

MIXED LIGAND COMPLEXES OF BIS (S-METHYL-N-ARYLIDENE HYDRAZINE CARBODITHIOATE) NICKEL (II) CHELATES WITH SOME AMINO ACIDS AND NITROGENOUS HETEROCYCLES

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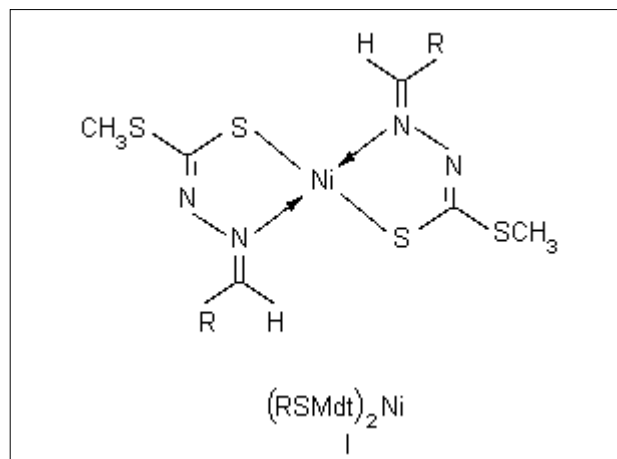
SUMMARY: The mixed ligand complexes of bis (S-methyl-N-arylidene hydrazine carbodithioate) nickel (II) chelates (I; R=C₆H₅, p-CH₃C₆H₄ and p-NO₂C₆H₄) with glycine, β-alanine, imidazole and the sodium salts of morpholine and piperazine dithiocarbamate are prepared and isolated in different solvent, and analyzed. Structures are suggested on the basis of IR and UV-VIS spectran and magnetic measurement. The results obtained suggest the formation of octahedral with imidazole and 1:1 displaced tetrahedral with the others.

Key Words: Glycine, β-alanine, imidazole.

INTRODUCTION

Due to the good ability of the square planar nickel (II) chelates of S-methyl hydrazine carbodithioate Schiff bases to act as Lewis acids and their carcinostatic activity, much attention has been attracted to study their interaction with different types of nitrogenous Lewis bases (1-5). Such study throws some light on the mode of the action of these chelates within the biological system. The antitumor activity of some transition metal chelates of Schiff bases derived from S-methyl hydrazine carbodithioate has been reported (6, 7).

In continuation of the previous studies on the reactions of these chelates with nitrogenous Lewis bases, the mixed ligand complexes of nickel (II) chelates of S-methyl-N-arylidene hydrazine carbodithioate (I; R=C₆H₅, p-CH₃C₆H₄ and p-NO₂C₆H₄) with glycine, β-alanine, imidazole and the sodium salts of morpholine and piperazine dithiocarbamate have been prepared and characterized using magnetic and spectral data.



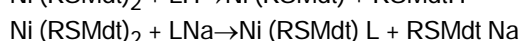
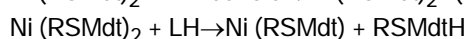
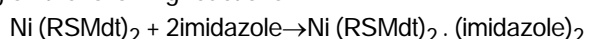
RESULTS AND DISCUSSION

Diamagnetic square-planar chelates of bis (S-methyl-N-arylidene hydrazine carbodithioate) nickel (II) (I; R=C₆H₅, p-CH₃C₆H₄ and p-NO₂C₆H₄) react with glycine, β-alanine, imidazole and the sodium salts of morpholine and piperazine dithiocarbamate to yield the corresponding mixed ligand complexes. The analytical data

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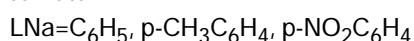
obtained for the isolated complexes suggest that the reaction of imidazole with I; R=C₆H₅, p-CH₃C₆H₄ and p-NO₂C₆H₄ in benzene gives rise to bis-six-coordinate adducts, while the reactions of these chelates with glycine or β-alanine in (1,4-dioxan + H₂O) and with sodium salts of morpholine or piperazine dithiocarbamate in (CH₃CN + H₂O) were found to yield the corresponding (1:1) displaced mixed ligand complexes. The analytical data of the complexes together with their electronic spectra and magnetic moment are given in Table 1.

