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Author(s): Makhlouf, Jawher; Valkonen, Arto; Smirani, Wajda Sta

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Growth, single crystal investigation and Physico-chemical Properties of Thiocyanate Coordination Compounds based on 1,4-dimethylpiperazine

Jawher Makhlouf [a], Arto Valkonen [b] and Wajda Smirani [a*]

a- Labortory of Material Chemistry, Faculty of Sciences of Bizerte, University of Carthage, Bizerte Zarzouna, Tunisia

b- Departement of Chemistry, University of Jyvaskyla, 40014 Jyvaskyla, Finland

Corresponding author: wajda_sta@yahoo.fr

Abstract

Four novel hybrid organic-inorganic compounds based on 1,4-Dimethylpiperazine, $(C_6H_{16}N_2)M(SCN)_4(H_2O)_2$ (M= Co(1), Ni(2)), $(C_6H_{16}N2)Cd(SCN)_4$ (3) and $[C_6H_{16}N_2(SCN)_2]$ (4), were prepared by evaporation crystal growth method at room temperature. Theses complexes were characterized by X-ray crystal structure, spectroscopic methods such as the FTIR analysis supported for the presence of surface ligands groups of thiocyanates and to identify the vibrational absorption bands. Optical studies such as the UV-visible spectroscopy showed the optical transparency of the complexes to have the cutoff wavelength at the range of 346 to 579 nm for (1), (2) and (3), and 280 nm for (4). Thermal analyses were also occurred in the range of [273–600 K] and showed the decomposition of the complexes.

Based on the results of these techniques, the formation of the desired complexes was confirmed. Hence, the piperazinium ring adopts a slightly distorted chair conformation which is more stable because it does not have any steric hindrance or steric repulsion between the hydrogen bonds and which favors the entities coordination. Intermolecular interactions were investigated by Hirshfeld surfaces and contact enrichment tools. In the crystals, Extensive intermolecular interactions have been used in the self-assembly of motifs, ranging from strong H-bonds, the components are linked mainly by N-H…S, O-H…S, N-H…N hydrogen-bonding interactions, resulting in a three-dimensional network.

The arrangements of the anions and cations in the solids are governed not only by the size and symmetry of the cations, but also by the non-covalent bonds in the crystal structures.

Keywords: Inorganic chemistry, Materials chemistry, DRX, crystal structure, heterocyclic aromatic bases, anti-oxidant behavior.

1. Introduction

Transition metal complexes represent a growing subject during recent years because of their enormous biological significance as well as unique catalytic and optical properties **[1-5].** Recently synthesized transition metal complexes have been used for the study of biological activities such as antibacterial, antifungal, toxicity **[6-7].** The d9 configuration of the Co(II), Cd(II) and Ni(II) cations favor either square planar, square-pyramidal or square-bipyramidal geometries. For several reasons, coordination compounds based on transition metal add to thiocyanates ligand have become of increasing interest in the last few years. First of all, the thiocyanate anion is a versatile ligand that can coordinate to metal cations in different ways leading to compounds with a large structural variety **[8–19].**

Organic-inorganic coordination materials may also have potential applications in fuel cells, liquid crystal-materials, dielectric responses and drug delivery **[20,21].** Transition metal complexes have been known for their wide range of applications in biochemistry, photochemistry and photophysics **[22]** and the significance in medicinal chemistry **[23]** and functions in host defense as part of microbicidal pathway, the antibacterial activity of thiocyanic-metal entities is often attributed to its ability to cross the bacterial cell wall before oxidizing critical metabolic elements, this may be a result by the reaction of the HSCN's protonated forms **[24].** The synthesis of coordination compounds by solid state synthesis is nothing unusual and also other approaches are reported **[25–30]**. Furthermore, amine salts of thiocyanic acid have been prepared by the reaction of amines with thiocyanogen **[8,10]** and by the reaction of hydrochloride with potassium thiocyanate. Isolation of the product by these methods was troublesome and rather low yields were obtained. The reaction of thiocyanate salt with organic amines **[10]** to form these compounds apparently has attracted little investigation. By means of this synthesis, amine salts of thiocyanic acid can be prepared by a simple procedure and the products can be readily isolated in high yields. In these complexes,

the motifs of the organo-amin and their counter inorganic species are stabilized by H-bonds. The energetics of H-bonds and their possible role in supramolecular chemistry of inorganic-organic hybrid solids have been shown **[29,30].** In particular, large sets of coordination materials from thiocyanate and divalent metal ions (Co, Ni, Cd) have been researched **[33].** The studies on transition metal and 1,4-dimethylpiperazine complexes have become increasingly important since these types of complexes found use as photo-active components of supramolecular assemblies such as the Thorium complex with 2-methyl piprazinuim add to thiocyante ligand ((2-Me-pip) Th $(NCS)_4$) **[34].**

1,4-dimethylpiperazine is a bi-dentate neutral N ligand system which show a high ability to donate towards a wide range of transition metal ions giving rise to very stable complexes **[35-37]**, which has also an aromatic nitrogen atom which unshared electron pairs are excellently located to act together in binding to metal ions, is known as a good π-acceptor **[38, 39]** and has been extensively used as a ligand in both analytical and preparative coordination chemistry **[40]**.

