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Complexes of thiophene-2,3-dicarboxaldehyde bis(oxime) (2,3BTCOH$_2$) with nickel(II) and copper(II): Synthesis, characterization, crystal structure of 2,3BTCOH$_2$. Rearrangement reaction with nickel(II) bromide

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ABSTRACT

Reacting with nickel(II) chloride, copper(II) chloride and bromide, thiophene-2,3-dicarboxaldehyde bis(oxime) (2,3BTCOH$_2$) leads to metal complexes formulated as [NiCl$_2$(2,3BTCOH$_2$)], [CuCl$_2$(2,3BTCOH$_2$)] and [CuBr(2,3BTCOH)]$_2$ respectively. In the case of nickel(II) bromide, we have observed the rearrangement of 2,3BTCOH$_2$ into 2-acetamido-3-thiophene carboxaldoxime (ACTOH) instead of the expected complex. The crystal structures of 2,3BTCOH$_2$ and ACTOH have been determined by X-ray diffraction methods and all other structures are proposed using usual spectroscopic techniques.

1. Introduction

The development of new ligands with less commonly used functional groups contributes to expand our understanding of coordination chemistry and allows the discovery of new transition-metal catalysts [1]. The chemistry of aldoxime ligands and aldoxime containing metal complexes is impressively rich and is far from being exhausted. In all cases, the ligand could act as neutral oxime or as an oximato anion.

Mono-aldoximes with heterocycles and their metal complexes were often described. Among them, pyridyl oximes and their metal complexes were recently reviewed [2]. Review papers have also pointed out some unconventional syntheses and reactivities of oxime and/or oximato metal complexes [3,4]. In our laboratory, various furan mono-aldoximes were described [5–8]. The dimethylglyoxime, one of the simplest bis(oximes), was used to obtain insoluble complex nickel(II) compound for gravimetric determination [9], even in presence of other metal like iron [10]. α-Furyl dioxime was also used as a reagent for qualitative and quantitative determination of nickel [11].

The oxime group can undergo a rearrangement, especially in the presence of protons or of a Lewis acid to give the corresponding secondary amide, and this rearrangement is known as Beckmann's rearrangement [12–14]. It can also undergo another type of rearrangement in the presence of metal catalysts (Fig. 1) to give the primary amide via another pathway in which nickel(II) derivatives are often used as catalysts [15,16].

The isomerisation of oximes in the presence of various catalysts has been described in the literature. In 1961, Field et al. published an article about the isomerisation of oximes (e.g. benzaldoxime) to give the corresponding amide in the presence of nickel(II) acetate tetrahydrate, nickel(II) carbonate and other metal derivatives (various salts, oxides...). They suggest that the benzaldoxime can form a complex ion with the catalyst, as intermediate, and in this case, of the oxime reacts as an acid. They also found the catalytic effect to appear with only some metals, their oxides or their salts with weak acids while their salts deriving from strong acids (i.e. chlorides) have no catalytic effect [17].

In 1973, Bourguignon et al. have synthesized the bis(oxime) thiophene-2,3-dicarboxaldehyde and described the isomerisation of the two oxime groups into amide groups simultaneously, in the presence of a slight excess of sodium carbonate [18].

As far as we know, there is no paper dealing with metal complexes deriving from thiophene-2,3-dicarboxaldehyde bis(oxime) (Fig. 2). In this article, we report the synthesis and the characterization of nickel(II) chloride and copper(II) chloride and bromide complexes with this ligand. In addition, we have observed, that when reacting with anhydrous nickel(II) bromide, thiophene-2,3-dicarboxaldehyde bis(oxime) undergoes the isomerisation of the oxime group in position 2 only to give 2-acetamido-3-thiophene carboxaldoxime instead of the expected metal complex.

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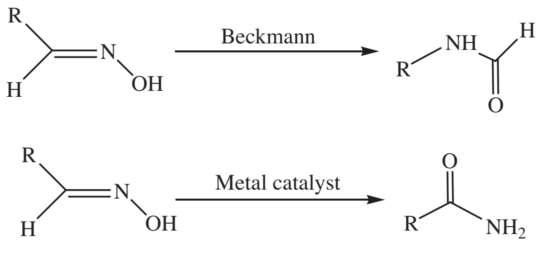

Fig. 1. Rearrangement of oximes.

