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Author(s): Hannachi, Anissa; Valkonen, Arto; Gómez García, Carlos J.; Rzaigui, Mohamed; Smirani, Wajda

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Anissa Hannachi, ArtoValkonen, Carlos J. Gómez García, Mohamed Rzaigui, Wajda. Smirani

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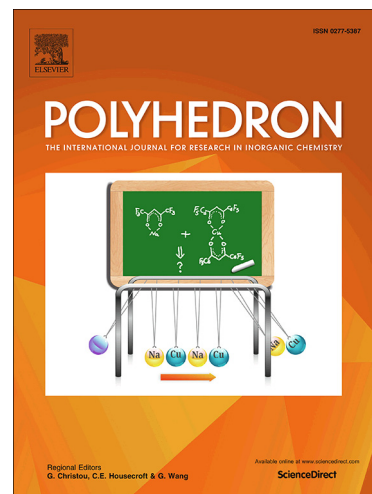
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Synthesis of isomorphous cobalt and nickel thiocyanate coordination compounds: Effect of metals on compound properties.

Anissa Hannachi^a, Arto Valkonen^b, Carlos J Gómez García^c, Mohamed Rzaigui^a and Wajda Smirani^{a*}

- a- Laboratory of Material Chemistry, Faculty of Sciences of Bizerte, University of Carthage, Bizerte, 7021 Zarzouna, Tunisia
- b- Department of Chemistry, University of Jyväskylä, 40014 Jyväskylä, Finland
- c- Instituto de Ciencia Molecular (ICMol), University of Valencia

Corresponding author: wajda_sta@yahoo.fr

Abstract

The reaction of 2-methylpiperazine with the thiocyanate ligand and two transition metals leads to the production of two new isomorphous $[ML_2SCN_4]$ where L is the 2-methylpiperazine and $[M = Co$ (1), and Ni (2)], presenting an octahedral configuration. These compounds were characterized by single crystal X-ray crystallography, TG-DTA analysis, as well as infrared and UV-Vis spectroscopy and TG-DTA. The magnetic and antibacterial properties were also determined. Through the link with N-H \cdots S hydrogen bonds, a global 3D network was established. The studied compounds show the metal center's impact leading to different properties. Indeed, the first compound shows high spin orbit coupling, whereas the second one shows a weak antiferromagnetic interaction. The antibacterial activity is enhanced for the cobalt compound compared with the nickel compound and the DTA/TG curves show a phase transition for the nickel compound.

Keywords; Nickel coordination compound, cobalt coordination compound, isomorphous structure, antibacterial activities, magnetic properties

1. Introduction

Many researches focus on metal coordination compounds due to their catalytic [1], fluorescent [2] and magnetic properties [3-8] and to their high biological activity as a result of the enzymes' active sites [9, 10], especially due to their capacity to stabilize the structure and to control metabolism [11]. These properties were enhanced when introducing the thiocyanate ligand. The contribution of this pseudohalide to the supramolecular network construction, acting as a hydrogen bond acceptor [12], and its ability to propagate the magnetic interactions between paramagnetic centers [5], have made it the subject of many studies [13-15].

The central metal ion and the organic co-ligand have an influence on the thiocyanate coordination compounds' geometry [16-18]. In this context, researches deal with polymorphs by changing the metals and studying the differences in behavior. Some significant similarities were seen [5] when the different characteristics were studied, while differences were seen in some aspects [6].

According to recent research [9, 19-22], terminal thiocyanate coordination is more widely known than bridged coordination. In view of these particular properties, the presence of the thiocyanate ligand makes the final coordination compounds, which we predict to obtain, a necessary quality, especially with the presence of cobalt and nickel as transition metals.

The aim of this work was to explore the effect of the two studied metals on the final coordination compounds and their characteristic behaviors using infrared, UV-Vis spectroscopies, magnetic properties and antibacterial activities.

2. Experimental

2.1. Materials and physical measurements

Using the Nicolet IR200 FT-IR spectrometer in the [400, 4000 cm^{-1}] range, the infrared spectra were measured at room temperature. The UV-Vis spectra [200-700 nm] were recorded on a Perkin

Elmer Lambda 11 UV/D68/Vis spectrophotometer. The simultaneous TG-DTA analyzer was used to perform the thermal measurements. The resulting curves were obtained with a heating rate of 10°C/min under inert gas from 0 to 500 °C. The ^{13}C NMR spectra were measured with a Bruker spectrometer. Magnetic susceptibility measurements were carried out in the [2-300 K] temperature range with an applied magnetic field of 0.1 T, on a polycrystalline sample, with a Quantum Design MPMS-XL-5 SQUID spectrometer. The diamagnetic contributions were estimated using Pascal's constant tables [23].

