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Synthesis and characterization of a novel coordination compound based on 2, 6-dimethylpiperazine

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Abstract

Here we show the synthesis and complete characterization, including single crystal X-ray structure determination, of the first compound containing the monoprotonated 2,6-dimethylpiperazinium cation: $(C_6H_{15}N_2)^+$. Compound $[Co(NCS)_4(C_6H_{15}N_2)_2]$ (**1**) crystallizes in the monoclinic $P2_1/n$ space group and contains an octahedral Co(II) ion surrounded by four -NCS and two protonated 2,6-dimethylpiperazine ligands $(C_6H_{15}N_2)^+$. There are some N-H...S intermolecular hydrogen bonds that generate a three-dimensional H-bonded network. Compound **1** has been characterized by single-crystal and powder X-Ray diffraction, infrared, UV-vis and RMN spectroscopies, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The magnetic properties in the temperature range indicate the presence of isolated high spin Co(II) ions with the expected spin-orbit coupling. The antibacterial activity of compound **1** shows a higher antibacterial activity than other related complexes due to the presence of the piperazine-derivative ligands.

Introduction

Piperazine and its derivatives have been extensively studied in the last years [1,2], due to their potential bridging abilities [3] to generate many different coordination polymers [4]. Furthermore, they may give rise to supra-molecular structures due to their weakly terminal amino protons [5]. Piperazine-derivative ligands are considered as important building blocks in drug discovery industries [3]. Among these piperazine derivatives, 2,6-dimethylpiperazine has been widely used in numerous studies, including the synthesis of an excellent antimicrobial agent as sparfloxacin [6], a potent agent for inhibiting the proliferation of SGC-7901 and HeLa cells [7] and, recently, as 2,6-allosteric inhibitors of CPS1 [8].

The thiocyanate (SCN^-) ligand has also been extensively used to obtain hybrid organic/inorganic materials thanks to its high coordination and bridging abilities [9]. It is well-known that NCS^- can be either terminal or bridging, giving rise to a wide variety of coordination modes and topologies [10]. When acting as terminal ligand, it can coordinate through the N or S atoms depending on the hard/soft acid character of the metal ion. Additionally, the thiocyanate ligand can form hydrogen bonds with adjacent species, usually observed through the nitrogen end of the ligand, giving rise to two- or three-dimensional networks [10–14].

Coordination compounds based on thiocyanate and different metals with interesting topologies and magnetic properties have been intensively investigated in order to determine the different factors influencing the final geometry, topology and properties [15–17], especially when the thiocyanate coordination mode can be affected by several factors [18–20].

In this work, we prepare and characterize a novel Co(II) coordination compound using thiocyanate and 2,6-dimethylpiperazine ligands [21]. The resulting complex, formulated as $[\text{Co}(\text{NCS})_4(\text{C}_6\text{H}_{15}\text{N}_2)_2]$ (**1**) contains a high spin Co(II) ion coordinated by four -NCS^- ligands in the equatorial plane and two monoprotonated 2,6-dimethylpiperazinium cations in axial positions. We also show that compound **1** shows a high antibacterial activity thanks to the presence of the two terminal protonated 2,6-dimethylpiperazinium ligands. Interestingly, a search in the CCDC database (performed on April 2022) reveals that compound **1** is the first reported compound with the monoprotonated 2,6-dimethylpiperazinium cation ($\text{C}_6\text{H}_{15}\text{N}_2$)⁺. Thus, to date there are only four reported compounds (CCDC codes: ASOPAC [22], OGICEM [23], TAYVEX [24] and XAVZEC [25]) containing doubly protonated 2,6-dimethylpiperazine-1,4-dium cations, but none containing the monoprotonated 2,6-dimethylpiperazinium cation ($\text{C}_6\text{H}_{15}\text{N}_2$)⁺.

