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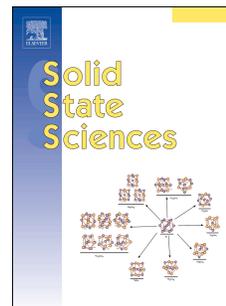
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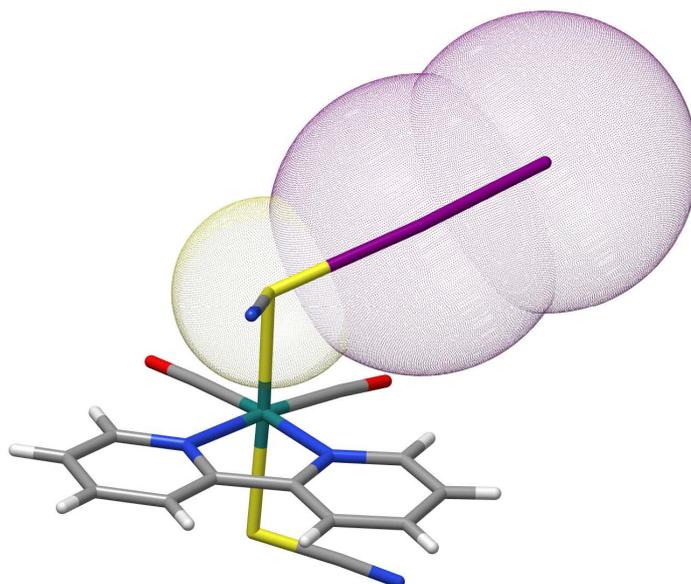
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Graphical abstract for

**Halogen Bond Preferences of Thiocyanate Ligand
Coordinated to Ru(II) via Sulphur Atom**Xin Ding,^a Matti Tuikka,^a Pipsa Hirva^b and Matti Haukka,^a^a University of Jyväskylä, Department of Chemistry, P.O.Box 35, FI-40014 University of Jyväskylä, Finland. E-Mail: matti.o.haukka@jyu.fi.^b University of Eastern Finland, Department of Chemistry, P.O. Box 111, FI-80101 Joensuu, Finland.

Halogen bonding (XB) between $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S}-\text{SCN})_2]$ (bpy = 2,2'-bipyridine) and I_2 was studied by co-crystallizing the metal compound and diiodine from dichloromethane solution. Halogen bond between Ru coordinated S and I_2 was found to be the preferred halogen bond mode. No crystalline XB adduct with $\text{I}\cdots\text{N}$ contact was observed.

Halogen Bond Preferences of Thiocyanate Ligand Coordinated to Ru(II) via Sulphur Atom

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KEYWORDS: *Halogen bond; Ru; Iodine; thiocyanate*

Abstract: Halogen bonding between $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ (bpy= 2,2'-bipyridine), I_2 was studied by co-crystallising the metal compound and diiodine from dichloromethane. The only observed crystalline product was found to be $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ with only one $\text{NCS} \cdots \text{I}_2$ halogen bond between I_2 and the metal coordinated S atom of one of the thiocyanate ligand. The dangling nitrogen atoms were not involved in halogen bonding. However, computational analysis suggests that there are no major energetic differences between the $\text{NCS} \cdots \text{I}_2$ and $\text{SCN} \cdots \text{I}_2$ bonding modes. The reason for the observed $\text{NCS} \cdots \text{I}_2$ mode lies most probably in the more favourable packing effects rather than energetic preferences between $\text{NCS} \cdots \text{I}_2$ and $\text{SCN} \cdots \text{I}_2$ contacts.

Introduction

Halogen bond (XB) refers to non-covalent interactions between a polarised halogen atom with its electron-poor region (Lewis acid) and an entity (molecule, atom, or anion) with an electron-rich region (Lewis base).[1] In this context the Lewis acid is called XB donor and the Lewis base as XB acceptor. Halogen bond as a tool for crystal engineering has attracted increasing interests since 1990s, due to its comparable bond strength to hydrogen bond, strong directionality, and more hydrophobic nature compared with hydrogen bond.[2-11] Most commonly used XB donors are organic halogen compounds but entities such as dihalogens or halonium ions can also act as donors.[1] Typically, XB donors follow a general rule that the more easier polarizable halogen atoms tend to form stronger the XB bonds.

