Investigation of structure-directing interactions within copper(i)thiocyanate complexes through X-ray analyses and non-covalent interaction (NCI) theoretical approach


This version is available from Sussex Research Online: http://sro.sussex.ac.uk/id/eprint/71266/

This document is made available in accordance with publisher policies and may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher's version. Please see the URL above for details on accessing the published version.

Copyright and reuse:
Sussex Research Online is a digital repository of the research output of the University.

Copyright and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable, the material made available in SRO has been checked for eligibility before being made available.

Copies of full text items generally can be reproduced, displayed or performed and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

http://sro.sussex.ac.uk
Investigation of structure-directing interactions within copper(i) thiocyanate complexes through X-ray analyses and non-covalent interaction (NCI) theoretical approach†

Khodayar Gholivand, a, b Kaveh Farshadfar, a S. Mark Roe, b Mahdieh Hosseini a and Akram Gholami a

Herein, we reported the synthesis of copper(i) thiocyanate complexes with ortho-pyridinyl carbohydrazones containing a thiophene (L1) or a furyl ring (L2) as a mixture of two different crystals for each compound, linkage isomers of C16, [Cu(NCS)(L1)PPh3], and C15, [Cu(SCN)(L2)PPh3], for L1, whereas monomeric and polymeric structures C2N, [Cu(NCS)(L2)PPh3], and C2P, [−(NCS)(Cu(L2))−], for L2. Crystallographic information and theoretical calculations, mainly noncovalent interaction reduced density gradient (NCI-RDG) analyses, were pursued to generate a profound understanding of the structure-directing interactions in these complexes. The supramolecular assemblies are first driven by cooperative π⋯π interactions and hydrogen bonds followed by CH⋯π, S⋯–S and S⋯π linkages. In the case of the linkage isomers, intermolecular interactions may have a significant role in the formation of the less stable S-bound isomer C15.

Introduction

Copper(i) compounds have attracted a growing interest because of their high structural diversity,1–4 catalytic activity5–7 and photophysical properties.3,8–10 They have applications in different areas such as organic light-emitting diodes (OLEDs),11–22 supramolecular assemblies, oxygen sensors and biological probes. The rich structural features and utilitarian considerations have motivated researchers to focus on the synthesis and characterization of Cu(i) complexes with various donor ligands. The formation of structural variations is greatly influenced by several parameters such as the synthetic conditions or steric/electronic effects exerted by the ligand.

The triatomic pseudohalide, thiocyanate anion (SCN−), is an excellent versatile ambidentate ligand with two donor atoms, S or N.23 It can coordinate to metal ions both in terminal and bridging coordination modes and potentially provide fascinating examples of linkage isomerism.24–26 When SCN− acts as a terminal ligand, it affords potential interaction sites to generate non-intermolecular interactions and, accordingly, can direct the crystal packing. Controlling the self-assemblies in the solid state on the basis of molecular structures and through the use of weak interactions is a long-standing goal of supramolecular chemistry.27

Very recently in our previous work, cuprous halide complexes of ortho-, meta- and para-pyridinyl carbohydrazones were introduced.28 The influence of ligand structure and halide variations on the molecular structures and supramolecular arrays of the complexes were studied both experimentally and theoretically. In the following, we employed cuprous pseudohalide, CuSCN, for the synthesis of complexes with two ortho-pyridinyl carbohydrazones. Copper(i) thiocyanate compounds are very interesting in solar cell applications as a p-type semiconductor.29–31

In this contribution, we report the structural characteristics of complexes from the reaction of CuSCN with PPh3 and
ortho-pyridinyl carbohydrazones containing a thiophene (L₁) or a furyl ring (L₂); see Scheme 1. The former resulted in two
linkage isomers: C₁N [Cu(NCS)(L₁)PPh₃] and C₁S [Cu(SCN)(L₁)-
PPh₃], while the latter afforded monomeric and polymeric complexes of C₂N [Cu(NCS)(L₂)PPh₃] and C₂P [-(NCS)(Cu(L₂))]-. We have also used a recently introduced alternative interpretive
technique, the non-covalent interaction (NCI) approach, to
manifold the diverse NCIs at the crystal packing structures.
This method is based on the analysis of the electron density
and enables us to identify and visualize the interactions.32
Various non-covalent interactions, including hydrogen bond-
ing,33 S⋯S, S⋯π,34 π⋯π35 and CH⋯π36 interactions, have been investigated in this work.

