Synthesis, X-ray powder diffraction study, thermal analysis, Hirshfeld surface analysis and Optical Properties of New Crystalline Polymer:  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ 

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## **Research Highlights**

- Crystal structure of a new polymeric compound:  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  is reported.
- The compound exhibited optical band gap (Eg) around 3.61 eV.
- The Urbach energy, optical conductivity, and electrical conductivity were also estimated from other optical parameters.
- The HOMO-LUMO energies and related molecular properties were evaluated.

Journal Prevention

Synthesis, X-ray powder diffraction study, thermal analysis, Hirshfeld surface analysis and Optical Properties of New Crystalline Polymer: {(C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)(MnCl(NCS)<sub>2</sub>)<sub>2</sub>}<sub>n</sub>

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## Abstract

Synthesis, structural and optical properties are given for a new organic manganese pseudo halide material. The crystal structure has been solved by ab initio using direct methods from powder data and has been confirmed by additional single-crystal data collected with a CCD area detector. The structure of the { $(C_2H_{10}N_2)(MnCl(NCS)_2)_2$ }<sub>n</sub> reveals that the adjacent Mn(II) centres are bridged by a pair of SCN<sup>-</sup> anions to form a 1-D array giving rise to the anionic chains (MnCl(NCS)<sub>2</sub>)<sup>*n*-</sup>. These chains are themselves interconnected by means of N– H•••Cl(S) hydrogen bonds originating from the organic cation [(NH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>. Optical parameters, such as extinction coefficient, refractive index, permittivity refractive, optical conductivity, electrical conductivity and electrical susceptibility were studied using the absorbance spectra UV-vis spectrophotometer in the spectral range 200-800 nm. Atomic Mulliken charges, energies of frontier molecular orbitals (E<sub>HOMO</sub> and E<sub>LUMO</sub>), energy band gap (E<sub>HOMO</sub>–E<sub>LUMO</sub>), chemical hardness (η), global electrophilicity index( $\omega$ ) and *Electronegativity* ( $\chi$ ) were calculated by Density functional theory (DFT) using B3LYP method. The direct optical band gap energy deduced from the UV–VIS spectroscopy is  $E_g$ = 3.61 eV.

#### 1. Introduction

Hybrid inorganic–organic thiocyanate materials exhibit interesting physical properties such as electrical conductivity and dielectric relaxation process [1] and have promising applications in nonlinear optics and luminescence [2, 3]. Amine, amino acid and Schiff bases [4–8] have recently been the focus of coordination chemists due to their preparative accessibilities, structural varieties, and varied denticities. Pseudohalides, like heteroatomic ambidentate thiocyanate [9–13], result in different molecular architectures through its versatile ligation modes (Fig. 1). Actually NLO materials play a major role in the field of photonics including optical information processing, sensor protector applications, optical communication, optical computing, biological imaging, signal processing, and image reconstruction technologies [14-19]. Different structural geometries of manganese thiocyanate complexes 1D, 2D, 3D may be obtained according to the diversity of bridging modes of (SCN<sup>-</sup>) ligands. [20–22]. In these compounds, the thiocyanate (SCN) anion is a versatile ambidentate ligand, with a capacity to link the cadmium center in end-to-end or in end-on mode by their terminal S and N-bonding modes respectively. Several, may lead to intriguing architectures and topologies often generating many coordination polymers of one, two, and three-dimensional infinite frameworks involving manganese (II) is formed.

We report herein the synthesis, crystal structure, CP/MAS NMR spectroscopy, DSC, XRD and the Hirshfeld surface analysis, fingerprint plots, excitation energies, and Mulliken, natural population analysis, electrostatic potential contour surface and molecular electrostatic potential of a new Mn(II) thiocyanate complex: of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ .

#### 2. Experimental details

#### 2.1. Synthesis of $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$

The crystals of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  were synthesized by firstly the synthesis of  $Mn(NCS)_2$  by the reaction of Ba(SCN)2.3H2O (29.19 g) with  $MnSO_4 \cdot H_2O$  (17.39g) in  $H_2O$ . The colorless precipitate of  $K_2SO_4$  was filtered and the filtrate was concentrated to dryness in a rotary evaporator giving the colorless powder of  $Mn(NCS)_2$  by Neumann method [23].

$$Ba(SCN)2 \cdot 3H2O + MnSO4 \cdot H2O \xrightarrow{H2O} Mn(NCS)2 + BaSO4$$
(1)

In a second stage, a solution of ethylendiamonium dichloride was prepared by mixing  $C_2H_8N_2$  (2.68ml) with KCl (5g) by adding nitric acid (HNO<sub>3</sub>) (4.64ml) in methanol to precipitate KNO<sub>3</sub>, according to the following reaction:

$$C2H8N2 + 2KCl + 2HNO3 \xrightarrow{alcohol} C2H10N2Cl2 + 2KNO3$$
(2)

$$C2H10N2CL2 + 2Mn(SCN)2 \xrightarrow{alcohol} {(C_2H_{10}N_2)(MnCl(NCS)_2)_2}_n$$
(3)

Crystals of the title compound were obtained by dissolving a stoichiometric mixture of eq.(I) and eq.(II)(molar ratio 1:2). Well shaped colorless crystals of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)\}_n$  were obtained after slow evaporation of the solvent.

