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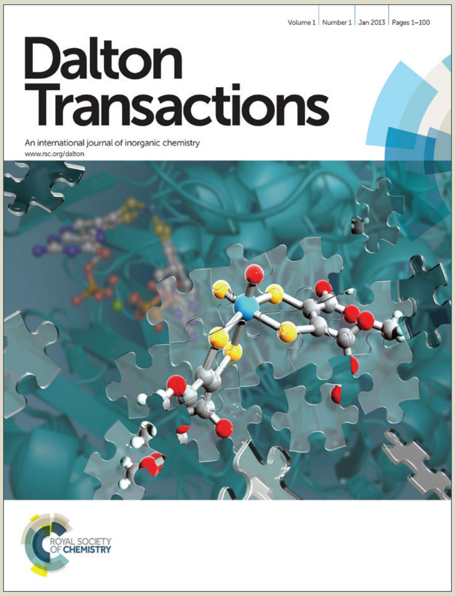

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ARTICLE TYPE

The influence of H-bonding on the 'ambidentate' coordination behaviour of thiocyanate ion to Cd(II): A combined experimental and theoretical study

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Two new trinuclear hetero-metallic copper(II)–cadmium(II) complexes $[(CuL)_2Cd(NCS)_2]$ (**1**) and $[(CuL^R)_2Cd(SCN)_2]$ (**2**) have been synthesized using [CuL] and $[CuL^R]$ as "metalloligand" (where H_2L = N,N′-bis(salicylidene)-1,4-butanediamine and H_2L^R = N,N′-bis(2-hydroxybenzyl)-1,4-butanediamine) respectively. Both the complexes were characterized by elemental analysis, various spectroscopic methods and single crystal XRD. Complex **1** is an angular trinuclear species, in which two terminal four-coordinate square planar "metalloligand" [CuL] are coordinated to a central Cd(II) through double phenoxido bridges along with two mutually *cis* nitrogen atoms of terminal thiocyanate ions. In complex **2**, which is linear, in addition to the double phenoxido bridge, two SCN^- coordinate to the *trans* positions of the central octahedral Cd(II) *via* S atoms. Theoretical calculations on the energetic difference between the two possible coordination modes of the thiocyanate anion to the Cd atom reveal that N-coordination is preferred over S-coordination in agreement with the much more abundance of the reported N-bonded structures. In **2**, there is a strong N–H···NCS–Cd H-bonding interaction, binding energy of which is computed to be approximately –9.3 kcal/mol, which is sufficient to compensate the 9.0 kcal/mol of energetic cost due to the Cd–SCN coordination unusual mode.

Introduction

The linear triatomic pseudohalide, thiocyanate (SCN^-) is a versatile ambidentate ligand with two donor atoms N and S.[1-4] It provides very interesting examples of linkage isomerism[5-7] in coordination chemistry, which are essential part of many undergraduate chemistry text books[8] to visualize the HSAB (hard soft acid base) principle[9] and its interplay with the steric and electronic effects around the metal centres.[10] It coordinates to hard metal centers through nitrogen end and soft centers *via* sulfur end. If the metal centers are border line one, like Cd^{2+}, then it can coordinate through either nitrogen or sulfur atom. The electronic and steric factors of the other ancillary ligands[11] attached to the metal ion have a very great effect on the coordination behavior of SCN^- ion. If the ancillary ligands increase the electron density on the metal center then thiocyanate ion uses preferentially the S end in binding to the metal by using π acceptor MO. On the other hand, the electron withdrawing ligands decrease the electron density on metals and SCN^- ion prefers to bind through the π-donor MO of N end.[12] However, the stability of the N-bonded and S-bonded compounds cannot be explained by electronic arguments alone as steric effect also plays an important role.[13] Generally, the SCN^- ion is linear when N-bonded[14] and bent when S-bonded.[15] Because of the greater steric requirement of the bent S-bonded thiocyanate, bulkier ancillary ligands favour coordination through N-atom. The bonding of SCN^- to borderline metal ions through either N or S in different complexes is therefore generally rationalized in terms of a balance between steric and electronic effects.

A CSD search (*vide infra*) of the terminally coordinated SCN^- to Cd reveals that there are 186 X-ray structures (257 fragments) where thiocyanate is coordinated to Cd through N atom and only in 17 structures (23 fragments) where the SCN^- is coordinated to Cd through the S atom (Cd···SCN) indicating a clear preference for the N coordination to Cd(II). Unlike other borderline metal ions such as Pd(II)[16] and Pt(II)[17] the 'ambidentate'[4,10] coordination behavior of thiocyanate to Cd(II) in most cases cannot be explained by steric and electronic effects. However, a careful look into the structures of the terminally coordinated thiocyanate to Cd(II) reveals that in majority of the complexes the free N atom or the S atom is involved in H-bonding which may be assumed to play a key role in stabilizing a particular structure. The N atom being more electronegative is capable of stronger H-bond formation and therefore, greater possibility of H-bonding should facilitate S-coordination to Cd(II).

In order to study this effect in a systematic way we synthesize and structurally characterized a trinucler complex $[(CuL)_2Cd(NCS)_2]$ (**1**) where H_2L = N,N′-bis(salicylidene)-1,4-butanediamine. The thiocynate ions show usual N-coordination to the Cd ion.To increase the possibility of the formation of H-bonding but keeping the ligand system similar, we reduced the C=N bonds of the Schiff base to produce N,N′-bis(2-hydroxybenzyl)-1,4-butanediamine (H_2L^R) and using it we synthesize the complex $[(CuL^R)_2Cd(SCN)_2]$ (**2**). The structure of the compound vindicate our prediction as the thiocyanate ions are S-bonded to Cd(II) and the N atoms are strongly H-bonded to the imine hydrogen. To have a deeper insight as well as quantitative idea a theoretical study has been performed using DFT calculations at the BP86-D3/def2-TZVPD level of theory and it is shown that the N coordination to Cd(II) is energetically favored one but formation of H-bond involving the uncoordinated N atom can tilt the balance toward apparently disfavoured Cd–SCN coordination.

Experimental

Starting materials

The salicylaldehyde, 1,4-butanediamine, sodium borohydride were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Synthesis of the Schiff base ligand N,N′-bis(salicylidene)-1,4-butanediamine (H_2L) and the "metalloligand" [CuL]

The di-Schiff base ligand was synthesized by a standard method. 5 mmol of 1,4-butanediamine (0.440 g) was mixed with 10 mmol of the salicylaldehyde (1.04 mL) in methanol. The resulting solution was refluxed for *ca.* 4 h, and allowed to cool in a freezer for overnight. The yellow solid mass was collected by filtration and then washed with cold methanol. This yellow mass was dissolved in methanol by simple heating on water-bath for 10 min. The methanolic solution (H_2L) was used directly for complex formation. To a methanolic solution (20 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.852 g, 5 mmol) was added a methanolic solution of H_2L (5 mmol, 10 mL) to prepare the "metalloligand"[CuL][18].