The mixed ligand complexes were prepared according on the following reactions:



where LH= glycine or β-alanine.

LNa = sodium salts of morpholine or piperazine dithiocarbamate



IR spectra

The most important i.r. bands of the complexes are given in Table 2. Comparison of the i.r. bands of the complexes are given in Table 2. Comparison of the i.r.

spectrum of nickel (II) chelates (I; R=C₆H₅, p-CH₃C₆H₄ and p-NO₂C₆H₄) with that of their corresponding bis-imidazole adducts indicates a new broad band at (3200-3185) cm⁻¹ which may be due to ν NH stretching vibration. On the other hand, the thioureide C=N band (8) of the parent chelates which appears at 1490 cm⁻¹ (3) is found to shift to a lower frequency of (1480-1470) cm⁻¹ due to the rearrangement of the in-plane ligand as a results of octahedral formation. The band of the azomethine group (C=N) at 1600 cm⁻¹ is not shifted in the base-adducts, but its intensity is increased. These data suggest the coordination of the imidazole molecule through its tertiary nitrogen atom as shown in Figure 1c.

The appearance of stretching bands of both the symmetric COO⁻ at 1380-1395 cm⁻¹ and νNH₂ at 3220-3190 cm⁻¹ in the i.r. spectra of the mixed ligand complexes of glycine and β-alanine indicates that the amino and carboxyl groups are chelated to the nickel atom as shown in Figure 1a. It is worth noting that the band responsible for the anti-symmetric stretching vibration of the COO⁻ (1500-1650 cm⁻¹) (9) is presumably overlapped by the high intensity bands of the C=C stretching vibration observed in the region 1415-1620 cm⁻¹ (10).

Table 1: Analytical data, electronic spectra and magnetic moments for the complexes.

Complex	Ni (%) Calc. found	S (%) Calc. found	μ _{eff} (B.M)	λ _{max} (nm)
Ni (p-HSMdt) ₂ .(imidz.) ₂	9.5 9.9	20.8 21.1	3.1	610,400
Ni (p-CH ₃ SMdt) ₂ .(imidz.) ₂	9.1 9.5	19.9 19.6	2.9	620,410
Ni (p-NO ₂ SMdt) ₂ .(imidz.) ₂	8.3 8.7	18.2 17.8	3.2	590,395
Ni (p-HSMdt).Li	13.6 14.0	29.7 29.4	3.6	690,480
Ni (p-CH ₃ SMdt).Li	13.2 13.5	28.8 28.6	3.4	710,490
Ni (p-NO ₂ SMdt).Li	12.3 12.7	26.9 26.4	3.4	630,420
Ni (p-HSMdt).Lii	13.6 13.9	29.8 29.4	3.8	680,468
Ni (p-CH ₃ SMdt).Lii	13.2 13.0	28.9 28.7	3.5	700,475
Ni (p-NO ₂ SMdt).Lii	12.3 12.5	27.0 27.4	3.9	625,416
Ni (p-HSMdt).Liii	17.1 17.5	18.7 18.3	3.5	700,470
Ni (p-CH ₃ SMdt).Liii	16.5 16.3	17.9 17.6	3.4	695,480
Ni (p-NO ₂ SMdt).Liii	15.1 15.0	16.5 16.1	3.9	675,430
Ni (p-HSMdt).Liv	16.5 16.1	17.9 18.4	3.6	714,495
Ni (p-CH ₃ SMdt).Liv	15.8 15.4	17.3 17.7	3.4	690,500
Ni (p-NO ₂ SMdt).Liv	14.6 14.9	15.9 16.3	3.8	660,440

