SYNTHESIS, SPECTROSCOPIC AND MAGNETIC CHARACTERISATION OF SOME NICKEL(II) COMPLEXES WITH 2-AMINO-1,3,4-THIADIAZOLE-5-THIOL

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abstract: A series of complexes of Ni(II) with 2-amino-1,3,4-thiadiazole-5-thiol (HTDA) have been synthesised and characterised. The bonding and stereochemistry of the complexes have been characterised by IR and electronic studies, magnetic susceptibility at room temperature and conductivity measurements. The Ni(II) complexes exhibit octahedral or trigonal bipyramidal stereochemistry. Thiadiazole in monoanionic form is coordinated as chelate through cyclic nitogen (N^4) and exocyclic sulfur of the tioamide moiety while in neutral form acts as unidentate through N^4. The effective magnetic moments at room temperature agree with proposed stereochemistry. Data concerning thermal behaviour of complex $[Ni(TDA)Cl(H_2O)_3]\cdot 2H_2O$ are presented.

keywords: nickel(II) complex, 2-amino-1,3,4-thiadiazole-5-thiol

Introduction

There is a much interest in heterocyclic ligands and their main group or transition metal complexes with particular attention focused on bioinorganic studies. It was shown that the mono- and disubstituted 1,3,4-thiadiazoles have pharmacological properties [1] and are versatile coordinating agents [2, 3]. Moreover, the complexes with 1,3,4-thiadiazole derivatives are biologically active having applications as fungicide [4]. We described homo- and heteronuclear complexes with 2-amino-1,3,4-thiadiazole-5-thiol (HTDA) which exhibit good inhibitory properties toward carbonic anhydrase [5÷8].

We report here the new complexes of Ni(II) with 2-amino-1,3,4-thiadiazole-5-thiol prepared and studied in order to evidence the coordination behaviour of this ligand in alkaline medium and at high metal: ligand molar ratio. The complexes were formulated on the basis of analytical, spectral and magnetic data.

Experimental

IR spectra (200-4000 cm^{-1}) were recorded in KBr pellets with a Specord M80 spectrophotometer. Electronic spectra were recorded by diffuse reflectance technique using

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MgO as standard with a VSU-2P Zeiss Jena instrument. Magnetic measurements were carried out using a Faraday balance at 25^0C, with $Hg[Co(NCS)_4]$ as standard. The molar conductivities of 10^{-3} M solution in DMSO or DMF were obtained on a Radelkis OK-120/1 conductivity bridge (having the cell constant 0.68), at room temperature.

The ligand, 2-amino-1,3,4-thiadiazole-5-thiol, $NiCl_26H_2O$ and $Ni(CH_3COO)_22H_2O$ were purchased from Merck. Nickel, chloride and sulphur were determined gravimetrically while nitrogen was determined by microcombustion.

Preparation of the complexes (1)-(5)

Compound $[Ni(TDA)(AcO)(H_2O)_2]$ (**1**) and $[Ni(TDA)(Cl)(OH_2)_3]\cdot 2H_2O$ (**2**). To a magnetically stirred metal salt solution (2 mmoles nickel(II) acetate or chloride) in 20 mL EtOH:H_2O (1:1, v/v) was added a solution of HTDA (2 mmoles) in 40 mL hot EtOH. The pH was adjusted at 8-9 with a solution of NaOH (10%) and the mixture was stirred 8h until a green compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air dried. Analysis, found: Ni, 21.09; ; N,14.82; S, 22.72, $NiC_4H_9N_3O_4S_2$ requires: Ni, 20.62; N,14.68; S, 22.38, $\Lambda_M = 3\Omega^{-1}cm^2mol^{-1}$; analysis, found: Ni, 18.77; N,13.31; S, 20.12; Cl,11.46; mass loss at 120°C, 11.29, $NiC_2ClH_{12}N_3O_5S_2$ requires: Ni, 18.64; N,13.27; S, 20.22; Cl,11.22; mass loss at 120°C, 11.37, $\Lambda_M = 3\ \Omega^{-1}cm^2mol^{-1}$.

