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Synthesis and structural study of complexes of nickel(II) with 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine

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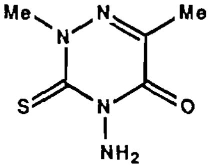
Abstract

Bis-ligand nickel(II) complexes with 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine have been prepared by reaction between the triazine and the corresponding nickel salt in the 2:1 molar ratio, respectively. Conductance, magnetic, and infrared and visible spectroscopy data have been used for structural assignments. Pseudooctahedral structures are proposed for the complexes with the triazine molecule acting either as a monodentate N-donor ligand or a bidentate N- and S-donor ligand. An X-ray structural determination carried out with $[Ni(triazine)_2(H_2O)_2](ClO_4)_2$ shows that the triazine acts as a bidentate ligand via the 4-amino nitrogen and the 3-thioxo sulfur (Ni–S = 2.377 Å; Ni–N = 2.079 Å) and the two H_2O molecules complete the hexacoordination of nickel(II) (Ni–O = 2.135 Å).

Introduction

Compounds containing the 1,2,4-triazine ring are found in natural materials and some of these have biological activity [1]. A group of biochemically active 1,2,4-triazines are the 4-amino-1,2,4-triazine-5-ones, some of which are widely used as herbicides [2].

A number of Co(II) and Ni(II) complexes with both 4-amino-6-methyl-5-oxo-3-phenylamino-4,5-dihydro-1,2,4-triazine [3] and 4-amino-6-methyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine [4, 5] have been synthesized. In the latter case the triazine may exist in thione and thiol forms [6] and can coordinate as a neutral or monoanionic ligand.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This paper deals with the synthesis and structural study of some nickel(II) complexes with the recently reported 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine [7], hereafter abbreviated as L. Prototropic tautomerism cannot occur in this heterocyclic thione because of the presence of the 2-methyl group, and the thiocarbohydrazide system N–N–C(S)–N–N is involved in coordination to the metal centre. Monodentate (4-amino) nitrogen donation or bidentate (4-amino and 3-thioxo) nitrogen–sulfur donation are the proposed coordination modes of the triazine, depending on the identity of the nickel salt, the experimental conditions and the presence or absence of H_2O in the complex.

Experimental

The C, H and N analyses were performed with a Perkin-Elmer 240C microanalyzer, and nickel was determined by titration with EDTA [8]. IR spectra were recorded on a Perkin-Elmer 1430 spectropho-

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tometer, with samples as Nujol mulls between polyethylene sheets and/or KBr discs. Electronic spectra were recorded on a Hitachi U 2300 instrument. Magnetic susceptibilities were measured by the Faraday method, using a DSM-5 magnetometer calibrated with Hg[Co(SCN)$_4$] ($H=15$ kG; $H(\delta H/\delta z)=29$ kG cm^{-1}. Thermal decomposition studies were carried out with a Mettler TG-50 thermobalance. Conductivities were measured with a Crison 525 conductimeter and the experimental results were compared with those reported in the literature [9].

The starting compounds $Ni(ClO_4)_2 \cdot 6H_2O$ and $Ni(BF_4)_2 \cdot 6H_2O$ were prepared from nickel carbonate and either perchloric or tetrafluoroboric acid, respectively. Ethanol solutions ($c \approx 0.29$ M) of $Ni(SCN)_2$ were prepared through the metathetic reaction between $Ni(NO_3)_2 \cdot 6H_2O$ and KSCN in ethanol and removal of the precipitated KNO_3 by filtration. The remaining nickel salts were commercial products. The solvents were dried before use, by methods described in the literature. 4-Amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (L) was synthesized as described elsewhere [7] and was recrystallized from ethanol.

Crystal data

$C_{10}H_{16}N_8O_2S_2Ni \cdot 2H_2O \cdot 2ClO_4$, $M=638.07$, triclinic, $a=7.559(2)$, $b=7.791(4)$, $c=12.563(2)$ Å, $\alpha=67.60(4)$, $\beta=68.30(2)$, $\gamma=62.71(4)°$, $V=590$ A^3, $Z=1$, $D_c=1.79$ M gm^{-3}, space group $P1$, flat blue crystals. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer in the range $1>\theta>25°$ using the flat psi mode to minimize absorption effects. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN 11/84 [10] refined by full-matrix least-squares technique with SHELX-76 [11] to $R=0.058$ and $R_w=0.062$ where $w=1/(\sigma^2(F)+0.003813F^2)$ over 874 observed reflections ($I>2\sigma(I)$).