Li = morpholine dithiocarbamate
Lii = piperazine dithiocarbamate

Liii = glycine
Liv = β-alanine

IR spectra of the mixed ligand complexes of morpholine and piperazine dithiocarbamate exhibit new bands around 1100, 1155 and 3180 cm^{-1} which may be assigned, respectively, to stretching frequencies of C-O, C-N and N-H groups and two bands at 980 and 945 cm^{-1} which may be, respectively, due to the asym. and sym. stretching modes of the CSS^- group (11). On the basis of this evidence, it is concluded that the morpholine and piperazine dithiocarbamate may be chelated to the central nickel atom as shown in Figure 1b.

Electronic spectra and magnetic measurements

The magnetic moment values, μ_{eff} , measured for all complexes at room temperature (298 K) and the electronic spectra of the complexes recorded in the solid state as Nujol mulls are given in Table 1. The μ_{eff} values measured for the mixed ligand complexes obtained with the amino acids and morpholine or piperazine dithiocarbamate fall in the range 3.4-3.9 B.M which are expected for a tetrahedral environment around Ni (II). The ground term in tetrahedral complexes $^3T_1(F)$ is orbitally triply degenerate and magnetic moment of such complexes are expected to contain some orbital contribution which raises

Figure 1: Suggested structures for the mixed ligand complexes.

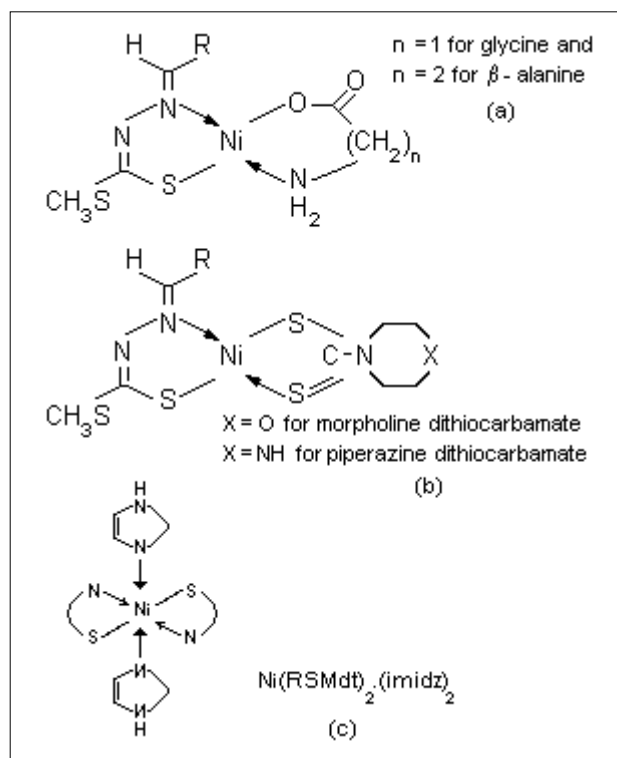


Table 2: Infra red bands for the complexes.