Materials and methods

Materials and physical characterization

All the reagents are commercial and were used as received. The IR spectra were recorded on a Nicolet IR200 FT-IR spectrometer in the 400-4000 cm^{-1} range at room temperature. The UV-vis spectra were recorded in the 200-700 nm range on a Perkin Elmer Lambda 11 UV/D68/Vis spectrophotometer. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurements were performed in the range 300-773 K with a Thermogravimetric analyzer: SETSYS 1750 (SETARAM): DTA- TGA coupled. The ^{13}C NMR spectra were carried out with a Bruker spectrometer Ultrashield Plus 500. Magnetic susceptibility measurements were measured with a Quantum Design MPMS-XL-5 SQUID susceptometer in the temperature range 2-300 K with an applied magnetic field of 0.1 T using a polycrystalline sample of compound **1** with a mass of 16.929 mg. Isothermal magnetization measurements were realized at 2 K with magnetic fields up to 5 T. The susceptibility data were corrected for the sample holder previously measured using the same conditions and for the diamagnetic contribution calculated with the Pascal tables [26].

*Synthesis of $[\text{Co}(\text{NCS})_4(\text{C}_6\text{H}_{15}\text{N}_2)_2]$ (**1**)*

An ethanolic solution (10 mL) containing 2,6-dimethylpiperazine (1 mmol, 100 mg) was mixed with (10 mL) of an ethanolic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 238 mg). The resulting solution was added to (10 mL) containing of the thiocyanate anion obtained by cation exchange of KSCN (2 mmol, 116 mg) with a protonated Amberlite IR 120 resin. The resulting acid solution was stirred for several minutes at room temperature until the colour changed from cloudy blue to pink. After 6 days, orange-brown crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solution at room temperature. Elemental analysis for $(\text{C}_{16}\text{H}_{30}\text{CoN}_8\text{S}_4)$ ($521.65 \text{ g mol}^{-1}$): Anal. Calc.: C, 36.84%; H 5.75,%; N, 21.47% and S 24.59%. Found: C, 35.55%; H, 5.03%; N, 20.04% and S, 25.18%.

X-ray data collection

A good quality single crystal with size $0.18 \times 0.17 \times 0.17 \text{ mm}^3$ was collected for the single crystal X-ray diffraction study using a Bruker-Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was refined by 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. Molecular graphics were prepared using Diamond IV [27].

Antibacterial activity

The antibacterial activity of compound **1** was studied for five different bacteria: two Gram-positive (*Staphylococcus aureus* and *Enterococcus faecium*), two Gram-negative (*Escherichia coli* and *Salmonella typhimurium*) and the pathogenic yeast *Candida albicans*. A suspension of the compound was tested using the disc diffusion method mixed in a tube already incubated overnight at 37°C . The mixture was adjusted to 0.5 McFarland turbidity standards. The dilution of solutions was realized in sterile water, then placed in inoculated plates on a sterile paper disc. Ampicillin (10 $\mu\text{g}/\text{disc}$) was used as a positive control for all strains, whereas for *Candida albicans*, the Nystatin (100 $\mu\text{g}/\text{disc}$) was used. The antibacterial activity was determined by measuring the growth inhibition zones.

Results and discussion

*Single crystal structure of $[\text{Co}(\text{NCS})_4(\text{C}_6\text{H}_{15}\text{N}_2)_2]$ (**1**)*

The asymmetric unit contains one Co(II) ion, located on an inversion centre, two *N*-coordinated thiocyanate ligands and one 2,6-dimethylpiperazinium cation. The application of the inversion centre leads to the monomeric neutral complex of formula $[\text{Co}(\text{NCS})_4(\text{C}_6\text{H}_{15}\text{N}_2)_2]$ (Fig. 1). Note that the 2,6-dimethylpiperazinium cation is formed by the protonation, under the strong acidic synthetic medium, of the 2,6-dimethylpiperazine molecule used in the synthesis of compound **1**. Tables 1 and 2 show the crystal data and selected bond distances and angles for compound **1**.