In order to contribute to the study of M-(1,4-dimethylpiperazine)(M= Co, Ni, Cd) complexes and the HSCN-(1,4-dimethylpiperazine) salt, in which we aim to discuss the transition metal precursor impact on thiocyanate complexes crystallization and their properties, we report here the synthesis and the characterizations of novel Cd(1,4-dimethylpiperazine) and M(1,4-dimethylpiperazine) (M = Co, Ni) complexes, add to the HSCN(1,4-dimethylpiperazine) salt.

The Hirshfeld surface analysis has been performed to completely characterize the intermolecular interactions and explain the crystalline architecture. Furthermore, the complexes were investigated by various spectroscopic and optical studies.

2. Experimental section of 1,4-Dimethylpiperazinium thiocyanate entities

2.1. Reagents

All materials were used as they were received without further purification. The amine 1,4-dimetylpiperazine, Cobalt bichlorate hexahydrate, Nickel bichlorate hexahydrate, Cadmium bichlorate tetrahydrate were obtained from Aldrich Chemical add to thiocyanate solution (KSCN) which was obtained from a cationic resin. All other solvents such as the ethanol used for synthesis and analysis were commercially available.

2.2. Preparation of $(C_6H_{16}N_2)M(SCN)_4(H_2O)_2$ (M = Co, Ni)

The solid metal complexes $(C_6H_{16}N_2)Co(SCN)_4(H_2O)_2$ and $(C_6H_{16}N_2)Ni(SCN)_4(H_2O)_2$ were prepared by mixing two drops (0.03 to 0.05 mL) the organic ligand dissolved in 25 mL of ethanolic solution and 25 mL of an aqueous solution of $CoCl_2.6H_2O$ for (1) and $NiCl_2.6H_2O$ for (2), and stirred together. The thiocynic acid solution obtained from a cationic resin exchange $H\text{-}SO_3$ using KSCN was added dropwise to the well stirred blue mixture until the color change to the pink for (1) and green mixture for (2). The obtained mixtures were left to evaporate for a week at ambient temperature. The solids were filtered and finally stored.

2.3. Preparation of $[C_6H_{16}N_2\ Cd(SCN)_4]$

Two drops (0.03 to 0.05mL) of 1,4-dimetylpiperazine dissolved in 30 mL water added to 30 mL of an aqueous solution of $CdCl_2$ and well stirred. An aqueous solution of KSCN was carefully added under continuous stirring until we reach the electro neutrality of the final mixture. The final solution was evaporated slowly at room temperature. White crystals suitable for single crystal X-ray structure analysis were obtained after 2 weeks.

2.4. Preparation of $[C_6H_{16}N_2\ (SCN)_2]$

The title compound $[C_6H_{16}N_2\ (SCN)_2]$ has been synthesized by reacting 10 mL of an aqueous solution of 1,4-Dimethylpiperazinium with 10 mL of thiocyanic solution (SCN^-) at 75–85 °C,

The obtained mixture was left to evaporate for a week at ambient temperature. The solids of $C_6H_{15}N_2^+.SCN^-$ were filtered and then recrystallized using ethanol as recrystallization solvent.

3. Investigation techniques

3.1. X-ray crystallography

In order to analyze the crystal structure of the obtained compound, an X ray automated four circle diffractometer (Bruker-Nonius Kappa CCD, diffractometer).

Single crystal X ray diffraction measurement were carried out on an automated four circle diffractometer (Bruker-Nonius Kappa CCD, diffractometer), containing a monochromatized-mirror using a graphite-monochromated MoKα (λ= 0.71073 Å) as radiation at 170 K. The structure was solved and reined on F^2 with the direct methods using the SHELXL software **[41]** incorporated in the wing X program package **[42].** A summary of Crystal data and experimental details are shown in **Table 1.**

3.2. Physical measurements

3.2.1. Infrared spectroscopy

IR measurement was performed using a spectrometer, scans were run over the range 400-4000 cm^{-1}.

3.2.2. UV Solid state spectroscopy

UV measurement was performed using a Perkin Elmer Lambda spectrophotometer. Scans were run over the range 200-800 cm^{-1}.

3.2.3. In situ high-pressure XRPD experiments

Powder X-ray diffraction (PXRD) measurements for hand-ground polycrystalline samples were carried out on a Miniflex600 Rigaku powder X-ray diffractometer using Cu Kα radiation (λ = 1.540598 Å) at room temperature. Diffraction data in the angular range of 2θ = 0–70°

were collected with a scan step width of 0.05° and a fixed time of 0.2 s. Rietveld refinement was applied to model the data sets using the GSAS package incorporated with the EXPGUI interface **[43].** The structure derived from single-crystal XRD was used as a template. Scale factor, background, lattice parameters, and zero point were refined until convergence.