2.2. Preparation of $\text{Co}(\text{SCN})_4(\text{C}_5\text{H}_{13}\text{N}_2)_2$ (1) and $\text{Ni}(\text{SCN})_4(\text{C}_5\text{H}_{13}\text{N}_2)_2$ (2)

All materials were used as received without further purification. 10 mL of ethanol solution containing (1mmol, 0.100 g) of 2-methylpiperazine were mixed with 10 mL (1mmol, 0.238g) of $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$ (where $\text{M}=\text{Co}$ for compound (1) and $\text{M}=\text{Ni}$ for compound (2)). After stirring well each solution, 10 mL (2 mmol, 0.116 g) of the thiocyanate solution, obtained from a cationic resin, were added slowly until the color changed from blue to light pink for (1) and from cloudy green to light green for (2). Violet (1) and orange-brown (2) crystals were collected after 7 days.

Elemental analysis for $(\text{C}_{14}\text{H}_{26}\text{CoN}_8\text{S}_4)$ (493.60 $\text{g}\cdot\text{mol}^{-1}$): Anal. Calc. (%) C 34.03%, H 5.27%, N 22.69%, S 25.93% found (%) C 33.65%, H 5.19%, N 23.04%, S 26.58% and for $\text{C}_{14}\text{H}_{26}\text{N}_8\text{NiS}_4$ (493.38 $\text{g}\cdot\text{mol}^{-1}$): Anal. Calc. (%) C 34.05%, H 5.27%, N 22.7%, S 25.93% found (%) C 33.65%, H 5.18 %, N 23.03 %, S 26.63%. The calculated and the experimental XRPD patterns are shown in Fig. S1. Their peak positions are in good agreement with each other.

2.3. X-ray structural analysis

After a week, violet (1) and orange-brown (2) crystals were obtained. These were suitable for X-ray diffraction studies with dimensions of $(0.26 \times 0.24 \times 0.18)$ and $(0.28 \times 0.22 \times 0.17)$ for (1) and (2) respectively. These were put on a Bruker–Nonius Kappa CCD with graphite monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were analyzed using Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 using Shelx programs. The hydrogen atoms were treated with a mixture of independent and constrained refinement.

2.4. Biological activity

In order to test the antibacterial activities for the two studied coordination compounds, five different bacteria were used. The compounds were tested using the disc diffusion method against two Gram positive bacteria (*Staphylococcus aureus*, *Enterococcus faecium*), two negative Gram bacteria (*Escherichia coli*, *Salmonella typhimurium*) and *Candida Albicans*, mixed in a tube with a suspension of the tested compounds, already incubated overnight at 37°C. The mixture was adjusted to 0.5 McFarland turbidity standards, and then the solutions were diluted in sterile water placed in inoculated plates on a sterile paper disc. Ampicillin (10µg/disc) was used as positive control for all strains except for *Candida Albicans* for which Nystatin (100µg/disc) was used. The evaluation of the antibacterial activities was carried out by measuring the growth inhibition zones.

3. Results and discussion

3.1. Structure descriptions

The molecular structures of compounds (1) and (2) are shown in Figs. 1a and 1b respectively. The crystal details, the selected bond distances and the angles for the two compounds are listed respectively in Tables 1 and 2. The structures $[M(2\text{-methylpiperazine})_2(\text{SCN})_4]$, where (M: Co, Ni) are presented as centro-symmetrical coordination compound cations. The metal is coordinated by two 2-methylpiperazinium ligands in the equatorial plane and four thiocyanate anions in a trans-axial arrangement, forming a slightly distorted octahedral geometry with crystallographic inversion symmetry. The metal is coordinated to each thiocyanate ligand through symmetrical N-M bonds varying between 2.0530(18) Å and 2.0693(16) Å for the cobalt compound and between 2.091(2) Å and 2.108(2) Å for the nickel compound and is then linked to the nitrogen amide. The bond is located in the [2.25 (3), 2.256 (3)] Å range and the [2.202 (2), 2.212 (19)] Å range for the Ni and Co coordination compounds respectively. The 2-methylpiperazine shows a disordered group, with an occupancy ratio of 0.894 / 0.106 for (1) and a ratio of 0.900 / 0.100 for (2).

Bond lengths involving amides are longer than those involving thiocyanate ligands which is in accordance with previous research, including SCN ions and amides such as $[\text{Co}(\text{NCS})_2(\text{apm})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{NCS})_4(\text{Hhtm})_2]$ (htm=hexamethylenetetramine, apm = 2-amino-pyrimidine)[12]. This is an indication of the high coordination of the anionic thiocyanate group compared to 2-methylpiperazine. As observed for the studied coordination compounds, all coordination bond lengths for the cobalt compound are shorter than those for the nickel compound unlike the variation of the atomic radii of the metals [16].

