Synthesis and Structural Characterization of Zinc Complexes with Sulfonamides containing 8-Aminoquinoleine

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 60th Birthday

Abstract. Sulfonamides obtained by reaction of 8-aminoquinoline with benzenesulfonyl, toluene-4-sulfonyl and naphthalene-2-sulfonyl chlorides have been used to synthetize coordination compounds with Zn^{II} with a ZnL_2 composition. Determination of the crystal structures for the resulting complexes by X-ray diffraction shows a distorted tetrahedral environment for the Zn^{2+} ions, sul-

fonamides acting as bidentate ligands through the nitrogen atoms from the sulfonamidate and quinoline groups. FT-IR, ¹H and ¹³C NMR and mass spectra of these compounds are also discussed.

Keywords: Zinc; Sulfonamide complexes; 8-Aminoquinoline; Crystal structures

Synthese und Strukturen von Zink-Komplexen mit Sulfonamid-8-aminochinoleinen

Inhaltsübersicht. 8-Aminochinolin-Sulfonamide mit Phenylsulfonyl-, 4-Tolylsulfonyl- und 2-Naphthylsulfonyl-Resten wurden zur Synthese von Zn^{II} -Komplexen der Zusammensetzung ZnL_2 eingesetzt. Die Bestimmung ihrer Kristallstrukturen zeigt verzerrt tetrae-

Introduction

Coordination chemistry of sulfonamides has undergone a noticeable development in recent years because of their interesting properties, both academic (groups involved in coordination to the metal ion and the effect of the sulfonyl group on the donor ability of the adjacent nitrogen atom [1-8]), as well as practical, due to the huge number of applications [9-12]. Although many of the coordination compounds prepared so far contain copper as the metal ion, many compounds have been prepared with zinc; the structures of some of these complexes have been solved [13], and their applications as carbonic anhydrase inhibitors [10, 14-16], antifungal activity [17] or as potentially powerful probes of intracellular zinc chemistry [18] have been investigated.

We have previously reported on the synthesis and characterization of three sulfonamides: N-quinolin-8-yl-benzenesulfonamide (Hqbsa), N-quinolin-8-yl-toluenesulfonamide

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Dpto. Química Inorgánica, Facultad de Farmacia Campus Unamuno E-37007-Salamanca/Spain Fax: 34-23-294515 e-mail: bmacias@usal.es drische Umgebung der Zn²⁺-Ionen, wobei die Ligandengruppen als zweizählige Chelatliganden über die N-Atome von Sulfamidinat- und Chinolin-Gruppe fungieren. FT-IR-, ¹H-, ¹³C-NMR- und Massenspektren werden mitgeteilt.

(Hqtsa) and N-quinolin-8-yl-naphthalenesulfonamide (Hqnsa), which have been used to prepare the corresponding coordination compounds with nickel [19] and copper [20, 21], which nuclease activity has been also tested.

Because of the interesting properties displayed by these complexes with Zn^{II} , we here report the synthesis and characterization of the coordination compounds formed by Zn^{II} with the above mentioned sulfonamides. In addition to structural determination ¹H and ¹³C NMR spectral properties are also reported.

Experimental

Materials and Methods

8-aminoquinoline and 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 analyser from Perkin-Elmer. Zinc was determined on an ICP spectrometer (Perkin-Elmer model 2380 Plasma 2). FT-IR spectra were recorded using KBr mulls and a Perkin-Elmer FT-IR 1730 instrument. 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. ¹H and ¹³C NMR spectra were obtained in CDCl₃ on a Bruker DX400 instrument.

Preparation of the compounds

The sulfonamide ligands were prepared by direct synthesis between 8-aminoquinoline with the corresponding sulfonyl chloride, following the method described elsewhere [19-21].

The complexes were prepared by direct reaction between the sulfonamide ligands and Zn^{II} salts. Although the copper complexes were prepared in a neutral medium [20, 21], addition of a base for deprotonating the amine nitrogen atom was necessary to prepare the zinc complexes. The process can be summarized as follows: 1.5 mmol of the sulfonamide are dissolved in 75 ml methanol and 2 ml 2M NH₃ are added. While this solution is magnetically stirred, 0.75 mmol ZnCl₂ dissolved in 50 ml methanol are dropwise added. When addition is completed a yellow precipitate is formed which is separated by filtration. Yield is 80-85 %.

Analytical data: [Zn(qbsa)₂]: Found: C, 56.70; H, 3.32; N, 9.05; Zn, 10.69. Calculated for $ZnC_{30}H_{22}N_4O_4S_2$: C, 57.02; H, 3.51; N, 8.87; Zn, 10.34 %.