Results and discussion

Synthesis

Ligands L₁ and L₂ were prepared by mixing equivalent amounts of 2-thiophenecarboxylic acid hydrazide (1) or fur(o)
hydrazide (2) and 2-pyridinecarboxaldehyde in methanol
solution.

A solution of the ligand in CHCl₃ was added dropwise to a
mixture of copper(i) thiocyanate and PPh₃ while stirring in
CH₂CN and then the mixture was filtered off. After slow diffusion of diethyl ether in the filtered solutions, two different
crystals were obtained for each compound including the light
orange needle crystals (C₁N) and clear light red irregula-
crystals (C₁S) for L₁ and orange needle crystals (C₂N) and dark or-
ange hexagonal crystals (C₂P) for L₂. A mixture of the isomeric
crystals C₁N and C₁S is shown in Fig. 1.

Various ratios of acetonitrile and chloroform solvents were
assessed in the crystallization of C₁. Upon using more chloro-
form, the percentage of C₁N was dominant, whereas a higher amount of acetonitrile in the reaction pot increased the
percentage of C₁S. For C₂, the formation of crystals depended on the concentration of the reaction mixture. At a high concen-
tration, the polymeric compound precipitated fast and we only
obtained crystals of C₂N, but slower diffusion of diethyl ether
in the more dilute solution afforded crystals of both C₂P (as
the dominant product) and C₂N suitable for X-ray diffraction.

ORTEP diagrams of the molecular structures are shown in
Fig. 2. The crystallographic data of the complexes are listed in
Table 1. Selected bond distances and angles are summa-
ized in Table 2.

Structural analysis

Cu[NCS](L₁)PPh₃ (C₁N). The title compound crystallizes in
the triclinic space group P₁. Ligand L₁ binds to the copper
atom in a bidentate chelating manner via N2 (pyridine) and
N3 (imine). An isothiocyanate anion (N-donor) and one PPh₃
occupy the other coordination sites (Fig. 1). Houser and co-
workers suggested an angular index (τ₄) which determines
the geometry of the four-coordinate metal centres as follows:

\[ \tau₄ = \frac{360 - (\alpha + \beta)}{141} \]

(α and β are the two largest angles around a four-coordinate metal centre). The values of τ₄ will
range from 1.00 for a perfect tetrahedral geometry to zero for
a perfect square planar environment. Intermediate structures
including trigonal pyramid and seesaws fall within the range of
0 to 1.00.37 According to the τ₄ value for C₁N (0.79), the
coordination polyhedra of the copper centre can be described as trigonal pyramid.

In the structure of C₁N, each molecular unit of the com-
plex is joined to the neighbouring unit by means of three 2-fold interactions including classical and non-classical hy-
drogen bonds N4–H4···S1 and C7–H7···S1, respectively
(Table 3), and π₅₇(π)–π₇₈(π) (Table 4).

The dimers are further connected to each other through
π₅₇(π)–π₇₈(π) and C5–H5···π₇₈(π) interactions along the a-direction
(Fig. 3a) to afford chains which are laterally linked together
via various intermolecular interactions to generate a 3D net-
work. The interactions which link the chains along the b-axis include (i) S1···S1, (ii) C3H3···S1, (iii) C11–H11···π₅₇(π) (iv) C2–H2···π₇₈(π)
and (v) C14–H14···π₇₈(π) linkages (Fig. 3b). In addition, C21H21···S2 H-bonds plus weak C27–H27···π₅₇(π) interactions (C···Cg: 4.090 Å) connect them along the
c-direction (Fig. 3c). The distance of the S···S interaction was
found to be about 3.456 Å which is 4% shorter than the sum
of the van der Waals radii of two sulfur atoms. A summary of the parameters for the other interactions mentioned above
are presented in Tables 3 and 4.