The four coordinated SCN ions are linear, showing angle values of about 179.6 and 178.38, slightly bent because of the metal centers' effect, with bond angles: C11-N10-Co (165.02°), C9-N8-Co (175.04°), for the cobalt compound and C11-N10-Ni (175.2°), C9-N8-Ni (165.3°) for the nickel compound. These values are similar to those obtained in the coordination compound with metal centers, thiocyanate anions and N-bound co-ligands [24].

An intermolecular hydrogen bonding interaction is established forming and stabilizing the supramolecular networks. The uncoordinated sulfur from the thiocyanate ligands got the neighboring nitrogen amides involved in the N-H...S hydrogen bonds, consolidating the crystal structures. The complex network presented in Fig 2 can be reduced to combinations of various graph sets as mentioned in Angrew's research [25]. Two ring sets are shown ($R_2^2(18)$ and $R_2^3(28)$).

3.2. Spectroscopic properties

3.2.1. IR spectra and UV-Vis

The infrared spectra of the two compounds are shown in Fig 3. The thiocyanate ion is revealed by the presence of two bands at 2102 cm^{-1} and 2096 cm^{-1} , which correspond respectively to coordination compounds 1 and 2. These peaks that don't exceed 2110 cm^{-1} , prove the presence of N-bonded frequency vs. S-bonded thiocyanates [5]. The nitrogen terminal coordination modes for both compounds are also confirmed through the presence of the bands at 860 cm^{-1} considering that the

coordination through N- and S- bonded terminal thiocyanates is frequently observed in the 860-780 cm^{-1} range [9]. The peaks occurring at around 2920 cm^{-1} and 1598 cm^{-1} indicate the presence of the ν (C-H) and ($\nu(\text{C}=\text{N}),\nu(\text{C}=\text{C})$) stretches respectively. The $\nu(\text{C}-\text{N}),\nu$ (C-C)) vibrations appear in the [960-1480 cm^{-1}] range [6, 26]. These infrared vibration bonds reveal the presence of the organic compound: 2-methylpiperazine.

At room temperature, the luminescence of the two compounds was studied in their solid state. As shown in Fig 4, each spectrum presents two peaks. The different emissions at around 320 nm and 335 nm for (1) and (2) respectively, are a good indication of the charge transfer from thiocyanate to metal, which is similar to that observed in other works [5, 14]. The recorded broad bands that appear at 476 nm and 506 nm for the two compounds are assigned to d-d transition metals [22].

3.3. Thermal analysis

The thermal curves of the two coordination compounds (cobalt and nickel respectively) are given in Figs. 5a and 5b. With an isomorphous structure, the two compounds present different thermal behaviors. Compound (1) shows a weight loss in the [539, 545K] range, complying with the decomposition of the organic part, and some of the thiocyanate ligands from the cobalt compound. The obtained experimental value is 67 % which is in agreement with the theoretical value of 64.38% and complying with the possible removal of the two organic compounds and two thiocyanate ligands.

The nickel compound is thermally stable up to 413 K and then a strong sharp peak is observed at 457 K without weight loss. To confirm the presence of a new phase, compound (2) was heated at that temperature.

The endothermic peak at 457 K is assigned to the reversible phase transition detected by DSC at around $T = 457/428$ K (heating and cooling) Fig. S2. The XRPD of the two experimental patterns for the coordination compounds before and after heating are shown in Fig S3. The two patterns

obtained show a difference, confirming the phase transition phenomenon due to the rearrangement of new atoms.

The decomposition in the [513-573 K] range has the same variation as the first compound. The calculated value of about 64.41 % is close to the experimental value which reveals a similar decomposition behavior. The decomposition of the resulting $M(NCS)_2$ is carried out at a higher temperature [27].

3.4. NMR

The ^{13}C NMR spectra of the two coordination compounds, as depicted in Fig. 6 show great similarities due to their isomorphous structures. In the piperazine ring the carbons appear at 51.490 ppm, 45.396 ppm and 40.52 ppm and are assigned to the C5, C6 and C3 for the cobalt compound whereas the singlet peaks at 51.955 ppm, 46.014 ppm and 40.589 ppm are proof of their presence in the nickel compound structure. The methyl carbon singlet is seen at 14.912 ppm for the cobalt compound and 15.284 ppm for the nickel compound. The thiocyanate carbon appears at 131.42 ppm for the cobalt compound and at 132.56 for the nickel one. All the peaks in the two coordination compounds studied are considerably de-shielded due to the coordination with the metal centers [28].

