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Synthesis and characterization of sulfonamides containing 8-aminoquinoline and their Ni(II) complexes. Crystalline structures of the Ni complexes

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Abstract

Reaction between 8-aminoquinoline and benzenesulfonyl, toluene-4-sulfonyl and naphthalene-2-sulfonyl chlorides in a basic medium leads to the formation of the corresponding sulfonamides. Reaction of these sulfonamides with Ni(II) salts leads to the formation of the corresponding complexes, with a NiL_2 stoichiometry. Determination of the crystalline structure by X-ray diffraction shows an octahedral environment for the Ni(II) ions, sulfonamides acting as bidentate ligands and two solvent molecules completing the octahedral coordination. The spectroscopic and magnetic properties of these compounds are also discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nickel complexes; Sulfonamide complexes; 8-Aminoquinoline; X-ray crystal structures

1. Introduction

Coordination chemistry of nickel with ligands containing N-donor atoms has been widely studied in the literature and in recent years such studies have been mostly addressed to ligands with a biological interest, such as peptides [1,2]; the Ni(II)-promoted hydrolysis of these peptides has been one of the aims of these sorts of studies [3]. Recent findings showing the role of Ni(II) ions in several processes taking place in living organisms (where it is coordinated by N-donor ligands) have been probably the origin of these studies [4]. However, complexes of this ion with sulfonamides are not well known, and only a few examples have been described in the literature [5], despite the fact that complexes formed by sulfonamides and other transition metal cations, especially copper, have been studied, probably because they may act as chemical nucleases [6–9].

In the present paper, we describe the synthesis of three new sulfonamides derived from 8-aminoquinoline and benzenesulfonyl, toluene-4-sulfonyl and naphthalene-2-sulfonyl chlorides, which have then been used as ligands to coordinate Ni(II) ions.

2. Experimental

2.1. Materials and methods

8-Aminoquinoline and the sulfonyl chlorides were provided by Aldrich and Fluka, respectively, and all reagents were of analytical grade.

Chemical analyses for carbon, hydrogen and nitrogen were performed on a 2400 elemental analyzer from Perkin–Elmer. Nickel was determined on an ICP spectrometer (Perkin–Elmer model 2380 Plasma 2).

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FT-IR spectra were recorded using KBr mulls and a Perkin–Elmer FT-IR 1730 instrument. Electronic spectra were recorded on a Shimadzu 8452A diode spectrophotometer.

Molecular masses were measured by Servicio de Masas (Universidad Autónoma de Madrid, Spain) by the FAB method with samples held on a nitrobenzyl alcohol (NBA) matrix.

Magnetic susceptibility measurements at room temperature (r.t.) were taken with a fully automatized AZTEC DSM8 pendulum-type susceptometer. Mercury tetrakis(thiocyanate)cobaltate(II) was used as a susceptibility standard. Corrections for diamagnetism were estimated from Pascal's constants.

2.2. Synthesis of the ligands

The sulfonamides were prepared by direct synthesis between 8-amino quinoline with the corresponding sulfonyl chloride, using pyridine as solvent. The procedure is as follows: 5 mmol 8-amino quinoline and 5 mmol sulfonyl chloride are dissolved in 10 ml pyridine and the mixture is heated under reflux at 110–120 °C for 30 min. The solution is then left to cool down to 70 °C and is added to a beaker containing 10 ml water. A brown precipitated is formed; this is filtered and washed with distilled water until all pyridine has been removed. Yield is 85–90%.

Analytical data: For N-quinolin-8-yl-benzenesulfonamide, Hqbsa: Found: C, 63.30; H, 4.04; N, 10.25%. Calculated for $C_{15}H_{12}N_2O_2S$: C, 63.37; H, 4.25; N, 9.85%. For N-quinolin-8-yl-*p*-toluenesulfonamide, Hqtsa: Found: C, 64.38; H, 4.69; N, 9.47%. Calculated for $C_{16}H_{14}N_2O_2S$: C, 64.44; H, 4.73; N, 9.43%. For N-quinolin-8-yl-naphthalene-2-sulfonamide, Hqnsa: Found: C, 68.08; H, 4.07; N, 8.32%. Calculated for $C_{19}H_{14}N_2O_2S$: C, 68.24; H, 4.22; N, 8.38%. The most significant IR bands are listed in Table 3. λ_{max} nm (ε, M^{-1} cm^{-1}): 250 (16 000), 320 (7000).

