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Mixed Ligand Complexes of Nickel(II) with some Aminoacids and Dithiocarbamates and their Triphenylphosphine Adducts

Mikkat Z. Hamdi **Ihsan A. Mustafa**
Department of Chemistry/ College of Science/ University of Mosul
Mikkat2009@yahoo.com **Ihsan_mustafa@yahoo.com**

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ABSTRACT

Mixed ligand complexes of the type [Ni (L)(L^-)] and [Ni(L)(L^-)(PPh_3)] were synthesized[HL= aminoacid = glycine, alanine, valine and methionine; L^- = N-methylcyclohexyldithiocarbamate and benzyldithiocarbamate anion]. The amino acids anions(L= Gly, Ala, Val and Met) coordinate through N and O and the dithiocarbamate coordinate through the two sulfur atoms giving square planar Ni(II) complexes. The reaction of the ternary complexes [Ni (L)(L^-)], with triphenylphosphine in 1:2 molar ratio yields quaternary complexes, [Ni(L-Met) (L^-)(PPh_3)], with the retainment of square planar geometry with the dithiocarbamates behave as monodentate ligands. On the other hand, the [Ni(Met)(L^-)(PPh_3)] complexes are octahedral with the methionine anion behave as tridentate ligand coordinating through N,O and S and the dithiocarbamates as bidentate anions coordinating through the two sulfur atoms. The synthesized complexes were characterized by i.r and uv-visible spectra, molar conductance, magnetic susceptibility measurements, metal analysis and some of them by CHNS analysis and (^{1}H-nmr) spectra.

Keywords: Mixed ligand, nickel(II) complexes, adduct.

معقدات ليكاندات مختلطة للنيكل (II) مع عدد من الأحماض الامينية و الثنائي ثايوكارباميت و مركبات الإضافة لثلاثي فنيل الفوسفين

الملخص

يتضمن البحث تحضير معقدات مختلطة للنيكل(II) مع عدد من ليكاندات الأحماض الامينية والثنائي ثايوكارباميت ذات الصيغة [Ni (L)(L^-)] حيث (HL= الأحماض الامينية كلايسين والانين وفالين وميثيونين و-N=L-مثيل سايكلوهكسيل ثنائي ثايوكارباميت و بنزيل ثنائي ثايوكارباميت). كذلك تم تحضير معقدات إضافة مع ثلاثي فنيل الفوسفين ذي الصيغة [Ni(L)(L^-)(PPh_3)] وذلك من تفاعل [Ni (L)(L^-)] مع ثلاثي فنيل الفوسفين بنسبة مولية (2:1). شخصت المعقدات المحضرة باستخدام التوصيلية الكهربائية وأطياف الأشعة تحت الحمراء والالكترونية والقياسات المغناطيسية إضافة إلى التحليل الدقيق للعناصر و بروتون الرنين النووي المغناطيسي لعدد من هذه المعقدات. أثبتت الدراسة أن المعقدات [Ni (L)(L^-)] تمتلك أشكال المربع المستوي إذ تسلك الايونات السالبة للأحماض الامينية وكذلك ليكندات الثنائي ثايوكارباميت بشكل ليكاندات ثنائية السن أحادية الشحنة السالبة. كذلك تمتلك المعقدات [Ni(L-Met)(L^-)(PPh_3)] أشكال المربع المستوي إذ تسلك ليكاندات الثنائي ثايوكارباميت بشكل أحادية السن في حين ان المعقدات [Ni(Met)(L^-) (PPh_3)] تمتلك شكل ثماني السطوح و يسلك المثيونين بشكل ثلاثي السن و ليكاندات الثايوكارباميت بشكل ثنائية السن.

INTRODUCTION

The chemistry of nickel has been rapidly expanded to the increasing number of nickel complexes of biological interest reported in the literature (Andrews *et al*., 1988). In this respect structurally characterized nickel complexes have been reported to possess antiepileptic (Bombiez *et al.*, 2001), anticonvulsant (Morgant *et al*., 2006), antifungal (Sathyadevi *et al*., 2012) and anticancer (Afrasiabi *et al*., 2005) activity.

Mixed ligand complexes have been extensively studied following recognition that they play an important role in biological processes and serve as suitable models in the elucidation of enzymatic prosses of biological relevance (Reddy *et al*., 2000). Also, mixed ligand complexes showed a significant antifungal (Parekh *et al*., 2006) and antibacterial (Abd El-Wahab *et al.*, 2008) activity. Consequently, there has been a considerable interest in the coordination chemistry of mixed ligand complexes. However, mixed ligand complexes of nickel (II) with amino acids and dithiocarbamates are not known. The paper reports the synthesis and characterization of nickel(II) mixed ligand complexes with some amino acids (glycine, alanine , valine and methionine) and dithiocarbamates (N-methylcyclohexyl and benzyl), in addition to the reaction products of these complexes with triphenylphosphine.