Syntheses

[NiL$_2$Cl$_2$]·H$_2$O] (1)

Triazine (250 mg; 1.453 mmol) was added to a solution of $NiCl_2 \cdot 6H_2O$ (172.7 mg; 0.726 mmol) in ethanol (5 ml), and the reaction mixture was stirred at room temperature for 30 min. Diethyl ether (40 ml) was then added dropwise with constant stirring, whereupon green crystals of **1** precipitated. These were filtered off, washed with diethyl ether and vacuum-dried in a P_2O_5-desiccator.

[NiL$_2$(H$_2$O)$_2$Br$_2$]·H$_2$O (2)

Triazine (250 mg; 1.453 mmol) dissolved in diethyl ether (40 ml) was added to a solution of $NiBr_2 \cdot 3H_2O$ (198 mg; 0.727 mmol) in ethanol (4 ml), whereupon a blue–green solid precipitated. The suspension was stirred at room temperature for 4 h and the colour became light blue. The solid was separated by filtration, washed with diethyl ether and vacuum-dried in a P_2O_5-dessicator.

a-[NiL$_2$Br$_2$] (3)

This compound was obtained when a sample of **2** (100 mg; 0.162 mmol) was heated at 140 °C for 15 min in the stove and then cooled to room temperature in a P_2O_5-desiccator.

b-[NiL$_2$Br$_2$] (4)

This isomer was prepared from a solution of **2** (160 mg; 0.260 mmol) in acetonitrile (3 ml). Green crystals precipitated when the solution was stirred at room temperature for 4 h. The crystals were collected by filtration, washed with diethyl ether and vacuum-dried under nitrogen.

[NiL$_2$(H$_2$O)$_2$I$_2$] (5)

A solution of the triazine (200 mg; 1.163 mmol) in diethyl ether (200 ml) was added to an ethanol (20 ml) solution of $NiI_2 \cdot H_2O$ (192 mg; 0.581 mmol), whereupon a precipitate was formed. The suspension was stirred at room temperature for 4 h, then the solid was filtered off and recrystallized from methanol–diethyl ether. The resulting green crystals were collected by filtration, washed with diethyl ether and vacuum-dried in a P_2O_5-desiccator.

[NiL$_2$(NCS)$_2$] (6)

A solution of the triazine (500 mg; 2.907 mmol) in diethyl ether (50 ml) was added dropwise to a 0.29 M ethanolic solution (5 ml) of $Ni(NCS)_2$. After 10 min with constant stirring, a yellowish green solid began to precipitate. The suspension was stirred at room temperature for 30 min and concentrated under reduced pressure until about 30 ml. The solid was filtered off, washed with diethyl ether and vacuum-dried in a P_2O_5-desiccator.

[NiL$_2$(H$_2$O)$_2$(ClO$_4$)$_2$ (7)

A solution of the triazine (250 mg; 1.453 mmol) in diethyl ether (40 ml) was added dropwise, with constant stirring, to a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (265.8 mg; 0.727 mmol) in ethanol (2 ml), and a light blue precipitate was formed. The suspension was stirred at room temperature for 4 h, and the solid was collected by filtration, washed with diethyl ether and dried under nitrogen. The compound was recrystallized from acetone–hexane. Crystals suitable for X-ray diffraction were obtained by solvent diffusion (acetone–hexane) at room temperature.

$[NiL_2(H_2O)_2](BF_4)_2$ (8)

The procedure was similar to that used for the perchlorate analogue, but $Ni(BF_4)_2 \cdot 6H_2O$ was the starting nickel salt. The blue product was recrystallized from acetone–diethyl ether.

$[NiL_2(CH_3CN)_2](ClO_4)_2$ (9) and
$[NiL_2(CH_3CN)_2](BF_4)_2$ (10)

The procedure was similar for both compounds. A solution of the aqua-complex, $[NiL_2(H_2O)_2]X_2$ ($X = ClO_4$ or BF_4; 0.245 mmol) in acetonitrile (10 ml) was refluxed for 8 h. Partial evaporation of the solvent resulted in the precipitation of a violet solid, which was collected by filtration, washed with diethyl ether and vacuum-dried in a P_2O_5-desiccator.