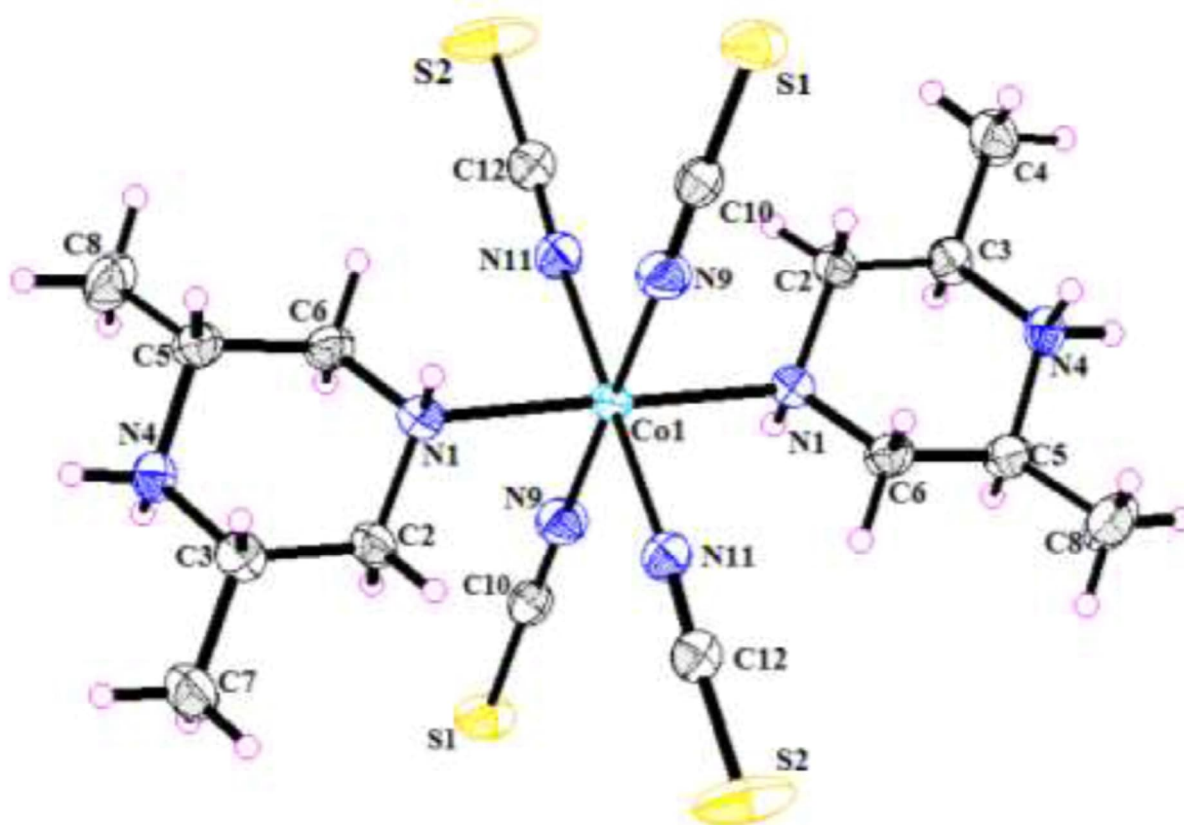


Fig. 1. ORTEP drawing of the asymmetric unit of compound $[\text{Co}(\text{NCS})_4(\text{C}_6\text{H}_{15}\text{N}_2)_2]$ (**1**). Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary size.

Table 1 Crystal data and structure refinement details for compound **1**.

Parameters	Compound
Empirical formula	$\text{C}_{16}\text{H}_{30}\text{CoN}_8\text{S}_4$
Formula weight (g mol^{-1})	521.65
Crystal system	Monoclinic,
Space group	$P2_1/n$
a (\AA)	7.0359(6)
b (\AA)	13.7865(6)
c (\AA)	13.0596(10)
β ($^\circ$)	90.464(3)
Volume (\AA^3)	1266.75(16)
Z	2

ρ_{calcd} (g cm ⁻³)	1.368
Absorption coefficient, μ (mm ⁻¹)	1.03
F(000)	546
Temperature (K)	170 K
Reflections collected	4784
Independent reflections	3140
Refinement	
R [$F^2 > 2 \sigma(F^2)$]	0.064
wR (F^2)	0.146
S	1.06
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.41, -0.40

Table 2 Selected bond distances (Å) and angles (°) for compound **1**.