EXPERIMENTAL

Materials

Sodium salt of N-methylcyclohexyl and benzyl dithiocarbamates were prepared as cited in the literature (Vogel, 1968). Hydrated nickel chloride, glycine, alanine, valine, methionine, N-methylcyclohexyl amine, benzylamine,triphenylphosphine, carbon disulfide and sodium hydroxide were either Aldrich, BDH or Fluka products.Organic solvents (ethanol, dichloromethane, chloroform, dimethylformamide) were reagent grade chemicals and were used without further purification.

Preparation of nickel(II) complexes:

Preparation of [Ni(N-MeCHdtc)(Gly)]

A solution of nickel(II) chloride hexahydrate (0.001 mol, 0.237g) in water (10cm^3) was added with stirring to solution containing a mixture of sodium N-methylcyclohexyldithiocarbamate. (NaN-MeCHdtc) (0.001 mol, 0.211g) in (10 cm^3) water and aqueous solution of sodium glycinate (NaGly) [prepared by dissolving (0.001 mol, 0.075g) of glycine in 5cm^3 of H_2O followed by the addition of aqueous solution of NaOH to PH~7.5]. The resulting precipitate was filtered, washed several times with water and air dried.

Complexes of[Ni (N-MeCHdtc)(Ala)], [Ni (N-MeCHdtc)(Val)], [Ni (N-MeCHdtc)(Met)] ,[Ni (Bzdtc)(Gly)] , [Ni (Bzdtc)(Ala)] , [Ni (Bzdtc)(Val)] and [Ni (Bzdtc)(Met)] were prepared by the same method using (0.001 mol, 0.089g) of alanine, (0.001 mol, 0.117 g) of valine and (0.001 mol,0.149g) of methionine and (0.001 mol, o.204 g) of NaBzdtc.

An alternative method is the reaction of bis(aminoacid) nickel(II) complex with bis (dithiocarbamate) nickel(II) complex in refluxing chloroform e.g:

$$[Ni(N\text{-}MeCHdtc)_2] + [Ni(Ala)_2] \longrightarrow 2[Ni(N\text{-}MeCHdtc)(Ala)]$$

Where (0.002 mol,0.178 g) of HAla dissolved in (15 cm^3) water was adjusted to PH~7.5-8 by the addition of aqueous solution of NaOH and added with stirring to $NiCl_2.6H_2O$ (0.001 mol,0.237g) dissolved in (10 cm^3) H_2O. The well defined crystals formed after 4 days was pulverized and added with vigorous stirring to a chloroform solution containing dissolved [Ni(N-MeCHdtc)$_2$] (obtained by the reaction of Na N-MeCHdtc(0.002 mol,0.422g) dissolved in (10 cm^3) H_2O with $NiCl_2.6H_2O$. (0.001 mol,0.237 g) in (10 cm^3) H_2O and the precipitate formed, was filtered washed with water and ether and air dried). The mixture was heated under reflux for 20

min. and filtered hot to remove any undissolved particles. Reflux continued for 2h., and the resulting precipitate formed on cooling, was filtered, washed with chloroform and air dried.

Preparation of [Ni(N-MeCHdtc)(Gly)PPh_3]

This complex was prepared by mixing (0.0001 mol, 0.0321g) of the nickel(II) complex, [Ni(N-MeCHdtc)(Gly)] dissolved in(15cm^3) dichloromethane and (0.0002 mol, 0.0524g) triphenylphosphine dissolved in (10cm^3) ethanol with vigorous stirring and refluxed for 2h. The mixture was cooled to room temperature and the resulting precipitate was filtered, washed several times with ethanol and dried in air.

The following complexes were obtained following the same procedure:
[Ni(N-MeCHdtc)(Ala) PPh_3], using (0.0001 mol, 0.0335 g) of [Ni(N-MeCHdtc)(Ala)], [Ni(N-MeCHdtc)(Val) PPh_3], using (0.0001 mol, 0.0363 g) of [Ni(N-MeCHdtc) (Val)], [Ni(N-MeCHdtc)(Met)PPh_3], using (0.0001 mol, 0.0395 g) of [Ni(N-MeCHdtc)(Met)], [Ni(Bzdtc)(Gly)PPh_3], using (0.0001 mol, 0.0315 g) of [Ni(Bzdtc)(Gly)], [Ni(Bzdtc)(Ala)PPh_3], using (0.0001 mol, 0.0329 g) of [Ni(Bzdtc)(Ala)], [Ni(Bzdtc)(Val)PPh_3], using (0.0001 mol, 0.0357 g) of [Ni(Bzdtc)(Val)], [Ni(Bzdtc)(Met)PPh_3] , using (0.0001 mol, 0.0389 g) of [Ni(Bzdtc)(Met)].