Complex	ν_{NH} cm^{-1}	$\nu_{\text{C=N}}$ cm^{-1}	sym. COO^- cm^{-1}	$\nu_{\text{C-N}}$ cm^{-1}	$\nu_{\text{C-O}}$ cm^{-1}
$\text{Ni}(\text{p-HSMdt})_2(\text{imidz.})_2$	3200	1600	-	1165	-
$\text{Ni}(\text{p-CH}_3\text{SMdt})_2(\text{imidz.})_2$	3196	1600	-	1158	-
$\text{Ni}(\text{p-NO}_2\text{SMdt})_2(\text{imidz.})_2$	3185	1600	-	1160	-
$\text{Ni}(\text{p-HSMdt}).\text{Li}$	-	1590	-	1145	1109
$\text{Ni}(\text{p-CH}_3\text{SMdt}).\text{Li}$	-	1590	-	1159	1100
$\text{Ni}(\text{p-NO}_2\text{SMdt}).\text{Li}$	-	1585	-	1152	1098
$\text{Ni}(\text{p-HSMdt}).\text{Lii}$	3182	1590	-	1151	-
$\text{Ni}(\text{p-CH}_3\text{SMdt}).\text{Lii}$	3186	1595	-	1152	-
$\text{Ni}(\text{p-NO}_2\text{SMdt}).\text{Lii}$	3178	1600	-	1150	-
$\text{Ni}(\text{p-HSMdt}).\text{Liii}$	3196	1635	1390	1200	1100
$\text{Ni}(\text{p-CH}_3\text{SMdt}).\text{Liii}$	3210	1635	1395	1210	1110
$\text{Ni}(\text{p-NO}_2\text{SMdt}).\text{Liii}$	3190	1630	1380	1100	1090
$\text{Ni}(\text{p-HSMdt}).\text{Liv}$	3210	1625	1394	1190	1130
$\text{Ni}(\text{p-CH}_3\text{SMdt}).\text{Liv}$	3220	1630	1390	1195	1160
$\text{Ni}(\text{p-NO}_2\text{SMdt}).\text{Liv}$	3198	1628	1385	1115	1100

Li = morpholine dithiocarbamate
Lii = piperazine dithiocarbamate

Liii = glycine
Liv = β -alanine

the magnetic moment values as high as 3.9 B.M (12). This suggest may be supported by appearing two electronic spectra bands in the region 714-625 nm which can be ascribed to the transition ${}^3T_1(P) \rightarrow T_1(\nu_3)$ and a band located between 500-416 nm which is reasonably assigned due to charge transfer transition. It seems remarkable that the ligand fields in these complexes must include a large low-symmetry component in the complexes (13).

The magnetic moment values measured for the mixed ligand complexes obtained with imidazole (2.9-3.2 B.M) may be attributed due to the normal octahedral geometry (14). The electronic spectra of these complexes exhibit two broad bands in the vicinity of 410-395 nm and 620-590 nm which may be argued to ν_3 -transition, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ν_2 transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ respectively in octahedral geometry. The following structures are suggested, for the complexes, on the basis of the above analytical, spectral and magnetic data.

Experimental

All reagents and solvent required for the complexes preparations were of analytical grade.

Preparation of the mixed ligand complexes

A 50 ml benzene solution of each bis (S-methyl-N-arylidene hydrazine carbodithioate) nickel (II) chelate (I; R=C₆H₅, p-CH₃C₃C₆H₄ and p-NO₂C₆H₄) (1 m.mol) was mixed with a 20 ml benzene solution of imidazole (2 m.mol). The reaction mixture was heated under reflux for ca. 1 hr and then the solvent partially evaporated where upon the product precipitated. It was filtered off, washed with benzene and dried over P₄O₁₀.

1, 4-dioxan solution of each one of these chelates was mixed in 1:1 molar ratio with water solution of glycine or β -alanine and heating under reflux for ca. 2 hrs. In the same manner, CH₃CN solution of each chelate was mixed in 1:1 molar ratio with water solutions of the sodium salt of morpholine or piperazine dithiocarbamate and heating under reflux for ca. 2 hrs. The reaction mixture was concentrated to a small volume by evaporation. On cooling, the corresponding mixed ligand complexes which precipitated, were filtered off, washed and dried over P₄O₁₀ in a desiccator.

Physical measurements

The nickel content was determined gravimetrically. Sulphur analysis was carried out at the microanalysis was

carried out at the microanalysis laboratory, Faculty of Science, Cairo University. Electronic spectra in the solid state as Nujol mulls were recorded on a Spectronic 2000 spectrophotometer. The infrared spectra were measured as KBr pellets on a Perkin-Elme 599 B spectrophotometer. The magnetic measurements at room temperature were carried out by the Gouy method using Hg [Co(NCS)₄] as a calibrant. Diamagnetic corrections were made using Pascal's constants.

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