$[NiL_2(H_2O)_2](NO_3)_2$ (11)

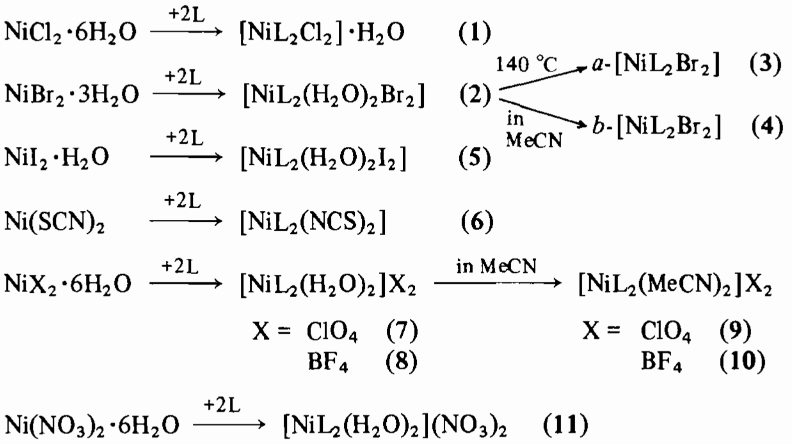
A solution of the triazine (250 mg; 1.453 mmol) in diethyl ether (40 ml) was added dropwise to an ethanol (5 ml) solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (140.8 mg; 0.484 mmol). A light blue precipitate was formed immediately, and the suspension was refluxed for 4 h. The product was filtered off, washed with diethyl ether and dried under nitrogen. It was recrystallized from ethanol.

Results and discussion

The results of our study are summarized in Scheme 1. The general procedure for the preparation of complexes **1**, **2**, and **5–8** is based on the reaction between the triazine (in diethyl ether) and the corresponding nickel salt (in ethanol) in the 2:1 molar ratio and under the conditions given in 'Experimental'. Complexes **2**, **7** and **8** have been used as precursors for **3**, **4**, **9** and **10** (Scheme 1). The stoichiometries, colours, yields, decomposition temperatures, partial elemental analyses and molar conductivities of the metal complexes are listed in Table 1.

Some infrared data relevant for structural assignments have been collected in Table 2. The changes in the stretching and deformation modes of the 4-NH_2 group indicate that in all the complexes the 4-NH_2 nitrogen is involved in coordination. However, the C=O stretching vibration, at 1665 cm^{-1} in free triazine, is shifted to higher wavenumbers (in the range 1710–1690 cm^{-1}) in all the complexes indicating that the carbonyl group remains uncoordinated and that the C=O oxygen of the free ligand is likely to be involved in hydrogen bonding. In the infrared spectrum of the free triazine two partially overlapped bands are observed at 1400–1380 cm^{-1}, attributed to the thioamide II band [12–14] and the symmetric methyl bending mode. In some of our complexes (**1–3** and **5**) only one band is found at *c.* 1380 cm^{-1}, but the presence of an additional band at *c.* 1340 cm^{-1} in the spectra of **4** and **6–11** is attributed to further coordination of the triazine by the S atom of the 3-thioxo group, i.e. as a bidentate N,S-donor ligand. As described below, this assignment has been confirmed for **7** by X-ray diffraction.

The visible spectra of the solid compounds display an absorption located in the range 14–18 kK which is assigned to $\nu_2[^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)]$ in O_h symmetry [15]. The room temperature (300 K) magnetic moments of the complexes lie in the range 3.42–3.20 BM (Table 3), which are the normal values for pseudooctahedral nickel(II) complexes [16] containing two unpaired electrons.



L = 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine

Scheme 1.

