

Synthesis and Characterization of Nickel(II) complexes of n-Butyl – and iso-Butyldicyandiamide in presence of alcohols

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ABSTRACT

Anhydrous nickel(II) chloride and nickel(II) nitrate hexahydrate promote addition of alcohols to n-butyl and iso-butyldicyandiamide. Hydrated nickel(II) chloride was found to be ineffective and could not produce alcohol addition product. Nickel(II) is found to be less efficient than copper(II) in forcing alcohol addition, a much longer reflux period being essential. The bis(ligand)nickel(II) complexes are all light yellow to orange yellow in color, diamagnetic i.e. no magnetic moment and absorb at around 22000-23000 cm^{-1} . In the nickel(II) complexes, the nitrile band of the substituted dicyandiamide is completely absent, instead new bands

appear at ca 1243 cm^{-1} /1250 cm^{-1} /1271 cm^{-1} mbr. The presence of these bands indicate the alcohol addition reaction has led to the formation of 1-n-butyldiamidino-O-methylurea(1-BuⁿAMeUH)(I) and 1-iso-butyldiamidino-O-methylurea(1-BuⁱAMeUH)(II).

They possess square planer $[\text{NiN}_4]$ geometry. Characterization of Nickel(II) complexes have been made on the basis of elemental analysis, conductance, electronic absorption spectra, magnetic moment and IR spectra. The free ligands are isolated in the crystalline state.

Keywords: Diamagnetic, Magnetic moment, Nitrile band, IR, Electronic absorption

I. INTRODUCTION

Barnard^[1] studied first the metal ion promoted addition reaction to 2-cyanopyridine. He reported that copper(II), nickel(II), cobalt(II) and iron(II) promote addition of alcohol to cyanopyridine forming complexes like $[\text{Cu}(\text{MePy})\text{Cl}_2]$, $[\text{Ni}(\text{MePy})_2(\text{H}_2\text{O})\text{Br}]\text{Br}$, $[\text{Ni}(\text{MePy})_3](\text{ClO}_4)_2$, $[\text{Co}(\text{MePy})\text{Cl}_2](\text{MePy} - \text{O} - \text{methylpyrine-2-carboximate})$ etc.

Similarly, in presence of alcohols transition metal ions like copper(II) and nickel(II) promote addition of alcohols^[2]. The resulting ligand is 1-amidino-O-methylurea($\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NH}-\text{C}(=\text{NH})-\text{OR}$). Hence, this ligand can form cationic complexes with Cu(II), Ni(II), Co(II) etc. All the complexes are orange

Dutta and Ray^[3] prepared the bis(ligand) Ni(II) complexes by refluxing Ni(II) salts and dicyandiamide in alcohol for 12 hr or more^[2,4]. So, Ni(II) catalysed the addition of alcohols to dicyandiamide, although, it was less efficient than Cu(II). All the complexes are orange yellow in colour. The complexes are all diamagnetic indicating a strong tetragonal distortion from the octahedral geometry.

n-Butyldicyandiamide and iso-Butyldicyandiamide also undergo alcohol addition reaction with Ni(II) salts forming complexes. All the complexes are found to be orange yellow colour, molar conductance values showing bi-univalent electrolytes^[5-7] and all diamagnetic indicating square planer complexes with $[\text{NiN}_4]$ chromophore.

II. EXPERIMENTAL

The complex $[\text{Ni}(\text{Bu}^n\text{MeUH})_2]\text{Cl}_2$ (III) is prepared in the following way. n-Butyldicyandiamide (2g) was dissolved in dry MeOH(50cm³) and anhydrous AR Ni(II)chloride(0.9214g) in MeOH(50cm³). The two solutions were mixed together and refluxed^[8] on a stream bath for about 90 hr until the green colour changed to reddish yellow. The reddish yellow solution was concentrated (~20cm³) and left in a refrigerator for

2 days. A golden yellow compound crystallized out which was further purified from MeOH and washed finally by acetone and dried in air. The other complexes $[\text{Ni}(\text{Bu}^n\text{AMeUH})_2](\text{NO}_3)_2$ (IV), $[\text{Ni}(\text{Bu}^i\text{AMeUH})_2]\text{Cl}_2$ (V) and $[\text{Ni}(\text{Bu}^i\text{AMeUH})_2](\text{NO}_3)_2$ (VI) are also prepared in the same manner as in complex III. The details of these complexes are given in Table I.