3.5. Biological activity

Examination of the biological activities shows that both compounds (1) and (2) present effective antibacterial activities against the studied bacteria. The growth inhibition zones increase with doses [29], but are still lower than commercial ones [10], showing the same behavior as in other tested compounds [30]. The IDZ values are depicted in Fig. 7. Bacteria such as *E. coli*, *S. typhimurium*, *E. feacium* and *C. albicans* give rise to similar behaviors for the two compounds. The cobalt compound was inactive against the gram positive bacteria (*S. aureus*) compared to the nickel compound. These differences in behavior indicate the possible effect of the metal nature on the

antibacterial activity where the nickel metal compound present a higher biological effect than the cobalt compound same as other research [31].

3.6. Magnetic properties

The thermal variation of the susceptibility of compound 1 at 300 K is about $3.0 \text{ cm}^3\text{K.mol}^{-1}$ per formula unit. These values are in the $2.8\text{-}3.4 \text{ cm}^3\text{K.mol}^{-1}$ range revealing an orbital contribution of the ${}^4T_{1g}$ ground state [6, 32-36]. Once the temperature decreases, the susceptibility also shows a progressive decrease reaching a value of $1.5 \text{ cm}^3\text{K.mol}^{-1}$ at 2 K (Fig. 8a). This behavior is attributed to the presence of spin-orbit coupling rather than an antiferromagnetic Co-Co. The observed value at 2K is very close to the values observed in many other Co (II)-containing octahedral coordination compounds[32, 34-36].

The isothermal magnetization of compound 1 shows a saturation value of about $2.1 \mu_B$ at 5 T (Fig. 8b), well below the expected one for an $S = 3/2$ with $g = 2$. The lower value is attributed to the fact that only the Kramers' doublet ground state is populated at 2 K, resulting in an effective $S_{\text{eff}} = 1/2$ ground spin state. With this effective spin ground state, the calculated g value is therefore 4.2, which is in good agreement with that observed in many other Co(II)-containing octahedral coordination compounds[27].

For the nickel compound, the thermal variation susceptibility at 300 K is about $1.2 \text{ cm}^3\text{K.mol}^{-1}$ per formula unit, which is an expected value for one nickel ion with $g = 2.19$. Below 5 K, the susceptibility shows an abrupt variation that decreases to reach a value of about $1.0 \text{ cm}^3\text{K.mol}^{-1}$ at 2 K (Fig. 8c) and then remains constant. Since this compound shows an isolated Ni(II) compound with an $S = 1$ spin ground state, the magnetic properties have been fitted to the monomer model with zero field splitting (ZFS), responsible for the sharp decrease at low temperatures [32].

This model reproduces very satisfactorily the magnetic properties in the whole temperature range with $g = 2.1897$ and $|D| = 2.3 \text{ cm}^{-1}$ (solid line in Fig 11a). Note that this value may include a very weak antiferromagnetic interaction between Ni(II) ions in neighboring compounds and that we cannot determine the sign of D with measurements on a polycrystalline sample. The D value is within the normal range found for other monomeric $S = 1$ Ni(II) compounds [2]. Further confirmation is provided by the isothermal magnetization at 2 K (Fig 8d) that shows a saturation value slightly above $2\mu_B$, as expected for an isolated $S = 1$ Ni(II) ion.

Conclusion:

Using the same reaction with two different metals, two coordination compounds were prepared. The metal center was found to be hexacoordinated with two 2-methylpiperazines and four NCSs through nitrogen bonds establishing an octahedral geometry. Both compounds have the same structure and the same configuration due to their isomorphous structure. The existence of a peak without any weight loss in the DTA/TG curves for compound (2) reveals a possible phase transition. The study of the magnetic properties shows high spin coupling for the cobalt compound and a weak antiferromagnetic behavior for the nickel compound. The thiocyanate coordination compounds have shown a positive result against different studied bacteria like *E. coli*, *S. typhimurium*, *E. feacium* and *C. albicans* except for *S. aureus* for the cobalt compound. These results are a good indication that the nature of the metals used has an important effect on the coordination compounds' characterization.