Atoms	Distance (Å)	Atoms	Atoms Distance (Å)
Co1-N9 ⁱ	2.085 (3)	Co1-N11	2.113 (3)
Co1-N9	2.085 (3)	Co1-N1 ⁱ	2.264 (3)
Co1-N11 ⁱ	2.113 (3)	Co1-N1	2.264 (3)
Atoms	Angle (°)	Atoms	Angle (°)
N9 ⁱ -Co1-N9	180.0	N11-Co1-N1 ⁱ	87.56 (11)
N9 ⁱ -Co1-N11 ⁱ	88.23 (12)	N9 ⁱ -Co1-N1	90.68 (12)
N9-Co1-N11 ⁱ	91.77 (12)	N9-Co1-N1	89.32 (12)
N9 ⁱ -Co1-N11	91.77 (12)	N11 ⁱ -Co1-N1	87.56 (11)
N9-Co1-N11	88.23 (12)	N11-Co1-N1	92.44 (11)
N11 ⁱ -Co1-N11	180.0	N1 ⁱ -Co1-N1	180.0
N9 ⁱ -Co1-N1 ⁱ	89.32 (12)	C2-N1-Co1	116.3 (2)
N9-Co1-N1 ⁱ	90.68 (12)	C6-N1-Co1	112.4 (2)
N11 ⁱ -Co1-N1 ⁱ	92.44 (11)	C10-N9-Co1	161.4 (3)
C12-N11-Co1	165.1 (3)	N9-C10-S1	179.3 (4)
N11-C12-S2	178.3 (4)		

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$. The Co(II) ion shows an octahedral coordination environment formed by four equatorial NCS^- ligands and two axial *trans* 2,6-dimethylpiperazinium cations coordinated through the non-protonated N atom. This coordination environment is similar to that observed for the closely related 2-methylpiperazine ligand [16]. The axial Co-N1 bond distances from the 2,6-dimethylpiperazinium cations (2.264(3) Å) are significantly longer than the two different Co-N9 and Co-N11 equatorial bond distances (2.085(3) and 2.113(3) Å), indicating a stronger SCN-Co interaction compared with the organic 2,6-dimethylpiperazinium ligands. The Co-N bond distances are similar to those reported for other thiocyanate coordination compounds of Co(II) with an octahedral geometry with thiocyanate and imidazole derivatives [16,21,28].

The C-C and C-N bond distances (in the range 1.502-1.515 Å and 1.465-1.502 Å, respectively) as well as the C-C-N, N-C-C, C-N-C and C-C-C bond angles in the 2,6-dimethylpiperazinium ligand are similar to those observed in other materials based on this 2,6-dimethylpiperazine ligand [29–31]. The N-C-S angles are almost linear, with values of 179.3 ° for the N9-C10-S1 ligand and 178.3 ° for the N11-C12-S2 one. The *cis* N9-Co1-N11 angles in the equatorial plane (88.23 ° and 91.77 °) slightly deviate from the ideal values due to the presence of several N-H...S hydrogen bonds that stabilize the structure (Table 3).

Table 3 Hydrogen bond geometry (Å, °) for the compound.

D-H ... A	D-H (Å)	H ... A (Å)	D ... A (Å)	D-H ... A (°)
N1-H1 ... S2 ⁱⁱ	0.88 (2)	2.88 (2)	3.674 (3)	150 (3)
N4-H4A ... S1 ⁱⁱⁱ	0.91 (2)	2.37 (2)	3.261 (3)	166 (3)
N4-H4B ... S2 ⁱⁱⁱ	0.90 (2)	2.43 (2)	3.313 (3)	170 (3)

Symmetry codes: (ii) $x + 1, y, z$; (iii) $x + 1/2, -y + 3/2, z + 1/2$.