 $\label{eq:constraint} \begin{array}{l} [Zn(qtsa)_2]: \mbox{ Found: C, 58.11; H, 3.91; N, 8.33; Zn, 9.75. Calculated} \\ for \ ZnC_{32}H_{26}N_4O_4S_2: \ C, \ 58.23; \ H, \ 3.94; \ N, \ 8.49; \ Zn, \ 9.91 \ \%. \end{array}$

$$\label{eq:constraint} \begin{split} &[Zn(qnsa)_2]: Found: C, \, 61.81; \, H, \, 3.54; \, N, \, 7.91; \, Zn, \, 9.14. \ Calculated \\ for \ ZnC_{38}H_{26}N_4O_4S_2: \, C, \, 62.34; \, H, \, 3.55; \, N, \, 7.66; \, Zn, \, 8.94 \, \%. \end{split}$$

To prepare the solids in crystalline form, the precipitates are dissolved in DMF (dimethylformamide) and, upon standing at room temperature yellow crystals, suitable for single crystal X-ray diffraction studies, are formed. As shown below, compound [Zn(qbsa)₂] crystallizes with a molecule of solvent (DMF), while complex [Zn(qtsa)₂] with half a molecule of water.

Crystal Structures Determination

A light yellow plate crystal of [Zn(qbsa)₂]·DMF was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by leastsquares refinement of the diffraction data from 25 reflections in the range of 14.09 $<\theta < 23.92^{\circ}$ on an Enraf Nonius CAD4 automatic diffractometer [22]. Data were collected using CuKa radiation and the ω -scan technique, and corrected for Lorentz and polarization effects [23]. A semi-empirical absorption correction wscan was made [24]. The structure was solved by direct methods [25] and subsequent difference Fourier maps, and refined on F² by a fullmatrix least-squares procedure using anisotropic displacement parameters [26]. All hydrogen atoms were located in their calculated positions (C-H 0.93-0.97 Å) and were refined using a riding model. Atomic scattering factors from "International Tables for X-ray Crystallography" [27]. Molecular graphics from PLATON [28] and SCHAKAL [29].

For the yellow complex $[Zn(qtsa)_2]$ data were collected on a four circle Seifert XRD 3003 SC diffractometer using CuK α radiation, graphite monochromator and the ω -2 θ scan technique. The unit cell parameters were determined by least squares refinement on the 2 θ values of 25 strong well centered reflections in the range 16 $< 2\theta < 40^\circ$. Scattering factors for neutral atoms and anomalous dispersion correction for Zn, C, N, O and S were taken from "International Tables for X-ray Crystallography" [27]. The structure was resolved by direct methods and refined in the monoclinic space group C2/c. Structure determination of the title compound afforded one water molecule at a fully occupied special position (4e) with point symmetry 2, but its hydrogen atoms were not found. 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 F² for all reflections, weighted R factors and all goodness of fit S are based on F², while conventional R factors are based on F; R factors based on F² are statistically about twice as large as those based on F, and R factors based on all data will be even larger. All calculations were performed using CRYSOM [30] software for data collection, XRAY8O [31] for data reduction, SHELXTL [32] to resolve and refine the structure and to prepare material for publication.

For the complex [Zn(qnsa)₂], a yellow prismatic crystal was mounted on a glass fiber and used for data collection. Crystal data were collected using a Bruker SMART CCD 1000 diffractometer. Graphite monochromated MoKa radiation was used throughout. The data were processed with SAINT [33] and corrected for absorption using SADABS (transmissions factors: 1.000-0.694) [34]. The structure was solved using the program SHELXS-97 [25] and refined by full-matrix least-squares techniques against F² using SHELXS-97 [26]. Positional and anisotropic atomic displacement parameters were refined using a riding model. Isotropic atomic displacement parameters for hydrogen atoms were constrained to be 1.2 times those of the respective C atoms. Criteria of a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.01 and no significant features in final difference maps. Atomic scattering factors from "International Tables for Crystallography" [27]. Molecular graphics from PLATON [28] and SCHAKAL [29].

A summary of the crystal data, experimental details and refinement results are listed in Table 1 for the three complexes. Table 2 shows some selected structural information. 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: 193501, 194345 and 194346].