Synthesis of the reduced Schiff base ligand, N,N′-bis(2-hydroxybenzyl)-1,4-butanediamine (H_2L^R) and its "metalloligand" [CuL^R]

The di-Schiff base ligand (H_2L) of 1,4-butanediammine and salicyldehyde was synthesized as stated above. 5 mmol of this ligand (H_2L) was dissolved in methanol and cooled, and then solid sodium borohydride (380 mg, 10mmol) was added slowly to this methanolic solution with stirring. After completion of the addition, the resulting solution was acidified with concentrated HCl (10 mL) and then evaporated to dryness.[19] The reduced Schiff base ligand H_2L^R was extracted from the solid mass with methanol, and this methanolic solution (*ca.* 20 mL) was used for the preparation of "metalloligand"(CuL^R)[20] followed by the similar procedure as for [CuL].

Syntheses of the complexes $[(CuL)_2Cd(NCS)_2]$ (1) and $[(CuL^R)_2Cd(SCN)_2]$ (2)

The precursor complex [CuL] (0.714 g, 2 mmol) was dissolved in methanol (20 mL) and then a water solution (1 mL) of anhydrous $Cd(ClO_4)_2$ (0.311 g, 1 mmol) followed by an aqueous solution (1 mL) of ammonium thiocyanate (0.159 g, 2 mmol) was added to this solution. The mixture was stirred for 1 h and then filtered. The filtrate was allowed to stand overnight when light green prismatic shaped X-ray quality single crystals of **1** appeared at the bottom of the vessel. The reddish green rhombic shaped single crystal of complex **2** was synthesized in the same procedure as described for complex **1** but using the "metalloligand" [CuL^R] instead of [CuL]. The crystals were washed with a methanol–water mixture and dried in desiccators containing anhydrous $CaCl_2$ and then characterized by elemental analysis, spectroscopic methods and single crystal X-ray diffraction.

Complex 1: Yield: 0.660 g (70 %). Anal. Calc. for: $C_{38}H_{36}Cd_1Cu_2N_6O_4S_2$, C 48.33; H 3.84; N 8.90%; Found: C 48.22; H 3.68; N 8.95 %. IR (KBr): ν(C=N) 1614 cm^{-1}, ν(SCN) 2083 cm^{-1}.UV/vis: λ_{max} (solid, reflectance) = 581 and 397 nm.

Complex 2: Yield: 0.758g (80 %). Anal. Calc. for: $C_{38}H_{44}Cd_1Cu_2N_6O_4S_2$, C 48.12; H 4.25; N 8.86 %; Found: C 48.32; H 4.36; N 8.92 %. IR (KBr): ν(N−H) 3207 cm^{-1}, ν(SCN) 2054cm^{-1}. UV/vis: λ_{max} (solid, reflectance) = 609 and 374 nm.

Physical measurements and crystallographic data collection and refinement

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–400 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in solid state (750–300 nm) were recorded in a Hitachi U-3501 spectrophotometer.

Suitable single crystals of each complex were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. The crystals were positioned at 60 mm from the CCD. Frames (360) were measured with a counting time of 5 s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. The hydrogen atoms bound to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 (or 1.5 for methyl groups) times those of the atom to which they were attached. Hydrogen atoms that bonded to N were located in a difference Fourier map and refined with distance constraints. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program.[21] All calculations were carried out using SHELXS 97,[22] SHELXL 97,[23] PLATON 99,[24] ORTEP-32[25] and WINGX system ver-1.64.[26] Data collection and structure refinement parameters and crystallographic data for the two complexes are given in Table 1. The selected bond lengths and bond angles are summarized in Table 2.

Theoretical methods

The energies of all complexes included in this study were computed at the BP86-D3/def2-TZVPD level of theory. The geometries of the preliminary study have been fully optimized and we have used the crystallographic coordinates for the theoretical analysis of the noncovalent interactions in the solid state. The calculations have been performed using the program TURBOMOLE version 6.4.[27] The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.[28] For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3).

Table 1. Crystal data and structure refinement of complexes **1** and **2**

Complexes	**1**	**2**
Formula	$C_{38}H_{36}Cd_1Cu_2N_6O_4S_2$	$C_{38}H_{44}Cd_1Cu_2N_6O_4S_2$
M	944	952
Crystal System	Monoclinic	Orthorhombic
Space Group	C2/c	Fdd2
a/Å	15.2789(7)	10.547(5)
b/Å	10.8642(7)	19.628(5)
c/Å	22.0898(11)	38.251(5)
α/°	90	90.000(5)
β/°	92.034 (2)	90.000(5)
γ/°	90	90.000(5)
V/Å^3	3664.44	7918.59
Z	4	8
D_c/g cm^{-3}	1.712	1.598
μ/mm^{-1}	1.890	1.749
F (000)	1904	3872
R(int)	0.050	0.051
Total Reflections	20127	8672
Unique reflections	3233	3351
$I>2\sigma(I)$	2923	2866
R1, wR2	0.0262, 0.0682	0.0346, 0.0872
Temp (K)	293	293

Results and discussion

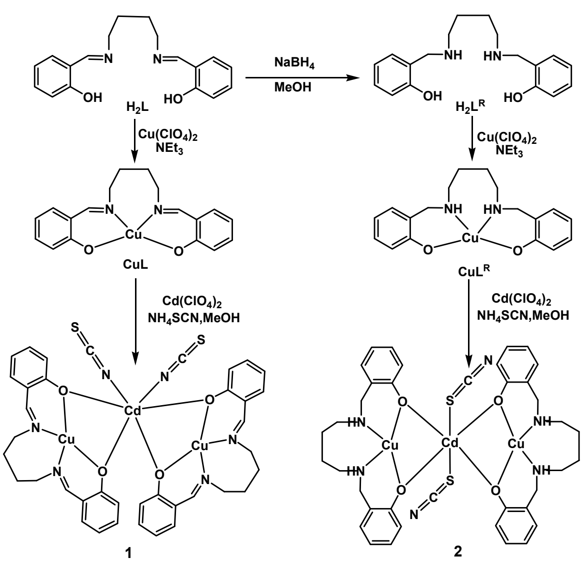
Syntheses

The Schiff-base ligand (H_2L), the reduced Schiff-base ligand (H_2L^R) and their Cu(II) complexes, [CuL] and [CuL^R] were synthesized using the reported procedures.[18-20] Both the "metalloligands", [CuL] and [CuL^R] on reaction with anhydrous cadmium perchlorate and ammonium thiocyanate in 2:1:2 molar ratio in MeOH–H_2O medium (10:1, v/v) resulted two new trinuclear heterometallic complexes, [$(CuL)_2Cd(NCS)_2$] (**1**) and [$(CuL^R)_2Cd(SCN)_2$] (**2**) respectively (Scheme 1).

