

Mixed Ligand Complexes of Nickel (II) with Some Aminoacids, Dithiocarbamates and their Triphenylphosphine

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Abstract - Mixed Ligand complexes of the type $[\text{Ni}(\text{L})(\text{L}^-)]$ and $[\text{Ni}(\text{L})(\text{L}^-)(\text{pph}_3)]$ were synthesized [HL = aminoacid = Leucine, Proline, methionine and iso-leucine; L^- = dicyclohexyl dithiocarbamate and diphenyl]. The amino and anions ($\text{L}=\text{Leu}$, Pro, Met and leu) coordinate through N and O and the dithiocarbamate coordinate through the two sulfur atoms giving square planar Ni(II) complexes. Reaction of the ternary complexes $[\text{Ni}(\text{L})(\text{L}^-)]$, with triphenylphosphine in 1:2 molar ratio yield quaternary complexes, $[\text{Ni}(\text{L-Met})(\text{L}^-)(\text{pph}_3)]$, with the refinement of square planer geometry with the dithiocarbamates behave as monodentate ligands. On the other hand the $[\text{Ni}(\text{Met})(\text{L}^-)(\text{pph}_3)]$ complexes are octahedral with the methionine anion behave as tridentate ligand coordinating through N,O and S and the dithiocarbamate as bidentate anions coordinating through the two sulfur atoms. The synthesized complexes were characterized by I.R and U.V-visible spectra, molar conductance, magnetic susceptibility measurements, metal analysis and some of them by CHNS analysis.

Keywords - Mixed Ligand, nickel (II) complexes, adduct

I. INTRODUCTION

The chemistry of nickel has been rapidly expanded to the increasing number of nickel complexes of biological interest reported in the literature [1]. In this respect structurally characterized nickel complexes have been reported to possess antiepileptic [2], anticonvulsant [3], antifungal [4] and anticancer [5] activity. Mixed Ligand complexes showed significant antifungal [6] and antibacterial [7] activity. Considerable interest in the coordination chemistry of mixed ligand complexes. also 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 process of biological relevance [8]. However, mixed ligand complexes of nickel (II) with amino acids and dithiocarbamates are not known. The paper report the synthesis and characterized of nickel (II) mixed ligand complexes with some aminoacid (Leucine, Proline, methionine, iso-leucine) and dithiocarbamates (dicyclohexyl and diphenyl), in addition to the reaction products of these complexes with triphenyl phosphine.

II. EXPERIMENTAL SETUP

Sodium salt of dicyclohexyl and diphenyl were prepared as cited in the literature [9]. Hydrated nickel chloride, Leucine, Proline, Methionine, iso-leucine dicyclohexyl amine, diphenyl amine triphenyl phosphine, carbon disulfide sodium hydroxide were either Aldrich BDH or Fluka products. Organic solvents (ethanol, dichloromethane, chloroform, dimethyl formamide) were reagent grade chemistry and were used without further purification.

Preparation of nickel (II) complex

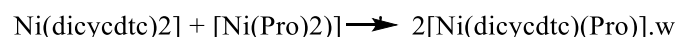
A. Preparation of $[\text{Ni}(\text{dicycdtc})(\text{Pro})]$

A solution of nickel (II) chloride hexahydrate (0.005 mol, 1.188 gm) in water (10 cm³) was added with stirring to solution containing mixture of Sodium dicyclohexyl dithiocarbamate (Nadicycdtc) (0.005 mol, 1.33g) in (10 cm³) water and aqueous Solution of Sodium Proline (NaPro) [prepared by dissolving (0.005 mol, 0.57 g) of Proline in (5 cm³) of H₂O 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(dicycrtc)(Leu)], [Ni(dicycrtc)(Met)], [Ni(dicycrtc)(iLeu)], [Ni(diphendtc)(pro)], [Ni(diphendtc)(Leu)], [Ni(diphendtc)(Met)] and [Ni(diphendtc)(iLeu)] were prepared by the same method using (0.005 mol, 0.655g) of Leucine (0.005 mol, 0.745 g) of Methionine (0.005 mol, 0.655g) of iso- Leucine. Alternative method is the reaction of bi (amino acid) nickel (II) complex with bis dithiocarbamate nickel (II) complex refluxing chloroform.

e.g.



