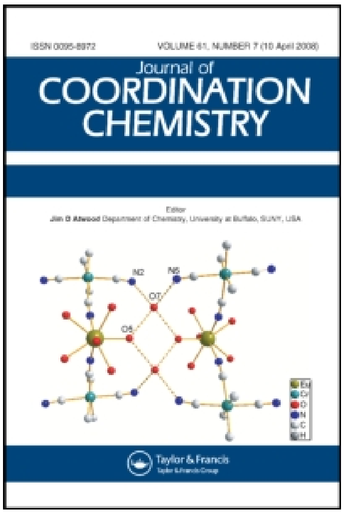

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Synthesis, spectroscopic characterization and crystal structure of disulfamethoxazole diaquo Ni(II) monohydrate

M. H. Torre[a]; S. Calvo[a]; H. Pardo[b]; A. W. Mombru[b]
[a] Cátedra de Química Inorgánica, DEC, Facultad de Química, UDELAR, Montevideo, Uruguay [b] Laboratorio de Cristalografía, DEQUIFIM, Facultad de Química, UDELAR, Montevideo, Uruguay

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Synthesis, spectroscopic characterization and crystal structure of disulfamethoxazole diaquo Ni(II) monohydrate

M. H. TORRE†*, S. CALVO†, H. PARDO‡ and A. W. MOMBRU‡

†Cátedra de Química Inorgánica, DEC, Facultad de Química,
UDELAR, Gral. Flores 2124, CC1157, Montevideo, Uruguay
‡Laboratorio de Cristalografía, DEQUIFIM, Facultad de Química,
UDELAR, Gral. Flores 2124, CC1157, Montevideo, Uruguay

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The novel disulfamethoxazole diaquo Ni(II) monohydrate, $[Ni(sulfamethoxazole)_2(H_2O)_2]\cdot H_2O$, was synthesized, characterized by infrared and electronic spectroscopies and the crystal structure determined. The compound crystallized in the monoclinic centrosymmetric space group $P2_1/c$, with four asymmetric units per unit cell. The nickel atoms are in slightly distorted regular octahedra, coordinated by four nitrogen atoms, two from *N*-arylamine and two from *N*-sulfonamide with the apical positions occupied by two oxygen atoms from the water molecules.

Keywords: Ni complexes; Sulfamethoxazole; Crystal structure

1. Introduction

Numerous metal complexes of sulfonamides have been studied as simple models for metal–protein interactions [1–4], and ligands containing a sulfonamide group have been investigated as reagents for the separation, concentration and selective determination of many first-row transition metal cations [5–7]. Many analytical tests using metal sulfonamides have been included in modern pharmacopoeias (Ph.Eur, BP, USP), and some metal sulfonamides have attracted attention because of their pharmacological activities. The antibacterial activity of sulfonamides, on the one hand, and the antimicrobial activity of heavy metals, on the other, have led to research on the combination of these chemical species. As a result, new metal complexes with higher antimicrobial activity than the free ligands or cationic metals were obtained [8–11]. Coordination compounds with sulfonamides and copper have also been used as reagents for the cleavage of nucleic acids [12–14].

Sulfamethoxazole, a well-known antibacterial sulfadrug, contains several groups with donor atoms that are able to interact with metal ions: Ar–NH_2, NH sulfonamide,

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*Corresponding author. Email: mtorre@fq.edu.uy

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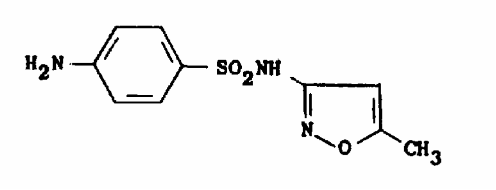

Figure 1. Sulfamethoxazole.

SO_2–R and N and O heterocyclic atoms (figure 1). Sulfamethoxazole can act as a monodentate or a bidentate ligand. Some metal complexes of sulfamethoxazole have been reported [15,16], but so far the crystal structure of a heteroleptic sulfamethoxazole aqua nickel complex has not been determined.