IR and solid state UV-Vis spectra

Besides elemental analysis, both complexes were initially characterized by IR spectra. The 'metalloligands' [CuL] and [CuL^R] are neutral and do not have any other anionic coligand, whereas complexes, **1** and **2** contain thiocyanate ion (Figs. S1 and S2). Therefore, the appearance of the characteristic intense peaks at 2083 and 2054 cm^{-1} for **1** and **2** respectively, indicate the formation of the trinuclear adducts. In the spectra of complex **1**, a strong and sharp band at 1614 cm^{-1} due to the azomethane ν(C=N) group of the Schiff base is found. On the other hand, there is no band in the region 1620−1650 cm^{-1} in the spectra of **2** due to the reduction of the imines group. Moreover, a moderately strong and sharp peak at 3207 cm^{-1} due to a N−H stretching vibration, for complex **2** also shows that the imines group of the Schiff base is reduced.[29]

The electronic spectra of these two compounds were recorded in the solid state (Fig. S3). Compounds **1** and **2** show broad absorption bands at 581 and 609 nm respectively while the band maxima for "metalloligands"[CuL] and [CuL^R] appear at 575 and 599 nm respectively.



Scheme 1 Formation of complexes **1** and **2**.

These bands are attributed to d–d transitions of Cu(II) ions for square planar environment. In addition, the two heterometallic compounds show a sharp single absorption maximum near 397 and 374 nm for **1** and **2** respectively and the two "metalloligands" [CuL] and [CuL^R] show absorption maxima at 365 and 373 nm respectively, attributed to ligand-to-metal charge transfer transitions.

Description of the structures of the complexes 1 and 2

The structure of **1** consisting of two "metalloligand" [CuL] (where H_2L = N,N'-bis(salicylidene)-1,4- butanediamine), one Cd(II) ion and two isothiocyanato ligands is shown in Fig. 1 together with the atomic numbering scheme. Dimensions of the metal coordination sphere of the complex **1** are given in Table 2.

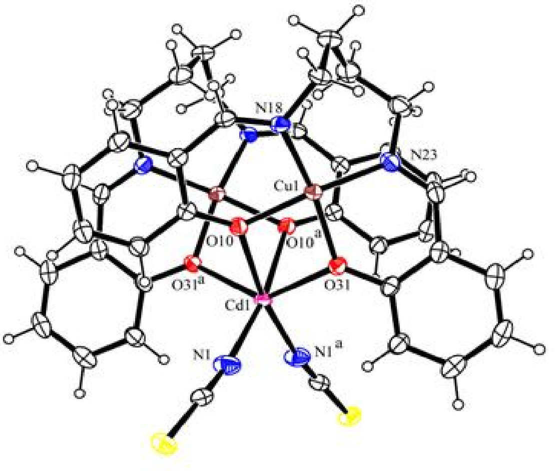


Fig. 1 The structure of **1** with ellipsoids at 30% probability. Symmetry transformation^a = 1-x, y, 1/2-z

The angular trinuclear entity of this complex of formula [$(CuL)_2Cd(NCS)_2$)] contains a crystallographic 2-fold axis which passes through the Cd centre. The six-coordinated cadmium has a distorted octahedral environment, constructed by the coordination of four oxygen atoms from the two "metalloligands" [CuL] and two mutually *cis* nitrogen atoms of isothiocyanate. The Cd–O distances are 2.394(2) and 2.279(2) Å while the Cd–N distance is 2.229(2) Å which is slightly shorter than Cd–O distances. However, the range of the *cis* [64.82(6)–135.75(6)°] and the *trans* [158.92(8)–171.13(8)°] angles indicates significant distortion from ideal octahedral geometry.

Each copper atom is bonded to two oxygen atoms and two nitrogen atoms of the tetra dentate Schiff-base ligand [H_2L]. Both the Cu–O bond distances [Cu(1)–O(10) 1.930(2) Å, Cu(1)–O(31) 1.930(2) Å] are shorter than Cu–N bond distances [Cu(1)–N(18)1.952(2) Å, Cu(1)–N(23) 2.002(2) Å]. The *trans* angles around Cu are O(10)–Cu(1)–N(23) 158.92(8)°, O(31)–Cu(1)–N(18) 165.97(8)° indicating that it suffers a tetrahedral distortion from the ideal square planar geometry. The tetrahedral distortion around Cu(1) is also apparent from the dihedral angles between the two N–Cu–O planes, which is 21.11°. This angle is 0° for a perfectly square-planar arrangement, and 90° for a perfect tetrahedral arrangement.

Table 2. Bond distances (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Cu(1)–O(10)	1.930(2)	1.945(4)
Cu(1)–O(31)	1.930(2)	1.935(4)
Cu(1)–N(18)	1.952(2)	2.014(5)
Cu(1)–N(23)	2.002(2)	2.018(4)
Cd(1)–O(10)	2.394(2)	2.273(4)
Cd(1)–O(31)	2.279(2)	2.302(4)
Cd(1)–N(1)/S(1)	2.229(2)	2.746(2)
O(10)–Cu(1)–O(31)	80.98(7)	82.76(16)
O(10)–Cu(1)–N(18)	92.37(8)	94.16(18)
O(10)–Cu(1)–N(23)	158.92(8)	173.13(17)
O(31)–Cu(1)–N(18)	165.97(8)	174.5(2)
O(31)–Cu(1)–N(23)	90.34(8)	92.95(17)
N(18)–Cu(1)–N(23)	99.85(9)	90.52(19)
O(10)–Cd(1)–O(31)	64.82(6)	68.19(14)
O(10)–Cd(1)–N(1)/S(1)	92.66(7)	88.73(10)
O(10)–Cd(1)–O(10)^a	81.96(6)	111.92(14)
O(10)–Cd(1)–O(31)^a	81.77(6)	177.40(12)
O(10)–Cd(1)–N(1)/S(1)^a	171.13(8)	94.99(10)
O(31)–Cd(1)–N(1) /S(1)	102.40(8)	87.61(10)
O(31)–Cd(1)–O(31)^a	135.75(6)	111.83(15)
O(31)–Cd(1)–N(1)/S(1)^a	107.55(8)	88.68(10)
N(1) /S(1)–Cd(1)–N(1)/S(1)^a	93.50(9)	173.37(10)

Symmetry element ^{a} = 1-x,y,1/2-z for **1** and ^{a} = -x,-y,z for **2**

This geometry is also confirmed by the so-called τ_4 index that measures the distortion between a perfect tetrahedron (τ_4= 1) and a perfect square planar geometry (τ_4= 0) with the formula: $\tau_4 = [360° - (\alpha + \beta)]/141°$, with α and β (in °) being the two largest angles around the central metal in the complex.[30] The τ_4 value for Cu(1) is 0.249. The four donor atoms in the equatorial plane around Cu show r.m.s. deviation of 0.247 Å while the metal atom is shifted by 0.061(1) Å from this mean plane. The Cd–Cu and Cu–Cu distances are 3.337(1) Å and 4.091 Å respectively.