2.3. Synthesis of the nickel complexes

Although direct synthesis between the sulfonamide and the metallic salt is possible with the copper complexes [6], addition of a base is required in the case of the Ni derivatives in order to deprotonate the sulfonamidate nitrogen atom. So 1.5 mmol sulfonamide are dissolved in 75 ml DMF and 2 ml NH_3 2 M are added. Then a solution containing 0.75 mmol Ni(II) chloride dissolved in 25 ml methanol is slowly added dropwise to the former solution. Once the addition has been completed, the original green color of the solution becomes enhanced. Upon very slow evaporation of the solvent, green crystals (suitable for structural determination by X-ray diffraction) were obtained.

Analytical data: $[Ni(qbsa)_2(H_2O)(MeOH)]$: Found: C, 55.31; H, 4.21; N, 8.43; Ni, 8.92%. Calculated for $NiC_{31}H_{28}N_4O_6S_2$: C, 55.13; H, 4.18; N, 8.29; Ni, 8.69%. MS: $m/z = 625$ $[M]^+$

$[Ni(qtsa)_2(H_2O)_2]$: Found: C, 56.01; H, 4.47; N, 8.33; Ni, 8.39%. Calculated for $NiC_{32}H_{30}N_4O_6S_2$: C, 55.75; H, 4.39; N, 8.13; Ni, 8.52%. MS: $m/z = 652.1$ $[M]^+$

$[Ni(qnsa)_2(H_2O)_2]$.2DMF: Found: C, 57.91; H, 4.91; N, 9.06; Ni, 6.55%. Calculated for $NiC_{44}H_{44}N_6O_8S_2$: C, 58.22; H, 4.89; N, 9.26; Ni, 6.47%. MS: $m/z = 725$ $[M]^+$.

The most significant IR bands are listed in Table 3. λ_{max} nm (ε, M^{-1} cm^{-1}): 266 (18 000), 370 (12 000), 585 (20), 785 (30).

2.4. X-ray data collection and processing

A green needle crystal of $[Ni(qtsa)_2(H_2O)_2]$ was mounted on an Enraf Nonius CAD4 automatic drifractometer to be used for the structure determination. X-ray diffraction data for $[Ni(qbsa)_2(H_2O)(MeOH)]$ and $[Ni(qnsa)_2(H_2O)_2]\cdot 2DMF$ were collected on a four circle Seifert XRD 3003 SC diffractometer. Data of these Ni(II) complexes were collected at r.t. using Cu Kα radiation and the $\omega-2\theta$ scan technique. The unit cell parameters were determined by least-squares refinement on the 2θ values of 25 strong well centered reflections in the range $13.5° < \theta < 27°$ for $[Ni(qtsa)_2(H_2O)_2]$ and $8° < \theta < 20°$ for $[Ni(qbsa)_2(H_2O)(MeOH)]$ and $[Ni(qnsa)_2(H_2O)_2]\cdot 2DMF$ compounds. Scattering factors for neutral atoms and anomalous dispersion correction for Ni, C, N, O and S were taken from 'International Tables for X Ray Crystallography' [10]. The structures of $[Ni(qtsa)_2(H_2O)_2]$ and $[Ni(qbsa)_2(H_2O)(MeOH)]$ were resolved by direct methods and refined in the monoclinic space groups $P2_1/c$ and $C2/c$, respectively. The structure of $[Ni(qnsa)_2(H_2O)_2]\cdot 2DMF$ was resolved by Patterson methods and refined in the monoclinic space group $P2(1)/n$. Full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms was carried out by minimizing $\omega(F_o^2-F_c^2)^2$. Refinement on F^2 for all reflections, weighted R factors ($R\omega$), and all goodness-of-fit S are based on F^2, while conventional R factors (R) are based on F; R factors based on F^2 are statistically about twice as large as those based on F, and R factors based on all data will be even larger.

Most of the calculations for $[Ni(qtsa)_2(H_2O)_2]$ were carried out using CAD4-EXPRESS [11] software for data collection, GENHKL [12] program for data reduction, SHELX-97 [13] to refine the structure and PLATON [14] for molecular graphics. All calculations for $[Ni(qbsa)_2(H_2O)(MeOH)]$ and $[Ni(qnsa)_2(H_2O)_2]\cdot 2DMF$ were performed using CRYSOM [15] software for data collection, X-ray8O [16] for data reduction, SHELXTL™ [17] to resolve and refine the structure and to prepare material for publication.