In this paper, the synthesis and characterization of a novel Ni(II) complex with sulfamethoxazole is described and its crystalline structure determined.

2. Experimental

2.1. *Synthesis of the complex and analytical characterization*

An aqueous solution of $NiCl_2 \cdot 6H_2O$ (2.5 mmol, Sigma) was added slowly to a solution of sulfamethoxazole (5 mmol, Sigma) was in basic water (NaOH 0.1 M). The solution was stirred for 0.5 h and left to concentrate at 40°C until green crystals of $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$ were obtained. The crystals were separated by filtration, washed with water and dried at room temperature. Anal. Calcd.(%): C 38.75, N 13.56, H 4.52, S 10.33, Ni 9.48. Found: C 38.70, N 13.65, H 4.37, S 10.24, Ni 9.01. Yield: 23%.

2.2. *Crystal structure determination*

X-ray data collection for $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$ was performed at room temperature [298(2) K] on a Rigaku AFC-7S diffractometer [17] using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) in the ω–2θ scan mode in a θ range 2.32–27.49°. Relevant crystallographic data are shown in table 1. During data collection the intensities of three standard reflections were monitored every 150 reflections to correct for intensity decay. Lorentz, polarization and absorption corrections were applied.

The structure was solved by direct methods locating most non-hydrogen atoms. The structure was completed by successive difference Fourier maps. Refinement was anisotropic for all non-hydrogen atoms. All hydrogen atoms were calculated at idealized positions, with fixed distances (0.93 Å for $C_{(aromatic)}$–H, 0.96 Å for $C_{(primary)}$–H and 0.86 Å for $N_{(primary)}$–H) and refined with isotropic displacement parameters related to the equivalent isotropic displacement parameter of the atom to which it is bonded.

The structure determination was achieved using SHELXS [18] and the refinement was carried out using the SHELXL programs included in the SHELX–97 [19] package. Geometric calculations and structural checking were performed with the PLATON

Table 1. Crystal data and structural refinement parameters for $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$.

Chemical formula	$C_{20}H_{20}N_6NiO_9S_2$
Formula weight	611.25
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	18.000(2)
b (Å)	8.725(5)
c (Å)	16.774(3)
α (°)	90
β (°)	77.647(12)
γ (°)	90
Volume (Å^3)	2573.4(15)
Z	4
Calculated density (Mg/m^3)	1.578
Absorption coefficient (mm^{-1})	0.977
F(000)	1256
Crystal size (mm)	$0.20 \times 0.15 \times 0.10$
Theta range for data collection (°)	2.32 to 27.49
Reflections collected/unique	7164/5745
Max. and min. transmission	0.9086 and 0.8285
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0693$, $wR_2 = 0.1765$

$R_1 = \sum \|F_0\| - \|F_c\| / \sum |F_c|$; $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]\}^{1/2}$.

program [20]. ZORTEP [21] was used to plot the drawings. Absorption correction was performed by ϕ-scan [17] and no extinction correction was applied. Other crystallographic data are summarized in the supplementary data.

2.3. *Spectroscopic measurements*

Electronic absorption spectra were recorded in the range 350–800 nm on a Nujol suspension using a Spectronic 3000 spectrophotometer. FTIR spectra were measured as KBr pellets in the range 4000–200 cm^{-1} on a Bomem MB 102 instrument.