Results and Discussion

Crystal Structure of the complexes

Molecular structures for the three zinc complexes are shown in Figures 1, 2 and 3, which show that, as expected, the local environment around the Zn^{2+} cations is similar in all three cases, bearing in mind the similarities among the three ligands. The structures correspond to highly distorted tetrahedron, where the sulfonamide acts as a bidentate ligand. Zn-ligand bonding takes place through the nitrogen atoms of the sulfonamide and quinoline groups. Bond distances, also similar in all three compounds, are slightly larger to the quinoline nitrogen than to the sulfonamide nitrogen atoms, as previously reported for the corresponding Ni and Cu compounds [19-21], and all them are in the range reported in the literature [15, 16, 18] for complexes of Zn with other sulfonamides. The distances between the zinc cation and the oxygen atoms of the sulfonyl groups are larger than 3.0 Å, thus indicating the lack of chemical bonding between these two atoms, so providing space for coordination of the amine nitrogen atom. The sulfonamide molecule forms a stable five-membered ring with the metal cation.

The bond angles N(11)-Zn-(N12) and N(21)-Zn-N(22), are in the $80-85^{\circ}$ range and depend on the precise param-

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		[Zn (qbsa) ₂]·DMF	[Zn (qtsa) ₂] ^{,1} / ₂ H ₂ O	[Zn (qnsa) ₂]	
Formula weight705,10668,06732,12Temperature213(2) K293(2) K293(2) KWavelength1.54184 Å1.54180 Å0.71073 ÅCrystal systemtricliniemonoclinicmonoclinicSpace groupP1 (No.2) $C2/c$ $P2_1/n$ (No.14)Unit cell dimensions: Z^2/c $P2_1/n$ (No.14) d Å10.241(3)23,849(5)9.9215(9) d Å10.434(3)17,035(3)14,7754(13) $d^2 \circ$ 79,890(16)9090 $d^2 \circ$ 79,890(16)90 $d^2 \circ$ 79,890(16)90 $d^2 \circ$ 79,890(16)90 $d^2 \circ$ 79,890(16)90 $d^2 \circ$ 861.9(20) Å^33315.5(5) Å^3 Z 284Calculated density1.421 g/cm ³ 1.514 g/cm ³ Absorption coefficient2.622 mm ⁻¹ 1.028 mm ⁻¹ F (000)72827521504Crystal size0.35x0.15x0.05 mm0.04x0.05x0.06 mm0.49x0.13x0.07 mm θ range for data collection5.27-64.95°2.63-59.64°1.65-26.41°Index ranges $-1<<1/2$ $-1<<<1/2$ $-1<<<1/2$ $-1<<2k<<12$ $-1<<<1/2$ $-1<<2k<<0$	Empirical formula	ZnC ₃₃ H ₂₉ N ₅ O ₅ S ₂	ZnC ₃₂ H ₂₆ N ₄ O _{4.5} S ₂	ZnC ₃₈ H ₂₆ N ₄ O ₄ S ₂	
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Data, restraints, parameters5560, 0, 3904041, 0, 4446752, 0, 442Goodness-of-fit on F^2 1.0181.1471.032Final R indices $[I>2\sigma(I)]$ $R_1=0.0751, wR_2=0.1797$ $R_1=0.0929, wR_2=0.2084$ $R_1=0.0474, wR_2=0.0996$ R indices (all data) $R_1=0.1416, wR_2=0.2138$ $R_1=0.2085, wR_2=0.2788$ $R_1=0.0999, wR_2=0.1234$ Largest diff. peak and hole1.052 and -0.662 e Å ⁻³ 0.665 and -1.426 e Å ⁻³ 0.663 and -0.357 e Å ⁻³	Refined method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	
Goodness-of-fit on F^2 1.0181.1471.032Final R indices $[I>2\sigma(I)]$ $R_1=0.0751, wR_2=0.1797$ $R_1=0.0929, wR_2=0.2084$ $R_1=0.0474, wR_2=0.0996$ R indices (all data) $R_1=0.1416, wR_2=0.2138$ $R_1=0.2085, wR_2=0.2788$ $R_1=0.0999, wR_2=0.1234$ Largest diff. peak and hole1.052 and -0.662 e Å ⁻³ 0.665 and -1.426 e Å ⁻³ 0.663 and -0.357 e Å ⁻³	Data, restraints, parameters	5560, 0, 390	4041, 0, 444	6752, 0, 442	
Final R indices $[I>2\sigma(I)]$ $R_1=0.0751$, $wR_2=0.1797$ $R_1=0.0929$, $wR_2=0.2084$ $R_1=0.0474$, $wR_2=0.0996$ R indices (all data) $R_1=0.1416$, $wR_2=0.2138$ $R_1=0.2085$, $wR_2=0.2788$ $R_1=0.0999$, $wR_2=0.1234$ Largest diff. peak and hole 1.052 and -0.662 e Å ⁻³ 0.665 and -1.426 e Å ⁻³ 0.663 and -0.357 e Å ⁻³	Goodness-of-fit on F ²	1.018	1.147	1.032	
R indices (all data) $R_1 = 0.1416, wR_2 = 0.2138$ $R_1 = 0.2085, wR_2 = 0.2788$ $R_1 = 0.0999, wR_2 = 0.1234$ Largest diff. peak and hole $1.052 \text{ and } -0.662 \text{ e} \text{ Å}^{-3}$ $0.665 \text{ and } -1.426 \text{ e} \text{ Å}^{-3}$ $0.663 \text{ and } -0.357 \text{ e} \text{ Å}^{-3}$	Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0751, wR_2 = 0.1797$	$R_1 = 0.0929, wR_2 = 0.2084$	$R_1 = 0.0474, wR_2 = 0.0996$	
Largest diff. peak and hole $1.052 \text{ and } -0.662 \text{ e} \text{ Å}^{-3}$ $0.665 \text{ and } -1.426 \text{ e} \text{ Å}^{-3}$ $0.663 \text{ and } -0.357 \text{ e} \text{ Å}^{-3}$	R indices (all data)	$R_1 = 0.1416, wR_2 = 0.2138$	$R_1 = 0.2085, wR_2 = 0.2788$	$R_1 = 0.0999, wR_2 = 0.1234$	
	Largest diff. peak and hole	1.052 and $-0.662 \text{ e} \text{ Å}^{-3}$	0.665 and $-1.426 \text{ e} \text{ Å}^{-3}$	0.663 and $-0.357 \text{ e} ^{-3}$	