#### 2.2. Powder data collection

The X-ray powder diffraction data were collected at room temperature 298(1)K, in  $\theta/\theta$  reflection mode using a Bruker D8 ADVANCE with monocromatized CuK $\alpha$  radiation ( $\lambda = 1.5406$  Å) using Bragg-Brentano geometry. The powder was ground for 1 h and mounted in a top-loaded sample holder [24] to minimize the preferred orientation effects. The diffractometer was operated at 40kV and 40mA. The specimen was scanned from 5° to 60°, with a step size of 0.04° and counting time of 0.04°/s per step. After data collection, the stability of the X-ray source was checked by recording again the diffraction lines at low angles. For pattern indexing, the extraction of the peak positions was carried out with the Socabim program PROFILE, which is a part of the DIFFRAC-AT software package supplied by Bruker AXS. Pattern indexing was performed with the program DICVOL06 [25]. The structure was solved ab initio by means of the program SHELXL-97 [26] and the structure refinement was carried out with FULLPROF [27], available in the software package WINPLOTR [28].

#### 2.3. Single-crystal data collection

This specimen was selected with a XRD Enraf-Nonius CAD4 diffractometer using monochromatic Mo Ka radiation ( $\lambda$ =0.7103 A) and  $\omega$ -2 $\theta$  scan mode. Lorentz and polarization corrections have been made. The crystal structure have been solved using the classical method: interpretation of the three Patterson function followed by successive difference Fourier maps after introducing anisotropic thermal factors for the non hydrogen atoms and isotropic ones for H atoms. All calculations are performed on a PC using the SHELXS-97 [29] programs included in the WinGX software package [30]. Diamond 3.2, supplied by

crystal impact [31] was used for drawing molecular graphics. The atomic scattering factors were taken from the International Tables for X-ray Crystallography [32]. The CIF file, including all crystal data of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  crystal has been deposited at the Cambridge Crystallographic Data Centre with deposition number: (CCDC 1993973, 2008638).

#### 2.4. Hirshfeld surfaces analysis.

Molecular Hirshfeld surfaces calculations were performed by using the CRYSTALEXPLORER [33] program. When the cif file of the title compound was read into the CRYSTALEXPLORER program for analysis, all bond lengths to hydrogen were automatically modified to typical standard neutron values (C-H = 0.97 Å). The 2D fingerprint plots displayed by using the standard 0.6-2.6 Å view with the de (the distance to the nearest atoms outside) and di (the distance to the nearest nucleus inside the surface) distance scales displayed on the graph axes.

#### 2.5. Thermal analysis

The crystals of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  have been investigated by the methods of differential scanning calorimetry (DSC) at the temperature range 90–450K. Measurements were carried out on PerkinElmer Pyris DSC 4000. The mass of the two specimens was 3 mg, and the rate of the temperature change was 5°C/min.

# 2.6. UV-vis investigation

The UV-vis spectra were recorded at room temperature on a computer-controlled PE Lambda 35 UV-vis spectrometer equipped with an integrating sphere in the 200–800 nm wavelength range. The absorption spectra were calculated from the diffuse reflection spectra by the Kubelka- Munk function:  $F(R = \frac{(1-R)2}{2R})$ , where R is the reflectance [34]. The optical band gap of the title compound was deduced with the use of a straightforward extrapolation method [35].

#### 2.7. Computational details

The molecular structures of New Crystalline Polymer were optimized using DFT (B3LYP) [36, 37] with the basis set 6-311G<sup>\*\*</sup> [38] by Gaussian03 [39]. The geometrical parameters, atomic charges such as Mullikan Population Analysis (MPA) and Natural Population

Analysis (NPA) and energy distributions (HOMO and LUMO) were analyzed using Gauss View program [40]. The electrostatic potential maps were also plotted using 3D plot.

#### 3. Results and discussions

#### 3.1. Structure solution and refinement

#### 3.1. 1. Powder pattern indexing

The first 20 lines of the powder pattern were indexed, using an absolute error of 0.04 (2 $\theta$ ) on the peak positions, on the basis of an monoclinic solution with the unit-cell dimensions a= 5.683(2) Å, b= 19.846(7) Å, c= 8.242(3) Å,  $\beta$ = 108.7584(3)° and V=880.1(5) Å<sup>3</sup> [F<sub>20</sub> = 45(0.005,89)], the powder diffraction data for  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  are presented in Table 1, This result compares well with the cell reported by Kroui et al. (2013) of [a=5.6941(10)Å, b=19.886(7)Å,  $\{(C_2H_{10}N_2)(SnCl(NCS)_2)_2\}_n$ c=8.2591(10)Å,  $\beta=108.758(10)^{\circ}$ [41]. In order to validate the correctness of the solution obtained in the present study, a powder diffraction pattern was generated on the basis of the structural data related phase. Fig. 2 shows reported for the parts of the pattern of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  observed in the present study and the calculated pattern. From the powder pattern indexing, the studied sample is pure and isotype to the structural model proposed. The indexed lines correspond to hkl reflections which are observed in the calculated pattern and, consequently, involves unit cell volume a of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ , which is even the cell volume reported by Karoui et al. (2013). The reflections hkl with h + l = 2n + 1 and 0k0 with k = 2n + 1 have been found to be compatible with the centrosymmetric space group  $P2_1/n$  only. According to the conditions for non-extinction, a refinement of all diffraction lines available led to the unit-cell dimensions given in Table 1, with the figures of merit  $F_{78} = 121(0.008,89)$ .

#### 3.1. 2. Ab initio structure determination from powder data

Integrated intensities were extracted from the iterative pattern decomposition algorithm available in FULLPROF, from which the manganese atoms only were located from direct methods by using the program SHELXS97[26]. A least-squares Rietveld refinement of the structure of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  was carried out in the angular range 5–60 using 2751 reflections. A pseudo-Voigt function was used to describe line profiles, with a possible variation of the mixing factors  $\eta$  as a linear function of the 2 $\theta$  angle. The final Rietveld refinement converged to the residual factors  $R_F = 0.0358$  and  $R_{wp} = 0.08973$ . The final

Rietveld plot (**Fig. 2**) shows the best agreement between experimental and calculated patterns. Crystallographic data and details of the Rietveld refinement are given in Table 1. Final atomic coordinates and isotropic atomic displacement parameters are displayed in Table 2.