3. Results and discussion

3.1. *Crystal structure of $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$*

An ORTEP drawing representation is shown in figure 2. Bond lengths and angles are listed in tables 2 and 3, respectively. Cell parameters were refined with 21 centered intensities in the θ range 26.40–34.50°. From the 7164 reflections collected in the range $-23 \leq h \leq 23$, $-1 \leq k \leq 10$, $-1 \leq l \leq 21$, 5745 were unique ($R_{\text{int}} = 0.0798$), while 3052 reflections were observed ($I > 2\sigma(I)$). This compound crystallized in the monoclinic centrosymmetric space group $P2_1/c$, and showed four asymmetric units per unit cell. Each asymmetric unit contains two independent Ni atoms in particular crystallographic positions, grouped into one dimeric unit. Each dimer is linked to other symmetry equivalent units forming a one-dimensional (1D) infinite chain that propagates along the [1 1 0] direction of the unit cell. This chain is related by the 2_1 axis with another 1D infinite

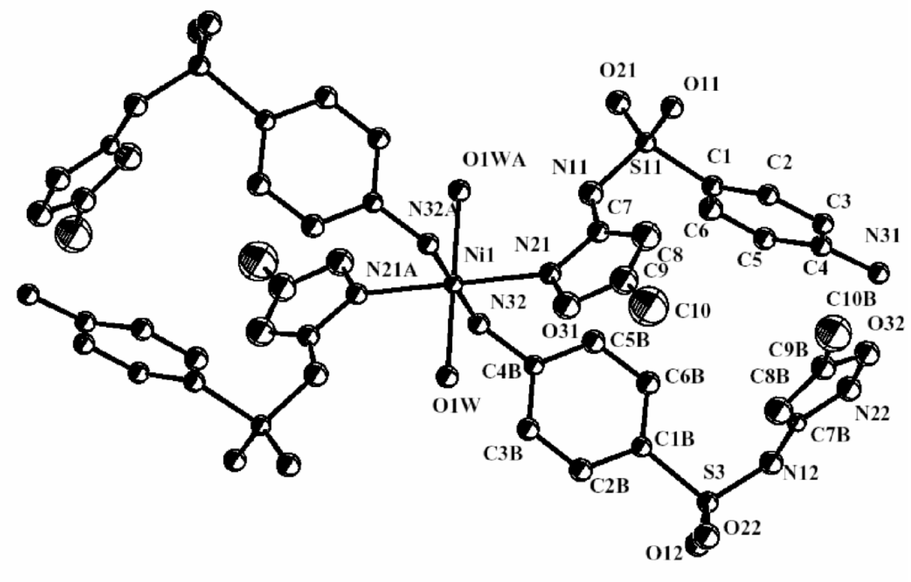

Figure 2. ORTEP drawing of $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$.

Table 2. Relevant bond lengths (Å) for $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$.

Ni(1)–N(21)	2.074(4)	S(3)–O(12)	1.449(4)
Ni(1)–O(1W)	2.094(4)	S(3)–O(22)	1.450(4)
Ni(1)–N(32)	2.188(4)	S(3)–N(12)	1.562(5)
Ni(2)–N(22)	2.052(4)	S(3)–C(1B)	1.769(5)
Ni(2)–O(2W)	2.106(4)	S(11)–O(11)	1.439(4)
Ni(2)–N(31)	2.186(4)	S(11)–O(21)	1.447(4)
		S(11)–N(11)	1.579(4)
		S(11)–C(1)	1.784(5)

chain with a resulting [0 1 0] translation direction of the unit cell as shown in figure 3. There are therefore two sets of translational equivalents chains in the unit cell. The nickel atoms are six coordinated, formed by two oxygen atoms from two coordinated water molecules, two nitrogen atoms from *N*-arylamine and two nitrogen atoms from *N*-sulfonamide (figure 2). The geometry can be described as a slightly distorted regular octahedron. The six- and the five-membered aromatic rings are planar within experimental error. As the nickel atoms are located at a special position (symmetry inversion center), each six- and five-membered ring is parallel to the symmetry equivalent one. Although no H water atoms could be located, the distances between the oxygen atoms in the surrounding water molecules and other groups suggest the existence of hydrogen bonds. The packing is determined by a fairly extensive hydrogen-bonding 3D network involving oxygen atoms from water, oxygen atoms from sulfonamide groups and nitrogen atoms from the amine group of sulfamethoxazole.