3.2.4. The thermal analyses

The thermal analysis spectra of was obtained with a simultaneous thermogravimetry-differential thermal analysis (TG-DTA) using PYRIS 1 TGA instrument using 9.8 mg for (1) , 10.4 mg for (2), 17.9 mg for (3) and 15.8 mg for (4), for a heating rate of 5 °C.min-1 for the titled compounds in the temperature range 300-880 K under inert atmosphere (nitrogen gas).

3.2.5. Hirshfeld surface

The intermolecular interactions, the fingerprint plots of internal and external distances (di, de) were carried out using the Crystal Explorer 3.1 software **[44]** imported on a CIF file.

3.3. Evaluation of anti-free radical activity by trapping free radical (DPPH)

The scanning activity of the DPPH radical was measured according to the protocol described by Louli et al. A solution of DPPH was prepared by dissolving 4 mg of DPPH in 90 mL of DMSO. The solution was then placed in the dark for three hours. In glass tubes, one prepares a series of dilutions of the extract as well as that of the positive control dichloromethane (DCM) with a concentration of the stock solution of (5 mg / 10 mL) in order to obtain the following concentrations (0, 20; 40; 60; 80µg / mL). After 5 ml of the DPPH solution are introduced. After shaking, the tubes are placed in the dark at room temperature for 30 minutes. Regarding the negative control, it contains only the DPPH solution and the ethanol with an equal volume of 2.5 mL. Reading is performed by measuring the absorbance at 515 nm using a UV / Vis spectrophotometer **[45].** Antioxidant activity is estimated using the following equation:

$$(I\ \%) = [Abs\ control\ _\ Abs\ sample\ /\ Abs\ control] \times 100$$

where:

(I %): percentage of anti-free radical activity

Abs sample: absorbance of the sample

Abs Control: absorbance of negative control

4. Results and discussion

4.1. X-ray diffraction

4.1.1. single X-ray diffraction

$(C_6H_{16}N_2)Co(SCN)_4(H_2O)_2$ (1) crystallizes in the monoclinic space group P $2_1/c$ with Z = 2 formula units in the unit cell. The asymmetric unit **(Fig 1.a)** consists of one half of $Co(SCN)_4(H_2O)_2$ anion, one half of 1,4 dimethylpiprazinium cation. The Co is sixfold coordinated to four N-bonding thiocyanate anions and two water molecules and connected to the 1,4 dimethylpiprazinium cation via N—H ... S and O—H... S hydrogen bounds to build a three-dimensional network **(Fig 1.c).** The bond lengths around the central Co atoms are comparable to those reported in literature and the bonding angles show that the octahedra are slightly distorted (**Table 3**). Therefore, hydrogen-bonding interactions play a major role in the stability of the compounds.

In the crystal structure, the discrete complex $(C_6H_{16}N_2)Co(SCN)_4(H_2O)_2$ is linked by intermolecular **O–H⋯S** hydrogen bonds between the H atoms of the water molecules and the thiocyanate S atoms into chains at y = 0 and y = $\frac{1}{2}$ (**Fig 1.b** and **Table 4**) add to the intermolecular **N–H⋯S** hydrogen bonds with between the H atoms of the N entity belongs to the cation molecules and the thiocyanate S atoms into layers parallel to the (a,b) plane. These layers are further connected by intermolecular hydrogen bonding into a 3D network (**Fig 1.c**).

It is noted that this topology of the thiocyanate network is quite rare and usually observed with the more Co (II) cations as for $2(C_5H_6N_2)$ $Co(SCN)_2$ **[46].** Similarly for the crystal structure of the most 1.4-dimethypiperazine deficient compound $(C_6H_{16}N_2)Ni(SCN)_4(H_2O)_2$ (2) (**Fig 2.a**) was determined and refinement using the crystallographic data of the isotopic Co compound (1). The Ni atoms are octahedral coordinated by four N -bonding thiocyanate anions and two water molecules (**Fig 2.b**). Additionally, the metal complexes are linked into chains by N-H…S and O-H…S hydrogen bounds (**Fig 2.c**). These chains are further connected into chains by the sulfur atoms via Ni1S2 and Ni1S1 units.

While for the $(C_6H_{16}N_2)$ $Cd(SCN)_4$ (3) complex, crystallizes in the triclinic space group $P\bar{1}$ with Z = 1 formula in the unit cell. The asymmetric unit consists of one Cd atom, located on a center of coordination of the thiocyanic anions add to one 1,4-dimethypiperazinium co-ligands in general positions (**Fig 3.a**). The Cd atoms are sixfold coordinated by two terminally N-bonded thiocyanate anions (N2) and four S-bonded thiocyanate anions (S1,S2) into discrete complexes (**Fig 3.b**) ,the central Cd atoms are linked by pairs of μ-1,3-bridging thiocyanate anions into corrugated chains at z = 0 (**Fig 3.b**). For (3) the thiocyanate N and S atoms as well as the co-ligand are in trans-position whereas for Cd1 the thiocyanate-related S and the 1.4-dimethypiperazinium N atoms are cis, whereas the thiocyanate N atoms are still trans, leading to an alternating all-trans and cis-cis-trans coordination.