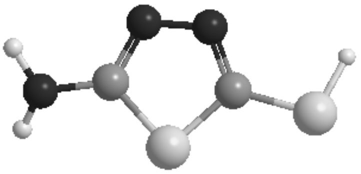
Compound $[Ni(TDA)_2(H_2O)_2]$ (**3**). To a magnetically stirred solution of 2 mmoles nickel (II) chloride in 20 mL EtOH:H_2O (1:1, v/v) was added a solution of HTDA (4 mmoles) in 40 mL hot EtOH. The pH was adjusted at 8-9 with a solution of NaOH (10%) and the mixture was refluxed for 6h until a brown-green compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air dried. Analysis, found: Ni, 16.89; N,23.49; S, 35.44, $NiC_4H_8N_6O_2S_4$ requires: Ni, 16.43; N,23.39; S, 35.65, $\Lambda_M = 14\ \Omega^{-1}cm^2mol^{-1}$.

Compound $[Ni(TDA)_2\ (HTDA)_2]$ (**4**). To a magnetically stirred solution of 2 mmoles nickel (II) chloride in 20 mL EtOH:H_2O (1:1, v/v) was added a solution of HTDA (8 mmoles) in 100 mL hot EtOH. The pH was adjusted at 8-9 with a solution of NaOH (10%) and the mixture was refluxed for 2h until a light green compound was formed. The microcrystaline product was filtered off, washed with EtOH, Et_2O and air dried. Analysis, found: Ni, 9.98; N, 28.52; S, 43.46, $NiC_8H_{10}N_{12}S_8$ requires: Ni, 10.02; N, 28.52; S, 43.46, $\Lambda_M = 8\ \Omega^{-1}cm^2mol^{-1}$.

Compound $[Ni(HTDA)_5]Cl_2$ (**5**). To a magnetically stirred solution of 1 mmole nickel II) chloride in 10 mL EtOH:H_2O (1:1, v/v) was added a solution of HTDA (10 mmoles) in 100 mL hot EtOH. The mixture was refluxed for 4h until a brown compound was formed. The microcrystaline product was filtered, and washed with EtOH, Et_2O and air dried. Analysis, found: Ni, 9.98; N, 28.52; S, 43.46, $NiC_8H_{10}N_{12}S_8$ requires: Ni, 10.02; N, 28.52; S, 43.46, $\Lambda_M = 8\ \Omega^{-1}cm^2mol^{-1}$.

Results and discussion

In this paper, we report the preparation and the physical-chemical characterisation of new complexes of Ni(II) with 2-amino-1,3,4-thiadiazole-5-thiol (HTDA).



2-amino-1,3,4-thiadiazole-5-thiol (HTDA)

All the complexes are polycrystalline solids with a low solubility in MeCN, THF, MeOH, EtOH and soluble in DMSO and DMF. The molar conductivities values in DMF (10^{-3} M) are low suggesting that complexes (**1**) - (**4**) behave as nonelectrolytes. For complex (5) the value obtained for molar conductivity agrees with an 1: 2 electrolyte behaviour [10]

For compound (**2**) it was proved by thermogravimetric analysis that the degradation of it occurred in three steps in the range 200 - 650 °C, the final residue being NiO. The heating curves TG, DTG and DTA allowed us to evidence the following decomposition steps:

$$[Ni(C_2H_2N_3S_2)Cl(OH_2)_2]\cdot 2H_2O_{(s)} \xrightarrow{75^o C} [Ni(C_2H_2N_3S_2)Cl(OH_2)_2]_{(s)} + 2H_2O_{(g)} \quad (1)$$

$$[Ni(C_2H_2N_3S_2)Cl(OH_2)_2]_{(s)} + 8O_{2\,(g)} \xrightarrow{205-535^o C} NiCl_{2\,(s)} + NiO_{(s)} + 2CO_{2(g)} + \\ +3NO_{2\,(g)} + 4H_2O_{(g)} \quad (2)$$

$$NiCl_{2\,(s)} + NiO_{(s)} + 0.5O_{2\,(g)} \xrightarrow{535-650^o C} 2NiO_{(s)} + Cl_{2\,(g)} \quad (3)$$

The first decomposition step occurred in the temperature range 70-200°C (the maximum decomposition rate corresponds to 75°C) with a weak endothermic effect. This step corresponds to the loss of crystallisation water molecules. The next two steps correspond to the loss of the coordinated water molecule, oxidative degradation of thiadiazole derivative and also of the nickel chloride transformation in nickel oxide.

