

Bis(diethylenetriamine- κ^3N)nickel(II) 5-amino-1,3,4-thiadiazole-2-sulfon- amidate chloride monohydrate

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In the X-ray crystal structure of the title complex, $[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2](\text{C}_2\text{H}_3\text{N}_4\text{O}_2\text{S}_2)\text{Cl}\cdot\text{H}_2\text{O}$, the coordination polyhedron is composed of non-centrosymmetric $[\text{Ni}(\text{diethylenetriamine})_2]^{2+}$ cations in which the triamine ligands coordinate to the metal centre as tridentate ligands in a facial position. The Ni^{II} ions are linked to six N atoms in an octahedral arrangement, slightly compressed in one extreme. The sulfonamide behaves as a counter-ion instead of as a ligand. Important information about the deprotonated sulfonamide group conformation has been obtained.

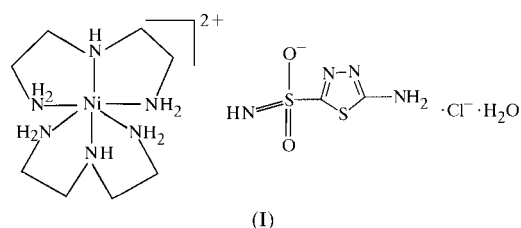
Comment

Heterocyclic sulfonamides constitute an important group of carbonic anhydrase inhibitors. The inhibition of this enzyme by sulfonamide drugs finds clinical application in the treatment of glaucoma, epilepsy and other disorders. Acetazolamide (5-acetamido-1,3,4-thiadiazole-2-sulfonamide) has been shown to be one of the most potent inhibitors (Evelhoch *et al.*, 1981). The search for new sulfonamides with major pharmacological potency, low toxicity and few side effects continues (Jallon, 1997). Hats (5-amino-1,3,4-thiadiazole-2-sulfonamide), an acetazolamide analogue, has been shown to be more potent than acetazolamide as an anticonvulsant in mice, despite its low inhibition ability on carbonic anhydrase (Chufán, Pedregosa, Baldini & Bruno-Blanch, 1999).

Knowledge of sulfonamide interactions with carbonic anhydrase (or its structural models) is of great pharmacological and therapeutic interest. Thus, metallic complexes with Hats were prepared and some crystal structures were determined (Chufán *et al.*, 1997; Borja *et al.*, 1998; Chufán, 1999). The crystal structure of $[\text{Zn}(\text{ats})_2(\text{NH}_3)]\cdot\text{H}_2\text{O}$, in which the sulfonamide presents two different coordination behaviours, *i.e.* as a monodentate ligand through the sulfonamide N atom

and as a bridging ligand, linking the zinc ions through the sulfonamide and thiadiazole N atoms, is reported (Borja *et al.*, 1998). Recently, we synthesized a new copper complex, $[\text{Cu}(\text{ats})_2(\text{dipn})]$ (dipn is dipropylentriamine), where the sulfonamide also presents two coordination modes, *i.e.* as a monodentate ligand, as in the zinc(II) complex described above, and as a bridging ligand, linking the copper ions through the sulfonamide N and O atoms (Chufán, Pedregosa, Ferrer & Borrás, 1999).

In the present paper, we report the crystal structure of $[\text{Ni}(\text{dien})_2](\text{ats})\text{Cl}\cdot\text{H}_2\text{O}$ (dien is diethylenetriamine), (I), in which the sulfonamide behaves as a counter-ion instead of as a ligand. It is noteworthy that this is the first reported metal complex structure where the Hats sulfonamide acts as a counter-ion.



The main structural difference between the sulfonamidate anion and free sulfonamide is the shortening of the N—S bond, see Table 3. This is due to deprotonation of the sulfonamide group and subsequent delocalization of the negative charge through the N—S bond. This phenomenon is also present in $[\text{Zn}(\text{ats})_2(\text{NH}_3)]\cdot\text{H}_2\text{O}$, but to a lesser degree because of the sulfonamide N atom being in a coordination site. The increasing length of the (C—S) exocyclic bond is also attributed to electronic delocalization after deprotonation. These facts are evidence that structural properties are more affected by deprotonation than by coordination effects, as was concluded from vibrational spectroscopic data for similar metal complexes (Chufán, Pedregosa, Ferrer & Borrás, 1999).