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

Table 2 Selected bond lengths/Å and angles/° for zinc complexes

	[Zn(qbsa) ₂]	[Zn(qtsa) ₂]	[Zn(qnsa) ₂]
Zn-N(11)	2.054(6)	2.047(1)	2.054(3)
Zn-N(12)	1.940(5)	1.972(9)	1.958(3)
Zn-N(21)	2.041(6)	1.981(1)	2.051(3)
Zn-N(22)	1.954(6)	1.931(1)	1.966(3)
N(11)-Zn-N(12)	82.4(2)	85.0(5)	82.09(1)
N(21)-Zn- $N(22)$	82.5(2)	82.8(5)	82.69(1)
N(11)-Zn-N(21)	115.2(2)	108.2(5)	116.33(1)
N(12)-Zn-N(22)	142.1(2)	135.0(5)	135.87(1)
N(11)-Zn-N(22)	116.7(2)	117.9(5)	121.90(1)
N(12)-Zn-N(21)	120.4(2)	128.8(5)	121.94(1)



eters of the sulfonamide molecule. These values are reasonable for octahedral complexes, but are quite acute relative to the optimal 109° value for a tetrahedral center. This can be explained assuming that the sulfonamide oxygen atoms hinder the formation of both square planar and octahedral complexes, thus providing a steric selection for tetrahedral coordination [18]. Nevertheless, angle N(12)-Zn-N(22) is rather large (135–142°) for all three complexes.

It should be noted that the DMF and water molecules are not coordinated to the metal atoms in complexes $[Zn(qbsa)_2]$ and $[Zn(qtsa)_2]$, respectively, and are not shown in the figures.

Figure 1 Molecular structure of [Zn(qbsa)₂] showing the atom numbering scheme.

Mass spectrometry

Mass spectra of the complexes show a signal due to the complex molecular ion. The signal is recorded at m/z=631, 659, and 731, respectively, for compounds [Zn(qbsa)₂], [Zn(qtsa)₂], and [Zn(qnsa)₂]. The values for the first two



Figure 2 Molecular structure of $[Zn(qtsa)_2]$ showing the atom numbering scheme.



Figure 3 Molecular structure of $[Zn(qtsa)_2]$ showing the atom numbering scheme.

compounds correspond to the "bare" molecules, without the DMF nor water molecule, respectively, concluded from elemental chemical analysis and X-ray diffraction analysis, thus confirming the weak interaction between these molecules (not directly bonded to the metal ions) and the metal sites.