Physical Measurements

Nickel contents have been determined employing spectrophotometric measurements using PYE UNICAM SP9-AASpectro Photometer (Phillips). Elemental analysis of carbon, hydrogen, nitrogen, and sulfur for some of the prepared complexes were done using Euro Vactor Model EA 3000 A (Italy) and proton n.m.r. using BRUKER 300 MHZ(Al al bait University, Jordan), respectively, IR spectra were recorded on Fourier-Transform (FT.IR) Spectrophotometer, Tensor27Co.Brucker 2003 at a range (400-4000cm^{-1}) using KBr discs, Electronic spectra were recorded on a U.V-Vis. Spectrophotometer (Shimadzu,UV-1650PC-Spectrophotometer,UV-Vis Recording) using dimethyl formamide DMF(10^{-3}M) as a solvent at room temperature, the Magnetic susceptibility of the complexes have been measured by Bruker B.M.6. using the Farady method, Conductivity measurements have been carried out using DMF as solvent (10^{-3} M) at room temperature with the Conductivity Meter Model PCM3Jenway. Melting and Decomposition points were measured using Electriothermal 9300 Engineering LTD.

RESULTS AND DISCUSSION

The reaction of nickel(II) chloride, sodium salt of amino acid and sodium salt of dithiocarbamate ligands in 1:1:1 molar ratio, in addition to the attempts of adduct formation by reacting the resulting complexes with triphenylphosphine in 1:2 molar ratio may be represented by the following equations:

$$NiCl_2.6H_2O + NaL + NaL^- \longrightarrow [Ni(L)(L^-)] + 2NaCl + 6H_2O$$
$$[Ni(L)(L^-)] + 2PPh_3 \longrightarrow [Ni(L)(L^-)(PPh_3)] + PPh_3$$

An alternative method to obtain the complexes [Ni(L)(L^-)] by reacting [$Ni(L)_2$]and[Ni (L^-)$_2$] in 1:1 molar ratio was already represented by the equation given in the preparation section. The results obtained by the two procedures gave the same products which were confirmed by comparing their colours, melting points, i.r-spectra and magnetic susceptibilities. The limited availability of chemicals makes it difficult to carry the two procedures for all reactions. The first method was therefore used because it is less chemical and time consuming.

The reaction of the ternary complexes, [Ni(L)(L^-)] with triphenylphosphine did not offer the quaternary bis adducts as expected, instead only one PPh_3 molecule was coordinated. The reaction carried out in refluxing dichloromethane - ethanol mixture. Using DMF - ethanol or chloroform offers the same result with poorer yield. An attempt to obtain the bis adduct by reacting [$Ni(L)_2$],

$[Ni(L^-)_2]$ and PPh_3 in 1:1:4 molar ratio by refluxing in chloroform- ethanol mixture failed to give the expected $2[Ni(L)(L^-)(PPh_3)_2]$ and gave the same result with one PPh_3 in the coordination sphere of the complex as indicated by their elemental analysis Table (1).

Elemental analyses (Table1) revealed that the complexes have the compositions $[Ni(L)(L^-)]$ and $[Ni(L)(L^-)(PPh_3)]$. The molar conductivity of the complexes are measured using (10^{-3}M) dimethylformamide solutions and the values shown in (Table2 and 3) are those expected for non electrolyte (Geary,1971). (Table1) gives some physical properties in addition to the elemental analysis for the prepared complexes.

The magnetic moments of the complexes calculated from the corrected magnetic susceptibilities determined at room temperature are shown in (Table 2 and 3). The Ni(II) complexes$[Ni(L)(L^-)]$ and $[Ni(L\text{-}Met)(L^-)(PPh_3)]$ are all diamagnetic suggesting square planar geometries (Travnıcek *et al*., 2004). The paramagnetic nature of the two methionine complexes $[Ni(Met)(L^-)(PPh_3)]$ (12 and 16) with μeff= 2.98 and 2.81 B.M respectively, indicate the octahedral structure (Neelakantan *et al*., 2011) for the two complexes.

The electronic spectra of the Ni(II) complexes are given in Table (2). The electronic spectra of $[Ni(L)(L^-)]$ exhibited two absorption bands at (15974-21500cm^{-1}) attributed to $^1A_1g \longrightarrow {}^1A_2g$ transition(ν_1) and the second one appeared at (24320-26890cm^{-1}) which were assigned to$^1A_1g \longrightarrow {}^1B_1g$ transition(ν_2). The position and assignment of these bands are in agreement with square planner geometry for the Ni(II) complexes (Travnıcek *et al*., 2004 ; Lever *et al*., 1984). The absence of any band below (10000cm^{-1}) confirms the square planar geometry. The electronic spectra of $[Ni(Met)(L^-)(PPh_3)]$(12 and 16) showed bands at the positions (9750, 10237cm^{-1}), (17789, 15498cm^{-1}) and (25672, 24569cm^{-1}) which were assigned to $^3A_2g \longrightarrow {}^3T_2g(F)$ (ν_1), $^3A_2g \longrightarrow {}^3T_1g(F)$ (ν_2), $^3A_2g \longrightarrow {}^3T_1g(P)$ (ν_3) respectively. The position of the three bands are in agreement with octahedral geometry for Ni(II) complexes (Lever *et al*., 1984 and Khatib *et al*., 2009). Complexes (9,15) $[Ni(N\text{-}MeCHdtc)(Gly)(PPh_3)]$ and $[Ni(Bzdtc)(Val)(PPh_3)]$ exhibited similar electronic spectra to the ternary complexes $[Ni(L)(L^-)]$ with the two bands at (16025, 21278cm^{-1}) and (25510, 25773cm^{-1}) were assigned similarly to $^1A_1g \longrightarrow {}^1A_2g$ and $^1A_1g \longrightarrow {}^1B_1g$ respectively, to the square planar geometry of Ni(II).