[Cu(SCN)(L₁)PPh₃] (C₁S). The red irregular crystals of C₁S are
the second form resulting from the reaction of a 1 : 1 molar
ratio of L₁ and the mixture of cuprous thiocyanate and
PPh₃. X-ray diffraction analysis reveals that it crystallizes in
the triclinic space group P1. The central copper atoms are
again in trigonal pyramidal environments (τ₄ = 0.82, exactly
equal to that for C₁N) formed by N₇(π) and N₃(π) (from the
chelating ligand), PPh₃ moiety and thiocyanate anion (this time
as an S-donor) (Fig. 1). Changing the coordination site of the
ambidentate ligand, NCS⁻, alters the supramolecular archi-
tecture of C₁S compared to that of the N-bound isomer C₁N.
The crystal structure of C_{1S} contains hydrogen bonded dimers generated by three pairwise interactions, N4–H4⋯N1, C7–H7⋯N1 and C10–H10⋯N1 (Table 3 and Fig. 4a). It is worth noting that the coordination of sulfur to the Cu(i) atom...
These chains are held together by C11⋯S between the discrete molecules in the dimers. In addition, H⋯S interactions connect the dimers to form [001] chains.

and consequently the orientation of the N1 atom direct the formation of hydrogen bonds and lead to supernumerary slippage of molecules on each other. The offset of pyridine and thiophene rings prevents the formation of a πpy⋯πthiophene interaction, unlike in the structure C1IN. Thus, instead of a πpy⋯πthiophene interaction, a C≡O⋯π interaction is established between the discrete molecules in the dimers. In addition, S⋯S interactions connect the dimers to form [001] chains. The distance between two sulfur atoms is equal to 3.594 Å. These chains are held together by C11⋯C9 and C17⋯H17⋯πthiophene linkages (Table 4) along the a- and b-directions, respectively, which complete a 3D network (Fig. 4b-d).

[Cu(NCS)(L2)PPh3] (C2N). This compound crystallizes in the triclinic space group P1. A trigonal pyramidal configuration of the Cu(II) centres (τ1 = 0.80) has been formed by the bidentate chelating ligand, PPh3 and thiocyanate (N-donor). C2N has a similar coordination environment to that of C1IN leading to its being isosctructural with this complex. The supramolecular organization of C2N is also disciplined by the formation of dimers through the same kind of interactions in C1IN: N3–H3⋯S1, C6–H6⋯S1 and πpy⋯πfuryl stacking interactions. Pyridine rings participate in the other π⋯π interactions (πpy⋯πpy) which build up a chain of the dimers directed along the c-axis. The chains are further reinforced by C3–H3A⋯πpp3 and C4–H4⋯πpp3 contacts (see Table 4). On the other hand, S⋯S synthsons accompanied by C2–H2⋯S1, C15–H15⋯S1 and C10–H10⋯N4 hydrogen bonds as well as C1⋯H1⋯πfuryl interactions link the chains to create (110) sheets. The third dimension of the supramolecular assembly results from the connection of the layers via C21⋯H21⋯πfuryl linkages. Crystal packing diagrams of C2N are presented in Fig. 5.