The signals recorded in the mass spectra give some clue about the decomposition pattern of these compounds in the ionisation chamber, suggesting it goes through the break of

Table 3 Selected IR bands/cm⁻¹

	[Zn(qbsa) ₂]·DMF	[Zn(qtsa) ₂]	[Zn(qnsa) ₂]
$v_{as}(SO_2)$	1323,1276	1326,1284	1324,1279
$v_s(SO_2)$	1143,1120	1143,1119	1142,1117
$\delta(SO_2)$	594,582	577,549	569,551
vS-N	961	959	962
vC-S	692	661	656

the S-N bonds in two consecutive steps. So, for complex $[Zn(qnsa)_2]$, with a molecular formula $ZnC_{38}H_{26}N_4O_4S_2$ and a m/z = 731 two signals, corresponding to $ZnC_{28}H_{19}N_4O_2S$ and $ZnC_{18}H_{12}N_4$, both formed by consecutive removal of the naphthalene-2-sulfonyl ($C_{10}H_7O_2S$) are recorded at m/z = 540 and 349, respectively.

FT-IR spectroscopy

The positions of the most representative bands, together with their assignments [35], are given in Table 3. The band close to 3260 cm^{-1} , recorded in the spectra of the ligands and corresponding to the N-H stretching mode [19], is missing in the spectra of the complexes, confirming deprotonation of the nitrogen atom of the sulfonamide and its coordination to the metal ion. The bands due to the SO_2 group split in the spectra of the complexes, probably because of the different (non equivalent) spatial orientation of these two groups in the crystal. The bands due to the symmetric and antisymmetric modes of this group shift ca. 30 cm^{-1} to lower wavenumbers than in the free ligands, probably because a larger double bond character of the S-O bonds in the free ligands. A similar shift is also observed for the S-N stretching mode, in this case because the N atom is involved in the bonding to the metal atom. These shifts are a consecuence of the protonation and/or coordination of the sulfonamide group. The remaining bands are recorded in positions very similar to those of the free ligands [19], and in the same ranges as previously reported for other sulfonamide complexes [16, 20, 25].

NMR spectra

The data and their assignments [36] for the ligand molecules are summarized in Table 4. The signal at 9.23 (Hqbsa) or 9.37 ppm (Hqnsa) in the ¹H NMR spectra of the ligand is due to the proton of the amine group. The signal corresponding to the methyl group in the Hqtsa ligand is recorded at 2.26 ppm. The remaining signals are recorded in the 7.30-8.80 ppm range, and are due to the aromatic protons. Similar features are recorded in the ¹³C NMR spectra, where the signal due to the methyl group of ligand Hqtsa is recorded at 21.25 ppm and the signals due to ring carbon atoms are recorded in the 120-150 ppm range.

The spectra of the Zn complexes are rather similar to those of the free ligands; the signal due to the amine proton is not longer recorded; the signals due to hydrogen atoms Table 4 Chemical shifts/ppm from ¹H and ¹³C NMR spectra of the sulfonamide ligands



Hqbsa		Hqtsa		Hqnsa		
	$^{1}\mathrm{H}$	¹³ C	¹ H	¹³ C	$^{1}\mathrm{H}$	¹³ C
H(N)	9.23	_	_	-	9.37	-
a	8.74	148.66	8.78	150.24	8.72	148.65
b	7.90	122.13	7.73	123.14	7.73	122.36
c	7.92	127.12	7.80	123.91	7.85	127.71
d	-	132.80	_	127.59	_	129.15
e	8.08	121.90	8.20	117.49	8.01	121.90
f	7.33	126.76	7.20	123.55	7.40	126.74
g	7.82	115.05	7.53	106.34	7.52	114.91
h	-	138.49	_	137.50	_	138.45
i	-	136.17	_	129.76	_	131.87
j	-	139.38	_	137.81	_	136.16
k	7.37	128.13	7.47	130.40	8.52	128.73
1	7.37	128.13	7.17	128.31	_	122.19
m	7.44	128.81	_	145.27	_	136.28
n	7.40	133.70	7.17	128.31	7.89	128.79
0	7.44	128.81	7.47	130.41	7.75	128.12
р	-	_	2.26	21.25	_	-
q	-	_	_	_	7.90	129.25
r	-	_	_	_	7.36	133.68
s	-	_	-	_	7.32	127.36
t	-	-	-	-	7.50	134.82

away from the Zn atom are recorded in almost the same positions as in the free ligands, and the remaining signals slightly shift towards lower field values, as a consequence of electron density transfer from the ligand to the metal. Although similar features are recorded in the ¹³C NMR spectra, correlations are not as evident as for the ¹H spectra.

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