The bond lengths around the central Cd atoms are comparable to those reported in literature and the bonding angles show that the octahedron is slightly distorted (**Table 2**). In the crystal structure, the discrete complexes are linked by intermolecular N–H⋯N hydrogen bonds between the H atoms 1.4-dimethypiperazinium and the thiocyanate N atoms into layers parallel to the b/c plane, These layers are further connected to build a 3D network (**Fig 3.c** and **Table 4).** It is noted that this topology of the thiocyanate network is quite rare and usually observed with the more chalcophilic Cd(II) cations as for the case of $[(CH_3)_4N]_2[Cd(SCN)_4]$ and $[(CH_3)_4N]$ $[Cd(SCN)_3]$ **[47].**

The asymmetric unit of the title compound **(Fig. 4.a),** contains one 1.4-dimetylpiperazinuim cation (C2, C3, C5, C6, C7, C8/N1, N4) and two thiocyanate anions (S1, S2/C10, C12/N9, N11). The 1.4-dimetylpiperazinuim ring adopts a slightly distorted chair conformation **(Fig. 4.b)**, with puckering parameters: Q = 0.4179 Å, θ = 177.95 (18) °, and φ = 161 (5) °. For an ideal chair configuration, θ has a value of 0 or 180°.

The bond lengths **Table 2** and bond angles **Table 3** are in normal ranges and are comparable with those reported earlier for similar compounds (Bagabas et al., 2014; Shimada et al., 1955; Smith et al., 1994; Odendal et al., 2010). The different types of H-bonds for $[C_6H_{16}N_2(SCN)_2]$ are shown in **Fig. 4.c** as dashed light red lines and their relative geometrical parameters are listed in **Table 4**.

As a hydrogen donor, the organic molecule exhibits the **N—H … N** H-bond type which give rise to 3D chains. On the other hand, the organic cation with its NH_2 groups display the

N—H…N H-bond types which contribute to the linkage between the $(NCS)^{2-}$ anions and the $(C_6H_{14}N_2)^{2+}$ cation. All these intermolecular hydrogen bonds give rise to three-dimensional network in the structure and contribute to the cohesion and stability of the compound. Regarding the donor-acceptor bond lengths, all the hydrogen bonds in the studied system are found to be weak (D—A > 3 Å) and have an electrostatic interaction type **[48].**

4.1.2. Powder X-ray diffraction

Fig. S1 shows the resulting X-ray powder diffractogram for the $(C_6H_{16}N_2)Co(SCN)_4(H_2O)_2$, $(C_6H_{16}N_2)Ni(SCN)_4(H_2O)_2$, $[C_6H_{16}N_2\ Cd(SCN)_4]$ and $[C_6H_{16}N_2(SCN)_2]$ **.** Some peaks with very low intensities can't be indexed, which could be some impurities. The results confirmed that (1), (2), (3) and (4) has been formed as a crystallin phases.

4.2. Hirshfeld surface analysis

Currently, the application of Hirshfeld surface **[49]** analysis occupies a huge interest within the field of crystallography. Hirshfeld surfaces and fingerprint plots **[50]** were generated and based on the crystallographic information file (CIF) using Crystal Explorer **[51,53]**. Hirshfeld surfaces allow the visualization of intermolecular interactions. This technique is a powerful tool for visualizing and identifying interatomic compound interactions. It provides a virtual image where the different types of interactions are clearly identified by the shapes, outlines and colors provided by the calculation. The dnorm map analysis have graphically illustrated the relative positions of neighboring atoms belonging to molecules that interact with each other. The normalized contact distance (dnorm) was calculated via the following expression:

$$Dnorm = \frac{di - r_i^{\mathrm{U}dw}}{r_i^{\mathrm{Udw}}} + \frac{de - r_e^{\mathrm{Udw}}}{r_e^{\mathrm{Udw}}}$$

is the van der Waals radius of the atom that lies inside the surface of Hirschfeld, while reUdw is the van der Waals radius of the atom that lies outside of the surface of Hirshfeld.

The Hirshfeld surface of the title compound is illustrated in **Fig. 5**. In this latter a color gradient is used, which varies from red (distances shorter than sum of UdW with negative dnorm value) through white (represents the contact around UdW separation with a dnorm value of zero) to blue (distance longer than of UdW with positive dnorm value).