Table 3 Hydrogen bond geometries for compounds C1IN, C15, C2N and C2P

<table>
<thead>
<tr>
<th>Structure</th>
<th>D–H⋯A</th>
<th>d (Å)</th>
<th>D–H⋯A</th>
<th>d (Å)</th>
<th>D–A</th>
<th>Symm. codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1IN</td>
<td>N4–H4⋯S1</td>
<td>0.880</td>
<td>2.6800</td>
<td>3.5042(18)</td>
<td>157.00</td>
<td>1 – x, 1 – y, 1 – z</td>
</tr>
<tr>
<td>C15</td>
<td>C7–H7⋯S1</td>
<td>0.950</td>
<td>2.8700</td>
<td>3.6680(2)</td>
<td>143.00</td>
<td>1 – x, 1 – y, 1 – z</td>
</tr>
<tr>
<td>C1S</td>
<td>C3–H3⋯S1</td>
<td>0.930</td>
<td>2.8754</td>
<td>3.7910(2)</td>
<td>162.00</td>
<td>–x, 2 – y, 1 – z</td>
</tr>
<tr>
<td>C2P</td>
<td>C21–H21⋯S2</td>
<td>0.930</td>
<td>3.0230</td>
<td>3.5480(2)</td>
<td>116.00</td>
<td>1 – x, 1 – y, 1 – z</td>
</tr>
<tr>
<td>C2N</td>
<td>N4–H4⋯N1</td>
<td>0.880</td>
<td>2.6810</td>
<td>3.0760(3)</td>
<td>163.16</td>
<td>1 – x, 1 – y, 1 – z</td>
</tr>
<tr>
<td></td>
<td>N3–H3⋯S1</td>
<td>0.879</td>
<td>2.8469</td>
<td>3.6410(3)</td>
<td>141.80</td>
<td>1 – x, 1 – y, 1 – z</td>
</tr>
<tr>
<td></td>
<td>N6–H6⋯S1</td>
<td>0.949</td>
<td>2.7230</td>
<td>3.5320(3)</td>
<td>143.60</td>
<td>1 + x, 1 + y, z</td>
</tr>
<tr>
<td></td>
<td>C10–H10⋯N4</td>
<td>0.950</td>
<td>2.8812</td>
<td>3.8020(2)</td>
<td>163.60</td>
<td>2 – x, 2 – y, 1 – z</td>
</tr>
<tr>
<td>C2P</td>
<td>C2–H2⋯S2</td>
<td>0.950</td>
<td>2.9839</td>
<td>3.8270(3)</td>
<td>148.60</td>
<td>x, 1 + y, z</td>
</tr>
<tr>
<td>C1IN</td>
<td>N3–H3⋯O1</td>
<td>0.880</td>
<td>3.0140</td>
<td>3.3480(4)</td>
<td>139.30</td>
<td>x, 1/2–y, 1/2+z</td>
</tr>
<tr>
<td>C2P</td>
<td>N3–H3⋯O1</td>
<td>0.880</td>
<td>3.2140</td>
<td>3.1000(3)</td>
<td>148.70</td>
<td>x, 1/2–y, 1/2+z</td>
</tr>
<tr>
<td>C1IN</td>
<td>C2–H2⋯N4</td>
<td>0.950</td>
<td>2.6850</td>
<td>3.5830(4)</td>
<td>157.90</td>
<td>2 – x, 1/2 + y, 1/2 – z</td>
</tr>
<tr>
<td>C2P</td>
<td>C11–H11⋯O4</td>
<td>0.950</td>
<td>2.5310</td>
<td>3.1830(4)</td>
<td>113.10</td>
<td>1 – x, –1/2 + y, 1/2 – z</td>
</tr>
</tbody>
</table>
actions establish two-fold sheets of the neighbouring chains contribution in the crystal packing. Herein, \( \pi_{\text{py}} \cdots \pi_{\text{py}} \) interactions establish two-fold sheets of the neighbouring chains which are also fortified by bifurcated hydrogen bonds. The other side of the chains in the sheets is involved in \( \pi_{\text{py}} \cdots \pi_{\text{py}} \) interactions, creating the [100] chain; (b and c) side views of the crystal packing in the ac and ab planes, respectively, which show how the chains are connected in the 3D network.

Table 4  \( n \)-interaction geometries for compounds \( C_{1N}, C_{1S}, C_{2N} \) and \( C_{2P} \)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Interaction</th>
<th>C-C (Å)</th>
<th>P-P°</th>
<th>P-CC°</th>
<th>CH···Cgl</th>
<th>C···Cg (Å)</th>
<th>C-H-Cg (°)</th>
<th>Symm. code</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{1N} )</td>
<td>( \pi_{\text{py}} \cdots \pi_{\text{thiophene}} )</td>
<td>3.749</td>
<td>7.52</td>
<td>19.63</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_{1N} )</td>
<td>( \pi_{\text{py}} \cdots \pi_{\text{py}} )</td>
<td>3.486</td>
<td>0.0</td>
<td>7.88</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_{1S} )</td>
<td>( \pi_{\text{py}} \cdots \pi_{\text{py}} )</td>
<td>3.719</td>
<td>11.74</td>
<td>17.28</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_{2N} )</td>
<td>( \pi_{\text{py}} \cdots \pi_{\text{terpyridine}} )</td>
<td>3.133</td>
<td>0.0</td>
<td>5.15</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_{2P} )</td>
<td>( \pi_{\text{py}} \cdots \pi_{\text{py}} )</td>
<td>3.882</td>
<td>—</td>
<td>19.60</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_{2P} )</td>
<td>( \pi_{\text{py}} \cdots \pi_{\text{py}} )</td>
<td>3.801</td>
<td>0.0</td>
<td>28.19</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\( C_g \) stands for the centre of gravity of the mentioned ring: for \( C_{1N} \): Cg2: S2, C9–C12; Cg3: N2, C2–C6; Cg4: C13–C18; Cg6: C25–C30; for \( C_{1S} \): Cg7: C25–C30; for \( C_{2N} \): Cg2: O2, C8–C11; Cg4: C13–C18; Cg6: C25–C30; for \( C_{2P} \): Cg2: O2, C8–C11; Cg3: N1, C1–C5.