#### 3.1. 3. Structure solution from single-crystal data

A monoclinic cell was initially found from the 25 reflections collected with the Nonius CAD4 diffractometer, with the unit-cell parameters a=5.6941(10)Å, b=19.886(7)Å, c=8.2591(10)Å,  $\beta=108.758(10)^{\circ}$ , V = 885.5(4)Å<sup>3</sup>. This cell corresponds to that reported by Karoui et al. (2013). The actual unit cell obtained from powder pattern indexing was found after repeating the data acquisition for cell determination three times. The unit-cell dimensions were thus a=5.663(2)Å, b=19.831(7)Å, c=8.2289(10)Å,  $\beta=108.742(10)^{\circ}$  and V=875.1(5)Å<sup>3</sup>. The indexing by SHELXL97 from the first 20 data frames collected with the CAD4 diffractometer gave the actual monoclinic cell found from powder data. The refinement from the complete data set led to the cell dimensions reported in Table 1.

#### 3.2. Description of the crystal structure

Single-crystal X-ray structural analysis reveals that  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  crystallizes in the monoclinic space group P2<sub>1</sub>/n. The asymmetric unit is composed of one-half  $[(NH_3)_2(CH_2)_2]^{2+}$  cation and the (Mn(NCS)\_2Cl) anion (**Fig. 3**). The primary bonding contacts from manganese are one chlorine atom and two nitrogen atoms (NCS) together constitute the (Mn(NCS)\_2Cl) anion. The Mn–Cl distance 2.501(1)Å and Mn–N bond lengths range from 2.149(4)Å to 2.214(4)Å, respectively. The N(1)–Mn–N(2), N(1)–Mn–Cl and N(2)–Mn–Cl angles are respectively equal to 83.53 (2)°, 81.10 (1)° and 86.38 (1)°. Three longer second contacts (3.344(1)–3.5835Å) to sulfur atoms on neighboring (Mn(NCS)\_2Cl) anions complete six fold coordinate geometry of manganese (Mn(NCS)\_2(SCN)\_3Cl ) **Fig.4**.

The SCN ligands connect to Mn atoms using the end-to-end bridging mode, producing a linear 1-D chain along [10 0] via a double thiocyanate bridges (Mn•••Mn) separation within each chain a=5.6941(10)Å. All the bond lengths and angles are comparable with similar structures [42–45]. Both of these 1-D arrays are linked by a weak intermolecular interaction (Mn–S=2.683(1)Å). The shortest Mn–Mn distance between the adjacent chains is 4.894(1)Å. Interatomic distances and bond angles of this anion are reported in Table 3. In the MnN2S3Cl core, the Mn–S, Mn–N and Mn–Cl bond lengths are 3.298(1)Å, 3.244(1)Å and 2.683(1)Å, respectively. The doubly bridging action of SCN give rise to eight-membered Mn2(NCS)2 rings in a chair confirmation because of the almost linear SCN group N(1)–C(1)–S(1)=

178.86 (5)°, N(2)–C(2)–S(2)= 175.96 (5)°. The S–C and C–N distances range from 1.516(5)– 1.579(5)Å and 1.081(6)–1.130(7)Å, respectively. These geometric parameters agree well with those reported in Mn(SCN)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> and C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>2+</sup>.Cl<sup>-</sup>.SCN<sup>-</sup> [46, 47] where the S–C and C–N distances are equal to 1.6364 Å and 1.15165 Å, respectively, (the SCN angle being 178.49°). The average values of the distortion parameters of Mn(NCS)2(SCN)3Cl octahedron are calculated using the following equations (4)-(8) [45].

$$\Delta_{\rm oct} = \frac{1}{6} \sum_{j=1}^{6} \left[ \frac{(d_i - d_m)}{d_m} \right]^2 \tag{4}$$

$$\sigma_{\text{oct}} = \frac{1}{11} \sum_{j=1}^{12} [\alpha_j - 90]^2 \tag{5}$$

$$ID(Mn - X) = \frac{(\sum_{i=1}^{6} |d_i - d_m|)}{6d_m}$$
(6)

$$ID(X - Mn - X) = \frac{(\sum_{i=1}^{12} |\alpha_i - \alpha_m|)}{12\alpha_m}$$
(7)

$$ID(X - X) = \frac{\left(\sum_{i=1}^{12} |(X - X)_i - (X - X)_m|\right)}{12(X - X)_m}$$
(8)

With  $\alpha_i$ : (X–Mn–X) angle, d: (Mn–X) distance, X: (X–X) distance, m: average values.  $\Delta_{oct}$ =0.028,  $\sigma^2_{oct}$ = 36.05, ID(Mn–X)= 0.148 , ID(X–Mn–X)= 0.307 and ID(X–X) =0.303. These values exhibit a strong distortion of the MnN2S3Cl octahedron. Table 3 reports the principal geometrical factures of the [(NH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> cation; the C–N and the C–C bond lengths vary from 1.443(6)Å to 1.473(9)Å, respectively. They are similar to those observed in other ethylenediammonium salts [48, 49]. The ethylenediammonium cation is centrosymetric with a trans configuration with a N–C–C–N torsion angle of 178.18 (2)°. The intermolecular hydrogen bonding contacts N–H···Cl and N–H···S reported in Table 4. The stability and the cohesion of the polymeric structure were assured by the formation of N–H···Cl and N–H···S (NCS) hydrogen bonding contacts provide a linkage between the cationic entities [(NH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> and the anionic chain (MnCl(NCS)2)<sub>n</sub><sup>-n</sup> belonging to give rise to a three dimensional network in the structure (**Fig. 4**).