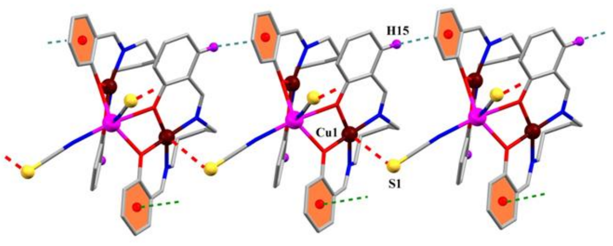


Fig. 2 The 1D chain of **1** formed by the Cu···S and C/H-π interactions. Other H-atoms have been removed for clarity.

The copper atoms of one unit is weakly coordinated to the sulfur atoms of another unit (symmetry: 1/2-x, 1/2+y, 1/2-z) at Cu(1)–S(1) = 3.132(1) Å (Fig. 2). In addition, an intermolecular C–H/π interaction is also observed between the centroid of phenyl ring and an aromatic H-atom (H15) (symmetry: 1/2-x, 1/2+y, 1/2-z) with a distance of 2.86 Å. These interactions give rise to 2D supramolecular entity parallel to the *ac* plane. This 2D supramolecular architecture has been further described in theoretical part.

The structure of **2** is shown in Fig. 3 together with the atomic numbering scheme. Dimensions in the metal coordination sphere are compared with **1** in Table 2. Complex **2** also contains a 2-fold axis passing through Cd metal center similar to complex **1**. All three metal atoms within the tri nuclear unit (two terminal Cu atoms and central Cd atom) are in a linear disposition. Thus, the geometry is very different from that observed in complex **1**. Like **1**, the central cadmium atom, Cd(1) has a six coordinate octahedral environment but the coordinating atoms and their relative arrangement around it is somewhat different with respect to **1**.

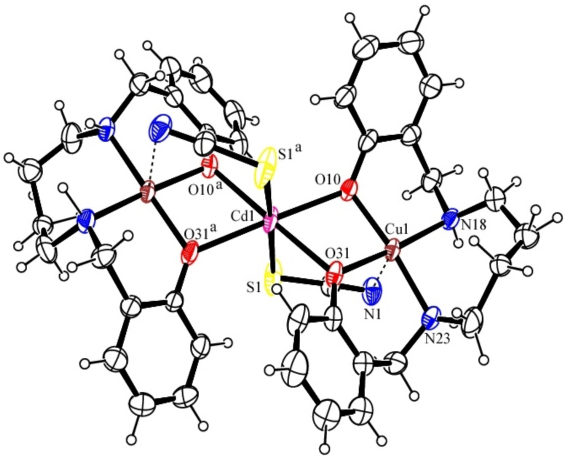


Fig. 3 The structure of 2 with ellipsoids at 30% probability. Symmetry transformation ^{a} = –x,–y,z. The weak bonds are indicated by dotted line.

It is bonded with the four oxygen atoms from the two "metalloligands"[CuL^R] at distances 2.273(4) and 2.302(4) Å and two mutually *trans* sulphur atoms from two thiocyanate ions at a distance of 2.746(2) Å. The distortions from octahedral geometry are small as the three *trans* angles are all within 7° of the ideal 180°. Like **1**, Cu(II) is bonded with the two nitrogen atoms and two oxygen atoms from the di-Schiff base ligand [H_2L^R], forming a square planar coordination around it. Both Cu–O (1.945(4) and

1.935(4) Å) and Cu–N (2.014(5) and 2.018(4) Å) bond distances are very similar to those of **1**. The r.m.s. deviation of the four basally coordinating atoms from the mean plane passing through them is 0.082 Å. The metal atom is shifted by 0.007(1) Å from this mean plane towards the axially coordinating nitrogen atom. However, the Cu atom suffers comparatively less tetrahedral distortion from the ideal square planar geometry as its *trans* angles (173.13(17) and 174.5(2)°) are closer to 180°.The lesser extent of tetrahedral distortion around Cu(1) with respect to **1**, is also clear from the dihedral angles (6.69°) between the two N–Cu–O planes and the τ_4 index (0.088). Moreover, unlike **1**, the axial position of Cu atom is weakly coordinated by the N end [Cu(1)–N(1) 2.811(4) Å] of the thiocyanato ligand whose S end binds to central Cd atom simultaneously. The Cd–Cu distance (3.30(2) Å) is considerably shorter than those found in complex **1** but the Cu–Cu separation (6.601 Å) is much longer than that of **1** as a consequence of the linear structure.

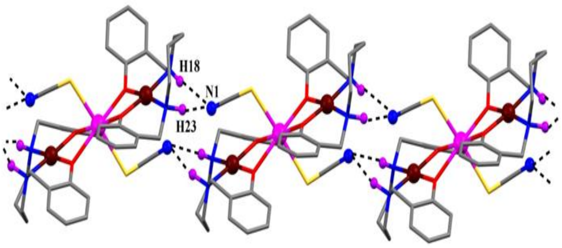


Fig. 4 The 1D chain of **2** formed by the bifurcated H-bonding interactions with N. Other H-atoms have been removed for clarity.

Like **1**, a 1D chain (Fig. 4) of complex **2** is constructed by the bifurcated H-bonding between the N atom of thiocyanato ligand of one unit with the hydrogen atoms (H18 and H23) of reduced imine moiety of other unit namely N(18)-H(18)···N(1) (1-x, 3-y, z) and N(23)-H(23)···N(1) (1-x, 3-y, z) with dimensions H···N2.33(6) and 2.17(6) Å, N-H···N172(5) and 165(4)° and N···N3.107(7) and 3.224(7) Å. This supramolecular architecture is further described and discussed in the theoretical section.

DFT and CSD studies

The theoretical study is devoted to rationalize the significant structural differences between compounds **1** and **2** that have been described above. That is, in compound **2**, both thiocyanate ligands are coordinated to the Cd(II) metal center using the sulfur atom whilst they are coordinated by the nitrogen atom in compound **1**. Moreover, the relative arrangement of the SCN^- ligands is *trans* in **2** and *cis* in **1**. These two differences provoke the formation of radically different supramolecular architectures in the solid state (*vide supra*). In compound **2**, the supramolecular assembly is formed by an extended hydrogen bond network between the reduced N=C Schiff base moieties and the thiocyanate anions. On the other hand, in compound **1** the solid state architecture is governed by a combination of C–H/π and ancillary S–Cu interactions.