Fig. 3  (a) Representation of dimeric units in \( C_{1N} \) and their association through \( n \)-\( n \) and \( C-H \cdots n \) interactions, creating the [100] chain; (b and c) side views of the crystal packing in the ac and ab planes, respectively, which show how the chains are connected in the 3D network.
stacking and H-bonding interactions, leading to the connection of the (011) layers along the \( a \)-direction to complete the overall supramolecular association (Fig. 6b). In other words, each coordination chain is associated with four other chains in a 3D arrangement, from one side through \( \pi \text{-furyl} \rightarrow \pi \text{-furyl}, C_{11-}H_{11} \cdots N_{4} \) and \( C_{11-}H_{11} \cdots O_{1} \) linkages and from the other side by \( \pi \text{-py} \rightarrow \pi \text{-py} \) stacking and \( C_{2-}H_{2} \cdots N_{4} \) interactions (Fig. 6c). In addition, these chains are laterally linked through interesting \( S \cdots \pi \text{-py} \) interactions in the \( b \)-direction (Fig. 6d).

### NCI approach

**Principle.** The non-covalent interaction (NCI) reduced density gradient (RDG) method has been recently developed as a theoretical strategy to visualize weak interactions. Investigation of the interactions using NCI-RDG analysis is quite concordant with the traditional method that recognizes them according to distances and angles. However, the NCI-RDG technique has more accuracy and precision, as it is based on fundamental computation. It provides a rich illustration of strong attractive, van der Waals interactions and also steric repulsions. The theory rests on the analysis and the graphical interpretation of two scalar properties, charge density \( \rho \) and its derivatives, namely the \( \lambda \) eigenvalue of its Hessian and its reduced gradient \( s(\rho) \), defined as:

\[
s = \frac{1}{2(3\pi^{3})^{1/3}} \frac{|\nabla \rho|}{\rho^{4/3}}
\]

where \( \nabla \rho \) is the gradient of \( \rho \). The non-covalent interactions are located in the regions with low RDG and density. Analysis of \( \text{sign}(\lambda_{2}) \) of the electron density Hessian can be used to discern different types of interactions. For the strong ones such as H-bonds, \( \text{sign}(\lambda_{2})\rho < 0 \); for the weak van der Waals types, \( \text{sign}(\lambda_{2})\rho \approx 0 \); and for the non-bonded interactions like steric repulsion, \( \text{sign}(\lambda_{2})\rho > 0 \).

As the sign of \( \lambda_{2} \) describes the essence of the interaction, 2D plots comprising \( \text{sign}(\lambda_{2})\times \rho \) versus RDG \( s \) would indicate a non-covalent interaction near-zero area in the horizontal axis. Close contacts between atoms change the behaviour of the reduced gradient signal more compared to the contacts among the atoms present in the tails, leading to troughs in the 2D NCI plots. These troughs, specially the \( \rho \) value at the troughs, are the basis of the NCI approach. The 2D NCI plots are then applied as inputs to construct 3D NCI plots, including isosurfaces of the reduced gradient of the density enabling the spatial visualization of the close contacts.