There are three H-bonds formed between the amine N1 atom and the sulphur S2 atom from a neighbouring complex, N1-H1...S2ⁱⁱ ($ii = x + 1, y, z$) and between the non-coordinated protonated amino N4 atom with two sulfur atoms from a neighbouring complex sitting at the $x + 1/2, -y + 3/2, z + 1/2$ position (Table 3). These H-bonds give rise to the supramolecular network shown in Fig. 2, containing two types of graph sets motifs [32]: $R_2^2(12)$ $R_4^3(22)$, as shown in Fig. 3.

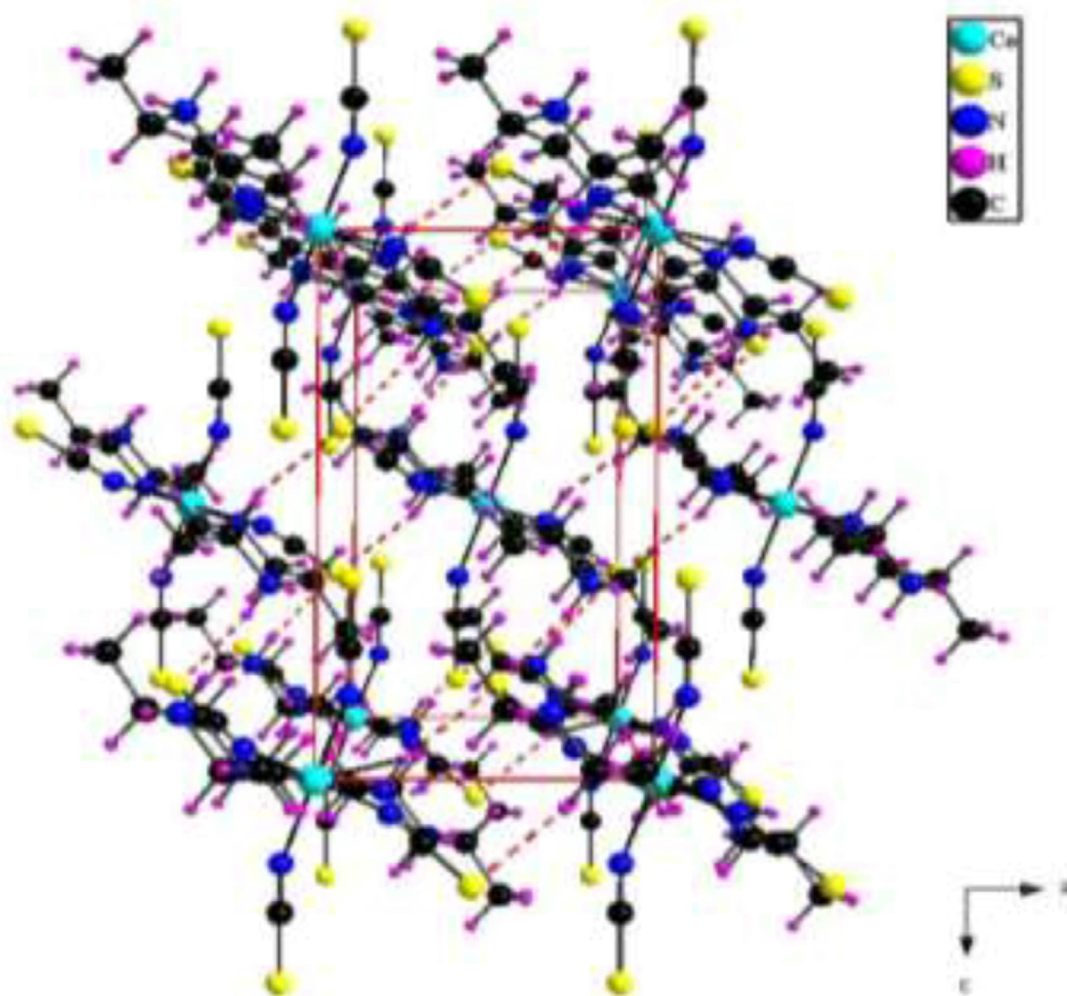


Fig. 2. Perspective view of the structure of compound **1** showing the intermolecular H-bonds.

