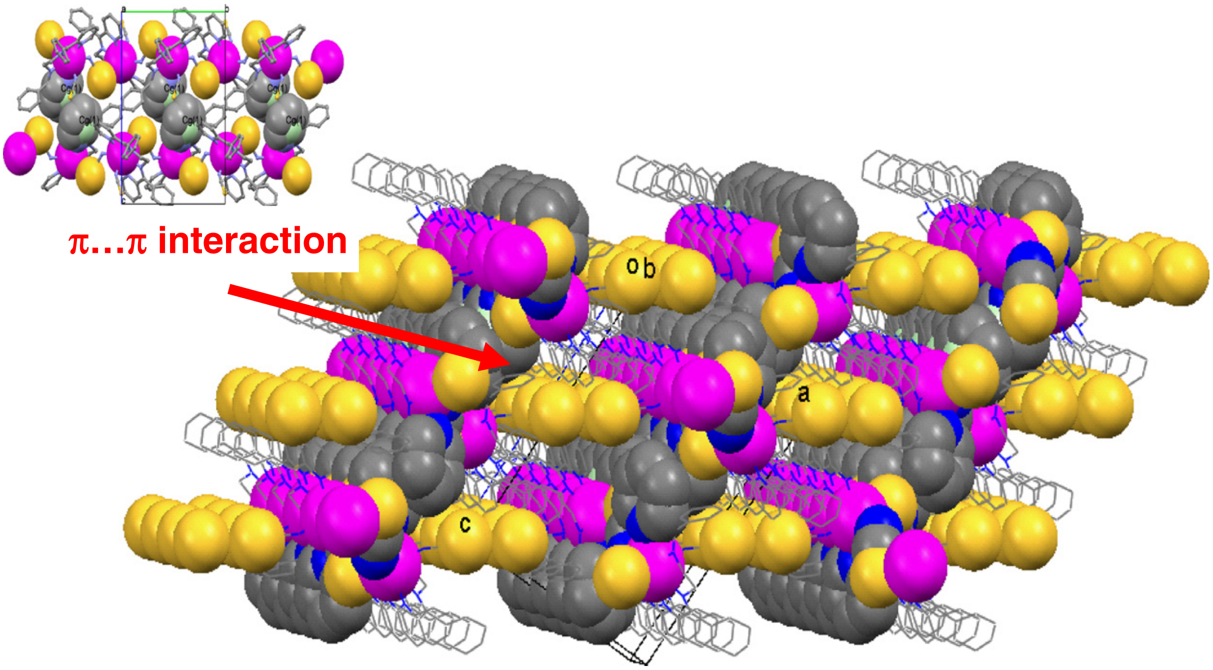

Fig. 3. 3D network structure in **1** formed through π…π stacking of 2D honeycombs along *c*-axis.