We applied this method to unravel the nature of supramolecular interactions in the title complexes. NCI analysis has been performed on the structure of complexes including the diverse noncovalent interactions. The considered structures were cut out directly from the CIF data. Since dimerization is the prominent feature of the crystal packing in the monomeric complexes (\( C_{1N}, C_{1S} \) and \( C_{2N} \)), the main NCIs are related to the interactions involved in the formation of dimers. The 2D and 3D NCI plots of dimers are shown in Fig. 7. Accordingly, we have done calculation once on the dimers.
including only the carbohydrazone ligands (Cu⁺ and SCN⁻ ions and PPh₃ moieties have been eliminated) and again for the whole dimeric units of complexes. Some of the other interesting intermolecular interactions in the crystal structures have also been investigated by the NCI method. The presence of noncovalent interactions is characterized by spikes at negative to near-zero sign of $\lambda^2$, whereas the peaks at positive sign indicate the repulsive steric contacts due to the ring formation. The spikes at the zero area ($\lambda^2\rho$ between ±0.015 au.) show vDW interactions. Notable points of the NCI calculations have been illustrated in the following:

(i) As shown in Fig. 7, for the ligand dimers, the spikes that appeared at 0.024 au. belong to the pyridine ring closure. These spikes shift to lower values (less repulsion) in the whole dimeric units of complexes. It can be explained by the effect of metal ion in the charge redistribution as well as the electrostatic interaction between atoms within the rings.

(ii) In the case of C_{1S}, the thiophene ring closure spike ($\lambda^2\rho$) is located between 0.042 and 0.044 au. while in the 2D plot and the 3D isosurface of C_{2N}, the furyl ring has a much lesser repulsion of ring closure than the thiophene alternative. It may be caused by the greater charge perturbation due to the presence of an oxygen atom which leads to more electrostatic interactions. Consistent with this, natural bond orbital (NBO) analysis also reveals the stabilizing energy of 54 kcal mol⁻¹ for the electronic delocalization “lone pair (O) → $\pi^*$ (C–C) orbital” which is more than that for the corresponding charge transfer energy in the thiophene ring (LP(S) → $\pi^*$ (C–C); 48 kcal mol⁻¹).

(iii) C_{1N} and C_{1S} compounds are linkage isomers, in a way that SCN⁻ is coordinated from N or S atoms, respectively. Optimization of the isomers, in the gas phase and also acetonitrile and chloroform solutions, indicates that the stability of C_{1S} is approximately 3–4 kcal mol⁻¹ less than that of C_{1S}; however, it has been also formed in the solid state. The formation of C_{1S} can be attributed to stronger intermolecular attractions particularly those involved in dimerization which compensate for the lesser stability of the discrete units of C_{1S}. RDG isosurfaces show stronger interactions in the C_{1S} dimer rather than in C_{1N}. Counterpoise calculations at the M06-2X/6-311G* level indicate that the binding energy of two complexes in a dimer, $\Delta E_{\text{dimer}}$, for C_{1S} is 2.8 kcal mol⁻¹ more than for C_{1N} as well.

Fig. 5 (a) Representation of dimeric units in C_{2N}; (b) association of these units through $\pi$–$\pi$ and C–H⋯$\pi$ interactions, creating the [100] chain; (c) and (d) side views of the crystal packing in the ab and ac planes, respectively; which show how the chains are connected in the 3D construction (PPh₃ moieties in (c) were omitted for more clarity).
(iv) It was thought to be of interest to further investigate the sulfur interactions to figure out their nature in the solid state structures. The sulfur atom, due to its large van der Waals radius and high polarizability, is able to establish several interactions with its local environment. Morgan and co-workers first proposed the hypothesis that a strong interaction exists between aromatic rings and divalent sulfur atoms. The importance of the $S\cdots\pi$ aromatic interaction is revealed in the high degree of its conservation across members in protein folding and stabilization.

Conclusions

Diverse coordination structures from the reaction of CuSCN with PPh$_3$ and ortho-pyridinyl carbonyldrazone containing a thiophene ($L_1$) or furyl ring ($L_2$) were presented. A mixture of thiocyanate linkage isomers, $C_{1N}$ and $C_{2S}$, was obtained for $L_1$, while the reaction with $L_2$ rendered two monomeric and polymeric compounds, $C_{2N}$ and $C_{2P}$, respectively. The molecular and supramolecular structures of these systems were elucidated using X-ray diffraction. The structure-directing interactions were also investigated by NCI-RDG calculations.