The red spots over Hirshfeld surface point out the inter-contacts included in hydrogen bonds. It is well observed in **Fig. 5** that the red circular collapsing is attributed to hydrogen-bonding interactions. In the dnorm map, the vivid red spots in the Hirshfeld surface are due to short normalized S—H distances corresponding to D— H···S interactions. Hydrogen-donor groups constitute the convex blue regions on the shape-index surface and hydrogen-acceptor groups appear in concave red regions. 3D graphics, Shape index (**Fig. S2**) and Curvedness (**Fig. S3**) are also used to identify the characteristic packaging modes existing in crystal. The small flat

segments delimited by the blue outline observed on the Curvedness graph indicate the absence of (π ... π) interactions so that there is no evidence of the adjacent red and blue triangles on the surface of Shape index (**Fig. S2**). This result was confirmed by a structural X-ray analysis.

The examination of the 2D fingerprints used to highlight the atoms participating in close contacts. In addition, the analysis of these footprints helped to reread numerical values to the surfaces previously described.

The characteristic features in the 2D-fingerprint plots (**Fig. S4**) obtained from the Hirschfeld were further investigated in order to find out the directional interactions. This analysis shows the relative contribution of each contact present in the compound. In these plots **di** corresponds to the closest internal distance from a given point of the Hirschfeld, and **de** to the closest external contacts (i.e., external distance). The two-dimensional fingerprint plots quantify the contributions of each type of non-covalent interaction to the Hirshfeld surface. The major contribution contacts, which represent van der waals interactions which are observed as two sharp peaks in the plot of **Fig. S4**.

The percentage of contacts between one (X…X) or two (X…Y) chemical elements in a crystal packing is information given by CrystalExplorer which can be used to indirectly calculate the enrichment ratios **[54].** The proportion of Hirshfeld surface contacts involving the (X,Y) pair of elements is referred to as CXY.

The proportion Sx of chemical type X on the molecular surface is obtained by the summation:

$$Sx = Cxx + \frac{1}{2} \Sigma\, CXY \textbf{ [54].}$$

The value of C_{XY} occurs both X…Y and Y…X contacts in the SX sum, where the X and the Y atoms are interior and exterior to the Hirshfeld surface. The factor $\frac{1}{2}$ relates to the fact that C_{XY} contributes to both Sx and SY summations. The summation of all the surface proportions is equal to unity:

$$\Sigma x\ Sx = 1$$ **[54].**

The ratio of random contacts R_{XY} between the two chemical elements X and Y is then introduced [62]. The R_{XY} values are defined as if all contact types X…Y in the crystal packing were equal distributed between all chemical types and are obtained by probability products:

$$R_{XX} = S_X S_X \quad \text{and} \quad R_{XY} = 2S_X S_Y$$ **[54]**

The corresponding fingerprint plots of both complexes (1), (2), (3) and (4) are shown with characteristic pseudo-symmetric wings in the d_e and d_i diagonal axes which are delineated mainly into H...S/S…H, H…C/C…H in (1), same (2) the main interactions are H...S/S...H, H...C/C...H for (3) H...S/S...H, H...C/C...H and H...N/N...H and S···H/H···S, H···H/H···H, N···H/H···N, contacts in complex (4).

The enrichment ratios E_{XY} were computed for sets of molecules belonging to several classes of molecules and were analyzed as a function of S_X values. Intermolecular interactions identified are assessed by an analysis of enrichment ratios (E_{XY}) which provide a quantitative measure of the probability of intermolecular interactions that occur on the Hirshfeld Surface (**Table S1**).

The contacts types are very similar on the three molecules as the correlation coefficient between the Cxy values of entities. The contacts types between the layer of $[Co(NCS)_4(H_2O)_2]$ for (1), for $[Ni(NCS)_4(H_2O)_2]$ (2), for $[Cd(NCS)_4]$ (3) and for (SCN) for (4) anions and their layers of organic cations are shown in **Table S1**.

It shows that the "N…H-S" is the strongest hydrogen bond for the compounds (1), (2) and (3), which constitute the major of the interface (54.25%) and are enriched at E = 1.600 for (1), the major of the interface (52.12%) and are enriched at E = 1.685 for (2),and the major of the interface for (3) also (42.3%) and are enriched at E = 1.390, while for (4) the "N…H-N" is the

strongest hydrogen bond which constitute the major of the interface (39.15%) and are enriched at E = 1.22.