The remaining four quaternary complexes (10,11, 13 and 14) showed bands in the range (10183-10288cm^{-1}),(15873-17331cm^{-1}) and (24630-26315cm^{-1}) in addition to a band observed around 21000cm^{-1}. The first three bands are characteristic of octahedral geometry with the usual assignment

$^3A_2g \longrightarrow {}^3T_2g(F)$ (ν_1), $^3A_2g \longrightarrow {}^3T_1g(F)$ (ν_2), $^3A_2g \longrightarrow {}^3T_1g(P)$ (ν_3) respectively. The additional band ~21000cm^{-1} may be assigned to

$^1A_1g \longrightarrow {}^1A_2g$ in square planar geometry. The diamagnetic properties for these four complexes in the solid state seem to suggest a change in their geometry on going from the solid state to solution in which case some sort of equilibrium between square planar and octahedral geometries seem to develop in solution (Cotton *et al*., 1999). The significant ir spectral data of the ligands and their nickel (II) complexes with their assignments are listed in Table (4). The ν(C-S) group in the ir spectra of the two dithiocarbamate ligands observed at 957 and 990 cm^{-1} shifted to lower frequencies 937-977 cm^{-1} in the ternary complexes $[Ni(L)(L^-)]$ and to 984 and 980 cm^{-1} in the quaternary complexes containing methionine $[Ni(Met)(L^-)(PPh_3)]$ (12 and 16) respectively, Table (4). The presence of only one band suggests the bidentate symmetrical coordination of the dithiocarbamates in these complexes. The remaining quaternary complexes $[Ni(L\text{-}Met)(L^-)(PPh_3)]$ (9-11 and 13-15) exhibited two C–S stretching bands in their ir spectra with more than 15 cm^{-1} difference in their positions suggesting that the dithiocarbamates are monodentate in these complexes. The ir spectra of the ν(C-N) observed at 1454 and 1469 cm^{-1} in the free dithiocarbamate

ligands, shift to higher frequencies (1476-1508)cm^{-1} in the complexes [Ni(L)(L^-)] and [Ni(Met)(L^-)(PPh_3)] respectively. The shift in ν(C-N) (thioureide) values to a higher wave number is due to the mesomeric drift of electron density from the ligand toward the metal atom and this increases the contribution of the polar thiouride form. In the case of complexes (9-11 and 13-15) [Ni(L-Met)(L^-)(PPh_3)] the ν(C-N) was shifted to a lower wave number or remains unchanged which is the case with monodentate dithiocarbamate ligands (Odola *et al*., 2011 ; Giovagnini *et al*., 2005).

The N–H vibration observed at (2956-3164cm^{-1}) in the free amino acids is shifted to higher wave numbers (2990-3236cm^{-1}) in the ir-spectra of the complexes suggesting coordination of the amino group which is in agreement with the published work (Patila *et al*., 2009; Tarallo *et al*., 2005).

The values of ν_{as}(COO) and ν_s(COO) for the aminoacid ligands are given in Table (4). The corresponding values for the prepared complexes indicate that the ν_s(COO) were shifted to lower wave numbers while the ν_{as}(COO) frequencies were shifted to higher wave numbers. The values $\Delta[\nu_{as}(COO) - \nu_s(COO)]$ for prepared complexes Table (4) are (230-274) cm^{-1} indicate the involvement of the carboxlyte anion in bonding (Reddy and Reddy, 2000; Molodkin *et al*., 2008; Onoa and Moreno, 1998) to the Ni(II) ion as monodentate ligand.

The ν(C-S-Me) in the ir spectra of methionine ligand observed at (1316cm^{-1}) (Onoa and Moreno,1998) remains almost in the same position on complex formation except for the quaternary complexes, [Ni(Met)(L^-)(PPh_3)] (12 and 16) where the shift to higher frequencies were observed suggesting the involvement of methionine sulfur in bonding for the two complexes and the non involvement of sulfur in the rest of the methionine complexes (Caubet *et al*., 1992).

The ir spectra of the complexes showed the appearance of non ligand bands observed at (537-565cm^{-1}) and (447-495cm^{-1}). These were assigned to ν(M-O) and ν(M-N), respectively.