In principle, any Lewis acid can act as XB acceptor. A variety of molecules with different electron donor atoms including oxygen, sulphur, nitrogen, and selenium as well as organic molecules with π -system have been reported as useful XB acceptors. In addition, metal complexes with suitable ligands, such as halogen atoms [12-14] or pseudohalogen groups [14-16], can also serve as XB acceptors. Thiocyanate ion is basically ambivalent ligand that can coordinate both through its nitrogen and sulphur atoms. Therefore, SCN^- ion as well as metal coordinated SCN -ligand can be involved as acceptor in halogen bonds that can be rationalized by σ -hole theory [6]. Thiocyanate can also participate in halogen interactions in which the donor-acceptor nature of the participating components is less obvious [17-29]. In principle both N, S ends of the thiocyanate can serve as halogen bond acceptor [17]. It has been suggested that the soft-hard nature of the two terminal atoms may play a significant role in formation of halogen bonds. It means that the soft sulphur end favours soft halogen bond donors such as iodine [17].

It is obvious that nitrogen-coordinated thiocyanate can only form halogen bonds through its sulphur atom since in this case the nitrogen atom is no longer available for further interactions. Adduct between $[\text{Ru}(\text{dcbpy})_2(\text{N-NCS})_2]$ and I_2 is a good example of such a case [16]. It also shows that sulphur can be involved in more than one XB simultaneously. There are some previous examples where S-coordinated thiocyanate forms a halogen bond or halogen interactions with soft halogen bond donor through its softer sulphur atom despite the sulphur is coordinated to a metal [28-29]. However, in most of these cases the thiocyanate nitrogen is either coordinated to another metal centre [28] or involved in hydrogen bonding [29].

In the current paper we investigated halogen bonding preferences of S-coordinated thiocyanate by co-crystallising $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-NCS})_2]$ with very soft halogen bond donor I_2 . Energetics and both possible halogen bond contacts, $\text{NCS}\cdots\text{I}_2$ and $\text{SCN}\cdots\text{I}_2$, were compared by computational QTAIM method [30].

Results, discussion

Crystals of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]\cdot\text{I}_2$ (**S \cdots I**)

Co-crystallisations of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ with I_2 from CH_2Cl_2 were carried out by using different molar ratios of the metal complex and I_2 (1:1, 1:2, 1:5, 1:10). In all cases the only observed crystalline product was an adduct where iodine formed halogen bond through sulphur (Figure 1). This happened even if the N-end of SCN had more sterical freedom for halogen bonding than the Ru coordinated S atom. Such results indicate a clear preference for soft-soft $\text{I}\cdots\text{S}$ contacts over soft-hard $\text{I}\cdots\text{N}$ interaction. On the other hand, the fact that only one of the thiocyanates was halogen bonded even if the amount of I_2 was increased 10-fold, may indicate that packing effects (i.e. other weak interactions) actually play a pivotal role in formation of the primary crystalline product.