3.2. *Infrared spectra*

Based on some general references [22–24] and previous studies of complexes with sulfonamides [25–28], a tentative assignment of the most important bands is given below.

Table 3. Relevant bond angles (°) for $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$ (#1 and #2 correspond to symmetry equivalent atoms).

N(21)#1–Ni(1)–N(21)	180.00(16)
N(21)#1–Ni(1)–O(1W)#1	92.20(15)
N(21)–Ni(1)–O(1W)#1	87.80(15)
N(21)#1–Ni(1)–O(1W)	87.80(15)
N(21)–Ni(1)–O(1W)	92.20(15)
O(1W)#1–Ni(1)–O(1W)	180.000(1)
N(21)#1–Ni(1)–N(32)	86.91(17)
N(21)–Ni(1)–N(32)	93.09(17)
O(1W)#1–Ni(1)–N(32)	87.91(16)
O(1W)–Ni(1)–N(32)	92.09(16)
N(21)#1–Ni(1)–N(32)#1	93.09(17)
N(21)–Ni(1)–N(32)#1	86.91(17)
O(1W)#1–Ni(1)–N(32)#1	92.09(16)
O(1W)–Ni(1)–N(32)#1	87.91(16)
N(32)–Ni(1)–N(32)#1	180.000(1)
N(22)#2–Ni(2)–N(22)	180.000(1)
N(22)#2–Ni(2)–O(2W)	89.91(17)
N(22)–Ni(2)–O(2W)	90.09(17)
N(22)#2–Ni(2)–O(2W)#2	90.09(17)
N(22)–Ni(2)–O(2W)#2	89.91(17)
O(2W)–Ni(2)–O(2W)#2	180.000(1)
N(22)#2–Ni(2)–N(31)	85.22(17)
N(22)–Ni(2)–N(31)	94.78(18)
O(2W)–Ni(2)–N(31)	89.21(18)
O(2W)#2–Ni(2)–N(31)	90.79(18)
N(22)#2–Ni(2)–N(31)#2	94.78(18)
N(22)–Ni(2)–N(31)#2	85.22(17)
O(2W)–Ni(2)–N(31)#2	90.79(18)
O(2W)#2–Ni(2)–N(31)#2	89.21(18)
N(31)–Ni(2)–N(31)#2	180.000(1)

The positions of the characteristic vibrations of the free sulfamethoxazole and the complexes are compared in table 4. As shown in table 4, the symmetric and antisymmetric bands assigned to $\nu(NH_2)$ in the ligand (3467 and 3378 cm^{-1}) were shifted to lower frequencies in the complex (3399 and 3331 cm^{-1}), indicating that two amine groups for each nickel were involved in coordination. However, the band attributed to $\nu(NH)_{amide}$ appeared in the ligand and in the complex almost at the same frequency, confirming that this group is neither deprotonated nor coordinated.

Although the SO_2 group did not participate in coordination, the $\nu_{as}(SO_2)$ shifted by 36 cm^{-1}, probably because of the different spatial orientation of the S=O group in the complex, while the $\nu_s(SO_2)$ remained almost unchanged. This behavior is frequently observed in other metal complexes [25,29,30].

The vibrational spectrum of isoxazole has been described by several authors [27,28]. Because of the rigidity of the penta-atomic ring, the spectrum cannot be interpreted in terms of localized vibrations. Similar to other simple metal complexes with isoxazole, in $[Ni(sulfamethoxazole)_2(H_2O)_2] \cdot H_2O$ only three isoxazole bands showed significant shifts. The bands of the ligands at 3144, 1502 and 886 cm^{-1} shifted to 3158, 1488 and 965 cm^{-1}, respectively, after coordination. Most of the other shifts were small.