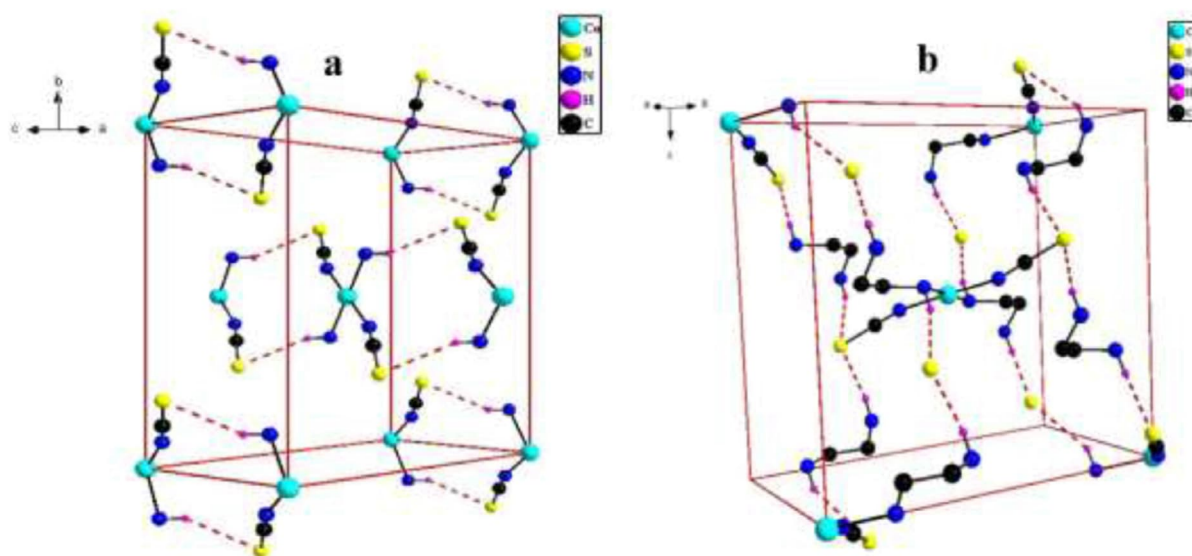


Fig. 3. (a) Graph sets of the type $R_2^2(12)$ and (b) $R_4^3(22)$ in compound **1**.

IR spectrum of compound 1

The infrared spectra of compound **1** shows a sharp peak at 2101 cm^{-1} due to the presence of the CN vibration bands of the NCS^- ligands (Fig. 4). The band corresponding to the C-S stretching vibration of the thiocyanate group appears at 971 cm^{-1} , in the typical range [$960\text{--}990\text{ cm}^{-1}$] observed for *N*-coordinated SCN^- ligands [20,33]. The band appearing at 1578 cm^{-1} can be attributed to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ stretching vibrations [34]. The bands at 3264 cm^{-1} and 3367 cm^{-1} can be attributed to the NH stretching vibrations. These bands appear at lower frequencies than in the free bases, confirming the coordination of the 2,6-dimethylpiperazinium cation through the NH group [35,36]. The broad peaks between 2740 cm^{-1} and 3100 cm^{-1} are assigned to the CH vibrations for the aromatic and aliphatic bonds of the piperazinium ligand [4].