The CrystalExplorer software gives us the opportunity also to determine the void surface in the crystal structures of the compounds. The void surface is focused on the sum of spherical atomic electron densities at the appropriate nuclear positions **[55].** The crystal-void calculation (results under 0.002 a.u. isovalue) shows (**Fig. 6**) the void volume of the compound (1) which is equal to 79.09 $Å^3$ and surface area in the order of 308.17 $Å^2$. The data gives by the monocrystal XRD analysis showed that the volume of the unit cell is equal 443.49 $Å^3$ (**Table 1**). 17.83% represents the calculated porosity value. For compound (2) (**Fig. 6)**, the void volume is equal to 76.75 $Å^3$ and surface area in the order of 307.10 $Å^2$. The data gives by the monocrystal XRD analysis showed that the volume of the unit cell is equal 443.27$Å^3$ (**Table 1**). 17.31% represents the calculated porosity value. For compound (3) (**Fig. 6)**, the void volume is equal to 31.92 $Å^3$ and surface area in the order of 112.33 $Å^2$. The data gives by the monocrystal XRD analysis showed that the volume of the unit cell is equal 460.93 $Å^3$ (**Table 1**). 6.92% represents the calculated porosity value, and for $C_6H_{16}N_2$ 2(SCN) (**Fig. 6)** the void volume is equal to 179.42 $Å^3$ and surface area in the order of 713.16 $Å^2$. The data gives by the monocrystal XRD analysis showed that the volume of the unit cell is equal 232.37 $Å^3$ (**Table 1**). 77.21% represents the calculated porosity value.

The electron density isosurfaces are not too closed around the components but are spaced out where there are interspecific approaches, e.g. N–H…S and N–H…N.

4.3. Vibrational IR spectra and assignments

For the determination of vibrational characteristics of (1), (2), (3) and (4) were add a vibrational study using infrared spectroscopy. In our study, wave numbers are in the ranges from 4000 to 400 cm^{-1}. The experimental IR spectrum is illustrated in **Fig. S5.**

The thiocyanate ion is revealed by the presence of bands at the range of 2130 cm^{-1} and 2096 cm^{-1}. The assignment of these bands to thiocyanate vibrations and the determination of its coordination mode are based on previously reported results such as for ($C_2N_6H_{12}$) [Co $(NCS)_4$]. H_2O **[56-58].**

These peaks that don't exceed 2110 cm^{-1}, prove the presence of N bonded frequency and S-bonded thiocyanates. The nitrogen terminal coordination modes for fourth compounds are also confirmed through the presence of the bands at 860 cm^{-1} considering that the coordination through N- and S- bonded terminal thiocyanates is frequently observed in the 860-780 cm^{-1} range. The peaks occurring at around 1598 cm^{-1} indicate the presence of the υ(C=N) stretches.

The nitrogen terminal coordination modes for the compound are also confirmed through the presence of the bands at 860 cm^{-1} considering that the coordination through N- and S- bonded terminal thiocyanates is frequently observed in the 860-780 cm^{-1} range.

We have estimated the vibration domain of the organic group which is located between 284 and 3200 cm^{-1} (**Fig. S5; a, b, c, d**) and shows the bands corresponding to the characteristic vibrational modes of cationic entity which compared with those of similar compounds.

In fact, the intense bands in 3100 cm^{-1} correspond to the valence vibrations of the groups (NH), so the broadening of these bands is due to the establishment of the hydrogen bonds, which effect the lowering of the frequencies of these groups. In the range1690-1660 cm^{-1}, the bands attributed to the valence vibrations of the group ν (C-C). The bands between 1490 and 1360 cm^{-1} are attributed to the valence vibrations ν (C - H) of the symmetric and asymmetric vibrations of the (-NH+), (-NH2) and (-CH3) groups. Finally, the observed weak band which is located towards 1200 cm^{-1} and 914 cm^{-1}, and between 1195 and 924 cm^{-1}, are attributed to the (C-N) deformation and its off-plane deformation **[59].**

4.4. UV Solid state spectroscopy

The luminescence properties of our compound have been studied in solution in dimethyl sulfoxide DMSO (10^{-2} mol. L^{-1}). The UV-Visible spectrum was recorded at room temperature by a Perkin Elmer Lambada 11 type spectrometer.

The compounds show different luminescence behaviors (**Fig S6; a, b, c**); the characteristic bonds at 482, 579 and 484 nm respectively for (1), (2) and (3) are assigned to d→d transition and 438, 456 and 437 for (1), (2) and (3) respectively are assigned π→π∗ transition. Also, we have the 346, 402, and 377 transitions which refers to the charge transfer transition.

The UV-Visible spectrum **(Fig. S6.d)** highlights the presence of a wide band at 279 nm which can be attributed to the transitions (n-π*) in the ring of the piperazinium. Furthermore, from the study by UV spectroscopy, we can determine the gap energy between the border orbitals (the highest energy orbital occupied by or less a HUMO electron and the lowest energy orbital not occupied by an electron (LUMO)), by adopting the method proposed by TAUC **[62]**. The value of the gap energy found are equal to 2.48, 2.09, 2.25 and 4.2 eV, which are determined by the tangent method following the intersection of the tangent to the curve with the baseline which is shown on **Fig.7.**

This result shows that the compounds (1), (2), (3) can be described as conductors and the compound [$C_6H_{16}N_2.(SCN)_2$], can be classified among the semiconductors **[61]**.

4.5. Thermal behavior of titled complexes

In metallurgy and materials science, thermal analysis is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable. It involves heating a material above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time and then cooling.