Proton Nuclear Magnetic Resonance (^{1}H-NMR) were recorded for the two complexes, [Ni(N-MeCHdtc)(Gly)] and [Ni(N-MeCHdtc)(Met)] using DMSO-d_6 as solvent (Pretsch *et al*., 2009)

The glycine complex showed a multiple signal at (1.16-1.33ppm) belongs to five protons of cyclohexyl in MeCHdtc. The multiple signal at (1.59-1.82ppm) belongs to the nine protons for (cyclohexyl and methyl group) in N-MeCHdtc. The singlet signal at (3.18ppm) belongs to the two protons of CH_2 in glycine. The broad signal at (4.19-4.23) belongs to the NH_2 group in glycine and the singlet signal at (2.50 ppm) belongs to DMSO-d_6. (Fig. 1)

The methionine complex showed multiple signal at (1.19-1.33ppm) due to six protons of cyclohexyl. The multiple signal at (1.63-1.82ppm) belongs to the ten protons for (six protons of cyclohexyl and four protons for $2CH_2$ group in methionine). The singlet signal at (3.13ppm) belongs to the three protons of CH_3 group in N-MeCHdtc. The singlet signal at (3.18ppm) belongs to the three protons of CH_3 group in methionine. The broad signal at (4.33-4.40ppm) belongs to the NH_2 group and the singlet signal at (2.50 ppm) belongs to DMSO-d_6. (Fig. 2)

CONCLUSION

Mixed ligand complexes of Ni(II) with four amino acids (L= Gly, Ala, Val and Met) and two dithiocarbamates (L^- = N-MeCHdtc and Bzdtc) were successfully prepared by simple mixing of solutions of Ni(II) with L and L^- sodium salts.

The results were square planar complexes [Ni(L)(L^-)] of Ni(II) with the dithiocarbamate behaving as bidentate ligand coordinating symmetrically through both sulfur atoms and the aminoacid anions coordinated through the oxygen of the carboxylate anion and the nitrogen atom of the amino group.

Attempts to prepare the triphenylphosphine bis adducts were unsuccessful and the reaction of [Ni(L)(L^-)] with PPh_3 in 1:2 molar ratio results in the formation of [Ni(L-Met) (L^-)(PPh_3)] in which the triphenylphosphine displace one sulfur atom leaving the dithiocarbamate to coordinate as monodentate with the retainment of the square planar geometry around the Ni(II). On the other

hand, the addition of one $PPh_3$to the two methionine complexes, $[Ni(Met)(L^-)(PPh_3)]$ results in changing the geometry from square planar to octahedral around Ni(II) with the methionine behaving as tridentate ligand coordinating through S, N and O and the triphenylphosphine occupies the sixth position of the octahedral geometry. The motive might be the preference to form square planar and octahedral geometries around Ni(II).

The quaternary complexes $[Ni(L\text{-}Met)(L^-)(PPh_3)]$ exhibited two different types of bands in their DMF solution electronic spectra, which were assigned to both octahedral and square planar complexes suggesting some sort of equilibrium between octahedral and square planar Ni(II) in solution. The octahedral configuration in solution might be formed through dimerization using the unbounded C=O of the carboxylate or a lone pair of one of the sulfur atoms to coordinate to neighbouring Ni(II) with the rearrangement of dithiocarbamate to become bidentate and the triphenylphosphine displaced to axial position. These observations need further studies to confirm it.

The following Figs. (3-6) give possible structure representation for the prepared complexes.

Table 1: Some physical properties and elemental analysis of the prepared complexes

Complex No.	Complex formula	Colour	M.P(°C) or Decomp. Temp.	Yield (%)	Elemental analysis, found /(calc.)				M%
					C%	H%	N%	S%	
1	[Ni(N-MeCHdtc)(Gly)]	Green	172-174	77	37.91 (37.40)	6.33 (5.65)	9.12 (8.72)	19.13 (19.96)	17.02 (18.28)
2	[Ni(N-MeCHdtc)(Ala)]	Green	168-170	81	-----	-----	-----	-----	16.40 (17.51)
3	[Ni(N-MeCHdtc)(Val)]	Green	187-189	75	-----	-----	-----	-----	15.63 (16.16)
4	[Ni(N-MeCHdtc)(Met)]	Pale green	196-198	72	40.36 (39.50)	6.69 (6.12)	7.41 (7.08)	22.67 (24.33)	15.23 (14.85)
5	[Ni(Bzdtc) (Gly)]	Grass green	132*	88	-----	-----	-----	-----	17.75 (18.63)
6	[Ni(Bzdtc) (Ala)]	Deep-beige	122*	75	-----	-----	-----	-----	16.92 (17.84)
7	[Ni(Bzdtc) (Val)]	Brownish-green	187*	75	44.36 (43.72)	5.33 (5.08)	8.06 (7.84)	17.35 (17.95)	15.75 (16.43)
8	[Ni(Bzdtc) (Met)]	Green	220*	76	-----	-----	-----	-----	14.33 (15.08)
9	[Ni(N-MeCHdtc)(Gly)(PPh_3)]	Pale green	88*	79	58.28 (57.83)	5.98 (5.67)	5.78 (4.81)	7.78 (10.99)	9.32 (10.06)
10	[Ni(N-MeCHdtc)(Ala) (PPh_3)]	Pale green	177*	84	-----	-----	-----	-----	11.23 (9.82)
11	[Ni(N-MeCHdtc)(Val) (PPh_3)]	Pale green	145*	66	60.19 (59.53)	6.21 (6.28)	4.99 (4.47)	8.71 (10.25)	10.04 (9.38)
12	[Ni(N-MeCHdtc)(Met) (PPh_3)]	Green	179*	75	60.41 (56.64)	5.83 (5.94)	4.88 (4.26)	15.89 (14.62)	10.23 (8.92)
13	[Ni(Bzdtc) (Gly) (PPh_3)]	Brown	198*	76	-------	------	------	-------	9.28 (10.16)
14	[Ni(Bzdtc) (Ala) (PPh_3)]	Brown	254*	82	-------	------	------	-------	9.35 (9.92)
15	[Ni(Bzdtc) (Val) (PPh_3)]	Orange	98*	65	-------	------	------	-------	7.68 (9.47)
16	[Ni(Bzdtc) (Met) (PPh_3)]	Orange-violet	267*	77	61.06 (57.15)	5.62 (5.11)	4.78 (4.30)	16.56 (14.76)	10.34 (9.01)