Pyridine, thiophene and furyl rings, the polarized aromatic systems, have an important role in governing the supramolecular assembly of the complexes by establishing $\pi\cdots\pi$ interactions. However, the coordination of sulfur to the Cu(I) atom in $C_{1S}$ leads to supernumerary slippage of the neighbouring molecules which prevents the formation of $\pi_{\text{py}}\cdots\pi_{\text{thiophene}}$ connections. CH–$\pi$ interactions between PPh$_3$ moieties contribute to further stabilization of the self-association in the monomeric complexes ($C_{1N}$, $C_{1S}$ and $C_{2N}$).

A prominent feature of the crystal packing in the monomeric complexes is the formation of the dimeric motifs via hydrogen bonding and $\pi\cdots\pi$ stacking interactions. Formation of the less stable S-bound isomer $C_{1S}$ can be attributed to stronger intermolecular attractions particularly those involved in dimerization which compensate for the lesser stability of the discrete units of $C_{1S}$ compared to $C_{2N}$.
Another interesting feature of the solid state structures is the presence of the lesser known S⋯S and S⋯π interactions. NCI-RDG analysis clearly indicates the significant contribution of these interactions in maintaining favourable packing interactions in the complex.

**Experimental**

**Materials and methods**

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker (Avance DRS) 250 MHz spectrometer. IR spectra were recorded on a Nicolet 510P spectrophotometer using KBr disks. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

**Synthesis procedures**

The ligands were prepared from the reaction of two equivalent amounts of 2-thiophenecarboxylic acid hydrazide or 2-furoic hydrazide and 2-pyridinecarboxaldehyde in methanol solution. A solution of ligand (0.20 mmol) in CHCl$_3$ (4 mL) was added dropwise to a stirred solution of a mixture of copper(I) thiocyanate (0.20 mmol) and triphenylphosphine (0.20 mmol) in CH$_3$CN (2 ml). The colour of the reaction mixture turned from orange to red. The reaction mixture was filtered; slow diffusion of diethyl ether in the filtered solution afforded suitable single crystals (total yields for the mixture of C$_{1N}$ and C$_{1S}$: 81%, and for that of C$_{2N}$ and C$_{2P}$: 76%). The complexes were obtained in good yields. Physical and spectroscopic data of the compounds are presented below:

(ortho-Thiophene)C(O)NHNCH$_2$(ortho-pyridine) (L$_1$). Mp: 177–179 °C. Selected IR peaks (cm$^{-1}$): 3433 w, 3065 w, 1641 s, 1584 m, 1374 s, 1157 m, 733 m. $^1$H NMR (CDCl$_3$, δ ppm): 7.20–7.35 (m, 2H), 7.73–7.81 (m, 2H), 8.18–8.26 (m, 3H), 8.66 (s, 1H), 10.52 (s, 1H).

(ortho-Furyl)C(O)NHNCH$_2$(ortho-pyridine) (L$_2$). Mp: 157–160 °C. Selected IR peaks (cm$^{-1}$): 3422 w, 3005 w, 1662 s, 1579 s, 1468 m, 1308 m, 1187 m, 756 m. $^1$H NMR (CDCl$_3$, δ ppm): 6.49 (s, 1H), 7.25–7.53 (m, 3H), 7.69 (s, 1H), 8.10 (d, 1H), 8.41–8.55 (d, 2H), 10.64 (s, 1H). $^{13}$C NMR (CDCl$_3$, δ ppm): 112.23, 116.32, 121.16, 124.26, 125.69, 136.48, 137.68, 144.82, 148.17, 148.27, 152.81.

[Cu(NCS)[$L_1$]PPh$_3$] (C$_{1N}$). Orange crystals. Mp: 211–214 °C. Anal. calcd for C$_{30}$H$_{24}$CuN$_4$OPS$_2$: C, 58.57; H, 3.93; N, 9.11. Found: 58.49; H, 3.96; N, 9.17. Selected IR peaks (cm$^{-1}$): 3437 s, 2925 s, 2032 s, 1670 m, 1540 m, 1431 w, 1264 s, 1142 w, 696 s, 517 w.