Where, (0.002 mol, 0.22 g) of HPro dissolved in (10 cm³) water adjusted to PH ~ 7.5-8.0 by the addition of aqueous solution of NaOH and added with string to NiCl₂ .6H₂O (0.001 mol, 0.237 g) dissolved in (10 cm³) of water. The well defined crystals were formed after 2 days was Pulverized and added with vigorous stirring to a chloroform solution containing dissolved [Ni(dicycrtc)₂] (obtained by reaction of Nadicycrtc) (0.002 mol, 0.52g) dissolved in (10 cm³) of water with NiCl₂. 6H₂O.

(0.001 mol, 0.237g) in (10cm³) of water 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 2hr and the resulting precipitate formed on cooling was filtered, washed with chloroform and air dried.

B.Preparation of [Ni(dicycrtc)(Pro)(pph₃)]

This complex was prepared by mixing (0.0001mol, 0.043g) of the nickel(II) complex , [Ni(dicycrtc)(pro)] dissolved in (THF) and (0.0002mol, 0.052g) triphenylphosphine dissolved in (10cm³) ethanol with vigorous stirring and refluxed for 2hr. The mixture was cooled to room temperature and the resulting severed times with ethanol and dried in air .The following complexes were obtained following the same procedure:

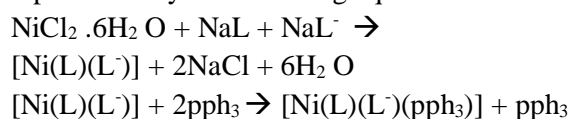
[Ni(dicycrtc)(leu)(pph₃)] , using (0.0001mol , 0.044g) of [Ni(dicycrtc)(leu)], [Ni(dicycrtc)(Met)(pph₃)], using (0.0001mol, 0.046g) of [Ni(dicycrtc)(Met)], [Ni(dicycrtc)(ileu)(pph₃)] , using (0.001mol , 0.044g) of [Ni(dicycrtc)(ileu)], [Ni(diphendtc)(pro)(pph₃)] , using (0.0001mol, 0.0418g) of [Ni(diphendtc)(pro)], [Ni(diphendtc)(leu)(pph₃)], using (0.0001mol , 0.043g) of [Ni(diphendtc)(leu)], [Ni(diphendtc)(Met)(pph₃)], using (0.0001mol, 0.045g) of [Ni(diphendtc)(Met)], [Ni(diphendtc)(ileu)(pph₃)] , using (0.0001mol , 0.043g) of [Ni(diphendtc)(ileu)].

Physical Measurements:

Nickel contents have been determined employing spectro photometric measurements using PYE UNICAM SpA-AA Spectro photometer (Philips).Elemental analysis of carbon , hydrogen , nitrogen , and sulfur were done using Euro Veetor Model EA 3000A (Italy) , IR spectra were recorded on Fourier _ Transform (FT. IR) Spectro photometer , Tensor 27Co . Bruckner at a range (400_4000cm⁻¹) using KBr disc. Electronic spectra were recorded on a U.V-vis spectro photometer (Shimadzu,) using dimethyl formamide DMF (10⁻³M) as a solvent at room temperature , Magnetic susceptibility of the complexes have been measured by Bruker B .14.6 using Faraday method , Conductivity measurements have been carried out using DMF as solvent (10⁻³M) at room temperature with the conductivity and Decomposition points were measured using Electro-thermal 9300 Engineering LTD .

III.RESULTS AND DISSCUSIONS

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 triphenyl phosphine in 1:2 molar ratio may be represented by the following equations:



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 the preparation section. The results obtained by the two procedures gave the same products which were confirmed by comparing their colors 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. The reaction carried out in refluxing dichloromethane-ethanol mixture Using DMF – ethanol offer the same result with poorer yield. Attempt to obtain bis adduct by reacting [Ni(L)₂], [Ni(L⁻)₂] and pph₃ in 1:1:4 molar ratio by refluxing in chloroform ethanol mixture failed to give the expected 2[Ni(L)(L⁻)(pph₃)₂] and gave the same result with one pph₃ in the coordination sphere of the complex as indicated by their elemental analysis table I.