TABLE 1. Analytical data, decomposition temperatures and yields for the nickel complexes

Complex	Colour	Yield (%)	Decomposition temperature (°C)[a]	Analysis: found(calc.) (%)			
				C	H	N	Ni
$[NiL_2Cl_2]\cdot H_2O$ (**1**)	green	72	150	24.6	3.4	22.9	11.7
				(24.4)	(3.7)	(22.8)	(11.9)
$[NiL_2(H_2O)_2Br_2]\cdot H_2O$ (**2**)	green	85	80	19.3	3.2	18.4	9.8
				(19.5)	(3.6)	(18.2)	(9.5)
a-$[NiL_2Br_2]$ (**3**)	green	100	197	20.9	3.1	19.6	10.3
				(21.3)	(2.8)	(19.9)	(10.4)
b-$[NiL_2Br_2]$ (**4**)	green	76	166	21.1	2.8	19.7	10.1
				(21.3)	(2.8)	(19.9)	(10.4)
$[NiL_2(H_2O)_2I_2]$ (**5**)	green–blue	62	107	17.0	3.2	15.9	8.2
				(17.3)	(2.9)	(16.2)	(8.5)
$[NiL_2(NCS)_2]$ (**6**)	green–yellow	73	200	27.7	3.0	26.7	11.6
				(27.8)	(3.1)	(27.0)	(11.3)
$[NiL_2(H_2O)_2](ClO_4)_2$ (**7**)	blue	81	150	19.1	3.3	17.3	8.9
				(18.8)	(3.1)	(17.6)	(9.2)
$[NiL_2(H_2O)_2](BF_4)_2$ (**8**)	blue	85	133	19.9	3.2	18.6	9.2
				(19.6)	(3.3)	(18.3)	(9.6)
$[NiL_2(CH_3CN)_2](ClO_4)_2$ (**9**)	violet–blue	71	120	24.9	3.3	20.2	8.4
				(24.6)	(3.2)	(20.5)	(8.6)
$[NiL_2(CH_3CN)_2](BF_4)_2$ (**10**)	violet–blue	72	138	25.6	3.5	20.9	8.6
				(25.5)	(3.3)	(21.3)	(8.9)
$[NiL_2(H_2O)_2](NO_3)_2$ (**11**)	blue	68	123	21.4	3.6	25.2	10.4
				(21.3)	(3.6)	(24.9)	(10.4)

[a] Data from thermogravimetric curves.

The presence of a band at 230 cm^{-1} in the spectrum of **1** is indicative of bridging nickel–chlorine bonds [17], and since no band is observed at 1340 cm^{-1} the triazine should not be bonded via the S atom of the 3-thioxo group. Thus a polymeric tetragonally distorted structure with four bridging chlorine atoms and two N-donor L molecules at the axial positions may be proposed for $[NiL_2Cl_2]\cdot H_2O$. The H_2O molecule gives absorptions at 3400 (νOH) and 1640 (δHOH) cm^{-1}, and the thermogravimetric trace shows that this H_2O molecule is released at 150 °C (weight loss 3.8%; theoretical weight loss 3.7%). The compound is insoluble in acetone but soluble in acetonitrile; the solution is almost non-conducting and shows a visible absorption at 16.3 kK (compared with 15.3 kK for the solid). It is likely that the acetonitrile causes cleavage of the polymeric structure to form $[NiL_2(MeCN)_2Cl_2]$ but attempts to obtain this acetonitrile species were unsuccessful.

The lower ability of bromine to be involved in bridging systems compared to chlorine is manifested in complex **2**. The lack of a band at *c*. 1349 cm^{-1} in the spectrum of **2** suggests that the triazine behaves as a monodentate N-donor in this complex. A sharp, strong band at 3500 cm^{-1} indicates the presence of coordinated H_2O. The thermogravimetric data support the presence of two different types of water molecules in the structure. The compound loses three H_2O molecules at 181 °C (experimental weight loss 8.8%; theoretical value 8.7%), but the thermogravimetric trace shows an inflexion at 127 °C indicating the possible formation of an intermediate $NiL_2Br_2\cdot H_2O$ according to eqn. (1).

$$[NiL_2Br_2(H_2O)_2]\cdot H_2O \xrightarrow[-2H_2O]{127\ ^{\circ}C} (NiL_2Br_2\cdot H_2O)^{\#} \xrightarrow[-H_2O]{181\ ^{\circ}C} [NiL_2Br_2] \qquad (1)$$

The difference between the experimental weight losses (6.8% and 2.0%, respectively) and the theoretical ones (5.8% and 2.9%, respectively) can be attributed to overlapping of the two decomposition stages. On the basis of the above data we propose for **2** a hexacoordinate structure, $[NiL_2(H_2O)_2Br_2]\cdot H_2O$, containing monodentate L, which is consistent with the visible absorption at 16.1 kK found in the electronic spectrum of the solid sample. **2** is soluble and non-conducting in acetone, but the electronic spectrum of the solution shows that the H_2O molecules are replaced by acetone molecules (absorption maximum at 15.3 kK).