Despite the fact that the linkage isomerism of thiocyanate is well known,[5-7] we have performed a search in the Cambridge Structural Database (CSD) in order to achieve a better understanding of the different binding modes of the thiocyanate anion (monodentate, not bridging ligand) and to know if the metal coordination using the sulfur atoms is uncommon. It is well-known that the CSD is a convenient and reliable tool for analyzing geometrical parameters.[31] Interestingly, we have found only 17 X-ray structures and a total of 23 fragments where the SCN^- is coordinated to Cd through the S atom (Cd···SCN). It should be mentioned that we have eliminated those hits where the SCN^- is acting as bridging ligand in any of the two modes represented in Fig. 5. In sharp contrast, we have found 186 X-ray structures (257 fragments) where the SCN^- is coordinated to Cd through the N atom (Cd···NCS). For this search we have also eliminated those hits where the SCN^- ligand is simultaneously coordinated to more than one metal center. The histogram plots represented in Fig. 5 clearly show a preference of the coordination *via* the nitrogen atom, due to the significantly larger number of hits observed for this coordination mode. Another interesting aspect is the dissimilar coordination angle observed for each type of complex. In the Cd–SCN histogram plot, it can be observed a preference for a Cd-S-C angle between 90 and 110 degrees and in the Cd–NCS plot a wider range of values is observed centered around a Cd-N-C angle of 155 degrees.

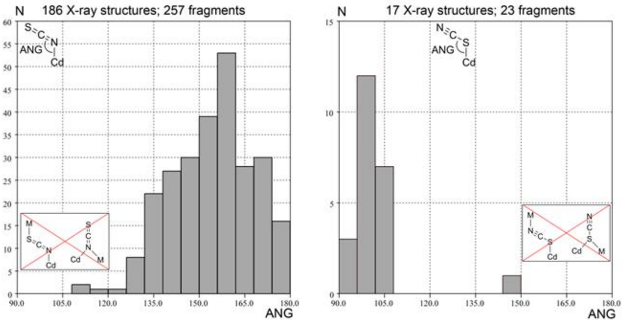


Fig. 5 Histogram plots of Cd-NC (left) and Cd-SC (right) angles in Cd–NCS and Cd–SCN complexes.

For comparison purposes, we have performed the same searches for the related $SeCN^-$ and OCN^- ligands. The number of hits is very limited for the cyanato ligand. That is, we have found only one structure for O-coordination and four structures for the N-coordination. For the $SeCN^-$ search, we have found 18 fragments (7 X-ray structures) for Cd-SeCN binding mode and only 8 fragments (4 X-ray structures) for the Cd–NCSe. Therefore, for the $SeCN^-$ ligand the Se-coordination to the Cd(II) metal is likely favoured with respect to the N-coordination, in contrast to the observed for the SCN^- ligand where the N-coordination is favoured. For the OCN^- ligand the number of hits is too small to extract any consistent conclusion.

In order to further analyze and rationalize the results obtained from the CSD searches we have performed a preliminary study using a reduced model as a theoretical approach. We have evaluated the energetic difference between the two possible coordination modes of the cyanate, thiocyanate and selenocyanate anions to the Cd atom. The theoretical models used (**A** and **B**) are shown in Fig.6 (top), where only two ligands have been used to minimize steric effects that may influence the coordination angle and energy. For the SCN ligand, the most stable geometry is **B**, where both SCN^- anions are coordinated to the Cd by the nitrogen atom in agreement with the CSD analysis that showed a clear preference for this binding mode. In addition, the theoretical angles observed in the optimized complexes are also in reasonably agreement with the data retrieved from the CSD (see histogram plots in Fig. 5), which confirm that the Cd–SCN complexes have preference for smaller Cd–S–C angles (~90º, **A**) than that in Cd–NCS complexes (~140°, **B**). It is important to note that these values are computed free from other influences as additional interactions (ancillary N/S···M or H-bonding interactions) that can be present in the solid state. Therefore there is significant geometric preference in the coordination angle depending on the binding mode adopted by the SCN^{-} ligand. The OCN^{-} anion also shows preference for the N-coordination, however the energetic difference between both binding modes is very large (61.6 kcal/mol). Therefore a very strong preference for coordination via the nitrogen atom is expected. In contrast, for the SeCN^{-} anion, the coordination via the chalcogen atom is preferred by only 4 kcal/mol (see Table 3), in agreement with the CSD analysis that reveals more X-ray structures with this binding mode. We have also compared the behaviour of Cd to Zn regarding the complexation to ChCN^{-} anions (Ch = O, S and Se). Several interesting differences have been found. A strong preference for the coordination using the nitrogen end of the ligands is found both theoretically and experimentally (see relative energies and CSD results in Table 3). In addition, the optimized Zn(NCCh)$_2$ complexes exhibit larger Zn–N–C angles than the corresponding Cd–N–Ch complexes (see Fig. 6). In fact, complexes Zn(NCS)$_2$ and Zn(NCSe)$_2$ present almost linear coordination angles. Similarly to Cd, the coordination of cyanate ligand to Zn shows a very strong preference for the N-coordination since the energetic difference is very large (66.4 kcal/mol, see Table 3)

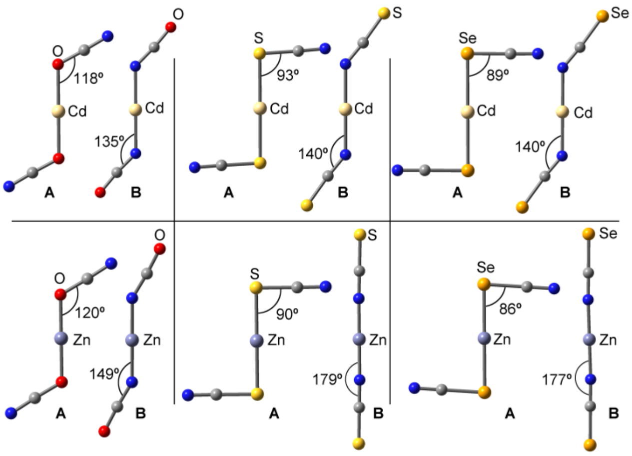


Fig. 6 Optimized geometries of ML$_2$ (M = Cd, Zn and L = OCN, SCN and SeCN) complexes **A** and **B**.

Table 3. Relative energies (kcal/mol) for the **A** and **B** binding modes for complexes of Cd(II) and Zn(II) with cyanate, thiocyanate and selenocyanate anions, and the number of hits obtained from the CSD searches

ML$_2$	Relative energy		Number of hits	
	A	**B**	M-ChCN	M-NCCh
Cd(cyanate)$_2$	61.6	0.0	1	4
Cd(thiocyanate)$_2$	9.0	0.0	17	186
Cd(selenocyanate)$_2$	**0.0**	**4.0**	**7**	**4**
Zn(cyanate)$_2$	66.4	0.0	0	15
Zn(thiocyanate)$_2$	21.2	0.0	0	283
Zn(selenocyanate)$_2$	10.3	0.0	0	7

Ch: chalcogen atom

In order to consider the electronic effect from the bonded oxygen atoms in compounds **1** and **2**, we have used several theoretical models with additional O-donor ligands (see Fig. 7). We have computed both binding modes (**A** and **B**) placing the SCN^{-} ligands in both *cis* and *trans* disposition to mimic compounds **1** and **2**. We have assumed that the electron density of the nitrogen atoms binding to the Cu(II) atoms is approximately the same in both compounds (**1** and **2**) and that it is not differently affecting the electron density in the oxygen atoms binding to the Cd(II) centre. Obviously, we cannot use a more elaborated theoretical model including the Cu atoms since extra stabilization in the S-coordinated isomers would be obtained due to the Cu···N ancillary interaction. The results of Fig. 7 indicate that the N-coordination of the SCN^{-} ligand to Cd is energetically favoured for both *cis* and *trans* isomers and that the energetic difference between the **A** and **B** binding modes is similar to the previously observed in the model shown in Fig. 6. This result suggests that the influence of the oxygen coordination upon the S/N coordination preference of the SCN^{-} ligand is negligible.