Elemental analyses (Table I) revealed that the complexes have the compositions [Ni(L)(L⁻)] and [Ni(L)(L⁻)(pph₃)], The molar conductivity of the complexes are measured using (10⁻³ M) dimethylformamide solutions and the values shown in (Table II and III) are those expected for non-electrolyte [9] (Table I) give some physical properties in addition to 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 tables II and III. The Ni(II) complexes [Ni(L)(L⁻)] and [Ni(L-Met)(L⁻)(pph₃)] are all diamagnetic suggesting square planar geometries [10]. The pure magnetic nature of the two methionine complexes [Ni(Met)(L⁻)(pph₃)] (11 and 15) with Meff = 2.97 and 2.81 B.M respectively, indicate the octahedral structure [11] for the two complexes.

The electronic spectra of the Ni (II) complexes are given in table II. The electronic spectra of [Ni(L)(L⁻)] exhibited two absorption band at (16650 – 21500 cm⁻¹) attributed to ¹A_{1g} → ¹A_{2g} transition (ν₁) and the second one appeared at (24320 – 26890 cm⁻¹) which were

assigned to ¹A_{1g} – ¹B_{1g} transition (ν₂). assigned to ¹A_{1g} → ¹B_{1g} transition (ν₂).

The position and assignment of these bands are in agreement with square planer geometry for the Ni (II) complexes [10,12]. The absence of any band below (10000cm⁻¹) confirm the square planer geometry. The electronic spectra of [Ni(Met)(L)(L⁻)(pph₃)] (11 and 15) showed bands at the positions (10204, 10237), (16106, 17789) and (24970, 25672) which were assigned to ³A_{2g} → ³T_{2g} (ν₁), ³A_{2g} → ³T_{1g} (f)(ν₂), ³A_{2g} → ³T_{1g} (p)(ν₃) respectively. The position of the three bands are in agreement with octahedral geometry for Ni(II) complexes [12,13]. Complexes (9,10,12) [Ni(dicycldtc)(Leu)(pph₃)], [Ni(dicycldtc)(pro)(pph₃)] and [Ni(dicycldtc)(ilue)(pph₃)] similar electronic spectra to the ternary complexes [Ni(L)(L⁻)] with the two bands at (16077 – 21278cm⁻¹) and (25555, 25773cm⁻¹) were assigned similar to ¹A_{1g} → ¹A_{2g} and ¹A_{1g} → ¹B_{1g} respectively, to the square planar geometry of Ni(II). The remaining three quaternary complexes (13, 14 and 16) 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} → ³T_{2g} (f)(ν₁), ³A_{2g} → ³T_{1g} (f)(ν₂), ³A_{2g} → ³T_{2g} (p)(ν₃) respectively.

The additional band ~ 21000cm⁻¹ may be assigned to ¹A_{1g} → ¹A_{2g} in square planar geometry. The diamagnetic properties for these, three complexes in the solid state seems 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 seems to develop in solution [14]. The significant IR spectral data of the ligands and their nickel (II) complexes with their assignments are listed in table IV. The ν (c-s) group in the IR spectra of the two dithiocarbamate ligands observed at 951 and 955cm⁻¹ shifted to lower frequencies 934-984 cm⁻¹ in the ternary complexes [Ni(L)(L⁻)] in the quaternary complexes containing methionine [Ni(Met)(L⁻)(pph₃)] (11 and 15) respectively, table IV. The presence of only one band