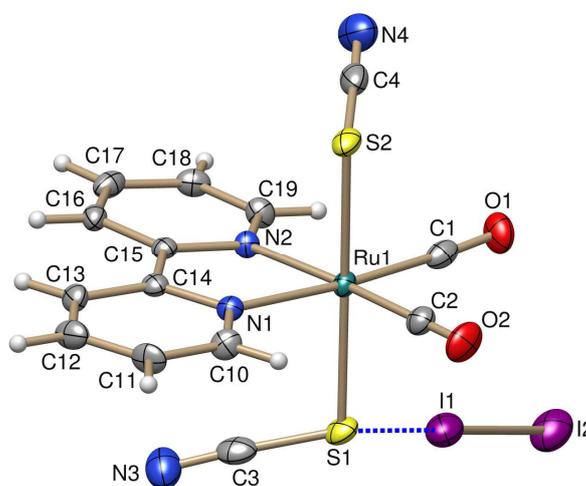


Figure 1. Crystal structure of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]\cdot\text{I}_2$ (**1**). The anisotropic displacement ellipsoids are drawn at 50 % probability level. Selected bond lengths (\AA) and angles ($^\circ$): Ru1-S1: 2.445(2), S1-C3: 1.658(8), C3-N3: 1.166(10), Ru1-S2: 2.422(2), S2-C4: 1.668(8), C4-N4: 1.148(10), S1 \cdots I1: 3.146(2), I1-I2: 2.7143(8), Ru1-S1-C3: 103.5(2), S1-C3-N3: 177.1(7), Ru1-S2-C4: 102.0(3), S2-C4-N4: 176.8(7), Ru1-S1 \cdots I1: 107.62(6), I2-I1 \cdots S1: 172.87(4), C3-S1 \cdots I1: 113.3(3).

In the structure shown in Fig. 1, the iodine atom I1, acts as XB donor and the sulphur atom, S1, as XB acceptor. As mentioned above, the other thiocyanate sulphur S2 is not involved in halogen bonds. Similarly, only one end of I_2 participates in XB contacts. The S1 \cdots I1 distance is 3.146(2) \AA , which is about 83% of the sum of Bondi's van der Waals radii of I and S [30]. The angle I2-I1 \cdots S1 is nearly linear (172.87(4) $^\circ$) as expected in a XB system with I_2 donor. The Ru1-S1 \cdots I1 and Ru1-S1-C3 angles of 107.62(6) $^\circ$ and 103.5(2) $^\circ$ are in line with bonds

and contact angles found in compounds that contain ruthenium coordinated SCN ligands [32-36].

Topological QTAIM charge density analysis

The goal was to study if the soft-soft I...S halogen bond is energetically favoured over soft-hard I...N interaction by comparing $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ molecule and $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]\cdot\text{I}_2$ adducts with I...S and I...N halogen bonds. Computationally established models of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ molecule as well as its I...S and I...N halogen bonded I_2 adducts were optimized to the energetically most favourable geometries using DFT technique. The obtained geometries with selected bond distances, angles are presented in Figure 2.

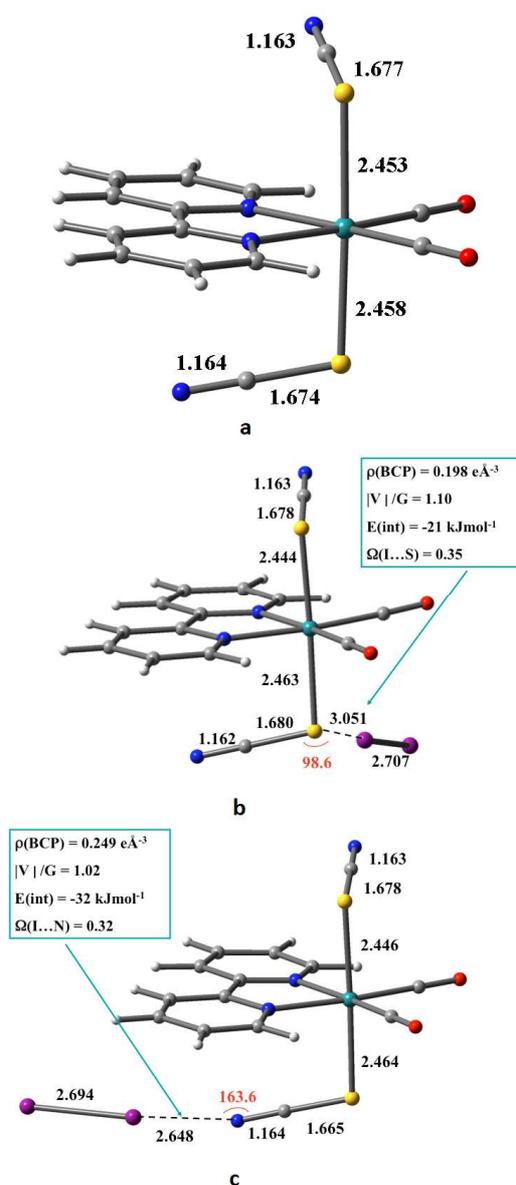


Figure 2. Optimized structures of the models for a) an isolated $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ complex, b) molecular complex in the co-crystal structure with S...I contact, c) molecular complex in the co-

crystal structure with N...I contact. Colour scheme is the same as that of Figure 1. Legends include selected properties of the electron density at the (I, N) or (I, S) bond critical points: $\rho(\text{BCP})$ =electron density at the bond critical point; $|V|/G$ =ratio between potential energy density, kinetic energy density; $E(\text{int})$ = interaction energy at the BCP, Ω =delocalization index between I atom and N or S atoms.