Two structurally different compounds, *a*- and *b*-$[NiL_2Br_2]$, can be prepared from **2**. If this is heated

TABLE 2. IR data (cm^{-1}) for the nickel complexes

Compound	ν(NH)	$\delta(NH_2)$	ν(C=S)	Others
1	3200br	1595	1380	230 (νNiCl) 3400 (νOH), 1640 (δH_2O)
2	3140 3080	1605 1595	1380	3500 (νOH), 1630 (δH_2O)
3	3190 3100	1595	1380	
4	3180 3070	1610	1335	
5	3260 3170 3080	1600 1590	1380	3510 (νOH), 1630 (δH_2O)
6	3150 3090	1610	1330	2080 (νCN of SCN), 490 (δSCN)
7	3220 3140	1610	1330	3570, 3400 (νOH), 1640 (δH_2O) 1080 ($\nu_3 ClO_4$), 620 ($\nu_4 ClO_4$)
8	3230 3160	1610	1330	3560, 3460 (νOH), 1620 (δH_2O) 1100 ($\nu_3 BF_4$), 765, 525, 345 (BF_4)
9	3230 3190 3130	1605 1595	1335	2290 (νCN of MeCN), 2320 (δCH_3 + νCC combination)
10	3230 3200 3140	1605 1595	1330	2290 (νCN of MeCN), 2320 (δCH_3 + νCC combination)
11	3200 3140 3200sh	1600 1590	1330	3450 (νOH), 1630 (δH_2O), 1390 ($\nu_3 E'$ NO_3)
Free L	3320 3220	1520	1380	

at 140 °C in the stove, the *a* isomer (**4**) is obtained. Its infrared spectrum shows the absence of water and the presence of the triazine as a monodentate N-donor ligand. The nickel–bromine vibration cannot be studied because of the lowest limit of our spectrophotometer (200 cm^{-1}). A polymeric structure similar to that proposed for **1** is consistent with the visible absorption observed at 15.0 kK. In acetone solution the complex behaves as a non-electrolyte and the absorption found at 16.2 kK ($\epsilon = 213$ mol^{-1} 1 cm^{-1}) indicates the formation of a tetrahedral complex in solution [15], possibly $[NiL_2Br_2]$ containing monodentate triazine. If, however, **2** is refluxed in acetonitrile the *b* isomer (**4**) is isolated. Its infrared spectrum displays a band at 1335 cm^{-1} indicating coordination of the triazine as a bidentate N,S-donor ligand and, accordingly, the complex is considered as a pseudooctahedral structure based on the chromophore $[NiN_2S_2Br_2]$. The two absorptions observed in the electronic spectrum of the solid at 13.8 and 15.9 kK are attributed to the splitting of the $^3T_{1g}$ term, due to structural distortion. It is likely that in the formation of **4** an acetonitrile intermediate, $[NiL_2(MeCN)_2Br_2]$, is involved and the coordinated solvent should be replaced by the S atoms of two 3-thioxo groups. Complex **4** is insoluble in acetone but soluble in methanol where it behaves as a 1:2 electrolyte.

The spectroscopic data of **5** indicate that it should be formulated as $[NiL_2(H_2O)_2I_2]$. The complex is insoluble in acetone but soluble in acetonitrile where it behaves as a 1:2 electrolyte and gives an absorption at 16.8 kK (at 15.9 kK in the solid sample).

The yellowish green thiocyanato complex (**6**) gives bands at 1330 (bonded 3-thioxo) and 2080 cm^{-1}, the latter being consistent with N-bonded thiocyanate [18]. Complex **6** is thus considered as a pseudooctahedral compound containing bidentate triazine and isthiocyanate. The electronic absorption at 16.9 kK is consistent with the above formulation. **6** is insoluble in acetone but soluble in acetonitrile where it behaves as a non-electrolyte.