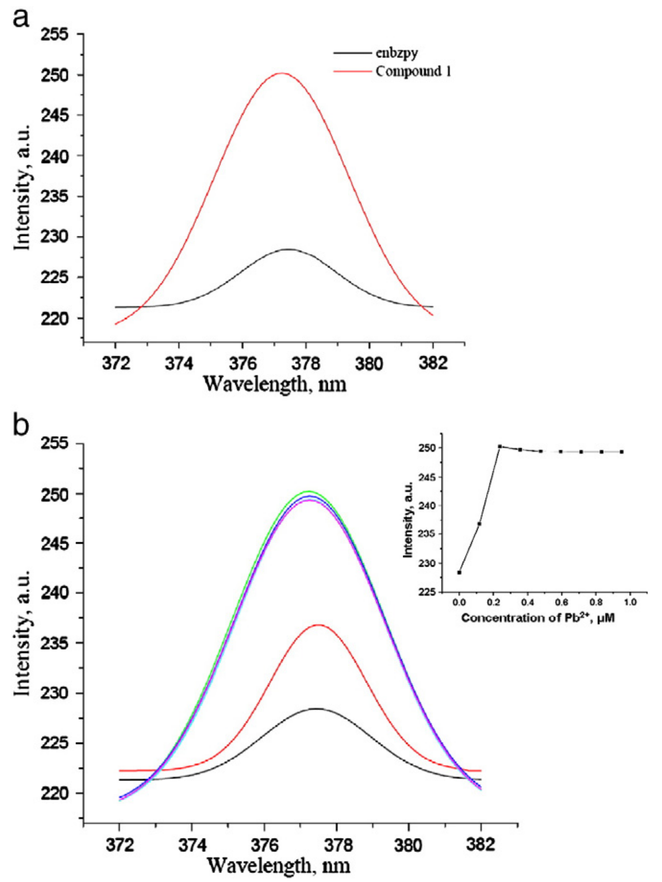

Fig. 4. (a) The Emission spectra of enbzpy and **1** in DMF solutions at room temperature and (b) Fluorescence spectra ($\lambda_{exc}=273$ nm) of ligand mixture (enbzpy, 0.197×10^{-6} M; NH_4NCS, 0.421×10^{-6} M) in DMF with increasing amounts of lead(II) ions. Inset: Fluorescence intensity values ($\lambda_{exc}=273$ nm, $\lambda_{em}=\sim378$ nm) vs concentration of added lead(II).

architecture harnessing strong covalent and weak non-covalent interactions towards crystal engineering to have directed functional behaviour with a heavy p-block metal ion.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Center (CCDC No. 832925 for **1**). Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary materials related to this article can be found online at doi:10.1016/j.inoche.2011.11.019.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.11.019.

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[30] *Synthesis of* $[Pb(enbzpy)(\mu_{1,3}\text{-}NCS)(NCS)]_n$ *(**1**)*: Enbzpy (0.390 g, 1 mmol) in methanol (15 cm^3) was added slowly to a $Pb(OAc)_2.3H_2O$ (0.379 g, 1 mmol) solution in the same solvent (15 cm^3). NH_4NCS (0.153 g, 2 mmol) in methanol (15 cm^3) was added dropwise to this mixture. After filtration through a fine glass frit, the supernatant light yellow solution was kept in air for slow evaporation. Light yellow crystals of **1** that deposited within a week, were collected by filtration and dried in *vacuo* over silica gel indicator. Yield: 0.514 g (72%). *Anal.* Calc. for $C_{28}H_{22}N_6S_2Pb$ (**1**): C, 47.1; H, 3.1; N, 11.8. Found: C, 47.3; H, 3.2; N, 11.6%. IR (KBr, cm^{-1}): ν(NCS) 2073, 2047, 2024; ν(C-S) 766, 749, 701; ν(C=N) + ν(C=C) 1621, 1584. UV–vis (λ, nm): 273.
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[33] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, sixth ed. John Wiley & Sons, New Jersey, 2009.
[34] *Crystal structure analyses:* Diffraction data of the single crystals of **1** were collected at 293 K on a Bruker SMART APEX II CCD area-detector diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å). The program SAINT was used for integration of diffraction profiles and absorption correction was made with SADABS program. The structure was solved by direct methods using the SHELXTL, and refined by full-matrix least-squares methods based on F^2 using SHELXL-97. *Crystal data for* **1**: M.F.: $C_{28}H_{22}N_6S_2Pb$, F.W.: 713.83, Monoclinic, $P2_1/c$, a = 12.8513(17) Å, b = 12.4666(16) Å, c = 17.686(3) Å, α = 90.00°, β = 93.486(4)°, γ = 90.00°, V = 2828.2(7) $Å^3$, Z = 4, T = 120(2) K, Crystal size = $0.28\times0.26\times0.24$ mm^3, D_c= 1.676 g/cm^3, F(000) = 1384, Reflections collected: 32088, final R indices [$I>2\sigma(I)$]: R = 0.0388, wR = 0.0975, R indices (all data): R = 0.0536, wR = 0.1049, index ranges: h/k/l = −15,15/-14,14/-21,21; independent reflections: 4979, (R_{int} = 0.049), θ ranges (°) = 1.59 to 25.00, data/restraints/parameters = 4979/399/334, goodness-of-fit on F^2 = 1.049, largest peak and hole ($eÅ^{-3}$) = 2.093 and −1.083, near heavy atoms, weighting scheme: $R = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, $wR = [\Sigma w(F_0^2\text{-}F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$. calc. $w = 1/[\sigma^2 (F_o^2)+(0.0515P)^2+7.6212P]$ where $P = (F_0^2+2F_c^2)/3$.
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