Appendix A. Supplementary material

CCDC 1905049 and 1905048 contain the supplementary crystallographic data for 1 and 2. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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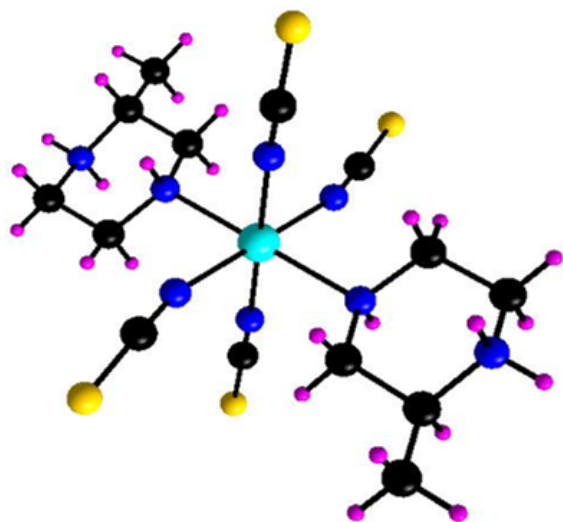
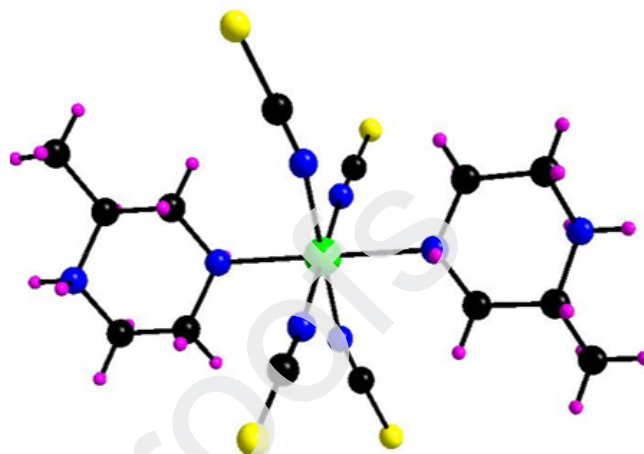
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Graphical abstract

2-methylpiperazine +HSCN

+

CoCl₂.6H₂O**NiCl₂.6H₂O****Graphical abstract (synopsis)**

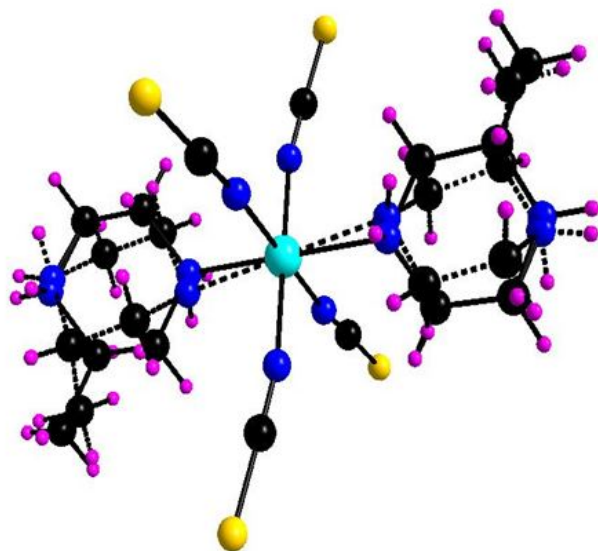
Two isomorphous coordination compound structures have been obtained using two different metals leading to different coordination compound behaviors.

- Two isomorphous structures are obtained
- The metal centers are hexacoordinated
- An effective antibacterial activities are observed for the two compounds
- The cobalt complex presents a spin-orbit coupling
- The nickel complex behaves as a weak antiferromagnetic material

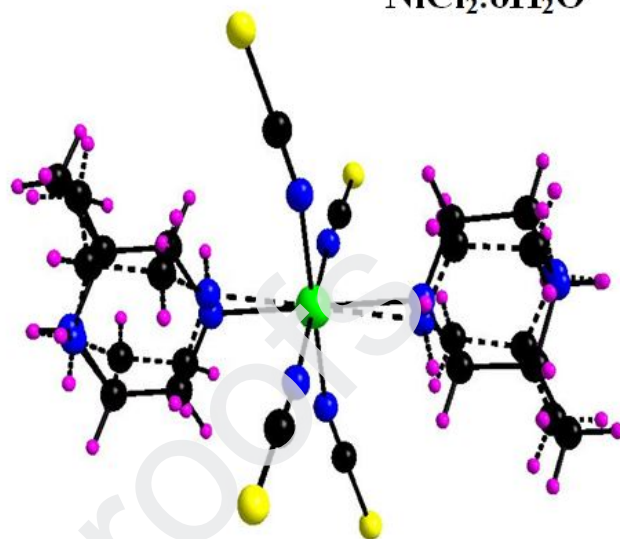
2-methylpiperazine +HSCN

+

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$



$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$



Journal Pre-proofs