*decomposition

Table 2: Electronic spectra of the ternary Ni(II) complexes (cm^{-1}), μeff (B.M.)and Molar Conductance (cm^2ohm^{-1} mol^{-1})

Complex no.	$^1A_1g \longrightarrow {}^1A_2g$	$^1A_1g \longrightarrow {}^1B_1g$	μeff B.M.	Molar Conductance (cm^2 ohm^{-1} mol^{-1})
1	21500	25252	dia	3.4
2	21186	25380	dia	4.2
3	15974	25380	dia	9.3
4	16025	25252	dia	3.2
5	20833	25906	dia	11.7
6	20833	25641	dia	8.5
7	20833	25773	dia	4.1
8	20746	25380	dia	9.5

Table 3: Electronic spectra of the quaternary Ni (II) complexes, μeff (B.M.)and Molar Conductance (cm^2ohm^{-1} mol^{-1}) (cm^{-1})

Complex No.	Electronic Spectra (cm^{-1})	μeff B.M.	Molar Conductance (cm^2ohm^{-1} mol^{-1})
9	16025,21276,25510,29411,32467,45454	dia	7.4
10	10183,11709,16077,21367,26315,30303,34482	dia	3.3
11	10288,11210,15873,21186,24752,27932	dia	3.7
12	9750,17789,25672,37456	2.98	9.3
13	10183,17331,21220,25125,30303	dia	3.6
14	10204,16200,20990,24630,29940	dia	14.3
15	15673,20833,25773,30120	dia	7.8
16	10237,15498,24569,33985	2.81	13.4

Table 4: Selected IR bands of the ligands and complexes(cm^{-1})

No.	ν (NH_2)	ν(COO^-)		Δ ν(COO)	ν(C–S)	ν(C–N)	ν(C-SMe)	ν (M– O)	ν(M–N)
		$\nu_{as}(COO^-)$	ν_s (COO)						
NaN-MeCHdtc	----	----	----	----	990	1469	----	----	----
NaBzdtc	----	----	----	----	957	1454	----	----	----
NaDiPrdtp	----	----	----	----	----	----	----	----	----
NadiBzdtp	----	----	----	----	----	----	----	----	----
Gly	3164	1615	1457	----	----	----	----	----	----
L-Ala	3082	1597	1413	----	----	----	----	----	----
L-Val	3080	1590	1410	----	----	----	----	----	----
L-Met	2956	1616	1408	----	----	----	----	----	----
1	3234	1635	1398	237	977	1506	----	543	493
2	3113	1623	1377	246	968	1498	----	539	475
3	3174	1638	1373	265	970	1498	----	541	488
4	3075	1634	1367	267	965	1498	----	544	468
5	3232	1637	1396	241	938	1489	----	559	486
6	3099	1633	1388	245	942	1508	----	537	447
7	3144	1628	1377	251	946	1488	----	533	463
8	3057	1638	1388	250	937	1496	----	542	495
9	3225	1633	1397	236	968,988	1460	----	559	486
10	3117	1642	1388	254	965,983	1464	----	546	492
11	3180	1638	1373	265	960,987	1462	----	553	482
12	3100	1637	1369	268	984	1477	1335	535	488
13	3232	1629	1398	231	937,953	1450	----	558	490
14	3120	1638	1386	252	934,950	1452	----	558	490
15	3210	1640	1379	261	939,955	1452	----	565	478
16	3143	1637	1375	262	980	1476	1337	547	492