The major *IR spectral* features of complexes, HTDA and NaTDA are listed in Table 1.

The band due to ν(SH) is absent in spectra of complexes. This information, together with the shifts of the four thioamide bands suggests the presence of 2-amino-1,3,4-thiadiazole-5-thiol in anionic form coordinated through nitrogen and sulfur of tioamide moiety in complexes (**1**) to (**3**). For these complexes the following modification were observed:

(i) the shift of TI and TIV bands towards lower wavenumbers by 15-30 cm^{-1};

(ii) the shift of TII band with 25-30 cm^{-1} towards higher wavenumbers.

For complexes (**4**) and (**5**) the spectra are more complex. The split and shift of the thioamide bands is in accord with the presence of both neutral and anionic form of thiadiazole. The following observation could be made:

(i) the TI and TII bands are splitted in two components;

(ii) the TIV band have also two components, both being shifted to lower wavenumbers, the former with 10 cm^{-1} and the second with 100 cm^{-1} in comparison with neutral ligand and with 20 cm^{-1} in comparison with sodium salt.

These modifications could indicate that the neutral form of ligand is coordinated as monodentate through N^4 and respectively that in monoanionic form the ligand is coordinated through N^4 and tioamide sulfur [11÷13].

Two bands at 1530 and 1400 cm^{-1} in the complex (**1**) spectrum may be assigned to the acetate coordinated as bridge ($\Delta\nu$ = 130 cm^{-1}) [14].

The presence of water molecule could be responsible by the fact that in spectra of complexes are present broad and strong bands in region 3400-3500 cm^{-1} and medium bands at ca. 560 cm^{-1} [15].

The new bands, observed in 460-480, 370-450 and 280-360 regions are assignable to ν(Ni-O), ν(Ni-N) and ν(Ni-S) respectively [15, 16].

Table 1. Absorption maxima (cm^{-1}) and assignments for HTDA, NaTDA and complexes (1) ÷ (5)

HTDA	NaTDA	(1)	(2)	(3)	(4)	(5)	Assignments
–	–	3420s	3400s	–	3450m	–	ν(OH)
3330m 3210m	3280m 3200m	3400s	3340s 3250m	3400s 3310s	3400m 3325m	3290s 3200s	ν(NH) cyclic
3110s 2885s	3050s 2900m	3230m 3140m	3120m 2920m	3250s 3150s	3165m 3135m	3050s 2870s	ν(NH) exocyclic
2585m	–	–	–	–	–	–	ν(SH)
–	–	1530vs	–	–	–	–	ν_{as}(COO)
1585s	1585s	1610s	1610s	1615s	1610s 1600s	1560vs	T I ν(C=N)
–	–	1400s	–	–	–	–	ν_s(COO)
1320s	1310s	1350m	1355m 1330m	1380m	1370s 1320s	1310vs 1285s	T II δ(NH) +ν(C=N)+ ν(C=S)
1040s	1030s	1050s	1055m	1080s	1055s	1020vs	T III ν(C=N)+ ν(C=S)
740m	680m	660m	640m	750m 665m	750m 660m	710s 680m	T IV ν(C=S)
–	–	540m	–	550w	–	–	$\rho_w(OH_2)$
–	–	435w	–	465w	–	–	ν(M–O)
–	–	410w	450w	410w 400w 390w	445w 420w 375w	430w	ν(M–N)
–	–	365w 310w	310w	350w 310w	310w 280w	–	ν(M–S)

Electronic spectral data of the complexes (**1**) ÷ (**5**) are presented in Table 2. The solid state d-d spectra of compounds (**1**) ÷ (**4**) show three characteristic bands of Ni(II) in a pseudooctahedral environment [17] as it is shown in Fig. 1 for complex (**1**). The assignment of the absorption about 12500 cm^{-1} to the spin forbidden $^3A_2 \rightarrow {}^1E$ transition is based on literature data [18].

The distortion from a regular octahedron, associated with the different nature of ligands and/or donor atoms, generated the broad aspect of the ν_1 and ν_2 bands. The average values of crystal field parameter falling in range 8,000-9,000 cm^{-1}, are consistent with the presence of oxygen, sulfur or chlorine as donor beside nitrogen, atoms that generates a weak field.