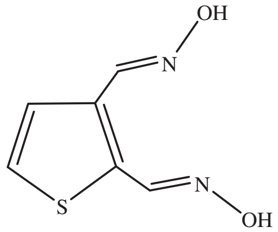

Fig. 2. Chemical structure of bis(oxime) thiophene-2,3-dicarboxaldehyde (2,3BTCOH$_2$).

2. Experimental

2.1. Reactants

All reactants and solvents were analytical grade. Thiophene-2,3-dicarboxaldehyde was purchased from Sigma–Aldrich (France). Hydroxylammonium chloride (Alfa Aesar, France), nickel(II) chloride hexahydrate, anhydrous nickel(II) bromide, copper(II) chloride dihydrate and anhydrous copper(II) bromide (Prolabo, France) were used as received.

2.2. Measurements

Elemental analyses were carried out by the service central of analyses (C.N.R.S. Vernaison, France). DSC diagrams were recorded in the 25–400 °C range with a Mettler DSC 822e unit, with the help of Mettler Toledo STAR^e SW 8.10 System software (Laboratoire de Physique, Faculté de Pharmacie, Angers); the heating rate was 10 °C/min. All measurements were made in 40 mm^3 closed Al crucibles. The IR spectra were recorded with a Bruker FTIR Vector 22 spectrometer between 4400 and 400 cm^{-1} (KBr disks). The far IR spectra were recorded with a Bruker Vertex FTIR spectrophotometer in the 650–50 cm^{-1} range using polyethylene disks (Institut des Matériaux Jean Rouxel, Université de Nantes (France).

2.3. Crystal data collection and processing

The crystal and instrumental parameters used in the unit-cell determination and data collection are summarized in Table 1.

The compound 2,3BTCOH$_2$ was crystallized from EtOH at room temperature. The monocrystals are monoclinic wit $C\,2/c$ space group. The crystal was placed and optically centered on a Bruker KAPPA APEX II diffractometer equipped with a Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The initial unit cell was indexed using the difference vectors method of a random set of reflections collected from three series of 0.5° wide omega-scans, 20 s per frame, and 12 frames per series that were well distributed in reciprocal space. The crystal to detector distance was 50 mm. A total of 1064 frames were collected to $\theta_{max} = 31.09°$ with 0.5° wide scans and an exposure time of 10 s per frame using the APEX2 software [19]. Unit cell refinement on all observed reflections and data reduction were performed using SAINT [20]. Scaling and a numerical absorption correction, based upon crystal size and faces indexing, were done using SADABS [20]. The structure was determined by direct methods with the successful location of all non-hydrogen atoms of the unique molecule within the asymmetric unit using the program SHELXS [21]. The structure was refined with SHELXL [22]. All non-hydrogen atoms were refined anisotropically.

Table 1
Crystallographic data for 2,3BTCOH$_2$ and ACTOH.

Name	2,3BTCOH$_2$	ACTOH
Formula	$C_6H_6N_2O_2S$	$C_6H_6N_2O_2S$
Formula weight	170.19	170.19
Crystal system	monoclinic	triclinic
Space group	$C\,2/c$	$P{-}1$
Unit cell dimensions		
a (Å)	24.1796(7)	4.9593(3)
b (Å)	4.2236(10)	5.8203(5)
c (Å)	15.7219(4)	12.9937(7)
α (°)	90	84.979(4)
β (°)	114.109(2)	86.753(5)
γ (°)	90	84.647(6)
V (Å^3)	1465.54(7)	371.54(4)
Z	8	2
Color	white	white
D_{calc} (g cm^{-3})	1.543	1.521
Crystal size (mm)	0.83 × 0.13 × 0.10	0.44 × 0.12 × 0.07
μ (mm^{-1})	0.387	0.382
hkl limits	$-34 \leqslant h \leqslant 34$	$-6 \leqslant h \leqslant 6$
	$-5 \leqslant k \leqslant 5$	$-8 \leqslant k \leqslant 8$
	$-22 \leqslant l \leqslant 22$	$-18 \leqslant l \leqslant 18$
θ_{min}, θ_{max} (°)	1.85, 31.09	3.53, 30.00
Number of variables	102	124
R_1 for $I > 2\,\sigma(I)$	0.0765	0.0534
wR_2 for $I > 2\,\sigma(I)$	0.2130	0.1181

Crystals of ACTOH obtained from low evaporation of EtOH solution are triclinic, with space group $P{-}1$. X-ray single-crystal diffraction data were collected at 293 K on a STOE-IPDS diffractometer, equipped with a graphite monochromator using Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K (MOLTECH-Anjou, UMR CNRS 6200, Université d'Angers). The structures were solved by a direct method and refined by a full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms with SHELX-97 program [22].