The variations in selected bond lengths, XB bond angles between the computational and experimentally obtained structures are due to the gas-phase calculations that tend to overestimate charge transfer effect and interactions between the ruthenium molecule, I_2 . This can be seen in shorter computational XB distance compared to the experimental results [17]. On the other hand, omitting the crystal environment should reveal possible differences in the actual I...S and I...N interaction energies and properties without interference of any packing effects. In addition to AIM parameters shown in Fig. 2, also the AIM defined atomic charges were calculated (Table 1).

Table 1. Atomic charges according to the AIM analysis for Ru, I, N, and S atoms in different configurations of the adducts $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S}-\text{SCN})_2] \cdot \text{I}_2$

Atom ^a	$[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S}-\text{SCN})_2]$	I...N	I...S
q(Ru)	0.949	0.951	0.949
q(S1)	0.120	0.163	0.146
q(S2)	0.113	0.121	0.123
q(N3)	-1.198	-1.231	-0.166
q(N4)	-1.191	-1.184	-0.180
q(I1)	—	0.095	0.008
q(I2)	—	-0.156	-0.135

^aNumbering scheme the same as in Fig.1.

It is known that strong XB contact with charge transfer or electron sharing will polarize the I_2 molecule [13,37]. The negative charge tends to accumulate on the iodine, which is not involved in halogen bonding (I2 in Fig.1). Similarly, the XB-bonded iodine (I1) is getting more positive charge. According to the AIM results, interaction of I_2 with the “hard” nitrogen atom induces more effective polarization on diiodine molecule than when I_2 is interacting with the “soft” sulphur atom. This generates larger charge difference between the two ends of I_2 . The ratio of potential energy density and kinetic energy density, $|V|/G$, at the bond critical point is indicative of the nature of the contact. If $|V|/G > 2$ the contact is a shared shell interaction (covalent) and if $|V|/G < 1$ the interaction is electrostatic [38-40]. Values between one and two indicate intermediate

between the two type of interactions. Another parameter defining the nature of the contact is delocalisation index Ω [38-40]. In an ideal pure electrostatic system the value of Ω should be close to zero and in a single covalent bond close to 1. In the case of I \cdots N and I \cdots S systems, there are no major differences in these two parameters (Fig. 2). In both systems the interaction is essentially electrostatic with some minor covalent character. It has been suggested that increase in charge transfer or electron sharing from the XB acceptor to donor will also elongate the I-I distance [13-37]. However, the longer I-I distance in I \cdots S adduct, where the charge difference between iodine atoms is smaller, does not support effect of charge transfer as the main reason for slight difference in I-I distance. It may be that small increase in electron sharing could be the reason for the longer I-I bond in this case.

The difference in interaction energies, $E(\text{int})$, between the I \cdots N and I \cdots S systems quite small, 11 kJ/mol, and can be overcome *via* other stabilising interactions in the crystal structure. According to the interaction energies the I \cdots N adduct should actually be the slightly more favourable one when these systems are compared. Obviously, none of the computational results rule out the existence of the observed sulphur-iodine interaction. Based on the over all similarity of the computational results of the two configurations, both structures should be fully possible and one should be able to isolate both of them. The fact that only I \cdots S crystals could be found suggests that the main factor, which determines the preferred primary crystalline form is due to the packing effects i.e. other weak intermolecular interactions. In other words, the overall packing of adduct with I \cdots S is simply more favourable.