The infrared spectra of complexes **7**, **8** and **11** indicate that they contain bidentate N,S-donor triazine with two H_2O molecules completing the hexacoordination of nickel, and their visible absorption maxima are consistent with the presence of a chromophore $[NiN_2S_2O_2]$. The presence of free perchlorate, tetrafluoroborate and nitrate in their respective compounds is shown by the bands at 1100,

TABLE 3. Visible spectra, magnetic moments and molar conductances for the nickel complexes

Compound	$\nu[^3A_{2g} \rightarrow {}^3T_{1g}]$	Λ_M[a]	μ_{eff} (BM)[b]
1	Nujol: 15.5		3.40
	MeCN: 17.3sh(43), 16.2(58), 15.4sh(43)	45	
2	Nujol: 16.1		3.42
	Me_2CO: 15.5(54), 14.2sh(40)	20	
3	Nujol: 15.0		3.35
	Me_2CO: 16.2(214)	19	
4	Nujol: 15.9sh, 13.8		3.25
	MeOH: 15.4(17)	167	
5	Nujol: 15.9		3.20
	MeCN: 16.6(22)	160	
6	Nujol: 16.9		3.27
	MeCN: 16.1(65)	28	
7	Nujol: 16.7		3.22
	Me_2CO: 16.9(23)	188	
8	Nujol: 17.0		3.23
	Me_2CO: 16.8(20)	182	
9	Nujol: 18.2		3.24
	Me_2CO: 16.9(22)	160	
10	Nujol: 17.9		3.25
	MeCN: 17.4(20)	156	
11	Nujol: 16.3		3.30
	Me_2CO: 15.6(27)	15	
	MeCN: 16.2(22)		

[a] ohm^{-1} cm^2 mol^{-1}. [b] At 300 K.

1070 and 1390 cm^{-1}, respectively [17]. Complexes **7** and **8** are soluble in acetone where they behave as 1:2 electrolytes, but the acetone solution of **11** is non-conducting, which may be attributed to replacement of the axial water molecules by nitrate ions. This is supported by the visible spectrum of the solution, since the absorption maximum (at 16.4 kK in the solid state) is found at 15.6 kK.

When both **7** and **8** are refluxed in acetonitrile the water molecules are replaced by solvent molecules to give $[NiL_2(CH_3CN)_2]X_2$, X being ClO_4 (**9**) or BF_4 (**10**). The visible absorption at 17.9–18.2 kK is in agreement with the presence of a chromophore $[NiN_4S_2]$. The infrared band at 2290 cm^{-1} is consistent with an end-on coordination of CH_3CN via the unshared electron pair on the nitrogen atom (free acetonitrile absorbs at 2254 cm^{-1}) [19].

Figure 1 gives a view of the structure of the cation in $[NiL_2(H_2O)_2](ClO_4)_2$. Bond lengths and bond angles, and fractional atomic coordinates are collected in Tables 4 and 5, respectively. The metal atom has a distorted octahedral environment. Each nickel atom is coordinated by a *trans*-N_2S_2 set involving the 4-amino (Ni–N_{1a} = 2.079 Å) and 3-thioxo (Ni–S_1 = 2.377 Å) substituents on the triazine. Two H_2O molecules at the axial positions (Ni–O = 2.135 Å) complete the hexacoordination of nickel. The Ni–N_{1a} and Ni–S_1 distances are in the range expected for this type of complex [20] and the double-bond character of the 3-thioxo is substantiated by the C_2–S_1 distance (1.665 Å) [6]. The S_1NiN_{1a} (83.2°) and C_2S_1Ni (96.5°) angles are quite similar to those reported for thiosemicarbazone–nickel complexes containing the same chelate ring [20].

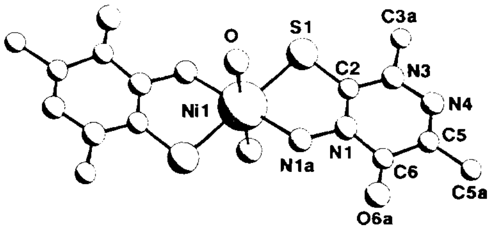


Fig. 1. Perspective view of $[NiL_2(H_2O)_2]^{2+}$ in the perchlorate compound with atom numbering.