2.4. Synthesis

2.4.1. Synthesis of 2,3BTCOH$_2$

This bis(oxime) was prepared by reacting thiophene-2,3-dicarboxaldehyde and hydroxylamine in a 1:2 M ratio. The hydroxylamine was obtained as follows: hydroxylammonium chloride (0.93 g, 14 mmol, 10 mL, MeOH) reacted with potassium hydroxide (0.77 g, 14 mmol, 10 mL, MeOH) for 10 min; potassium chloride precipitated and was removed by filtration. Thiophene-2,3-dicarboxaldehyde (1 g, 7 mmol, 15 mL, EtOH) was added to MeOH solution of hydroxylamine, the mixture is heated up to 30 °C for 24 h. After cooling to room temperature, the solution was concentrated under reduced pressure and small polycrystals were obtained. Monocrystals were produced by slow evaporation from ethanol. The DSC pattern shows the melting point of this compound at 196 °C. NMR spectra (DMSO-D6, TMS as internal reference): unequivalent hydroxyl protons at 11.34 (s) and 12.16 (s) ppm; unequivalent CH=N at 8.24 (s) and 8.55 (s) ppm, thiophenic protons at 7.71 (d) and 7.34 (d) ppm.

2.4.2. Reaction with NiBr$_2$: synthesis of ACTOH

The 2-acetamido-3-thiophene carboxaldoxime was obtained by the reaction of bis(oxime) thiophene-2,3-dicarboxaldehyde

($2,3BTCOH_2$) (0.43 g, 2.5 mmol, 15 mL, EtOH) with anhydrous nickel bromide $NiBr_2$ (0.59 g, 2.5 mmol, 15 mL, water) under reflux for 6 h, the solution was concentrated under reduced pressure, the product precipitates and was then filtered and recrystallized from ethanol. Pale yellow monocrystals were obtained. In its DCS diagram, this compound shows a fine exothermic crystallization peak at 161 °C, immediately followed by an endothermic peak at 163 °C attributable to its melting. NMR spectra (DMSO-D_6, TMS as internal reference): hydroxyl protons at 11.30 (s), NH_2 (amide) 7.60 (s) ppm; $CH{=}N$ 8.51 (s) ppm, thiophenic protons at 7.91 (d) and 7.32 (d) ppm.

2.4.3. Synthesis of [$NiCl_2$($2,3BTCOH_2$)]

The complex [$NiCl_2$($2,3BTCOH_2$)] was prepared by adding 20 mL of $2,3BTCOH_2$ (0.85 g, 5 mmol, EtOH) into a solution of nickel(II) chloride $NiCl_2,6H_2O$ (1.3 g, 5 mmol, 15 mL, EtOH) in an equimolar ratio. The mixture was maintained at room temperature and a green precipitate appeared after 6 h. It was filtered and washed with ethanol.

2.4.4. Synthesis of [$CuCl_2$($2,3BTCOH_2$)]

The synthesis of the complex [$CuCl_2$($2,3BTCOH_2$)] was achieved by addition of 15 mL of $2,3BTCOH_2$ (0.85 g, 5 mmol, EtOH) to a solution of $CuCl_2,2H_2O$ (0.91 g, 5 mmol, 15 mL, EtOH). The complex precipitated after one hour, the mixture was kept at room temperature for 3 h and then the complex was filtered and washed with ethanol.

2.4.5. Synthesis of [CuBr(2,3BTCOH)]$_2$

This complex was obtained by adding 15 mL of a solution of $2,3BTCOH_2$(0.85 g, 5 mmol, EtOH) to a solution of $CuBr_2$ (1.2 g, 5 mmol, 15 mL, EtOH), the complex precipitated after 5 h at room temperature, the complex was obtained with the above described procedure.