[Cu(SCN)[$L_1$]PPh$_3$] (C$_{1S}$). Red crystals. Mp: 211–213 °C. Anal. calcd for C$_{30}$H$_{24}$CuN$_4$OPS$_2$: C, 58.57; H, 3.93; N, 9.11. Found: 58.41; H, 3.90; N, 9.15. Selected IR peaks (cm$^{-1}$): 3437 s, 2927 w, 2074 m, 1665 m, 1545 m, 1426 w, 1226 m, 1126 w, 703 m, 512 m.

**Fig. 7** Left: The NCI RDG s vs. sign($\lambda_2$)/$\rho$ plots for dimers of ligands and complexes. Right: Coloured RDG-based NCI isosurfaces for the dimers of complexes.
[Cu(NCS)(I$_2$)PPh$_3$] (C$_{2N}$). Orange crystals. Mp: 204–206 °C. Anal. calcd for C$_{30}$H$_{24}$CuN$_4$O$_2$PS: C, 60.14; H, 4.04; N, 9.35. Found: 60.21; H, 4.05; N, 9.41. Selected IR peaks (cm$^{-1}$): 3435 w, 2083 s, 1686 s, 1533 m, 1469 s, 1284 s, 1179 s, 752 m, 696 m, 516 m.

[–(NCS)Cu(I$_2$)–]$_n$ (C$_{2P}$). Dark orange crystals. Mp: 238–240 °C (decomp.). Anal. calcd for C$_{12}$H$_9$CuN$_4$O$_2$S: C, 42.79; H, 2.69; N, 16.63. Found: 42.68; H, 2.69; N, 16.60. Selected IR peaks (cm$^{-1}$): 3277 w, 2112 s, 1672 s, 1543 m, 1464 m, 1295 m, 1186 m, 771 w.

Crystal structure determination

Single crystal X-ray diffraction data were collected for all compounds on an Agilent Gemini Ultra diffractometer equipped with an Eos CCD area detector and using either Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) or Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å). The data were collected at 173 K using an Oxford Cryosystems Cryostream 600. The data were processed with CrysAlisPro.$^{49}$ Semi-empirical absorption corrections were carried out using the Multi-Scan$^{50}$ program. The structures were solved by direct methods using SHELXT$^{51}$ and refined with full matrix least squares refinement using SHELXL-2013 (ref. 52) within Olex2.$^{53}$ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at calculated positions and refined using a riding model based on the parent atom. The CIF files have been deposited with the CCDC and have been given the deposition numbers 1401344, 1401345, 1469718 and 1469717 for C$_{1N}$, C$_{1S}$, C$_{2N}$ and C$_{2P}$, respectively.

Computational details

The NCI technique was carried out through the analysis of the reduced density gradient (RDG) with low densities$^{33}$ at the ωB97XD$^{54}$/6-311+G** level using the Gaussian 09 package$^{55}$ and Multiwfn program.$^{56}$ The calculated grid points are plotted for a defined real space function, sign($\lambda$(r))$\rho$(r) and reduced density gradient (RDG) and a visualization of the

Fig. 8 RDG-based NCI surfaces for S···S and S···π interactions.
gradient isosurface was depicted using the VMD 1.9.2 software. The colour of the isosurfaces was decided using the value of sign($\lambda_2$). Blue, green and red colour codes are commonly used to describe stabilizing H-bonding, van der Waals and steric interaction, respectively. Pictures are provided for an isosurface value of $s = 0.5$.

Natural bond orbital (NBO) analysis was performed on the crystal structure of the complexes using the NBO 3.1 module in Gaussian 09 at the B3LYP/6-311+(g)** level of theory. The binding energy of two complexes in a dimer, $\Delta E_{\text{dimer}}$, for $\text{C}_1\text{N}_1\text{C}_2\text{N}_2$ were calculated at the M062X/6-311G* level based on the energy difference between the dimer and its units. The interaction energies have been corrected for the basis set superposition error (BSSE) using the counterpoise (CP) procedure.

Acknowledgements

Financial support of this work by Tarbiat Modares University is gratefully acknowledged.

Notes and references

35. (a) H. Akpinar, J. T. Mague and P. M. Lahti, CrystEngComm, 2013, 15, 831; (b) M. M. Naseer and S. Hameed, CrystEngComm, 2012, 14, 4247; (c) B. Sarma, L. S. Reddy and...