Table 1
Summary of crystal parameters, data collection and refinement for the three crystal structures

	$[Ni(qbsa)_2(H_2O)(MeOH)]$	$[Ni(qtsa)_2(H_2O)_2]$	$[Ni(qnsa)_2(H_2O)_2]2DMF$
Empirical formula	$NiC_{31}H_{28}N_4O_6S_2$	$NiC_{32}H_{30}N_4O_6S_2$	$NiC_{44}H_{40}N_6O_8S_2$
Formula weight	675.40	689.43	903.65
Temperature (K)	293(2)	213(2)	293(2)
Wavelength (Å)	1.54180	1.54184	1.54180
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$ (No.14)	$P2_1/n$
Unit cell dimensions			
a (Å)	11.868(2)	13.361(12)	10.554(2)
b (Å)	16.161(3)	10.238(4)	30.480(6)
c (Å)	31.417(6)	24.056(16)	14.004(3)
α (°)	90	90	90
β (°)	100.06(3)	101.06(7)	109.58
γ (°)	90	90	90
Volume (Å^3)	5932.8(21)	3229.4(4)	4244.4(15)
Z	8	4	4
D_{calc} (g cm^{-3})	1.441	1.482	1.414
Absorption coefficient (mm^{-1})	0.838	2.491	0.617
$F(000)$	2672	1432	1880
Crystal size (mm)	$0.04 \times 0.04 \times 0.06$	$0.20 \times 0.10 \times 0.05$	$0.30 \times 0.04 \times 0.06$
θ Range for data collection (°)	4.88–67.26	5.48–65.01	1.45–64.34
Index ranges	$-14 < h < 14$	$-15 < h < 1$	$-12 < h < 11$
	$0 < k < 19$	$0 < k < 12$	$0 < k < 36$
	$0 < l < 31$	$-28 < l < 28$	$0 < l < 14$
Reflections collected, unique, R_{int}	5249, 5147, 0.0219	6243, 5476, 0.0509	5096, 4780, 0.0709
Refined method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data, restraints, parameters	5125, 0, 510	5476, 0, 410	4764, 0, 654
Goodness-of-fit on F^2	1.160	1.039	1.216
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0765$, $wR_2 = 0.1556$	$R_1 = 0.0595$, $wR_2 = 0.1184$	$R_1 = 0.0997$, $wR_2 = 0.1730$
R indices (all data)	$R_1 = 0.1130$, $wR_2 = 0.2030$	$R_1 = 0.1551$, $wR_2 = 0.1434$	$R_1 = 0.1724$, $wR_2 = 0.2290$
Largest differential peak and hole (e Å^{-3})	0.481 and −0.875	0.335 and −0.366	0.380 and −0.664

Crystal data and some details of the structural determination are given in Table 1. Table 2 shows some selected geometrical information.

3. Results and discussion

The synthetic route used to prepare the sulfonamides can be depicted as in Scheme 1 for N-quinolin-8-yl-naphthalene-2-sulfonamide, Hqnsa.

Deprotonation of the sulfonamide takes place in an ammonia medium to yield the sulfonamidate anion, qnsa$^-$, which readily reacts with Ni(II) ions to form complexes with a NiL_2 stoichiometry, although solvent molecules also exist completing the coordination around the Ni(II) cations.

3.1. Description of the crystal structures

As it could be readily expected, the local environment around the Ni(II) cations is very similar in all three cases, with a distorted octahedral structure (Figs. 1–3). The coordination polyhedron is formed by four N atoms from both sulfonamide molecules (one nitrogen atom from the sulfonamide group, and another from the quinoline group), which act as bidentate ligands, together with two oxygen atoms from two water molecules. The sulfonamide molecule forms a stable five-member ring with the metal cation. It should be noticed that the hydrogen atoms from the water molecules are not shown in the structural formula of the complex, $[Ni(qnsa)_2(H_2O)_2]\cdot 2DMF$, as they were not located by X-ray diffraction.

Selected bond distances and angles are summarized in Table 2. Only minor differences can be seen in the local environment of the nickel ions among the three complexes prepared, as expected bearing in mind that the organic chains differentiating the three ligands studied are rather far away from the coordinating (donor) sites of these molecules. From the bond angles given, it can be also concluded that the distortion is not too severe, the angle between *trans* atoms being close to 180°, and that between *cis* atoms close to 90°.