3. Results and discussion

As far as we know, the crystal structures of mono thiophene carboxaldoxime (in 2- or 3-position) or bis(oxime) thiophene-2,3-dicarboxaldehyde were not yet described. It is also the first report of a rearrangement occurring with one oxime group only in the case of bifunctional thiophene derivatives [18].

3.1. Rearrangement with nickel(II) bromide

All complexes were easily obtained at room temperature. In the case of nickel(II) bromide, were have not observed any complexation at room temperature. So, we have chosen to proceed under ethanol refluxing condition. After removing ethanol, we have obtained a solid which was not characterized as the expected complex but as 2-acetamido-3-thiophene carboxaldoxime. We have previously described the reaction of cobalt(II), nickel(II), copper(II) halides with thiophene-3-carboxaldoxime (3TCOH) and we have obtained a series of complexes: [CoX_2($3TCOH$)$_4$] and [NiX_2(3TCOH)$_4$] (X = Cl or Br) and [$CuCl_2$(3TCOH)$_4$], [$CuBr_2$(3TCOH)$_2$] without pointing out any rearrangement [23]. A rearrangement is observed in the case of mono-oximes in presence of nickel chloride, but the reaction took place at 155 °C and not at room temperature [15]. Many Ni(II) and Cu(II) chlorides complexes with *vic*-dioximes are obtained at room temperature without conversion of the ligand [24].

The ionic radii for Cl^- and Br^- are 1.81 and 1.96 Å respectively [25] and this difference is not sufficient to explain the behavior of nickel bromide. The hexahydrated nickel(II) chloride is an aquo complex in which Ni^{2+} exhibits an octahedral geometry and the complexation easily occurs *via* a substitution reaction. In the case of the anhydrous bromide, the nickel ion needs to change its surrounding before bonding to $2,3BTCOH_2$. That is why the coordination is not possible at room temperature. At higher temperature, Ni^{2+} could act as a catalyst [15] and the rearrangement is then observed.

3.2. Crystal structure of $2,3BTCOH_2$

The main crystal parameters are reported in Table 1. The monoclinic unit cell (space group $C\ 2/c$) contains eight molecules. The molecule of $2,3BTCOH_2$ with numbering scheme is given in Fig. 3. The molecule is quite planar with a feeble mean deviation to the plane. The most important deviation is observed for N1 and O1 (0.25 and 0.21 Å) respectively. In this oxime, the geometry of functional group in position 2 is *cis* around the C6–N2 carbon–nitrogen double bond while geometry is *trans* around the C5-N1 double bond for the oxime group in position 3.

Representative bond distances and angles for $2,3BTCOH_2$ are shown in Table 2. The bond lengths C5–N1 and C6–N2 are equal to 1.279 and 1.290 Å, respectively, and they correspond to carbon–nitrogen double bond [26,27].

The cohesion of the crystal is ensured by the presence of intermolecular hydrogen bonds (Table 4). The packing arrangement with hydrogen bonds in the unit cell is given in Fig. 4. The stability of a group of eight molecules is governed by intermolecular

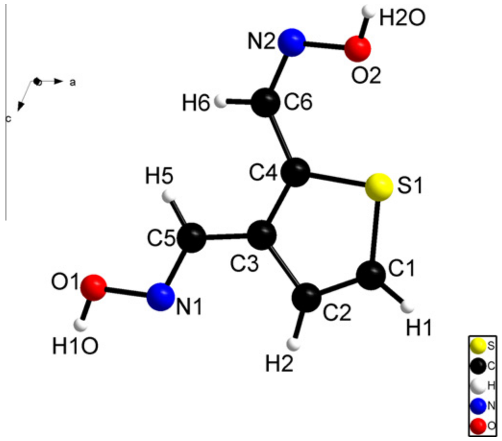

Fig. 3. Crystal structure and atoms numbering for $2,3BTCOH_2$.

Table 2
Selected bond lengths (Å) and angles (°) for $2,3BTCOH_2$.