#### 3.3. Hirshfeld surface

The Hirshfeld surface [50, 51] is an essential approach for investigating intermolecular interactions. All the molecular interactions occurring in the crystal packing are quantified, and the pie chart of molecular interactions is displayed in **Fig. S1**. To visualize and understand the

insights into the intermolecular interactions in the crystals, Crystal Explorer software package [26] is a graphical tool for Hirshfeld Surfaces analysis using CIF. The set of points in 3D space allows investigating the intermolecular interaction and the set of points in 2D space shows the overall contributions of intermolecular interactions using fingerprint plots [52–55]. The value of  $d_{norm}$  is negative or positive when intermolecular contacts are shorter or longer than van der Waals (vdw) radii, respectively. The none,  $d_{norm}$ , de, d<sub>i</sub>, Shape index and Curvedness surfaces of asymmetric unit of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  are shown in **Figure 5**. Also, the 2D plots were created by binning (d<sub>e</sub>, d<sub>i</sub>) pairs and coloring each bin (essentially a pixel) of the resulting 2D histogram as a function of the fraction of surface points in that bin, ranging from blue (few points) through green to red (many points). The normalized contact distance (d<sub>norm</sub>) based on both d<sub>e</sub> and d<sub>i</sub>, and the van der Waals (vdw) radii of the atom, given by the equation:

$$d_{norm} = \frac{d_{i+d_i^{rdw}}}{d_i^{rdw}} + \frac{d_{e-d_e^{rdw}}}{d_e^{rdw}} \tag{9}$$

The surfaces represented were mapped over d<sub>norm</sub>, d<sub>e</sub>, d<sub>i</sub>, curvedness and shape-index in the ranges -0.377to 1.078Å, 0.866 to 2.648Å, 0.861 to 2.552Å, -4.000 to 0.400 and -1.000 to 1.000Å, respectively. The distinct circular depressions (red spots) on the d<sub>norm</sub> surface (Fig. 5b) correspond to the Cl...H/H...Cl and S...H/H...S close contacts which are due to the hydrogen bonds N-H···Cl (22.2%) and N-H···S (15.3%). On the de surface, this feature appears as a relatively flat green region where the contact distances are similar (Fig. 5c). The presence of longer second contacts to sulfur atoms is also evident in the flat region of both sides of the groups anionic is clearly visible on the curvedness surface (Fig. 5e): the circular shape of the light blue outline on the curvedness surface unambiguously delineates the contacting patches of the anionic groups. Indeed, the pattern red and blue in the same region of the shape-index surface is characteristic of hydrogen bonding contacts; the pattern blue represent convex regions resulting from the presence of N–H···Cl and N–H···S intermolecular, while the red circular represent concave regions caused by chlorine and sulfur atoms . From the Hirshfeld surfaces, it is also evident that the molecules are related to one another by hydrogen bonding, as can be inferred from inspection of the adjacent red and blue circular on the shape-index surface (Fig. 5f).

The 2D fngerprint plots (**Figure 6**) provide us information about these intermolecular interactions. From the plots it is revealed that the Cl····H (22.2%) and S····H (15.3%) bonding appear to be a major contributors in the crystal packing, whereas the N····H (10.3%), Mn····S

(9.6%), N····S (7.3%) and S····S=H...H (7%) contacts has their significant contribution to the total area of the surface, remaining contacts are very low.

#### 3.4. NMR spectroscopy

The NMR spectra of { $(C_2H_{10}N_2)(MnCl(NCS)_2)_2$ }<sub>n</sub> rotating at 8 kHz are shown in **Figs. 7**. **Fig. 7a** shows <sup>13</sup>C CP/MAS NMR spectrum of compound consisting of three distinct resonance signals correspond to three different structural positions that carbon atoms occupy in the structure. This result is in agreement with the structure determination. The isotropic shift at about 40 ppm from TMS was attributed to the aliphatic carbon atom (C3) of the centrosymmetric ethylendiamonium cation and the above assignment is in line with the assumption that sp<sup>3</sup> carbon bonded to C **Fig. 7b**. Two distinct pairs around 140.59 ppm and 143.49 ppm were attributed respectively to the two carbon atoms C(1) and C(2) of two inequivalent thiocyanate SCN<sup>-</sup> anions. The observed triplet is caused by residual dipolar splitting arising from <sup>14</sup>N quadrupolar interaction. The measured J-coupling between <sup>13</sup>C and <sup>14</sup>N are J(<sup>14</sup>N, <sup>13</sup>C(1))=83 Hz for [N(1)–*C*(*1*)– S(1)] and J(<sup>14</sup>N, <sup>13</sup>C(2))=114 Hz for [N(2)–*C*(*2*)–S(2)].

# 3.5. Differential scanning calorimetry (DSC)

The DSC thermogram depicted in **Fig. 8** shows two mainly endothermic peaks at  $T_1$ = (331±1) K corresponding to the phase transition and  $T_2$ = 429 K corresponding to the melting of this compound. The enthalpy and entropy values for these transitions are respectively  $\Delta H_1$ =2.700 kJ mol<sup>-1</sup> and  $\Delta S_1$ =8.157 J mol<sup>-1</sup> K<sup>-1</sup> for the former and  $\Delta H_2$ =158.46 kJ mol<sup>-1</sup> and  $\Delta S_2$ =0.369 kJmol<sup>-1</sup> K<sup>-1</sup>.