The perchlorate ions are partially disordered in the crystalline cell. While the Cl and O_1 atoms are well positioned, the remaining three O atoms are simultaneously occupying two sites around the C_3 symmetry axis of the ClO_4 tetrahedron (each one with a occupancy factor of 1/2). These sites are named O_2 to O_4 for the first tetrahedron and O_5 to O_7 for the second one. There are four distances lower than 3.5 Å between O atoms of the coordinated

TABLE 4. Bond lengths (Å) and bond angles (°) with their e.s.d.s in parentheses

S1–Ni1	2.377(3)	N1a–Ni1–S1	83.2(0.3)
N1a–Ni1	2.079(9)	O–Ni1–S1	89.2(0.3)
O–Ni1	2.135(9)	O–Ni1–N1a	88.2(0.4)
C2–S1	1.665(12)	C2–S1–Ni1	96.5(0.4)
C2–N1	1.358(14)	C6–N1–C2	125.5(1.0)
C6–N1	1.389(14)	N1a–N1–C2	118.1(0.9)
N1a–N1	1.432(13)	N1a–N1–C6	116.3(1.0)
N3–C2	1.345(16)	N1–C2–S1	124.1(0.9)
N4–N3	1.372(14)	N3–C2–S1	121.2(0.9)
C3a–N3	1.474(16)	N3–C2–N1	114.7(1.0)
C5–N4	1.268(15)	N4–N3–C2	125.0(1.0)
C6–C5	1.464(19)	C3a–N3–C2	121.1(1.1)
C5a–C5	1.486(16)	C3a–N3–N4	113.6(1.0)
O6a–C6	1.222(15)	C5–N4–N3	118.7(1.1)
O1–Cl1	1.434(12)	C6–C5–N4	123.4(1.1)
O2–Cl1	1.372(23)	C5a–C5–N4	120.2(1.3)
O3–Cl1	1.521(24)	C5a–C5–C6	116.4(1.2)
O4–Cl1	1.332(23)	C5–C6–N1	112.5(1.1)
O5–Cl1	1.600(26)	O6a–C6–N1	121.9(1.2)
O6–Cl1	1.370(38)	O6a–C6–C5	125.6(1.1)
O7–Cl1	1.348(34)	N1–N1a–Ni1	115.1(0.7)
		N1a–H11–Ni1	76.2(0.3)
		O2–Cl1–O1	103.1(1.2)
		O3–Cl1–O1	107.2(1.0)
		O3–Cl1–O2	109.4(1.4)
		O4–Cl1–O1	107.2(1.1)
		O4–Cl1–O2	126.9(1.4)
		O4–Cl1–O3	102.0(1.3)
		O5–Cl1–O1	110.7(1.1)
		O6–Cl1–O1	112.1(1.5)
		O6–Cl1–O5	96.8(1.8)
		O7–Cl1–O1	122.0(1.6)
		O7–Cl1–O5	100.4(1.8)
		O7–Cl1–O6	111.2(2.3)

water molecules and perchlorate ions, evidencing hydrogen bonds between cation and anion in the crystalline cell. The shortest one is 2.864 Å with O_5(i) (i=x, $y-1$, z)

Supplementary material

Listings of anisotropic temperature factors and observed and calculated structure factors (6 pages) are available from the authors on request.

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TABLE 5. Fractional atomic coordinates (×10⁴) with the equivalent temperature factors

	x/a	y/b	z/c	B_{eq}
Ni1	0(0)	0(0)	0(0)	2.94
S1	878(6)	1208(4)	7905(3)	3.81
N1	2844(14)	−2758(13)	8449(9)	2.62
C2	2248(18)	−1019(16)	7614(11)	2.84
N3	2916(15)	−1204(15)	6497(9)	3.14
N4	4045(16)	−2976(15)	6178(9)	3.41
C5	4503(18)	−4582(17)	6984(13)	3.40
C6	3892(19)	−4648(18)	8245(13)	3.24
N1a	2253(16)	−2676(14)	9656(10)	3.42
C3a	2278(26)	523(19)	5503(13)	5.46
C5a	5700(27)	−6533(20)	6675(14)	5.93
O6a	4278(15)	−6160(12)	9052(8)	4.36
O	2332(15)	709(13)	10109(9)	4.80
Cl1	1438(6)	−6817(5)	12316(4)	4.72
O1	227(17)	−5586(16)	11458(11)	6.36
O2	2893(37)	−6005(34)	11988(25)	6.84
O3	59(34)	−6499(34)	13518(21)	7.49
O4	1770(38)	−8706(35)	12434(22)	7.55
O5	3401(40)	−8564(36)	11816(24)	5.53
O6	528(57)	−8026(57)	13240(35)	9.13
O7	2333(58)	−6084(53)	12699(38)	7.99

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