Bond lengths (Å)		Bond angles (°)	
C5–N1	1.279	N1–C5–C3	120.44
C6–N2	1.290	N2–C6–C4	129.10
N1–O1	1.404	C5–N1–O1	111.09
N2–O2	1.378	C6–N2–O2	112.41
C1–S1	1.688	C1–S1–C4	92.10

Table 3
Selected bond lengths (Å) and angles (°) for ACTOH.

Bond lengths (Å)		Bond angles (°)	
C5–N1	1.273	N1–C5–C3	119.40
C6–O2	1.240	O2–C6–N2	122.03
C6–N2	1.335	O2–C6–C4	120.98
N1–O1	1.398	N2–C6–C4	116.99
		C5–N1–O1	111.70

Table 4
Bond lengths (Å), angles (°) and positions of intermolecular hydrogen bonds for 2,3BTCOH$_2$ and ACTOH.

Compound	Hydrogen bonds	Distance (Å)	Angle (°)
2,3BTCOH$_2$	O1···H2O	2.86	145.08
	N1···H2 O	1.97	169.54
	O2···H1O	2.83	142.05
	N2···H1O	2.00	164.42
	N2···H1O′	3.16	112.23
ACTOH	O1···H1A	2.82	126.51
	O2···H2A	2.18	155.16
	O2···H2B	2.22	169.34

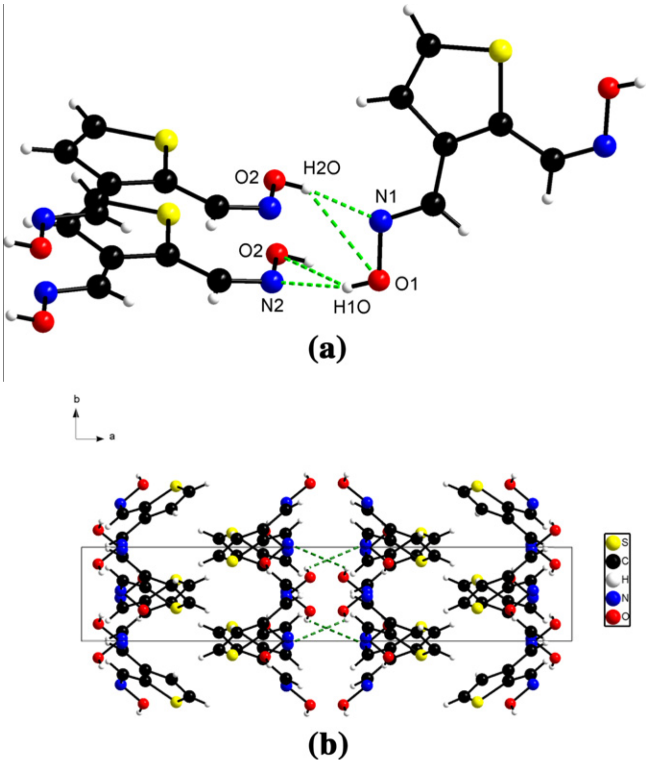

Fig. 4. Hydrogen bonding (a) and cell packing (b) for 2,3BTCOH$_2$.

hydrogen bonds (Table 4, Fig. 4a). The stacking of the molecules in the crystal lattice is made of symmetrical parallel double zigzag chains along c axis (Fig. 4b). Inside a series of molecules, the hydrogen bonds occur between N1 and H2O, O1 and H2O and, in the same way, between N2 and H1O and O2 and H1O. In both cases, the bonds through oxygen atoms are weaker than those obtained with N atoms.

Two symmetrical chains lead to a series of identical hydrogen bonds: N2···H1O′ where N2 is located on a chain and H1O′ is located on the symmetrical chain (Fig. 4b). Though this bond is weak, it can stabilize the crystal, because it is present in each molecule in the lattice [28].

3.3. Crystal structure of ACTOH

The main crystal parameters are reported in Table 1. Some representative bond lengths and angles are reported in Table 3. The triclinic unit cell (space group $P{-}1$) contains two molecules. The numbering scheme of a molecule is given in Fig. 5.

The bond lengths C6–O2 and C5–N1 are equal to 1.240 and 1.273 Å, respectively, and correspond to carbon–oxygen (acetamide) [29] and carbon–nitrogen (oxime) double bonds [27].