suggest the bidentate symmetrical coordination of the dithiocarbamates in these complexes. The remaining quaternary complexes $[\text{Ni}(\text{L-Met})(\text{L}^-)(\text{pph}_3)]$ (9,10,12-14,16) exhibited two ν (c-s) stretching bands in their IR spectra with more than 15cm^{-1} difference in their positions suggesting that the dithiocarbamate are monodentate in these complexes. The IR spectra of the ν (C-N) observed at 1455 and 1470cm^{-1} in the free dithiocarbamate ligands, shift to higher frequencies (1457 - 1508cm^{-1}) in the complexes $[\text{Ni}(\text{L})(\text{L}^-)]$ and $[\text{Ni}(\text{Met})(\text{L}^-)(\text{pph}_3)]$ respectively. The shift in ν (C-N) (thioureide) values to 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 thioureide form. In the case of complexes (9,10,12-14,16) $[\text{Ni}(\text{L-Met})(\text{L}^-)(\text{pph}_3)]$ the ν (C-N) were shifted to lower wave number or remain unchanged which is the case with monodentate dithiocarbamate ligands [15,16]. The ν (N-H) vibration observed at (2956 - 3100cm^{-1}) in the free amino acids are shifted to higher wave numbers (3044 - 3143cm^{-1}) in the IR spectra of the complexes suggesting coordination of the amino group which is in agreement with published work [17,18]. The values of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ for amino acid ligands are given in table IV. The corresponding values for the prepared complexes indicate the $\nu_{\text{s}}(\text{COO})$ were shifted to lower wave numbers while the $\nu_{\text{as}}(\text{COO})$ frequencies were shifted to higher wave numbers. The values $[\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})]$ for prepared complexes are (231 - 288cm^{-1}) indicate the involvement of the carboxylate anion in bonding [8,19-21] to the Ni(II) ion as monodentate ligand table IV. The $\nu(\text{c-s-me})$ in the IR spectra of methionine ligand observed at (1316cm^{-1}) [21] remains almost in the same position on complex formation except for the quaternary complexes $[\text{Ni}(\text{Met})(\text{L}^-)(\text{pph}_3)]$ (11 and 15) where the shift to higher frequencies were observed suggesting the involvement of methionine sulfur in bonding for the two complexes and the noninvolvement of sulfur in the rest of the methionine complexes [22]. The IR spectra of the complexes showed the appearance of non-ligand bands

observed at (535 - 575cm^{-1}) and (465 - 498cm^{-1}). These were assigned to ν (M-O) and ν (M-N) respectively.

IV. CONCLUSION

Mixed ligand complexes of Ni(II) with four amino acids (L=pro, leu, met and ileu) and two dithiocarbamates (L^- = dicycadtc, diphendtc) were successfully prepared by simple mixing of solutions of Ni(II) with L and L^- sodium salts. The results were square planar complexes $[\text{Ni}(\text{L})(\text{L}^-)]$ of Ni(II) with the dithiocarbamate behaving as bidentate ligand coordinating symmetrically through both sulfur atoms and the amino acid anions coordinated through the oxygen of the carboxylate anion and the nitrogen atom of the amino group. Attempts to prepare the triphenyl phosphine di adducts were unsuccessful and the reaction of $[\text{Ni}(\text{L})(\text{L}^-)]$ with pph_3 in 1:2 molar results in the formation of $[\text{Ni}(\text{L-Met})(\text{L}^-)(\text{pph}_3)]$ in which the triphenylphosphine displaces one sulfur atom leaving the dithiocarbamate to coordinate as monodentate with the retention of the square planar geometry around the Ni(II). On the other hand, the addition of one pph_3 to the two methionine complexes, $[\text{Ni}(\text{Met})(\text{L}^-)(\text{pph}_3)]$ result 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 triphenyl phosphine 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 $[\text{Ni}(\text{L-Met})(\text{L}^-)(\text{pph}_3)]$ 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.

V. REFERENCES

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Table I

Some physical properties and elemental analysis of the prepared complexes

Comp. No.	Complex Formula	colour	M.p(c) or Decomp	Elemental analysts found(calc)				
				C%	H%	N%	S%	M%
1	[Ni(dicycdtc)(pro)]	green	191	51.04 (50.25)	7.26 (6.20)	6.75 (6.50)	15.17 (14.87)	12.94 (13.64)
2	[Ni(dicycdtc)(leu)]	green	190	—	—	—	—	12.58 (13.15)
3	[Ni(dicycdtc)(met)]	green	195	47.65 (46.56)	7.34 (7.16)	6.21 (6.03)	20.98 (20.67)	12.17 (12.64)
4	[Ni(dicycdtc)(ileu)]	Deep green	198	—	—	—	—	12.55 (13.15)
5	[Ni(diphendtc)(pro)]	green	195	—	—	—	—	13.74 (14.03)
6	[Ni(diphendtc)(leu)]	Pale green	172	53.39 (52.55)	5.51 (5.33)	6.70 (6.44)	14.90 (14.74)	12.91 (13.51)
7	[Ni(diphendtc)(Met)]	green	180	48.72 (47.80)	4.86 (4.68)	6.43 (6.19)	21.72 (21.22)	12.10 (12.98)
8	[Ni(diphendtc)(ileu)]	Pale green	200	—	—	—	—	12.92 (13.51)
9	[Ni(dicycdtc)(pro) (pph ₃)]	Deep Brown	255	63.71 (62.43)	6.87 (6.69)	4.32 (4.04)	10.01 (9.24)	7.96 (8.47)
10	[Ni(dicycdtc)(leu) (pph ₃)]	Deep Brown	255	—	—	—	—	7.86 (8.28)
11	[Ni(dicycdtc)(Met) (pph ₃)]	Deep green	266	60.87 (59.50)	6.98 (6.65)	3.97 (3.85)	13.60 (13.21)	7.50 (8.07)
12	[Ni(dicycdtc)(ileu) (pph ₃)]	Brown	261	—	—	—	—	7.83 (8.23)
13	[(Ni(diphendtc)(pro) (pph ₃)]	Deep yellow	255	—	—	—	—	7.99 (8.62)
14	[Ni(diphendtc)(leu) (pph ₃)]	Deep yellow	255	64.92 (63.80)	5.89 (5.49)	4.63 (4.02)	9.99 (9.18)	8.02 (8.42)
15	[Ni(diphendtc)(Met) (pph ₃)]	yellow	240	61.55 (60.48)	5.7 (5.07)	4.21 (3.91)	14.03 (13.43)	8.42 (8.21)
16	[Ni(diphendtc)(ileu) (pph ₃)]	Deep green	260	—	—	—	—	7.94 (8.42)