## 3.6. UV-vis absorption analysis

The Kubelka–Munk theory is generally used for analyzing the diffuse reflectance spectra obtained from weakly absorbing samples. In this case, the Kubelka–Munk function is given by [57, 58].

$$F_{KM}(R) = \frac{(1-R)^2}{2R}$$
(10)

where R is the absolute reflectance of the sample and  $F_{KM}(R)$  is Kubelka–Munk function. Fig. 9(a) and 9(b) present the plots of the diffuse reflectance spectrum and the Kubelka-Munk curve of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ , respectively. The optical band gap of samples can then be determined from the following relation [59]:

$$\frac{F_{KM}(R)*h\vartheta}{t} = A(h\vartheta - E_g)^n \tag{11}$$

where t, h, n and Eg are thickness of the pellet (1 mm), Planck's constant, photon frequency and energy band gap, respectively. In equation (2), A is an energy-independent constant and n is a constant that determines the type of the optical transitions [(n = 2) for indirect allowed transition, (n = 3) for indirect forbidden transition, (n = 1/2) for direct allowed transition and (n = 3/2) for direct forbidden transition]. The plot of  $(F_{KM}(R) * h\vartheta)^2$  versus  $h\vartheta$  (Fig. 9(c)) is linear indicating a direct allowed transition for this phase. The optical band gap was deduced with the use of a straightforward extrapolation method [60]. The extinction coefficient as a function of photon energy is plotted as shown in Fig. 9(d). The energy band gap estimated from the linear extrapolation of  $(F_{KM}(R) * h\vartheta)^2$  values to zero absorption is 3.61 eV. The value of n = 0.53#1/2 is confirmed by the plot of  $(\ln(F_{KM}(R) * h\vartheta))$  versus  $\ln(h\vartheta - E_a)$  as shown in Fig. 9(e). The extinction coefficient and reflectance of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ single crystal were calculated from the above expressions shown in Fig. 9(f). The graph plotted between  $(\ln(F_{KM}(R) * h\vartheta))$  versus  $\ln(h\vartheta - E_g)$  the represented in **Fig. 9(e)** shows the linear behavior, and from this the slope value of 6.16902 was observed which clearly indicates that the crystal is highly crystalline in nature [61]. The Urbach energy is estimated by plotting  $ln(\alpha)$  vs. hv and fitting the linear portion of the curve with a straight line. The reciprocal of the slope of this linear region yields the value of Eg. The extrapolation of the straight line down to  $(\alpha h v)^2 = 0$  gives the value of direct electronic band gap energy Eg = 3.61eV. Hence, this grown polymeric compound crystal possessing such wide optical band gap can be an effectively used as a suitable candidate for optoelectronic application. The value of Urbach energy may be attributed to the decrease in edge broadening of the grown crystal which supports its good NLO performance.

#### 3.7. Optical constant determination

The prominent way to gain the potential of the material is getting knowledge of optical constants of the material. The finding of optical parameters was determined using the following theoretical formulas [62]. The extinction coefficient (K) is given by:

$$K = \frac{\alpha\lambda}{4\pi} \tag{12}$$

Optical conductivity is a material property which provides information about the frequency response of the material, and is related to [62].

$$\sigma_{op} = \frac{n\alpha c}{4\pi} \tag{13}$$

Also, optical conductivity means the measure of electrical conductivity of the crystal and is obtained using the relation [62].

$$\sigma_{ele} = \frac{2\lambda\sigma_{op}}{\alpha} \tag{14}$$

The optical conductivity and the electrical conductivity are correlated for  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  crystal and are shown in **Fig.10(a)** and **Fig.10(b)**, respectively. It is clear that the optical conductivity increases with photon energy having high magnitude  $(10^{11}\Omega m^{-1})$  which confirms the existence of very high photo response properly of the material. The low extinction value and electrical conductivity of the present work implicate the semiconducting nature of the material [63]. The electrical susceptibility was assessed from the refractive index of the crystal according to the formula [62].

$$\varepsilon_{r} = \varepsilon_0 + 4\pi \chi_c = n^2 - K^2 \tag{15}$$

$$\chi_C = \frac{n^2 - K^2 - \varepsilon_0}{4\pi} \tag{16}$$

where  $\varepsilon_0$  is the dielectric constant in the absence of any contribution from free carriers. Also, the complex dielectric constant could be worked out from

$$\varepsilon_{r=}n_x^2 - K^2 , \qquad \qquad \varepsilon_{i=}2n_x K \tag{17}$$

The plot of photon energy versus permittivity refractive and susceptibility for  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  single crystal is shown in **Fig. 10(c)** and **Fig. 10(d)**, respectively. Thus, the optical constants of the material with high band gap energy and low extinction coefficient and refractive index elucidate the suitability for device applications in processing and computing optical data [64].

#### 3.8. Frontier molecular orbital analysis (FMO)

The molecular orbital theory is most essential theory for chemists which plays significant role in the electronic properties and chemical reactions [65]. The energy levels for the title compound were computed by DFT-B3LYP/6-311G\*\*(d,p) method. The frontier molecular