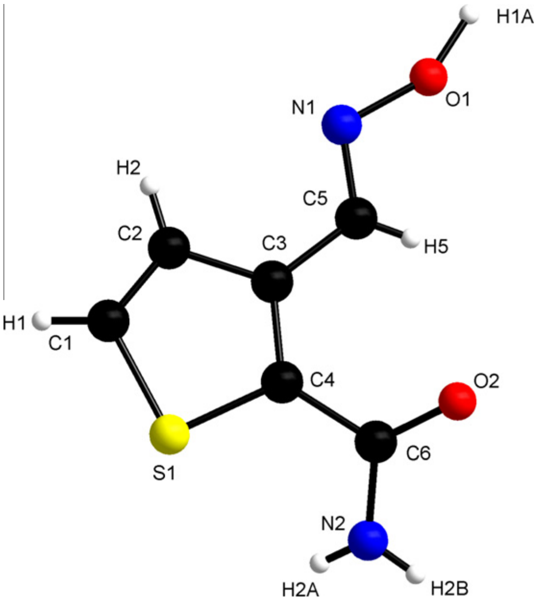

Fig. 5. Crystal structure and atoms numbering for 2-acetamido-3-thiophene carboxaldoxime (ACTOH).

The molecule is quite planar with a feeble mean deviation to the plane. The most important deviation are observed for N2 and O2 (0.63 and 0.43 Å) respectively. In the oxime functional group, the geometry around the carbon–nitrogen double bond C5–N1 is a *trans* geometry. There are not any intermolecular hydrogen bonds in this molecule.

Cohesion of the crystal is ensured by the presence of intermolecular hydrogen bonds whose characteristics are given in Table 4. They are established between identical functional groups.

Each oxime group shared two hydrogen bonds (O···H) with the same group of a second molecule (Fig. 6a) and these two bonds are identical. In some cases these bonds occurred through N (oxime) atoms [29] but in our structure these atoms are too far from hydrogen (quite 4 Å) to create a hydrogen bond.

The acetamide group of a molecule is linked with two neighboring molecules: O2···H2A (2.18 Å) and O2···H2B (2.22 Å). There are slightly longer than in the case of 2-thiophene carboxamide [29].

The packing arrangement in the unit cell is given in Fig. 6b. The stacking shows that the molecules lie in a family of parallel planes. These planes are associated together through O2···H2A hydrogen bonds along the plane.

3.4. Proposed structures

The main analytical data is given in Table 5. In all cases, the results of elemental analysis correspond to the proposed formulae.

The DSC diagrams of these complexes do not show endotherms corresponding to their melting. In the case of [NiCl$_2$(2,3BTCOH$_2$)], the exothermic peak 275 °C with a shoulder at 268° C is due to a first crystallization of a low stable polymorph (268 °C) which leads finally to a more stable crystalline form. In the [CuCl$_2$(2,3BTCOH$_2$)] pattern, the crystallization peak is located at 182 and 153 °C for the complex [CuBr(2,3BTCOH)]$_2$. In all cases, the peaks corresponding to their decomposition appeared for temperatures higher than 400 °C.

All complexes were found to be paramagnetic. The main infrared bands for the organic molecules and the complexes are listed in Table 6. In the IR spectrum of [NiCl$_2$(2,3BTCOH$_2$)], the band at