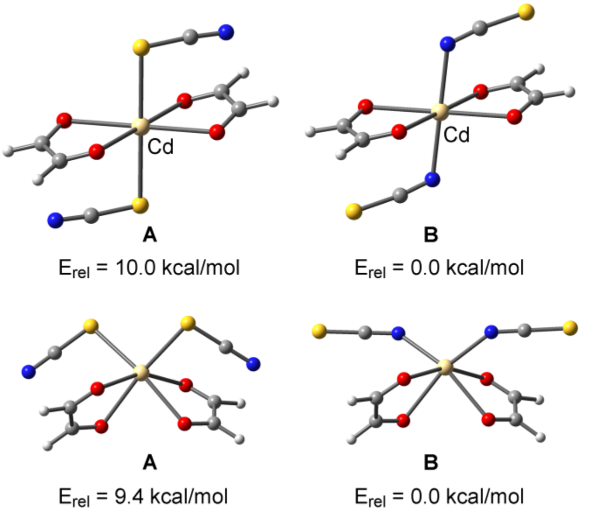


Fig. 7 Optimized geometries of several Cd model complexes complexes **A** and **B**.

We have also analysed the geometric and energetic features of the X-ray structures of compounds **1** and **2** theoretically, in order to give an explanation to the fact that the simple reduction of the imidic C=N bond of the organic ligand in **2** changes the more usual coordination mode of the SCN^{-} ligand. The most significant implication of the reduction of both C=N groups in **2** is the formation of two amino groups and, consequently, two strong hydrogen bond donors are available to interact with the SCN^{-} ligand. In fact, a careful examination of the CSD search of Cd–SCN complexes reveals that 12 structures out of a total of 17 present N–H···NCS–Cd hydrogen bonds that likely contribute to the stabilization of the Cd–SCN binding mode, which is energetically disfavoured (see Table 3).

Three selected examples are shown in Fig. 8 and it is worth mentioning that the XAKDUK structure presents two differently coordinated SCN^{-} ligands and that it is precisely the ligand coordinated through the sulfur atom that participates in the H-bonding interaction. In the KIBSUK structure the SCN^{-} ligand establishes a bifurcated hydrogen bond that is also observed in compound **2** (see Fig. 8) and probably compensates the unfavorable Cd–SCN binding mode, as it is further studied below.

For the theoretical study we have selected the crystal fragments shown in Fig. 9, which are dimers originated from the supramolecular interactions involving the SCN$^-$ ligand. Each dimer is part of an infinite 1D chain that is formed in the solid state architecture of the corresponding X-ray structure.

The binding energy computed for the self-assembled dimer of compound **2** is $\Delta E_1 = -37.4$ kcal/mol, which is large and negative due to the formation of four hydrogen bonding interactions. Thus the binding energy of each hydrogen bond is approximately –9.3 kcal/mol, which corresponds to a strong N–H···NCS–Cd interaction in agreement with the very short distance. The enhanced acidity of the hydrogen atoms of the amino group due to its coordination the Cu(II) ion in conjunction with the negative charge of the ligands most likely contribute to the strength of the interaction. Additionally, intramolecular ancillary interactions are established between the nitrogen atom of the SCN$^-$ ligand and the Cu^{II} atom (highlighted in red in Fig. 9) that obviously do not affect to the binding energy. In compound **1** (right) the dimer is formed basically due to the interaction between the sulfur atom of the SCN$^-$ ligand and a Cu^{II} metal. Furthermore, a supramolecular network of C–H/π interactions is also present along the crystal structure (see Fig. 9, right).

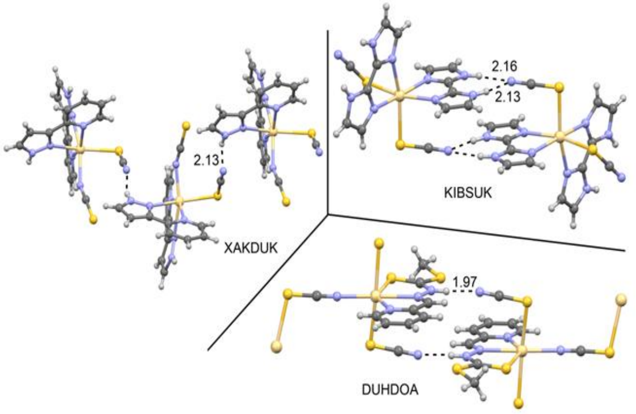


Fig. 8 Partial views of the X-ray structures KIBSUK, XAKDUC and DUHDOA. The N–H···NCS–Cd hydrogen bonds are represented by dashed lines. Distances in Å.

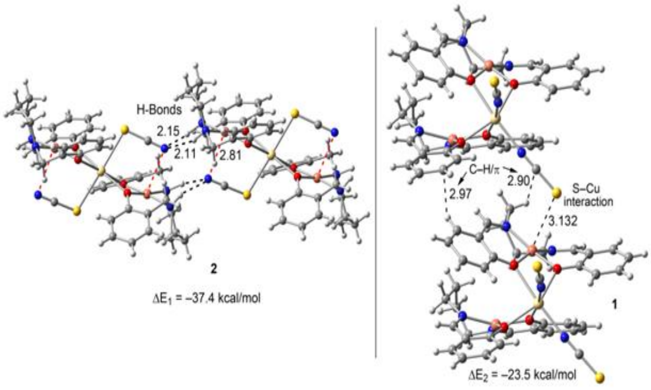


Fig. 9 X-ray crystal fragments of compound **1** (right) and **2** (left).

We have also evaluated the binding energy of this dimer that is $\Delta E_2 = -23.5$ kcal/mol. Remarkably, this interaction energy is considerably smaller (in absolute value) than ΔE_1, compensating the 9.0 kcal/mol of energetic cost due to the Cd–SCN coordination unusual mode observed in **1**. This explanation for the coordination mode observed in **1** can be probably extended to the CSD hits represented in Fig. 8, where the formation of H-bonded infinite chains energetically compensates the disfavored Cd–SCN coordination.