UV-vis spectrum of compound 1

The UV-vis absorption spectrum of compound **1** have been investigated in the solid state, at room temperature [37]. The experimental electronic spectrum of **1** shows two broad absorption bands: a very strong band, at 256 nm , that can be attributed to the $n\text{-}\pi^*$ transition confirming the presence of an intra-ligand transition in the thiocyanate ligand [28,38,39] and a second band, at 582 nm , indicative of the existence of d-d-type electronic transitions in the Co(II) metal [4,40]. These values are similar to those observed in other similar octahedral cobalt(II) complexes [16]. An energy gap of 3.72 eV can be determined for compound **1** with the Tauc method, [41] from the absorption spectrum by extrapolation at the origin of the curve $[\alpha h\nu]^2$ as a function of $h\nu$ (Fig. 5). This value indicates the insulating character of **1** [42].

NMR spectrum of compound 1

As depicted in Fig. 6, the ^{13}C NMR spectrum shows three resonances corresponding to three carbon atoms in different environments. The peak at 22.211 ppm is attributed to the C atom of the two CH_3 groups. The signals at 50.696 ppm and 56.940 ppm can be attributed to the C atoms (C3, C5) and (C2, C6) of the piperazinium cation. These resonances confirm the presence of 2,6-dimethylpiperazinium in the structure of compound **1**. The C atom of the thiocyanate groups appears at 133.2 ppm . All these peaks in compound **1** are de-shielded due to the coordination with the cobalt(II) ion, as observed in similar complexes [32].

X-ray powder diffraction of compound 1

The X-ray powder diffraction (XRPD) pattern of compound **1** at room temperature is very similar to the simulated one from the single crystal X-ray structure, confirming the phase purity of compound **1** (Fig. 7).

TGA and DTA of compound 1

As shown in Fig. 8, the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of compound **1** in the range $300\text{--}770\text{ K}$ under a N_2 atmosphere show an endothermic peak at around 440 K without weight loss, indicating the presence of a possible phase transition. The TGA plot shows an important weight loss of 68% starting at around 500 K with a maximum slope at approximately 550 K that is also clearly observed in the DTA plot with a double endothermic peak at 497 and 560 K . The weight loss of 68% agrees with the departure of two 2,6-dimethylpiperazinium and two thiocyanate ligands [4]. The decomposition of the residual compound $\text{Co}(\text{NCS})_2$ is expected to take place above 770 K [43] and, therefore, cannot be

observed in our measurements. This thermal behaviour is similar to the one observed in the related compound $[\text{Co}(\text{NCS})_4(\text{C}_5\text{H}_{13}\text{N}_2)_2]$ [16].

Biological activity

Several studies have shown that the antibacterial activity of some coordination compounds is better than that of the corresponding free ligands [44–48] since the metal ion may also have antibacterial properties [45]. Accordingly, we have examined the antibacterial activity of compound **1** for different bacteria types as *Enterococcus faecium* (*EF*), *Staphylococcus aureus* (*SA*), *Escherichia coli* (*EC*), *Salmonella typhimurium* (*ST*) and the yeast *Candida albicans* (*CA*).

The growth inhibition zone values are shown in Fig. 9. The measured diameters for the gram-positive bacteria *EF* and *SA* are higher than those of the gram-negative bacteria *EC* and *ST* and of the yeast *CA*. As shown in Fig. 9, for doses below 50 μg , there is no antibacterial activity, but for 100, 150 and 200 μg doses, compound **1** shows antibacterial activity for all the tested bacteria. As expected, the antibacterial activity increases as the dose increases. These results are comparable with previous results obtained by some of us for *SA* with a related Co(II) complex [16]. The examination of free ligands didn't show any antibacterial activity with the thiocyanate and reveals a weak behaviour for the 2,6-dimethylpiperazine in comparison with compound **1** (Fig. 9). It proves the effect of the coordination in improving antibacterial activities.