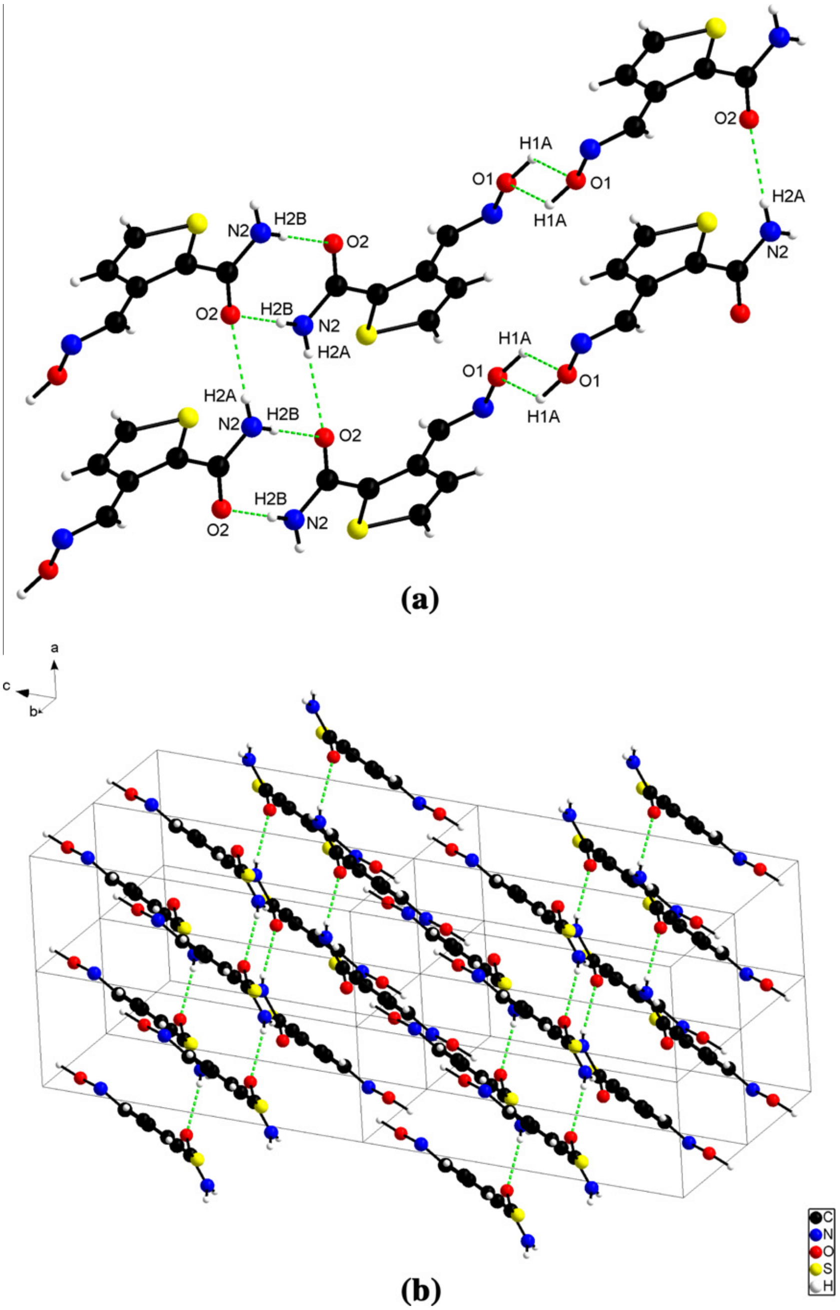

Fig. 6. Hydrogen bonding (a) and cell packing (b) for ACTOH.

Table 5
Analytical data.

Compound	Color	Yield (%)	Elemental analysis exp. (calc.)		
			C (%)	H (%)	N (%)
2,3BTCOH$_2$	white	83	42.09 (42.34)	3.47 (3.55)	16.43 (16.46)
[NiCl$_2$(2,3BTCOH$_2$)]	dark green	69	23.97 (24.04)	2.41 (2.02)	9.02 (9.34)
[CuCl$_2$(2,3BTCOH$_2$)]	dark orange	79	24.69 (23.66)	1.82 (1.99)	9.26 (9.20)
[CuBr(2,3BTCOH)]$_2$	dark orange	75	23.55 (23.05)	2.01 (1.61)	8.65 (8.96)

3330 cm^{-1} confirms the presence of the hydroxyle. The bands ν(Ni–N), ν(Ni–Cl) are observed at 379 and 218 cm^{-1} respectively. These results are consistent with non ionized oxime and the coordinating atoms are N (Oxime). In addition, the ν(C=N)

Table 6
Infrared data (cm^{-1}).