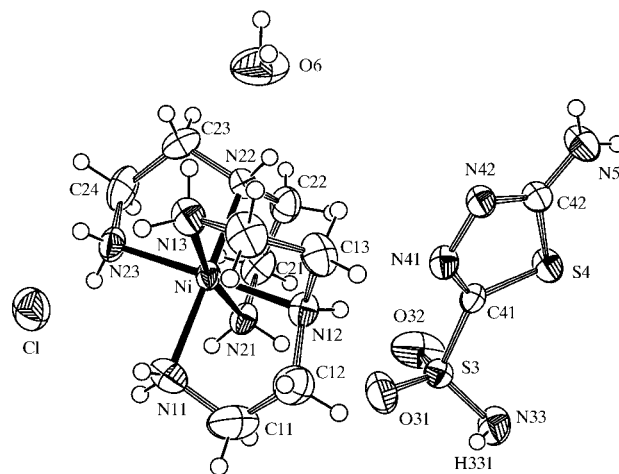


Figure 1
View (ORTEP; Johnson, 1976) of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

The coordination polyhedron consists of $[\text{Ni}(\text{dien})_2]^{2+}$ cations, in which the diethylenetriamine coordinates to the metal center as a tridentate ligand in a facial position. The Ni^{II} ions are linked to six N atoms, forming NiN_6 chromophores with octahedral geometry. On the other hand, the differences in the angles at Ni (see Table 1) are due to the spanning of the dimethylene groups.

The analogous complex $[\text{Cu}(\text{dipn})(\text{ats})_2]$ was synthesized with the same metal–triamine–sulfonamide molar ratio (1:2:2) under similar experimental conditions. The reason that the bis(triamine)–copper(II) complex is not formed is related to the fact that the copper(II) ion is subject to a Jahn–Teller effect whose typical distortion is an elongation along one fourfold axis, so that there is a planar array of four short Cu–L bonds and two long *trans* ones (Cotton & Wilkinson, 1988).

Experimental

The title complex, $[\text{Ni}(\text{dien})_2](\text{ats})\text{Cl}\cdot\text{H}_2\text{O}$, was prepared by mixing nickel(II) chloride hexahydrate (1 mmol), diethylenetriamine (2 mmol) and 5-amino-1,3,4-thiadiazole-2-sulfonamide (2 mmol) in ethanol (50 ml) at room temperature. Single crystals were obtained after one month from the resulting pale-purple solution.

Crystal data

$[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2](\text{C}_2\text{H}_3\text{N}_4\text{O}_2\text{S}_2)\cdot\text{Cl}\cdot\text{H}_2\text{O}$	$Z = 4$
$M_r = 497.73$	$D_x = 1.567 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.378 (6) \text{ \AA}$	Cell parameters from 25 reflections
$b = 11.099 (10) \text{ \AA}$	$\theta = 1.8\text{--}25.0^\circ$
$c = 23.042 (12) \text{ \AA}$	$\mu = 1.28 \text{ mm}^{-1}$
$\beta = 99.44 (5)^\circ$	$T = 293 (2) \text{ K}$
$\gamma = 90.00 (7)^\circ$	Prismatic, red
$V = 2114 (3) \text{ \AA}^3$	$0.15 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	2685 reflections with $I > 2\sigma(I)$
ω - 2θ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 9$
$T_{\text{min}} = 0.774$, $T_{\text{max}} = 0.880$	$k = 0 \rightarrow 13$
3706 measured reflections	$l = -27 \rightarrow 26$
3706 independent reflections	60 standard reflections every 1000 reflections
	intensity decay: 0.047%