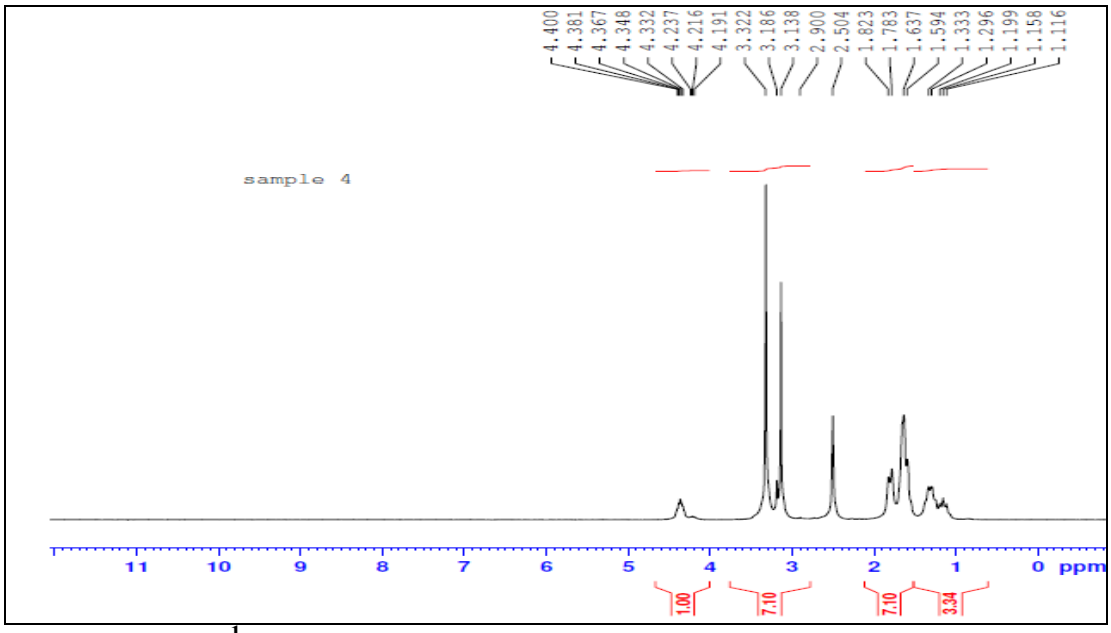

Fig. 1: (^{1}H-NMR) spectrum of complex [Ni (N-MeCHdtc)(Gly)]

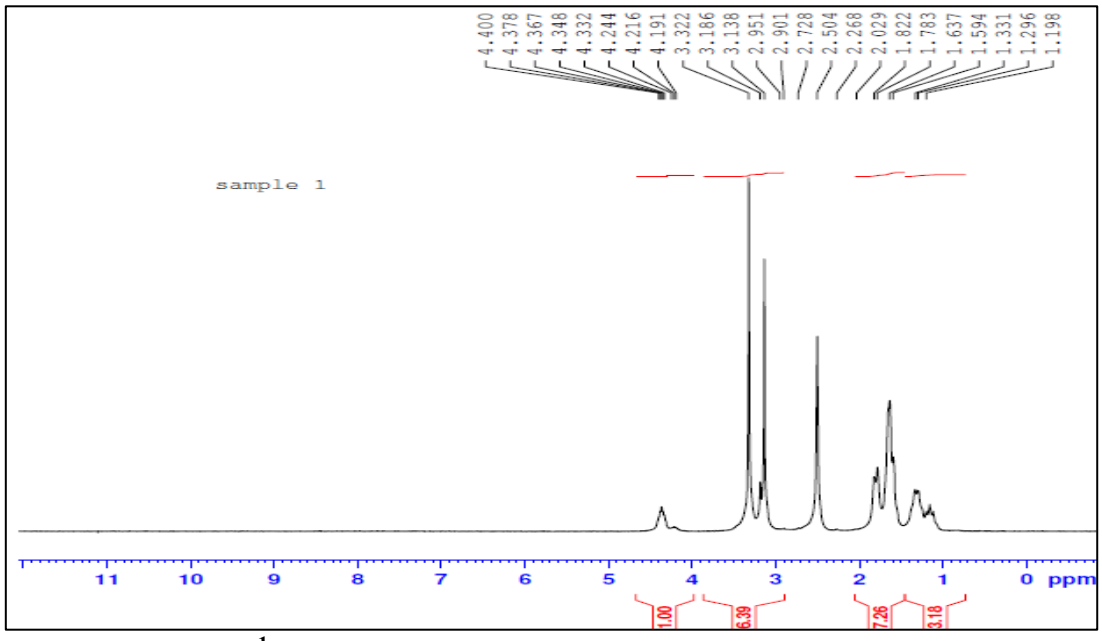

Fig. 2: (^{1}H-NMR) spectrum of complex [Ni(N-MeCHdtc)(Met)]

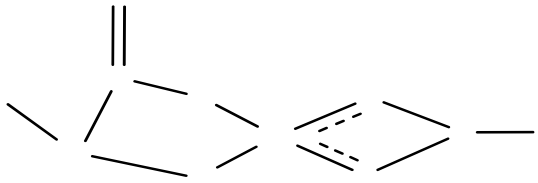

Fig. 3: Proposed structure for the complexes [Ni(L)(L$^-$)] M=Ni(II), (R =H when R$^-$ = benzyl, R = CH_3 when R$^-$ = cyclohexyl) R$^=$ = (Gly), -CH_3(Ala),-($CH(CH_3)_2$(Val). R$^=$ = $CH_2CH_2SCH_3$ (Met)