orbitals are used to identify the position of electron transfer from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of the molecule. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties. The lowest unoccupied molecular orbital (LUMO) energy of the molecule is -1.3375 eV and the highest occupied molecular orbital (HOMO) energy is -5.0173 eV. The energy gap of HOMO-LUMO explains the ultimate charge transfer interaction within the molecule and the frontier orbital energy gap of molecule is found to be 3.6798 eV. Fig. 11 shows the HOMO and LUMO map of the molecule. The global chemical reactivity descriptors calculated for the molecule using DFT are; chemical hardness (n), electronegativity ( $\chi$ ), electrophilicity ( $\omega$ ) ionization potential (I), and electron affinity (A) [66]. Chemical hardness is associated with the stability and reactivity of a chemical system. It measures the resistance to change in the electron distribution or charge transfer from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of the molecule. On the basis of frontier molecular orbitals, chemical hardness corresponds to the gap between the HOMO and LUMO. The larger the HOMO-LUMO energy gap, the harder and more stable or less reactive the molecule [67, 68]. The ionization energy (EI) and the electron affinity (EA) can be calculated by the HOMO and LUMO energies as  $E_I = E_{(HOMO)}$  and  $E_A = -E_{(LUMO)}$ . The ionization energy (I) and electron affinity (A) of the molecule calculated in gas phase value are 5.0173 eV and 1.3375 eV respectively. Chemical hardness is  $\eta = E_{(LUMO)} - E_{(HOMO)}$ , where  $E_{(HOMO)}$  and  $E_{(LUMO)}$  are the LUMO and HOMO energies. Table 5 contains the calculated chemical hardness of molecule. The results indicate that the molecule is harder and less reactive. From this study, we have confirmed that the molecules have high stability. The concept of electronegativity ( $\chi$ ) put forward by Pauling [69] is defined as the power of an atom in a molecule to attract electrons towards it. Higher is the electronegativity of the species, greater is its electron accepting power or rather the electrophilicity [70]. It has been observed that the molecule has an electronegativity and a large electron accepting electron power. The Electronegativity  $(\chi)$  of the complex is calculated using Koopman's theorem [71]:  $\chi = \frac{1}{2}(E_I + E_A)$ , the softness (S) is the reciprocal of hardness; S=  $1/\eta$ , global electrophilicity index ( $\omega = \chi^2/2\eta$ ), was calculated using the electronegativity and chemical hardness. The HOMO-LUMO gap value of the  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  compound was found to be 3.6798 eV. This value compared with the experimental UV-visible energy gap value (3.61 eV). This result is predictable, in fact it is admitted that the HOMO– LUMO gap decreases by increasing the number of chains in polymeric structures.

#### 3.9. Population analysis

Mulliken atomic charges calculated at the B3LYP levels with the 6-311++G (d, p) are collected in **Fig. S2**. The maximum negative charge belongs to Cl, N1 and N2 atoms and its value is -0.55. The maximum positive charge belonging to hydrogen (H1N3, H2N3 and H3N3) atom is 0.4. The atomic charges of all hydrogen atoms in the NH3 group are positive. The atomic charges of three hydrogen atoms involved in the hydrogen bonding interaction are 0.4. These charge variations clearly reveal the existence of N–H···Cl and N–H···S intermolecular hydrogen bonding. The electron withdrawing character of halide (Cl) and pseudo halid (NCS) group in {(C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)(MnCl(NCS)<sub>2</sub>)<sub>2</sub>}<sub>n</sub> studied is demonstrated by the decrease of electron density on manganese atom. The N1and N2 atom has negative charge due to the electronegativity of carbon atoms. From **Fig. S2**, the carbon atoms have positive charges between 0.154 and 0.38, similarly all of the ethylenediammonium cation hydrogen atoms have positive charge. As is standard for any DFT calculation on a neutral system, the total partial charge on the {(C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)(MnCl(NCS)<sub>2</sub>)<sub>2</sub>]<sub>n</sub> is zero.

## 3.10. Molecular electrostatic potential

The molecular electrostatic potential (MEP) is a plot of electrostatic potential mapped onto the constant electron density surface. The molecular electrostatic potential has been used to predict reactive sides for electrophilic and nucleophilic attack and hydrogen bonding interactions as well as their potential use in biological recognition studies [72, 73]. To predict reactive sites and hydrogen bonding interactions, Molecular electrostatic potential was determined using DFT/B3LYP with the basis set 6-311G\*\*method. Molecular electrostatic potential is the useful quantities to illustrate the charge distributions of molecules are used to visualize variably charged regions of a molecule. Therefore, the charge distributions can give the information about how the molecules interact with another molecule. At any given point r (x, y, z) in the vicinity of a molecule, the molecular electrostatic potential (MEP), V(r) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r. Te molecular electrostatic potential is related to the electronic density and a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogenbonding interactions. In **Figure S5**, whereas electrophilic reactivity is presented by the

negative (red) regions, nucleophilic reactivity is shown by the positive (white) regions of MEP. Te red region is localized on the vicinity of sulfur (SCN), nitrogen (NCS) and chlorine reflects the most electronegative region (excess negative charge). On the other hand, the nucleophilic reactivity of the molecules is localized on the hydrogen atoms. Furthermore, the total charge density contour map is given in the **Figure S4**. A contour plot is a two-dimensional XY plot of a three-dimensional XYZ surface showing lines where the surface intersects planes of constant elevation (Z). Te contour maps are used to show lines of constant density or brightness, such as electrostatic potentials and are drawn in the molecular plane. Te electron rich red lines are around sulfur (SCN), nitrogen (NCS) and chlorine whereas electron defcient region are shown by greenish-yellow lines. Te contour maps are also calculated by same basis sets at 0.0004 density values at same level of calculations of the MEP mapped surface of the molecules.

#### 4. Conclusion

A new crystalline polymer compound  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  was prepared and analyzed using single crystal XRD, NMR, DSC and UV-Vis spectroscopy. The crystal structure shows that manganese(II) atom is hexacoordinated by two cis N-bonded thiocyanato anions, three trans S-bonded thiocyanato anions and one cis chloride anions which generate 1D polymeric anionic the (MnCl(NCS)2) $_n^n$  chain. The stability and the cohesion of the compound network is assured by the existence of N-H…Cl and N-H…S (NCS) hydrogen bonding contacts between the  $(C_2H_{10}N_2)^{2+}$  cation and the  $(MnCl(NCS)2)_n^{-n}$  chains. The indirect spin-spin coupling between <sup>13</sup>C and <sup>14</sup>N are J(<sup>14</sup>N, <sup>13</sup>C(1))=83 Hz for [N(1)-C(1)-S(1)] and J( $^{14}N$ ,  $^{13}C(2)$ )=114 Hz for [N(2)–C(2)–S(2)] was studied by means of  $^{13}C$  CP/MAS with dipolar coupling constant. The DSC analysis shows that this compound undergoes a reversible phase transition at about (321±1) K. The indirect optical band gap energy deduced from the UV–Vis spectroscopy by the use of the Tauc model is Eg = 3.91 eV. Electronic structure and optical properties were determined using density functional theory (DFT) calculations. The estimated band gap between HOMO and LUMO calculation is 3.61 eV. The lowering in the HOMO and LUMO energy gap explains the eventual charge transfer interactions that take place within the molecules which is responsible for the high optical nonlinearity of the crystal.