The spectrum of complex (**5**) (Fig. 2) is consistent with a pentacoordination that could be associated with a trigonal bipiramidal stereochemistry for Ni(II) ion with a high spin configuration [19].

Table 2. Absorption maxima, assignement, crystal field parameters and magnetic moments for complexes (1)÷(5)

Complex	Absorption maxima (cm^{-1})	Assignment	B (cm^{-1})	β	$(\mu)_{HT}$ (μ_B)
$[Ni(TDA)(AcO)(OH_2)_2]$ (**1**)	26315 14600 12440 sh 8900	$^3A_2 \rightarrow {}^3T_2$ $^3A_2 \rightarrow {}^3T_1$ (F) $^3A_2 \rightarrow {}^1T_1$ $^3A_2 \rightarrow {}^3T_1$ (P)	855	0,82	3,16
$[Ni(TDA)(Cl)(OH_2)_3]\cdot 2H_2O$ (**2**)	25640 14925 12755 sh 9090	$^3A_2 \rightarrow {}^3T_2$ $^3A_2 \rightarrow {}^3T_1$ (F) $^3A_2 \rightarrow {}^1T_1$ $^3A_2 \rightarrow {}^3T_1$ (P)	880	0,85	2,93
$[Ni(TDA)_2(H_2O)_2]$ (**3**)	26660 15150 9170	$^3A_2 \rightarrow {}^3T_2$ $^3A_2 \rightarrow {}^3T_1$ (F) $^3A_2 \rightarrow {}^3T_1$ (P)	960	0,92	3,10
$[Ni(TDA)_2(HTDA)_2]$ (**4**)	(24710) 15150 10640	$^3A_2 \rightarrow {}^3T_2$ $^3A_2 \rightarrow {}^3T_1$ (F) $^3A_2 \rightarrow {}^3T_1$ (P)	768	0,64	3,20
$[Ni(HTDA)_5]Cl_2$ (**5**)	26315 19230 13123 9090	$^3E \rightarrow {}^3A_2$ $^3E \rightarrow {}^3E$ $^3E \rightarrow {}^3A_2, {}^3A_1$ $^3E \rightarrow {}^3E$			3,78

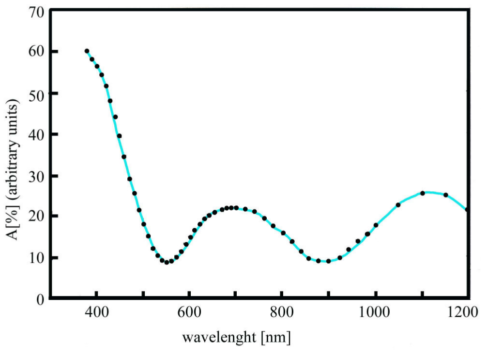


Fig. 1. *The electronic spectrum of* $[Ni(TDA)(AcO)(OH_2)_2]$

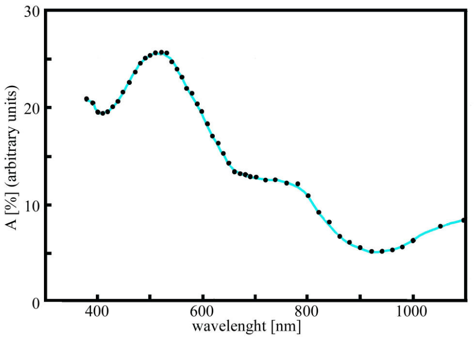


Fig. 2. *The electronic spectrum of* $[Ni(HTDA)_5]Cl_2$

The values of effective magnetic moments (Table 2) agree with this stereochemistry and suggest that there is no interaction between the metal centres at room temperature [20].

Conclusions

Five new Ni(II) complexes with 2-amino-1,3,4-thiadiazole-5-thiol have been synthesised.

The complexes were formulated on the basis of chemical analysis, molar conductivity measurements, electronic and IR spectral data and also magnetic behaviour at room temperature.

The complexes adopt distorted octahedral stereochemistry with the exception of complex (**5**) for which the electronic and magnetic data agree with a trigonal bypiramidal stereochemistry.

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