Complex No.1-8

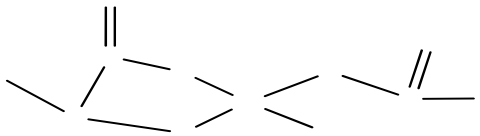

Fig. 4: Proposed structure for the complexes [Ni(L)(L$^-$)PPh$_3$] R,R$^-$, R$^=$, as defined in Fig. (3) Complex No. 9-11, 13-15

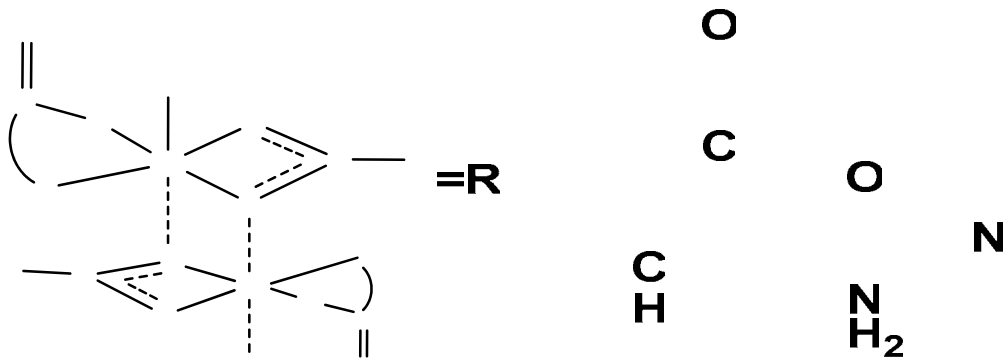

Fig. 5: Possible dimer formation of [Ni(L-Met)(L-)(PPh$_3$)] complexes in DMF solution Complex No. 10,11,13,14

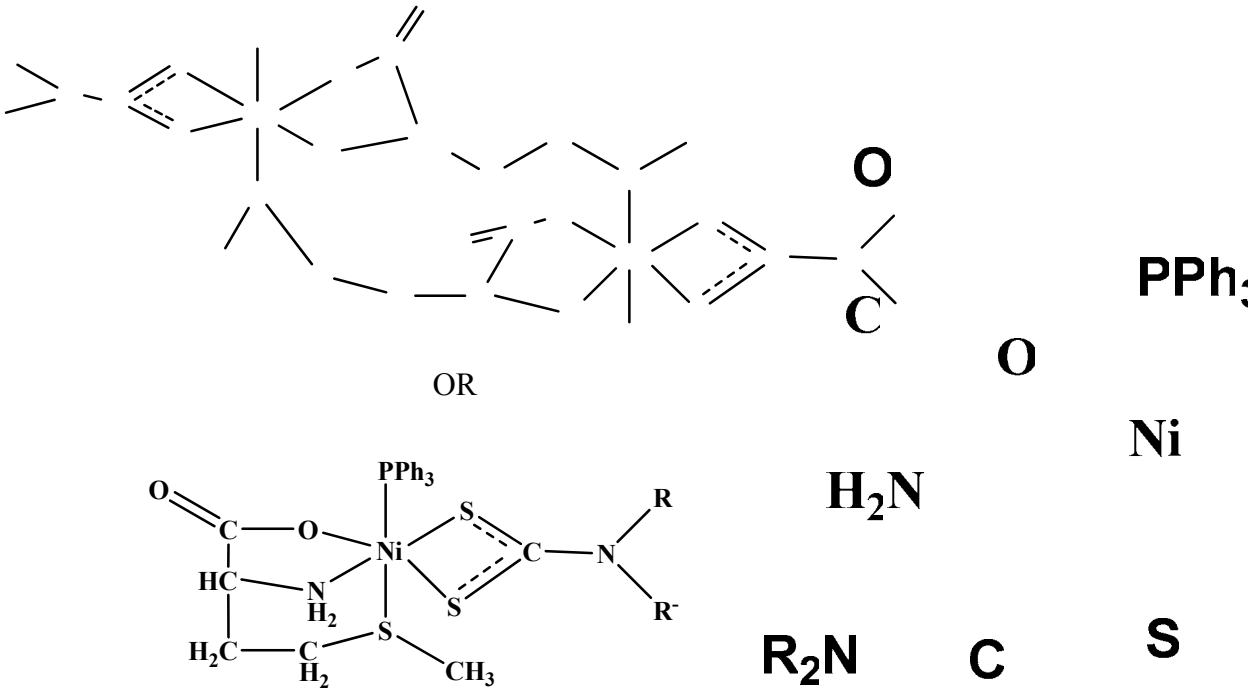

Fig. 6: Suggested structure for [Ni(Met)(dtc)PPh$_3$] R,R$^-$, as defined in Fig. (3) Complex No. 12 and 16

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