The most significant distortions are observed for the complex $[Ni(qsba)_2(H_2O)(MeOH)]$, where two different molecules (water and methanol) complete the octahedral coordination around the Ni(II) cation, opposite to the findings for the other complexes, where two water molecules exist. Consequently, the O1–Ni–O2 angle decreases to 85.3°, with respect to the values determined

Table 2
Selected bond lengths (Å) and angles (°) for nickel complexes

	[Ni(qbsa)$_2$(H$_2$O)(MeOH)]	[Ni(qtsa)$_2$(H$_2$O)$_2$]	[Ni(qnsa)$_2$(H$_2$O)$_2$]2DMF
Bond lengths			
Ni–N(21)	2.077(5)	2.049(4)	2.063(10)
Ni–N(11)	2.048(5)	2.060(5)	2.067(9)
Ni–O(1)	2.122(7)	2.098(4)	2.087(8)
Ni–N(12)	2.139(5)	2.119(4)	2.127(10)
Ni–N(22)	2.101(5)	2.136(4)	2.117(10)
Ni–O(2)	2.068(7)	2.152(4)	2.097(7)
Bond angles			
N(21)–Ni–N(11)	95.0(2)	91.7(19)	91.7(4)
N(21)–Ni–O(1)	176.9(2)	175.8(17)	176.4(4)
N(11)–Ni–O(1)	86.5(3)	92.3(17)	90.5(3)
N(21)–Ni-N(12)	91.1(2)	94.1(17)	94.0(4)
N(11)–Ni–N(12)	79.2(2)	79.4(17)	79.6(4)
O(1)–Ni–N(12)	91.9(3)	88.2 (16)	89.2(3)
N(21)–Ni–N(22)	78.8(2)	79.6(17)	78.4(4)
N(11)–Ni–N(22)	92.3(2)	91.5(18)	94.0(4)
O(1)–Ni–N(22)	98.4(2)	98.7(15)	98.6(3)
N(12)–Ni–N(22)	166.2(2)	168.8(18)	170.0(3)
N(21)–Ni–O(2)	93.2(3)	88.1(17)	90.8(3)
N(11)–Ni–O(2)	171.7(3)	177.4(18)	176.6(4)
O(1)–Ni–O(2)	85.3(3)	88.0(16)	87.0(3)
N(12)–Ni–O(2)	99.9(3)	98.1(17)	97.9(3)
N(22)–Ni–O(2)	90.1(3)	91.0(17)	88.7(3)

for the other two complexes (88.0° and 87.0°); similarly, the N11–Ni–O2 angle also decreases (171.7° vs. 177.43° and 176.6°), while angle N21–Ni–O2 is slightly larger (93.2° instead of 88.1° and 90.8°).

As expected, the angle formed by the Ni(II) cation with the two N atoms belonging to the same ligand molecule (N11–Ni–N12 and N21–Ni–N22) remain constant in all three complexes, although small differences are seen for angles formed between N atoms from both ligands (e. g. N11–Ni–N21), probably as a consequence of the changes in other angles commented above. The Ni–N(sulfonamidate) distances are also slightly larger than the Ni–N(quinoline) ones. In any case, the bond and angle distances measured for these complexes are very similar to those previously reported [5,18] for complexes similar to those prepared here.

3.2. FT-IR spectroscopy

Data are summarized in Table 3. It should be noticed that the removal of the band at 3260 cm^{-1}, due to the N–H stretching mode, in the complexes demonstrates the deprotonation of the N(sulfonamide) atom. It should also be mentioned that the splitting of bands due to the symmetric and antisymmetric stretching modes of the SO$_2$ group, probably because of the different spatial orientation of the S=O bonds upon coordination of the sulfonamide to the metal cation. Both bands shift approximately 30 cm^{-1} downwards when passing from the ligands to the complexes,

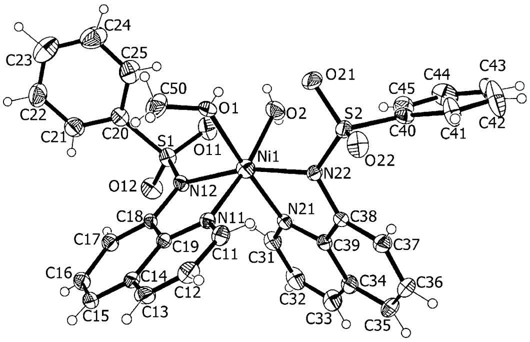
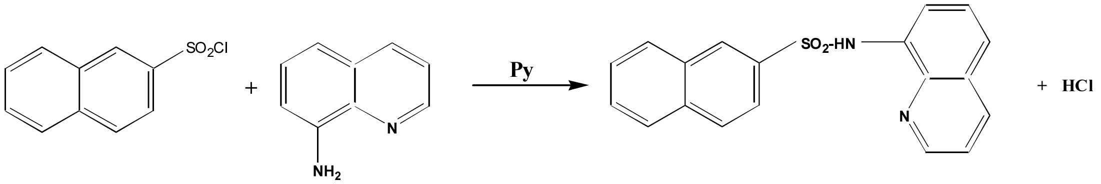


Fig. 1. Molecular structure of [Ni(qbsa)$_2$(H$_2$O)(MeOH)] showing the atom numbering scheme.