Table II

Comp.No	${}^1A_{1g} \rightarrow {}^1A_{2g}$	${}^1A_{1g} \rightarrow {}^1B_{1g}$	Meff B.M.	Molar conductance ($\text{cm}^2 \cdot \text{Ohm}^{-1} \cdot \text{Mol}^{-1}$)
1	18670	26456	dia	2.03
2	20500	24975	dia	4.70
3	21500	24998	dia	2.40
4	16650	26890	dia	3.50
5	20250	25897	dia	2.90
6	17769	26716	dia	1.80
7	19860	25675	dia	4.70
8	20656	24320	dia	4.30

Table III

Electronic spectra of the quaternary Ni (II) complexes(cm^{-1}), Meff (B.M) and Molar conductance ($\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{Mol}^{-1}$)

Complex No	Electronic spectra (cm^{-1})	Meff (B.M.)	Molar conductance ($\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$)
9	16077,25555	dia	5.60
10	21186,25670	dia	8.00
11	10204,16106,24970	2.97	9.10
12	21278,25773	dia	10.20
13	10210,15990,25670,21010	dia	6.70
14	10183,15873,24630,21025	dia	11.30
15	10237,17789,25672	2.85	4.30
16	10288,17331,26315,21015	dia	6.80

Table IV

Selected IR bands of the ligands and complexes (cm⁻¹)

No	ν (NH ₂)	ν(coo ⁻)		Δ	(Coo)ν	ν(c-s)	ν(c-N)	ν(c-sMe)	ν(M-o)	ν(M-N)
		vs(coo)	vas(coo)							
dicycdtc	—	—	—	—	—	951	1455	—	—	—
diphendtc	—	—	—	—	—	955	1470	—	—	—
Pro	3010	1597	1413	—	184	—	—	—	—	—
Leu	3082	1598	1408	—	190	—	—	—	—	—
Met	2956	1616	1403	—	213	—	—	—	—	—
iLeu	3100	1610	1440	—	170	—	—	—	—	—
1	3097	1637	1375	—	262	978	1490	—	558	490
2	3119	1638	1386	—	252	934	1482	—	553	482
3	3044	1640	1379	—	261	945	1487	1332	535	488
4	3132	1644	1370	—	274	942	1494	—	546	492
5	3075	1638	1379	—	259	939	1492	—	559	486
6	3113	1638	1388	—	250	938	1488	—	575	484
7	3074	1629	1390	—	239	980	1496	1331	553	488
8	3134	1629	1373	—	256	944	1508	—	545	492
9	3092	1637	1390	—	247	941, 972	1460	—	544	486
10	3107	1628	1390	—	288	946, 972	1456	—	539	488
11	3113	1630	1399	—	231	968	1458	1332	541	568
12	3143	1638	1376	—	262	951, 971	1475	—	543	493
13	3118	1638	1388	—	250	942, 973	1450	—	545	475
14	3110	1633	1388	—	245	952, 972	1458	—	538	465
15	3043	1628	1377	—	251	972	1457	1337	547	498
16	3120	1637	1396	—	241	939,971	1465	—	548	488