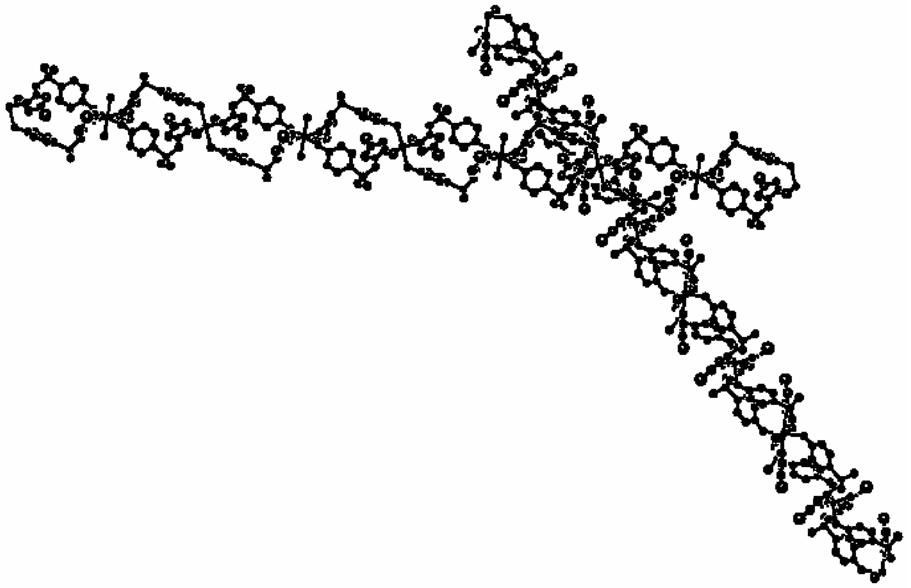

Figure 3. Perspective view of a detail of the molecular packing.

Table 4. Characteristic IR bands (cm^{-1}) of the spectra of sulfamethoxazole and the Ni-sulfamethoxazole complex.

Sulfamethoxazole	Ni-sulfamethoxazole	Assignment
–	3568 (m)	ν(OH)
3467 (s)	3399 (m)	$\nu_{as}(NH_2)$
3378 (s)	3331 (m)	$\nu_s(NH_2)$
3301 (s)	3296 (m)	ν(NH)amide
3144 (s)	3158 (w)	ν(=CH)isoxazole ring
1621 (s)	1617 (s)	$\delta(NH_2) + \nu$(isoxazole ring)
1597 (s)	1600 (sh)	$\nu(C=C)$ aromatic
1502 (s), 1471 (s)	1488 (s), 1471 (s)	ν(isoxazole ring)
1383 (s)	1383 (vw)	
1313 (s)	1277 (s)	$\nu_{as}(SO_2)$
1266 (s)	1263 (s)	ν(C–N)
1157 (s)	1159 (s)	$\nu_s(SO_2)$
1092 (s)	1100 (m)	δ(CH) aromatic
886 (s)	965 (s)	ρ(isoxazole ring)
–	265 (w), 281 (w)	$\nu(M–N_{heterocyclic})$ $\nu(M–N_{arylamine})$

The tentative assignment of the $\nu(Ni–N_{heterocyclic})$ to $265\,cm^{-1}$ is in agreement with the literature [27]. Another band, which may be assigned to $Ni–N_{arylamine}$, appeared at $281\,cm^{-1}$.

3.3. *Electronic spectra*

The reflectance spectra of the Ni(II) (d^8) compounds were typical of octahedral coordination. The absorption bands at 770, 610 and 363 nm can be assigned to $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, respectively [31].

4. Conclusion

[Ni(sulfamethoxazole)$_2$(H$_2$O)$_2$]$\cdot$H$_2$O was synthesized and structurally characterized. The sulfonamide coordinated as a monodentate ligand to Ni(II), through different N-atoms, giving a chain-like structure. The spectroscopic data are in agreement with the crystal structure.

Supplementary data

Crystallographic data for the structure reported in this article have been deposited in the Cambridge Crystallographic Data Center, CCDC No. 241717. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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