Finally, we have further analysed the weak coordination of S to Cu the Bader's theory[32] of "atoms in molecules" that has been widely used to characterize a variety of covalent and noncovalent interactions.[33] We have used a reduced model of compound **2** (see Fig 10) in order to keep the size of the system computationally approachable. In this model the tetradentate ligands that do not participate in the interactions have been simplified. The distribution of critical points and bond paths have been generated with AIMAll program[34] that uses dashed lines for noncovalent interactions (positive value of the Laplacian of the electron density at the bond critical point) and solid lines for covalent bonds (negative value of the Laplacian). It can be observed that the C–H/π interactions are characterized by the presence of a bond critical point (red sphere) connecting the hydrogen atom with either a carbon or a sulphur atom of the π-system (phenyl or NCS respectively). The S···Cu interaction is also characterized by the presence of a bond critical point connecting the S and Cu atoms. The value of the Laplacian is positive (2.66×10^{-2} a.u.) as is common in closed shell noncovalent interactions.[32]

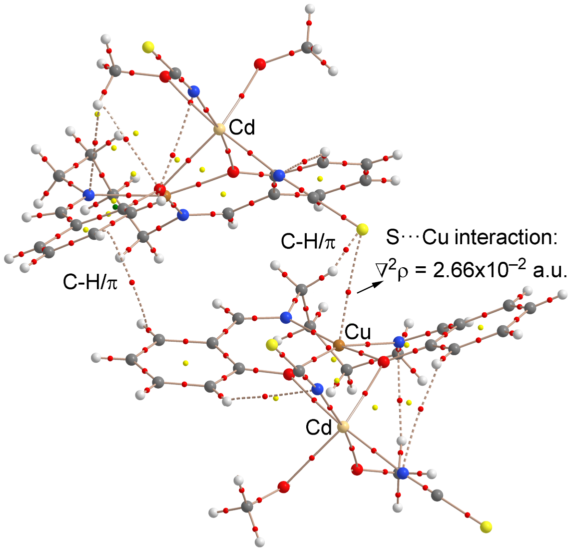


Fig. 10. Distribution of bond (red) and ring (yellow) critical points and bond paths in a model of an X-ray crystal fragment compound **1**.

Conclusions

In this present work, we synthesize one trinuclear complex, $[(CuL)_2Cd(NCS)_2]$ (**1**) [where H_2L = N,N′-bis(salicylidene)-1,4-butanediamine] in which the thiocyanate ions show usual N-coordination to the Cd(II) ion. However, in the complex with the corresponding reduced Schiff base ligand, $[(CuL^R)_2Cd(SCN)_2]$ (**2**) where the C=N bond is reduced (H_2L^R), the thiocyanate is in

S-bonded mode. From the analysis of the CSD and the preliminary DFT study we have demonstrated that the coordination of the NCS^- ligand to Cd(II) *via* the nitrogen atom is energetically favored with respect to the coordination *via* the sulfur atom. In the solid state structure of compound **2** strong N–H···NCS–Cd hydrogen bonds are present. We computed the binding energy of these hydrogen bonds and observe that it is crucial for the stabilization of the solid state structure, compensating the less favored Cd–SCN coordination. Thus, structurally characterizing two very similar complexes with different potentiality for H-bond formation and doing relevant theoretical calculations we show for the first time that the 'ambidentate' coordination behaviour of thiocyanate to Cd(II) cannot be explained only by the electronic and steric effects around the metal centre but the weak interactions such as H-bonding should also be taken in account.

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Notes and references

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*Electronic supplementary information (ESI) available: The electronic supplementary information file contains Fig. S1–S4. CCDC 972828 and 972829 for **1** and **2** respectively.*