In order to investigate the weak interactions in the crystal structure in more detail, we performed QTAIM analysis on the extended model comprising one I₂ molecule surrounded by five [Ru(bpy)(CO)₂(SCN)₂] complexes. The resulting bond paths and BCPs can be seen in Fig. 3. In addition to the main I \cdots S interactions, there are much weaker intermolecular I \cdots N and several CO \cdots I interactions from the neighbouring carbonyl complexes. Although the interaction energies are small, varying between -2 and -5 kJ/mol, and the nature of the CO \cdots I interaction is clearly electrostatic ($|V|/G \sim 0.8$), they are able to provide extra support for the sulphur coordination and explain the preference found in the

crystal structure of the adduct. It should be noted, that in the extended model, a weak I...N interaction is also found, supporting the computationally found similarity of the two halogen bond sites.

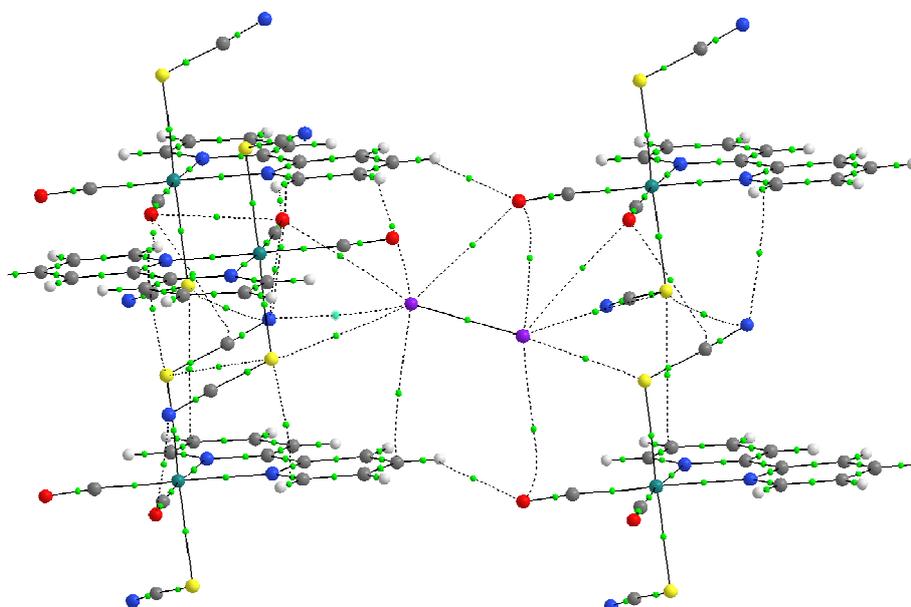


Figure 3. Bond paths and bond critical points (green dots) in the extended $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]_5 \cdot \text{I}_2$ model of the crystal structure.

Since experimental results showed that only one of the SCN ligands is involved in halogen bonding, we decided to analyse computationally if there are energetic reasons preventing formation of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot 2\text{I}_2$ adducts (Fig. 4). The results indicate that there is a little more electron sharing involved in I...S adducts and energetically the I...N mode should be slightly more favourable. However, despite the small differences both modes of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot 2\text{I}_2$ should be fully possible.

The nature of the frontier molecular orbitals was calculated to compare the doubly interacting compounds with adducts of only one diiodine. The appearance of the FMOs can be seen in Fig. 5. Regardless of the interaction site, whether it is the nitrogen or the sulphur end, the energies of HOMOs were found comparable with the systems having only one interacting SCN ligand. It means that the second XB contact is not contributing considerable additional

stabilization to the system. On the other hand, the LUMOs are stabilized in the doubly interacting system, which indicates reduced stability, when both SCN ligands are involved in halogen bonding.