Magnetic properties

Magnetic measurements show that the product of the molar magnetic susceptibility times the temperature ($\chi_{\text{m}}T$) for compound **1** at 300 K is 3.1 $\text{cm}^3 \text{K mol}^{-1}$ per Co(II) ion. This value is close to the expected for one Co(II) ion (in the range 2.8–3.4 $\text{cm}^3 \text{K mol}^{-1}$ due to the orbital contribution of the $^4\text{T}_{1\text{g}}$ ground state) [49–54]. When the temperature is lowered, $\chi_{\text{m}}T$ shows a progressive decrease to reach a value of 1.3 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K (Fig. 10 a). This progressive decrease is due to the presence of a spin-orbit coupling rather than an antiferromagnetic Co-Co coupling and the observed value at 2 K is very close to those observed in many other Co(II)-containing octahedral complexes [49–54].

The isothermal magnetization of compound **1** shows a saturation value of ca. 2.3 μB at 5 T (Fig. 10 b), well below the expected one for a $S = 3/2$ with $g = 2$. This lower value confirms that only the ground Kramers doublet 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, 4.6, in good agreement with those observed in many other Co(II)-containing octahedral complexes [49–54].

In order to confirm that the decrease in $\chi_{\text{m}}T$ on lowering the temperature is due to the spin-orbit coupling rather than to an intermolecular antiferromagnetic coupling, we have fit the thermal variation of $\chi_{\text{m}}T$ for compound **1** using the program PHI [55] with the following Hamiltonian:

$$\hat{H} = \alpha\lambda\hat{L} \cdot \hat{S} + \alpha^2 D [3\hat{L}^2 - \hat{L}^2] + \mu_B (\alpha\hat{L} \cdot I + 2\hat{S} \cdot I) \cdot \vec{B} \quad (1)$$

This Hamiltonian corresponds to an isolated Co(II) monomer in a distorted octahedral geometry and considers one magnetically isolated octahedral high spin Co(II) ion with an orbital reduction factor ($\alpha = \kappa A$) and a spin-orbit coupling (λ). We have also included a zero

field splitting parameter (D) to account for the axial distortions of the complex. This Hamiltonian reproduces very satisfactorily the thermal variation of $\chi_m T$ for compound **1** (solid line in Fig. 10 a) with the following parameters: $\lambda = -134.6(7) \text{ cm}^{-1}$, $\alpha = -1.40(1)$ and $|D| = 1.78(1) \text{ cm}^{-1}$. These values are within the normal range found for other isolated monomeric Co(II) complexes [49]. Note that the sign of D cannot be determined unambiguously from powder magnetic measurements.

Conclusion

We have successfully prepared and characterized the first compound with the protonated 2,6-dimethylpiperazinium cation. Single crystal X-ray structure determination of this compound, formulated as $[\text{Co}(\text{NCS})_4(\text{C}_6\text{H}_{15}\text{N}_2)_2]$ (**1**), shows that it presents an octahedral Co(II) ion surrounded by four NCS^- ligands in the equatorial plane and two protonated 2,6-dimethylpiperazinium cations in the axial positions. Compound **1** shows some N-H \cdots S hydrogen bonds that stabilize the structure. The UV-vis spectrum indicates that **1** is an optical insulator with a band gap of 3.72 eV. The NMR spectra confirms the purity of **1** and the X-ray powder diffraction pattern, its phase purity. The TGA and DTA shows the presence of a possible phase transition at 440 K followed by its thermal decomposition starting at about 500 K.

Biological tests revealed a high antibacterial activity of compound **1** for different bacteria, including two Gram-positive (*Staphylococcus aureus* and *Enterococcus faecium*), two Gram-negative (*Escherichia coli* and *Salmonella typhimurium*) and the pathogenic yeast *Candida albicans*.

The magnetic properties show that compound **1** behaves as an isolated high spin Co(II) ion with a spin-orbit coupling and a small zero-field splitting.

CRedit authorship contribution statement

Anissa Hannachi: Investigation, Methodology, Writing - original draft. **Carlos J Gómez García:** Experimental part, Writing - review & editing. **Arto Valkonen:** Experimental part, Structure determination. **Wajda Smirani:** Supervision, Reviewing & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.molstruc.2022.133569. CCDC 2128727 contain the supplementary crystallographic data for the obtained compound. 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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