Scheme 1. Formation of *N*-quinolin-8-yl-naphthalene-2-sulfonamide.

Table 3
Selected IR bands (cm^{-1})

		Hqbsa	Hqtsa	Hqnsa	[Ni(qbsa)$_2$(H$_2$O)(MeOH)]	[Ni(qtsa)$_2$(H$_2$O)$_2$]	[Ni(qnsa)$_2$(H$_2$O)$_2$]2DMF
ν_{N-H}		3218	3260	3245			
SO$_2$	ν_{as}	1359	1367	1375	1317 1276	1316 1273	1314 1274
	ν_s	1169	1160	1164	1130 1114	1129 1115	1141 1122
	δ_{SO_2}	585 559	570 545	558 546	596 584	578 550	567 549
ν_{S-N}		926	922	918	952	954	961
ν_{C-S}		686	666	679	692	658	655

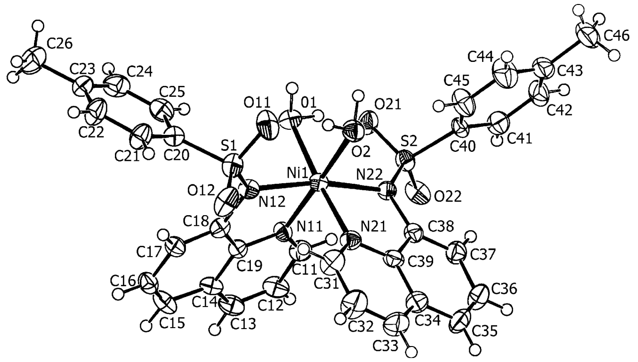


Fig. 2. Molecular structure of [Ni(qtsa)$_2$(H$_2$O)$_2$] showing the atom numbering scheme.

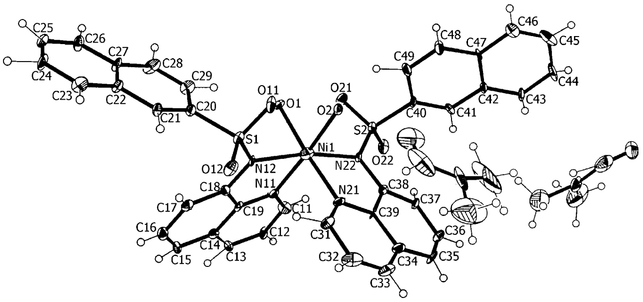


Fig. 3. Molecular structure of [Ni(qnsa)$_2$(H$_2$O)$_2$]·2DMF showing the atom numbering scheme.

probably due to a charge transfer from the deprotonated, negatively-charge N atom to the oxygen atom of the sulfonyl group [7]; consequently, the double bond character of the S=O group results larger in the free ligands than in the complexes.

The remaining bands are recorded in close positions both for the ligands and for the complexes, except the band due to the S–N stretching mode, which shifts approximately 30 cm^{-1} upwards, thus confirming the donor role of the N atom. Overall, the positions are similar to those previously reported for similar compounds [19].

3.3. Magnetic susceptibility and electronic spectra

The effective magnetic moments at room temperature of the complexes are in the range 2.95–3.13 BM, in agreement with the octahedral environment around the Ni(II) cations. These values are only slightly larger than that corresponding to the spin-only value (2.83 BM), thus suggesting an orbital contribution by mixing of the ground state with low energy excited states, or because the ground state is orbitally degenerated.

The two intense bands recorded in the electronic spectra of the complexes at 266 and 370 nm are probably due to charge transfer processes. The two bands at 785 and 585 nm are recorded in the ranges usually expected for transitions $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively, of octahedral Ni(II) (d^8) complexes [20].

4. Supplementary material

Complete lists with atomic coordinates, anisotropic displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center, 912 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) [CCDC 173676, 173677, 173866].

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