1 A. A. Newman (Ed.), *Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives*, Academic Press, New York, 1975, 222-275.
2 A. M. Golub, H. Kohler and V. V. Skopenko (Eds.), *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986.
3 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev*., 1971, **6**, 407-445.
4 J. L. Burmeister, *Coord. Chem. Rev*., 1990, **105**, 77-133.
5 L. Vandenburgh, M. R. Buck and D. A. Freedman, *Inorg. Chem*., 2008, **47** (20), 9134–9136.
6 (*a*) A. R. Khan, S. M. Socol, D. W. Meek and R. Yasmeen, *Inorg. Chim. Acta*, 1995, **234**, 109-113; (*b*) L. A. Epps and L. G. Marzilli, *J. Chem. Soc., Chem. Commun.*, 1972, 109-110; (*c*) M. J. Maroney, E. O. Fey, D. A. Baldwin, R. E. Stenkamp, L. H. Jensen and N. J. Rose, *Inorg. Chem*., 1986, **25**, 1409-1414.
7 S. Chowdhury, N. Koshino, A. Canlier, K. Mizuoka and Y. Ikeda, *Inorg. Chim. Acta*, 2006, **359**, 2472–2478.
8 (*a*) J. E. House, *Inorganic Chemistry*, Academic Press is an imprint of Elsevier, 2008, 313-315; (*b*) P. A. Cox, *Inorganic Chemistry*, Inorganic Chemistry Laboratory, New College, Oxford, UK, 390-391; (*c*) G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, Pearson international edition, 179-181.
9 (*a*) R. G. Pearson., *J. Am. Chem. Soc*., 1963, **85**, 3533-3539; (*b*) R. G. Pearson, Chemical Hardness, Wiley-VCH, Weinheim, 1997, 385; (*c*) R. G. Pearson, *Coord. Chem. Rev*., 1990, **100**, 403-425.
10 (*a*) C. T. Hunt and A. L. Balch., *Inorg. Chem*., 1982, **21**, 1242-1246; (*b*) C. –H. Hsieh, S. M. Brothers, J. H. Reibenspies, M. B. Hall, C. V. Popescu and M. Y. Darensbourg, *Inorg. Chem*, 2013, **52**, 2119−2124; (*c*) H. Zhang, X. Wang, K. Zhang and B. K. Teo, *Coord. Chem. Rev*., 1999, **183**, 157–195.
11 (*a*) E. Shurdha, S. H. Lapidus, P. W. Stephens, C. E. Moore, A. L. Rheingold and J. S. Miller, *Inorg. Chem*., 2012, **51**, 9655−9665; (*b*) C. K. Jorgensen, *Inorg. Chem*., 1964, **3**, 1201-1202.
12 (*a*) R. Clark and G. J. Palenik, *Inorg. Chem*., 1970, **9**, 2754-2760; (*b*) B. Barszcz, J. Masternak and W. S. Dobrowolska, *Dalton Trans*, 2013, **42**, 5960.
13 (*a*) J. M. Harrington, S. B. Jones, D. J. VanDerveer, L. J. Bartolotti and R. D. Hancock, *Inorg. Chim. Acta*, 2009, **362**, 1122–1128; (*b*) X. M. Hu, L. W. Xue and W. C. Yang, *Russ. J. Coord. Chem*., 2013, **39**, 636-640; (*c*) F. Basolo, W. H. Braddley and K. J. Weidenbaum, *J. Am. Chem. Soc.*, 1966, **88**, 1576-1578.
14 (*a*) Y. –Y. Liu, P. Yang and B. Ding, *Acta Crystallogr*., 2012, **E68**, m1095-m1096; (*b*) H. Zhu, M. Strobele, Z. Yu, Z. Wang, H. -J. Meyer and X. You, *Inorg.Chem.Commun*., 2001, **4**, 577-581; (*c*) P. Seth, L. K. Das, M. G. B. Drew and A. Ghosh, *Eur. J. Inorg. Chem.* 2012, 2232–2242; (*d*) S. Biswas and A. Ghosh, *Polyhedron*, 2011, **30**, 676–681; (*e*) L. K. Das, A. Biswas, A. Frontera and A. Ghosh, *Polyhedron*, 2013, **52**, 1416–1424; (*f*) L. K. Das, M. G. B. Drew and A. Ghosh, *Inorg. Chim. Acta*, 2013, **394**, 247–254; (*g*) S. Biswas, C. Diaz and A. Ghosh, *Polyhedron* 2013, **51**, 96–101; (*h*) S. Biswas and A. Ghosh, *Indian J. Chem., Sect. A*, 2011, **50**, 1356–1362.
15 (*a*) H. –C. Fang, X. –Y. Yi, Z.-G. Gu, G. Zhao, Q.-Y. Wen, J. –Q. Zhu, A.-W. Xu and Y. –P. Cai, *Cryst. Growth Des*., 2009, **9**, 3776-3788; (*b*) H. Cai, Y. Guo and J.-G. Li, *Acta Crystallogr., Sect. E:Struct.Rep.Online*, 2010, **66**, m1205; (c) A. D. Jana, A. K. Ghosh, D. Ghoshal, G. Mostafa and N. R. Chaudhuri, *CrystEngComm*, 2007, **9**, 304-312; (d) H.-L. Jia, M.-J. Jia, H. Ding, J.-H. Yu, J. Jin, J.-J. Zhao and J.-Q. Xu, *CrystEngComm* , 2012, **14**, 8000-8009; (*e*) S. Wöhlert, J. Boeckmann, I. Jessa and C. Näther, *CrystEngComm*, 2012, **14**, 5412-5420.
16 (*a*) F. J. Muñoz-Lara, Z. Arcís-Castillo, M. C. Muñoz, J. A. R. -Velamazán, A. B. Gaspar, and José A. Real, *Inorg. Chem*., 2012, **51**, 11126–11132; (*b*) A. D. Leóna, J. Ponsa, J. G.-Antóna, X. Solansb, M. F.-Bardíab and J. Rosa, *Polyhedron*, 2009, **28,** 2165-2170; (*c*) D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc*., 1970, **92**, 5351-5359.
17 (*a*) G. L. Thériault, C. Reber, C. Aronica and D. Luneau, *Inorg. Chem*., 2006, **45**, 2379–2381; (*b*) A. Kobayashi, Y. Fukuzawa, H. -C. Chang and M. Kato, *Inorg. Chem*., 2012, **51**, 7508-7519; (*c*) A. Turco and C. Pecile, *Nature*, 1961, **191**, 66-67.
18 H. H. Yao, J. M. Lo, B. -H. Chen and T. –H. Lu, *Acta Crystallogr., Sect.C:Cryst.Struct.Commun*., 1997, **53**, 1012-1013.
19 (*a*) G. J. Colpas, B. J. Hamstra, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1994, **33**, 4669-4675; (*b*) A. Biswas, M. G. B. Drew and A. Ghosh, *Polyhedron* 2010, **29**, 1029-1034.
20 M. K. Taylor, J. Reglinski, L. E. A. Berlouis and A. R. Kennedy, *Inorg. Chim. Acta*, 2006, **359**, 2455-2464.
21 SAINT, version 6.02; SADABS, version 2.03, Bruker AXS, Inc., Madison, WI, 2002.
22 G. M. Sheldrick, SHELXS 97, *Program for Structure Solution*, University of Göttingen, Germany, 1997.
23 G. M. Sheldrick, SHELXL 97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.
24 A. L. Spek, PLATON. *Molecular Geometry Program*, J. Appl. Crystallogr., 2003, **36**, 7-13.
25 L. J. J. Farrugia, *J. Appl. Crystallogr*., 1997, **30**, 565.
26 L. J. J. Farrugia, *J. Appl. Crystallogr*., 1999, **32**, 837-838.
27 R. Ahlrichs, M. Bär, M. Hacer, H. Horn and C. Kömel, *Chem. Phys. Lett*., 1989, **162**, 165-169.
28 S. B. Boys and F. Bernardy, *Mol. Phys*., 1970, **19**, 553–566.

29 (*a*) S. Ghosh, S. Biswas, A. Bauzá, M. Barceló-Oliver, A. Frontera and A. Ghosh, *Inorg. Chem.*, 2013, **52**, 7508–7523; (*b*) A. Biswas, R. Saha and A. Ghosh, *CrystEngComm*, 2011, **13**, 5342–5347.

30 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans*., 2007, **9**, 955-964.

31 A. Nangia, K. Biradha and G. R. Desiraju, *J. Chem. Soc., Perkin Trans*., 1996, **2**, 943-953.

32 (*a*) R. F. W. Bader, Atoms in Molecules—A Quantum Theory, Oxford University Press, Oxford, 1990; (*b*) R. F. W. Bader, *Chem. Rev*., 1991, **91**, 893-928.

33 (*a*) S. J. Grabowski, A. Pfitzner, M. Zabel, A. T. Dubis and M. Palusiak, *J. Phys. Chem. B*, 2004, **108**, 1831–1837; (*b*) A. Vila and R. A. Mosquera, *J. Mol. Struct.: THEOCHEM*, 2001, **546**, 63–72; (*c*) D. Chopra, T. S. Cameron, J. D. Ferrara and T. N. G. Row, *J. Phys. Chem. A*, 2006, **110**, 10465–10477; (*d*) A. Bauzá, T. J. Mooibroek, A. Frontera, *Angew. Chem. Int. Ed*., 2013, **52**, 12317–12321.

34 AIMAll (Version 13.11.04), T. A. Keith, TK Gristmill Software, Overland Park KS, USA, 2013 (aim.tkgristmill.com).

Graphical Abstract

The influence of H-bonding on the 'ambidentate' coordination behaviour of thiocyanate ion to Cd(II): A combined experimental and theoretical study

Alokesh Hazari, Lakshmi Kanta Das, Antonio Bauzá, Antonio Frontera* and Ashutosh Ghosh*

With the help of structural analyses and DFT studies of two hetero-metallic compounds bearing the Cu_2Cd cores with two similar di-Schiff base ligands it is shown that H-bonding plays an important role in stabilizing the unusual S-coordination of thiocyanate ion to Cd(II).