The combined DTA and DTG of the titled compounds in dynamic air atmosphere, with heating rate of 5°C min^{-1}, are shown in **Fig. S7**. Four well defined steps can clearly be observed, in the ATD and DTG curves.

TGA studies showed that the water molecules in (1) and (2) as well are removed between [350-365 K] associated with the endothermic loss, this step is common to all the complexes and is similar to the dehydration of many other complexes with water of crystallization **[62].**

The second step at 410 K for (1), 420 K for (2), 370 K for (3) and 323 K for (4) belongs to the phase transition without any weight loss.

An interesting observation in the thermal behavior of the four compounds as recently reported for other ligands **[63-64].** as well at the process of the loss of the amine C-N groups from the equatorial ligand at [450 - 530 K] for (1), (2) and (3) while for (4) the decomposition process begins at 453 K. During this endothermic process, the mass loss in this step can be attributed to successive decomposition of the titled complexes. This endothermic step take place when the intermolecular N.H⋯S hydrogen bonding breaks apart in the deamination process and one of the three amines N-H groups per complex molecule is no longer engaged in hydrogen bonding.

During the fourth process, the SO group, free from hydrogen bonding, is oxidized to SO_2 at [550 - 580 K] for (1), (2) and (3), while for (4) it takes part at 520 K **[65].**

4.6. Electronic density

Despite the relatively recent history of SCN as a promising hole-transporting material for numerous electronic applications, there have been only a handful of published theoretical studies of the electronic properties of compounds based on thiocyanates **[66],** This work mainly employs the electronic density functional (DFT) calculations for elucidating the electronic structure of thiocyanic components. In quantum mechanics, and in particular in

quantum chemistry, the density ρ corresponding to an N-electronic wave function Ψ (N) is the monoelectronic function given by:

$$\rho(x) = \int dx_2 \ldots dx_N \, |\Psi^{(N)}(x, x_2, \ldots, x_N)|^2$$

These quantities are particularly important in the context of density functional theory. The density functional theory (DFT, acronym for Density Functional Theory) is a quantum calculation method allowing the study of the electronic structure, in principle exactly. It is one of the most used methods in quantum calculations in both condensed matter physics and quantum chemistry due to its possible application to systems of very varied sizes, ranging from a few atoms to several hundreds. The Electronic density play a key role in the characterization of interaction energy between the electric charge produced by the electrons and the nuclei of the molecule. The Electronic density–is one of the best suitable tools for prediction of the presence of inter- and intramolecular interactions of the studied compounds. It is a useful descriptor to determine the active sites of electrophilic and nucleophilic attacks over the molecule for the study of biological recognition process as well as hydrogen-bonding interactions **[67]**.

The Electronic density surface was made by using the software crystal explorer **[51] (Fig. 8).** The mapping represents the donor atoms in blue regions with positive potential, is the most positive electrostatic potential (nucleophilic site) and it is localized hydrogen atoms and the acceptor atoms with negative potential in red regions represents the most electronegative potential (electrophilic sites) and it is mainly localized over anionic group (red, thiocyanic atoms), whereas the white color indicates the neutral region **[68].** This graph shows that the electrophilic sites are located around the hydrogen atoms, whereas the nucleophilic sites are located around the thiocyanic atoms.

Electronic density surface represents a proof of the formation of the hydrogen bond **[69],** it is defined as being a donor acceptor interaction. It proves that the electrostatic potential of the donor becomes less negative as the acceptor becomes more negative.

4.7. Dielectric Properties: Impedance Spectroscopy

In order to detect possible ionic conduction, we study the properties of electric transport of the compounds produced. A pellet whose geometric factor $g = e / s$ while $g = 0.197\ cm^{-1}$ was chosen to study the conductivity of the compound produced.

The study of electrical conductivity sheds light on the behavior of charge carriers under a dielectric conductivity field, their mobility and mechanism of conduction, the conductivity of the crystals in the higher temperature region is determined by intrinsic defects caused by thermal fluctuations **[70]**.

The impedance spectroscopy is a very convenient and powerful technique that helps to analyze and separate the contribution from grain boundary and material electrode interface in the materials. The high frequency semi-circular arc attributes to the contribution from grains and low frequency semicircular arc attributes to the contribution from grain boundary **[71].** The impedance spectrum of the titled compounds recorded between 303 and 333 K for (1), 373 and 403 K for (2), 328 and 358 K for (3) and between 163 and 243 K for (4) is shown in **Fig. S8,** this representation is called also a Nyquist diagram. These complex plots form arcs, and each experimental point corresponds to a frequency value. The semicircle diameter expresses the electrical resistivity of the sample at the specified temperature and the maximum value corresponds to the relaxation frequency w = 1/RC. The impedance curves show that the radius of the arc decreases with increasing of the temperature. This behavior is consistent with the Cole–Cole law **[72].**

The complex impedance Z* measurement can be expressed as a function of resistance R and capacitance C using the following equations:

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega)$$

Where: $Z'(\omega) = \frac{R}{1+\omega^2R^2C^2}$ and $Z''(\omega) = \frac{\omega CR^2}{1+\omega^2R^2C^2}$

are, respectively, the real and imaginary parts of the impedance given by the equations **[73].** The impedance data were fitted to the equivalence of R and C parallel network **[74].**

4.8. Antioxidant activities

The different concentrations of the 70% ethanolic solutions of the tested compounds (0, 2.5; 5; 8; 11; 13.85 µg / ml) showed antioxidant activities in a dose-dependent manner 0, 3.49, 4.12, 5.8, 7.1, 8.51% inhibition **[75].**

In **Fig.9**, it is shown that the percentage inhibition of the free radical DPPH (2,2-diphenyl-1-picrylhydrazyl) has the same pattern for the extract used. However, it has been observed that the percentage inhibition increases with the concentration of the 70% ethanolic solution of the tested compounds (**Table 5**), it is generally lower when compared to that of the synthetic antioxidant DPPH which shows a higher antioxidant activity of the inhibition percentage **Fig. 9.**

The study of the antioxidant activity of the extract from Stevia rebaudiana using the DPPH free radical scavenging method showed that the tested samples have significant antioxidant activity. However, this activity remains significantly lower than that of DPPH, but it is a crude extract containing a large number of different compounds. It is therefore very likely that it contains compounds which, once purified, may exhibit activity comparable to that of DPPH.

The antioxidant capacity is expressed in Trolox equivalent (TEAC) which gives a value of EC50 = 18.36± 0.05 µg / ml, EC50 = 20.74 ± 0.01 µg / ml, EC50 = 19.42 ± 0.08 µg / ml and EC50 = 16.29 ± 0.07 µg / ml respectively for (1), (2), (3) and (4); it corresponds to the concentration of Trolox which gives a value of EC50 Trolox = 21.642 µM, having the same activity as the substance to be tested at one concentration. The result is given in µM of Trolox equivalent per g of product with a value of 1.417, 0.958, 1.093 and 1.739 µmoles Trolox / mg

of (1), (2), (3) and (4) extracts. Scavenger effect of the DPPH radical. The anti-free radical activity of the various extracts **[76]** was evaluated by their inhibitory activity on a methanolic solution of DPPH, measured at 517 nm. We interpret this phenomenon by the transfer of the single electrons which are located in the external orbital of the DPPH, and after reaching a given concentration, the antioxidant will react completely with the radical, and when we increase the concentration, the antioxidant activity of the compound could be explained by the presence of an important capacity to act as donors of hydrogen or electron atoms, hence the reductive transformation of DPPH • into DPPH-H, and consequently the formation of the Yellow coloration was attributed to the presence of numerous bioactive molecules which is accompanied by the saturation of the electronic layers of the radical. Furthermore, we compare the antioxidant activity of the titled compounds to an innocent counter ion (without thiocyanate), the 1,4-dimethylpiperazine ($C_6H_{14}N_2$) shows a low activity comparing to titled compounds (**Table 5**). For a concentration of 100 µg / ml, ($C_6H_{14}N_2$) shows an inhibition percentage which values 27%, and we have 69.08% for (1), 37.19% for (2), 42.87% for (3) and 29.82% for (4) as an inhibition percentage, we conclude that the high antioxidant activity observed for the titled compounds (1), (2) and (3) is generated due to the presence of the groupment $[M(SCN)_4]$ while M= Co, Ni, Cd.

Conclusion

We have synthesized four novel inorganic-organic complex hybrid solids by the solution reaction of $CoCl_2$(1)/$NiCl_2$(2)/ $CdCl_2$(3) with heterocyclic aromatic base in strong thiocyanic acidic conditions. They all have lattice solvent molecules. The $Ni^{2+}/Co^{2+}/Cd^{2+}$ complexes are tetrahedrally coordinated by $(SCN)^-$. For the heterocyclic derivative, the ring N atoms are protonated. While for (4) has been synthesized by reacting an aqueous solution of 1,4-Dimethylpiperazinium with thiocyanate (SCN^-). These compounds display 3D network from the presence of N-H…S, N-H…N and O-H…S H-bonds interactions. These results are a good

indication that the nature of the metals used has an important effect on the coordination compounds characterization.

Furthermore, the optical properties were investigated by absorption measurements. It is found that the gap energy value of the formed compounds is 2.48 eV for (1), 2.09 eV for (2), 2.25 eV for (3) and 4.21 eV for (4), in the light of this result, we are able to predict that our finding is a conductor (for (1), (2), and (3)) and a semiconductor (for (4)). Addition to the interesting antioxidant behavior showing by [M(SCN)] where M=Co,Ni,Cd.

Appendix A. Supplementary material

A CCDC Deposition Number 2061180, 2081695, 2081696 and 2061182 respectively for (1), (2), (3) and (4) contain the supplementary crystallographic data for. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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