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## New CRediT author statement

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## **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Figure captions** 

Fig. 1. Different ligational motifs of thiocyanate

Fig. 2. Experimental and calculated RDX powder pattern of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ 

**Fig.3.** View of the asymmetric unit of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ 

Fig. 4. Packing diagram of the polymeric complex  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  with H-bonds interactions in dashed lines.

**Fig.5.** Hirschfeld surfaces of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$  (a) *none* (b)  $d_{norm}$  (c)  $d_e$  (d)  $d_i$  (e) *curvedness* (f) *Shapeindex*.

**Fig.6.** Two-dimensional fingerprint plots for the title compound and relative contributions of the atom pairs to the Hirshfeld surface.

Fig.7. <sup>13</sup>C MAS NMR spectra of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ .

Fig.8. Differential scanning calorimetry curves for  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ .

Fig. 9. Photon energy versus (a) kubelka-Munk (b) Diffuse reflectance R; (c) Tauc's plot

(d) Extinction coefficient K; (e) Plot of  $(\ln(F_{KM}(R) * h\vartheta))$  versus  $\ln(h\vartheta - E_g)$  (f) Absorption

coefficient ( $\alpha$ ) versus reflectance R and extinction coefficient K.

**Fig.10.** Plot of photon energy versus (a) optical conductivity (b) electrical conductivity (c) permittivity refractive and (d) electrical susceptibility.

Fig. 11. Frontier Molecular Orbitals (HOMO and LUMO) for  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ .

	Н	K	L	Dobs	D <sub>cal</sub>	D <sub>obs</sub> -D <sub>cal</sub>	I(%)
	0	2	0	9.943	9.944	-0.001	70
	1	1	0	7.278	7.278	0	57
	1	2	0	6.147	6.147	0	29
	1	3	0	5.056	5.056	0	75
	0	4	0	4.972	4.971	0.001	66
	0	2	1	4.739	4.74	-0.001	18
	0	3	1	4.184	4.183	0.001	32
	1	0	1	3.892	3.892	0	38
	2	1	-1	3.731	3.731	0	97
	0	4	1	3.655	3.655	0	20
	1	4	-1	3.628	3.63	-0.002	15
	1	5	0	3.548	3.545	0.003	23
	2	2	-1	3.548	3.548	0	77
		5	-1	3.182	3.182	0	64
	1	4	1	3.063	3.064	-0.001	14
	1	6	0	3.052	3.051	0.001	19
r	2	4	-1	3.018	3.018	0	83
	0	6	1	2.823	2.823	0	35
	2	1	1	2.743	2.743	0	26
	2	5	-1	2.747	2.743	0.004	23
	0	0	2	2.696	2.695	0.001	32
	2	0	-2	2.654	2.653	0.001	18
	1	3	-2	2.617	2.615	0.002	39
	3	2	-1	2.617	2.617	0	24
	0	8	0	2.485	2.485	0	23
	1	2	2	2.267	2.267	0	23
	0	5	2	2.231	2.231	0	15

Table 1 X-ray powder diffraction data for the  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ 

1	4	2	2.108	2.108	0	18
3	1	1	2.085	2.085	0	18

Table 2 Crystallographic data and processing parameters of  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ 

Formula	$\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$				
	single-crystal X-ray diffraction	X-ray powder diffraction			
Molecular weight /g.mol-1	475.229	475.229			
Crystal System	Monoclinic	Monoclinic			
Temperature/K	293	298			
Space group	P21/n	P2 <sub>1</sub> /n			
Unit cell dimension	a=5.663(2)Å	a= 5.683(2)Å			
	b=19.831(7)Å	b=19.846(7)Å			
	c=8.2289(10)Å	c= 8.242(3)Å			
	β= 108.742(10)°	β= 108.7584(3)°			
Volume/Å <sup>3</sup>	875.1(5)	880.1(5)			
Z	2	2			
Dm, $Dx(g.cm^{-3})$	1.803	1.793			
Diffractometer	ENRAF NONIUS CAD4	Bruker D8 ADVANCE			
Radiation, graphite	0.71073 (Mo K <sub>α</sub> )	1.5406 Å (Cu Kα <sub>1</sub> )			
monochromator					
Theta range for data collection	2.05, 25.67	5≤θ≤60			
Reflection measured	1832	154			
Reflections with $I > \sigma 4(I)$	1649	-			
Number of parameters	39	78			
R <sub>1</sub>	0.0624	0.0358			
wR <sub>2</sub>	0.1935	0.0897			
Computer programs	SHELXS97, SHELXL97 [26],	DICVOL06 [ 25], FULLPROFF			
	WINGX [30] and Diamond[31]	[27], WINPLOTR [28]			
Deposit CCDC number	2008638	1993973			

 $\label{eq:table 3} \begin{array}{l} \mbox{Table 3} \mbox{ Principal intermolecular distances (Å) and bond angles (°)} \\ \mbox{ in } \{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n. \end{array}$ 