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni–N23	2.094 (5)	S3–O31	1.459 (7)
Ni–N11	2.114 (6)	S3–N33	1.513 (7)
Ni–N13	2.123 (5)	S3–C41	1.792 (10)
Ni–N21	2.126 (5)	C41–S4	1.723 (9)
Ni–N22	2.129 (6)	N41–N42	1.383 (11)
Ni–N12	2.129 (5)	N42–C42	1.304 (8)
S3–O32	1.432 (6)		
N23–Ni–N11	94.2 (2)	N23–Ni–N12	172.9 (2)
N23–Ni–N13	92.6 (2)	N11–Ni–N12	82.0 (2)
N11–Ni–N13	95.0 (2)	N13–Ni–N12	81.8 (2)
N23–Ni–N21	94.0 (2)	N21–Ni–N12	92.2 (2)
N11–Ni–N21	93.0 (2)	N22–Ni–N12	102.1 (2)
N13–Ni–N21	169.2 (2)	N41–C41–S4	114.7 (5)
N23–Ni–N22	82.2 (2)	C41–S4–C42	86.7 (4)
N11–Ni–N22	173.1 (3)	C41–N41–N42	112.9 (5)
N13–Ni–N22	91.0 (2)	C42–N42–N41	111.9 (5)
N21–Ni–N22	81.5 (2)	N42–C42–S4	113.8 (5)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 4.4405P]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} = 0.042$
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
3706 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
264 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N5–H52···Cl ^v	0.86	2.44	3.242 (7)	156
N5–H51···N42 ^{iv}	0.86	2.22	3.066 (9)	166
N11–H11A···Cl	0.90	2.68	3.521 (7)	155
N11–H11B···O32 ⁱ	0.90	2.07	2.964 (9)	171
N12–H12···O31	0.91	2.46	3.158 (8)	134
N12–H12···N41	0.91	2.33	3.16 (1)	150
N13–H13A···O6	0.90	2.29	3.08 (2)	146
N13–H13B···Cl	0.90	2.52	3.374 (7)	159
N21–H21A···O31	0.90	2.21	3.108 (8)	171
N21–H21B···N33 ⁱ	0.90	2.40	3.28 (1)	162
N21–H21B···S3 ⁱ	0.90	2.93	3.796 (7)	162
N22–H22···O6	0.91	2.31	3.08 (1)	141
N23–H23A···O31 ⁱ	0.90	2.38	3.23 (1)	156
N23–H23A···S3 ⁱ	0.90	2.96	3.83 (1)	161
N23–H23B···N33 ⁱⁱⁱ	0.90	2.19	3.048 (9)	160
O6–H61···Cl ^{vi}	0.95 (7)	2.28 (7)	3.174 (8)	157 (10)
O6–H62···Cl ⁱⁱ	0.95 (6)	2.28 (5)	3.190 (8)	160 (10)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $1 - x, 1 - y, 2 - z$; (iii) $x, 1 + y, z$; (iv) $2 - x, -y, 2 - z$; (v) $1 + x, y - 1, z$; (vi) $1 + x, y, z$.

Table 3

Sulfonamide bond distances (\AA) for free Hats, $[\text{Ni}(\text{dien})_2](\text{ats})\text{Cl}\cdot\text{H}_2\text{O}$ and $[\text{Zn}(\text{ats})(\text{NH}_3)]\cdot\text{H}_2\text{O}$.

	N–S	S=O	S=O	S–C
Hats	1.569	1.427	1.432	1.767
ats ⁻¹ counter-ion	1.528	1.434	1.453	1.785
$[\text{Ni}(\text{dien})_2](\text{ats})\text{Cl}\cdot\text{H}_2\text{O}$				
ats ⁻¹ monodentate ligand	1.542	1.435	1.444	1.774
$[\text{Zn}(\text{ats})(\text{NH}_3)]\cdot\text{H}_2\text{O}$				
ats ⁻¹ bridging ligand	1.544	1.437	1.438	1.787
$[\text{Zn}(\text{ats})(\text{NH}_3)]\cdot\text{H}_2\text{O}$				

All H atoms were localized geometrically and refined as riding (C–H = 0.97 \AA), except for H331 bonded to N33 and water H atoms H61 and H62, which were located in subsequent difference Fourier maps and refined isotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1997); cell refinement: *CAD-4 Software*; data reduction: *PROCESS* in *MolEN* (Nonius, 1997); program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1492). Services for accessing these data are described at the back of the journal.

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