Compound	ν(OH)	ν(C=O)	ν(C=N)	ν(N–O)	ν(M–N)	ν(M–O)	ν(M–X)
2,3BTCOH$_2$	3124	–	1624	968	–	–	–
ACTOH	3172	1646	1607	964	–	–	–
[NiCl$_2$(2,3BTCOH$_2$)]	3330	–	1639	966	379	–	218
[CuCl$_2$(2,3BTCOH$_2$)]	3217	–	1640	974	337	–	218
[CuBr(2,3BTCOH)]$_2$	3225	–	1636	978	311	494	224

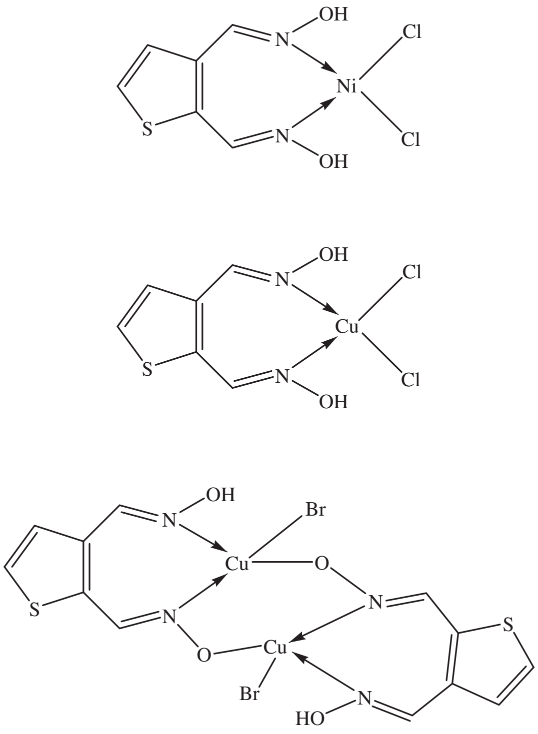

Fig. 7. Proposed structures for nickel(II) and copper(II) complexes.

vibration band at 1624 cm^{-1} (ligand) was shifted up to 1639 cm^{-1} (complex). As it has been already observed in similar compounds this complex is quite square-planar [30] (Fig 7).

For the complex [CuCl$_2$(2,3BTCOH$_2$)], the presence of the hydroxyle is confirmed by the presence of the band ν(OH) at 3217 cm^{-1}. The bands at 337 and 218 cm^{-1} respectively correspond to Cu–N coordination bonds and Cu–Cl bond. In addition, we have not found any bands corresponding to copper-oxygen coordination bond. The ν(C=N) appeared at 1640 cm^{-1}. In this complex, the copper(II) ion shows a geometry which is an intermediate between tetrahedral and square planar configurations (Fig 7) as already observed in similar complexes [31,32].

In this binuclear species [CuBr(2,3BTCOH)]$_2$, the band located at 3225 cm^{-1} is due to ν(OH) vibration. The bands ν(Cu–N), ν(Cu–O), ν(Cu–Br) are present at 311, 494 and 224 cm^{-1} respectively while the ν(C=N) vibration band is located at 1636 cm^{-1} (+22 cm^{-1} regarding the ligand). Each molecule of ligand is almost planar, each copper ion(II) shows a distorted tetrahedral geometry with coordination bonds as follows: (i) a coordination bond with each nitrogen atom of the oxime groups of one of the ligands, (ii) a bond with a bromide ion and (iii) a fourth link with the oxygen atom (oximato) of the second ligand molecule. Thus, these fourth bond lead to a bridge between the two symmetrical parts of the complex molecule (Fig 7). This structure has been already described for similar molecules [33,34].

4. Conclusion

Thiophene-2,3-dicarboxaldehyde bis(oxime) (2,3BTCOH$_2$) is able to complex hydrated nickel(II) chloride, copper(II) chloride and bromide. On the opposite side, the reaction with anhydrous nickel(II) bromide induces its rearrangement into 2-acetamido-3-thiophene carboxaldoxime (ACTOH); only the oxime functional group in position 2 is converted. As metal complexes were obtained at room temperature, they could be considered as thermodynamic products of the reaction. The rearrangement of oxime functionnal group occurs at higher temperatures (*e.g.* 110–155 °C) with anhydrous nickel(II) bromide. In all complexes, the nitrogen atoms of the two oxime groups are involved in chelation. In addition, in the dinuclear complex [CuBr(2,3BTCOH)]$_2$, one of the hydroxyle is ionized and bound to copper(II) while the second remains unchanged.

Appendix A. Supplementary material

CCDC 857506 and 857507 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.05.029.

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