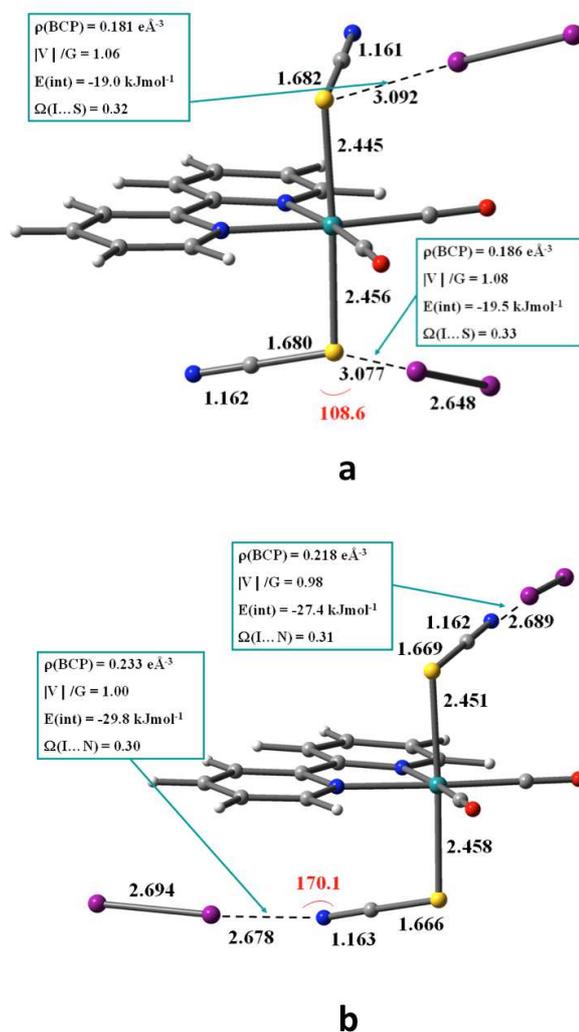


Figure 4. Optimized structures for interaction of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ with two I_2 molecules.

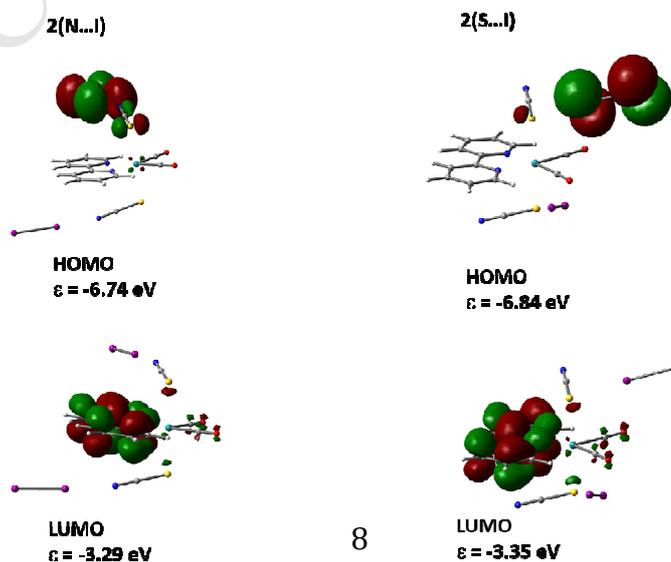


Figure 5. Frontier molecular orbitals of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot 2\text{I}_2$

Experimental

Synthesis

All starting materials are from Sigma-Aldrich or from Johnson & Matthey and were used as received. The synthesis of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ was carried out following the previously reported procedure [36]. The adducts were obtained by dissolving $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ and I_2 in CH_2Cl_2 and mixing the solutions at room temperature. A series of reactions were carried out varying the molar ratio of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ and I_2 (1:1, 1:2, 1:5, 1:10). After careful mixing the combined $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]/\text{I}_2$ solution was placed in a vial covered with parafilm. Crystals were obtained by using slow evaporation technique at room temperature. X-Ray quality crystals were collected after three days and the yield of crystalline $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ adduct range from 33%-45%. When collecting the product the solution was not allowed to evaporate to dryness. Among the collected crystalline material the dark red $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ was the only crystalline reaction product. The residual material consisted of starting compounds $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2]$ and I_2 . No other products were observed. The synthesis was not optimized for maximum yield. The goal was to collect the initial crystalline material to analyse the preferred primary product.