	MnCl(SCN) <sub>2</sub>							
Atomes	Distances (Å)	Atomes	Angles (Å)					
N(1)–C(1)	1.081(6)	N(1)–C(1)–S(1)	178.86 (5)					
N(2)–C(2)	1.130(7)	N(2)-C(2)-S(2)	175.96 (5)					
S(1)–C(1)	1.516(5)	N(1)-Mn-N(2)-C(2)	102.98(9)					
S(2)–C(2)	1.579(5)	N(2)-Mn-N(1)-C(1)	69.44(6)					
		Cl-Mn-N(1)-C(1)	156.78(6)					
		Cl-Mn-N(1)-C(1)	175.58(6)					
	Oc	tahedral [MnCl2N3S]						
$Mn-S(1)^{(i)}$	3.298(1)	N(1)–Mn–S(2) <sup>(iii)</sup>	156.04 (1)					
Mn–S(2) <sup>(ii)</sup>	3.244(1)	N(1)–Mn–S(2) <sup>(ii)</sup>	108.19 (1)					
Mn–S(2) <sup>(iii)</sup>	2.683(1)	N(1)–Mn–S(1) <sup>(i)</sup>	74.77 (1)					
Mn–Cl	2.501(1)	N(1)-Mn-N(2)	83.53 (2)					
Mn–N(1)	2.149(4)	N(1)–Mn–Cl	81.10 (1)					
Mn–N(2)	2.214(4)	N(2)-Mn-S(2)	80.34 (1)					
N(1) –C(1)	1.081(6)	N(2)-Mn-S(2)	121.47 (1)					
N(2)–C(2)	1.130(7)	N(2)-Mn-S(1)	156.04 (1)					
$S(1)^{(i)} - C(1)$	1.516(5)	N(2)–Mn–Cl	86.38 (1)					
$S(2)^{(ii)} - C(2)$	1.579(5)	S(1)–Mn–Cl	80.41 (4)					
		S(1)–Mn–S(2)	116.56 (3)					
		S(1)-Mn-S(3)	75.91 (3)					
		S(2)-Mn-Cl	80.31(3)					
		S(2)-Mn-S(3)	95.35 (4)					
		S(3)-Mn-Cl	150.93 (4)					
		1						

Symmetry codes:	: (i) x-1, y, z,	(ii) x-1, y, z, (iii	i) x-0,5, -y+1,5, z -0,5					
$[(NH_3)_2(CH_2)_2]^{2+}$								
C(3)–N(3)	1.443(6)	$N(3)-C(3)-C(3)^{(ii)}$	112.94(5)					
C(3)–C(3)	1.473 (9)	$C(3)^{(ii)} - C(3) - H(1C3)$	115.16(4)					
С(3)-Н(1С3)	1.071(6)	C(3) <sup>(ii)</sup> –C(3)–H(2C3)	116.93(4)					
C(3)-H(2C3)	0.877(6)	H(1N3)–N(3) <sup>(i)</sup> –H(2N3)	110.58 (6)					
N(3) <sup>(i)</sup> –H(1N3)	0.847(6)	H(1N3)–N(3) <sup>(i)</sup> –H(3N3)	106.44 (7)					
N(3) <sup>(i)</sup> –H(2N3)	0.774(6)	H(2N3)–N(3) <sup>(i)</sup> –H(3N3)	103.48(7)					
N(3) <sup>(i)</sup> –H(3N3)	0.816(8)	$N(3)^{(i)}-C(3)^{(ii)}-C(3)-N(3)$	178.12(2)					
Symmetry codes	(i) 1-x, 2-y, 1-z	(ii) 1-x,-y, 2-z	3					

Table 4 Hydrogen bond geometry in  $\{(C_2H_{10}N_2)(MnCl(NCS)_2)_2\}_n$ 

D-HA	N– H	HCl (S)	NCl (S)	N– HCl (S)
$N-H(1N3)Cl^{(ii)}$	0.847(6)	2.388(5)	3.301(5)	133 (6)
$N-H(2N3)S(1)^{(iii)}$	0.774(6)	2. 492(5)	3.231(5)	160 (5)
N– H(3N3)Cl <sup>(i)</sup>	0.816(8)	2. 347(6)	3.000(5)	131(7)
Symmetry codes (i) x-1,	y, z, (ii	) 1-x, 2-y, 1-z,	(iii) -x+2,-y	/+2,-z+1

Table 5 Calculated frontier molecular orbital energies (eV).

FMO	Energy
Еномо	-5.0173
E <sub>LUMO</sub>	-1.3375
Band gap $(E_{HOMO}-E_{LUMO})$	-3.6798
Ionization energy $(E_l)$	5.0173
<i>Electron affinity</i> $(E_A)$	1.3375
Chemical hardness (η)	3.6798
Softness (S)	0.2717
Electrophilicity ( $\omega$ ) indexes	1.3717
Electronegativity (χ)	3.1774

Туре	Mode of coordination					
Type (I) : Terminal	(Ia) M-S-C=N(S-coordination) thiocyanate			(I b Bridging) S=C-N-M(N-coordination) isothiocyanate		
Type (II): Bridging	(Ia) M-SCN-M		(IIb) M SCN M		(IIc) SCN $<_{\rm M}^{\rm M}$	
Type (III): Bridging	(IIIa) MSCN-MM-		(IIIb) -SCN	(IIIc) M M M SCN	ſ	
Type (IV): Bridging	$(IVa)$ $M \rightarrow SCN M$ $M$		(IVb) MSCNM MSCNM		(IVc) $M \longrightarrow SCN \underset{M}{\overset{M}{\underset{M}{\overset{M}{\overset{M}{\overset{M}{\overset{M}{\overset{M}{$	
(Va)			$M \qquad M \qquad M \qquad SCN \ll M \\ M \qquad M \qquad M \qquad M$		7 <b>b)</b> М М М	
Type (VI): Bridging			M M SCN (			
Figure 1						







Figure 4





Figure 6









Figure 10

Jour 1



# **Graphical Abstract**