Crystal structure determinations

The crystal of $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ was immersed in cryo-oil, mounted in a MiTeGen loop, and measured at 170 K on a Rigaku Oxford Diffraction Supernova diffractometer using $\text{Mo K}\alpha$ ($\lambda = 0.71073$) radiation. The *CrysAlisPro*⁴² program package was used for cell refinement and data reduction. Multi-scan absorption correction (*CrysAlisPro*) was applied to the intensities before the structure solution. The structure was solved by charge flipping method using the *SUPERFLIP*⁴³ software. Structural refinements were carried out using *SHELXL*-

2016.⁴⁴ Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95 Å, $U_{\text{iso}} = 1.2 \cdot U_{\text{eq}}$ (parent atom). The crystallographic details are summarized in Table 2.

Table 2. Crystal Data.[†]

Empirical formula	$\text{C}_{14}\text{H}_8\text{I}_2\text{N}_4\text{O}_2\text{RuS}_2$
fw	683.23
Temp (K)	170(2)
λ (Å)	0.71073
cryst. syst.	Triclinic
Space group	$P \bar{1}$
a (Å)	7.2729(3)
b (Å)	10.9807(4)
c (Å)	12.5479(4)
α (deg)	79.278(3)
β (deg)	74.862(4)
γ (deg)	82.918(4)
V (Å ³)	947.49(7)
Z	2
ρ_{calc} (Mg/m ³)	2.395
μ (Mo K α) (mm ⁻¹)	4.322
No. reflns.	7362
Unique reflns.	4642
GOOF (F ²)	1.032
R_{int}	0.0165
$R1^a$ (I $\geq 2\sigma$)	0.0469
$wR2^b$ (I $\geq 2\sigma$)	0.1297

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Computational details

All single molecule models were fully optimized with the Gaussian 09 programme package [45] at the DFT level of theory with a hybrid functional PBE0 [46]. The selected basis set included the standard all-electron basis 6-311++G(d, p) for C, H, S, N atoms, and relativistic effective core potential basis sets LANL2DZspdf for I atoms [47] and LANL2TZ (f) for Ru [48]. The DFT wave function was used in the topological charge density analysis with QTAIM [30], which was performed with AIMALL program [49].

The geometry of the extended model $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{SCN})_2]_5 \cdot \text{I}_2$ was taken directly from the experimental crystal structure, and the charge density analysis of the weak interactions was done without further optimization using the wavefunction obtained at the same DFT level than the smaller models.

Conclusions

Halogen bond preferences of the S-coordinated thiocyanate in $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ adduct were studied by using computational methods. Experimentally, soft XB-donor I_2 was found to favour soft sulphur atom as the primary XB acceptor. However, DFT and QTAIM analysis indicate that the XB contact between the dangling nitrogen of Ru-SCN and the I_2 donor should also be stable. In fact, energetically this should even be slightly more favourable option compared to the observed XB-system. Also, computational results indicate that both SCN-ligands should be able to act as XB acceptors simultaneously. The fact that only one of the thiocyanates was found to be involved in halogen bonding in experimental structure is most probably due to the highly favourable packing of the experimentally observed $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ adduct. It has been suggested that soft XB acceptors favour soft XB donors such as I_2 . This could explain that the only observed crystalline product was $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{S-SCN})_2] \cdot \text{I}_2$ with $\text{I} \cdots \text{S}$ contact. However, computational analysis did not reveal any strong evidence that $\text{I} \cdots \text{S}$ interaction is energetically superior to $\text{I} \cdots \text{N}$ contact. The reason for $\text{I} \cdots \text{S}$ contact as the primary halogen bond mode can be found from the packing effects, especially from supporting weak $\text{CO} \cdots \text{I}$ contacts, which further stabilize the preferred crystal structure.

Acknowledgements

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Supporting information

†CCDC 1524888 contains the supplementary crystallographic data for compound $[\text{Ru}(\text{bpy})(\text{CO})_2(\text{SCN})_2] \cdot \text{I}_2$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336- 033; or e-mail: deposit@ccdc.cam.ac.uk

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ACCEPTED MANUSCRIPT

Highlights

- Halogen bond preferences of ruthenium coordinated SCN-ligands with I₂ halogen bond donor have been studied.
- The reason for the observed NCS...I₂ mode lies most probably in the more favourable packing effects rather than energetic preferences between NCS...I₂ and SCN...I₂ contacts.
- The preferred contact is supported especially by weak CO...I contacts.