Table I: Physical parameters of the Ni(II) complexes

Complex	Formula	Reflux time (hr)	Colour	Found(Calcd)				
				C	H	N	Ni	Cl
1	$[\text{Ni}(\text{Bu}^n\text{AMeUH})_2]\text{Cl}_2$	90	Golden yellow	35.62 (53.51)	7.00 (6.84)	23.70 (23.60)	12.30 (12.26)	15.00 (15.01)
2	$[\text{Ni}(\text{Bu}^n\text{AMeUH})_2](\text{NO}_3)_2$	76	Golden yellow	31.98 (31.93)	6.11 (6.08)	26.70 (26.61)	11.00 (11.02)	-
3	$[\text{Ni}(\text{Bu}^i\text{AMeUH})_2]\text{Cl}_2$	64	Golden yellow	35.59 (35.51)	7.01 (6.84)	23.66 (23.67)	12.30 (12.26)	15.03 (15.01)
4	$[\text{Ni}(\text{Bu}^i\text{AMeUH})_2](\text{NO}_3)_2$	76	Golden yellow	32.00 (31.93)	6.12 (6.05)	26.65 (26.61)	11.08 (11.02)	-

III. RESULT AND DISCUSSION

n-Butyl/iso-Butyldicyandiamide reacts with MeOH in the presence of anhydrous Ni(II) chloride and Ni(II)nitrate hexahydrate to give orange yellow to golden yellow complexes(Table1). Reactions of n-Butyl and iso-Butyldicyandiamide with hydrated Ni(II)chloride in presence of MeOH to produce bis(ligand) Ni(II)complexes were not successful. This may be due to the formation of hydroxide. Attempts to prepare mono(ligand) Ni(II)complexes were not fruitful while bis(ligand) Ni(II)complexes are formed in a single step^[9,10].

A. Magnetic Moment

All the Ni(II)complexes of the BuⁿAMeUH and BuⁱAMeUH were found to be diamagnetic(Table II). These diamagnetic natures and their strong absorption band at ca 23000cm⁻¹ including shoulder at

From EtOH onwards all the higher alcohols fail to provide the bis(ligand) Ni(II)complexes. This is because of the steric hindrance between one alkyl group(n-Butyl or iso-butyl) and bulky alkyl group of the second ligand in a square planer around Ni(II). It may be noted that none of the above substituted dicyandiamides alone reacted with MeOH. These dicyandiamides can be recovered unchanged in m.pt and nitrile band positions even after 40-60 hr reflux from alcohol. This shows that methanolysis(alcoholysis) can not take place without Ni(II) ions.

ca 19000cm⁻¹ in DMF strong support to a square planer geometry^[10-14]. Like 1-amidino-O-alkylurea^[9] and biguanide^[15], BuⁿAMeUH and BuⁱAMeUH set strong enough a ligand field around Ni(II), a square planer complex of Ni(II) may be either paramagnetic^[16] depending on the strength of the ligand field^[17].

B. Conductance

The molar conductance values of $[\text{Ni}(\text{Bu}^{\text{p}}\text{AMeUH})_2](\text{NO}_3)_2$ and

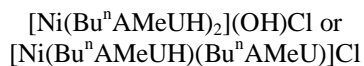
$[\text{Ni}(\text{Bu}^{\text{i}}\text{AMeUH})_2](\text{NO}_3)_2$ indicate bi-univalent electrolyte^[9,12,18] in both MeOH and DMF. It is observed that conductance values of the Ni(II) complexes in MeOH are higher than those in DMF solution.

Table II: Conductance data of Ni(II) complexes in MeOH and DMF solution

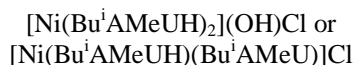
Complex	Magnetic Moment	Solvent	Concentration	Conductance at 25 ^o C $\lambda_{\text{m}}(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$
1	Diamagnetic	MeOH	2	84.29
			1	85.48
		DMF	2	35.22
			1	44.25
2	Diamagnetic	MeOH	2	113.79
			1	118.58
		DMF	2	45.17
			1	43.65
3	Diamagnetic	MeOH	2	140.79
			1	141.58
		DMF	2	102.67
			1	113.35
4	Diamagnetic	MeOH	2	135.75
			1	127.58
		DMF	2	99.67
			1	111.35

The conductance values of Dutta and Ray^[3] and Dutta and Manihar^[10] on Ni(II) complexes of 1-amidino-O-alkylurea and 1-phenylamidino-O-alkylurea have shown that the bases are all obtained in the anhydro form there having no water of constitution or crystallization whatsoever. The conductance values of $[\text{Ni}(\text{Bu}^{\text{p}}\text{AMeUH})_2]\text{Cl}_2$ and

$[\text{Ni}(\text{Bu}^{\text{i}}\text{AMeUH})_2]\text{Cl}_2$ in both MeOH and DMF show the uni-bivalent electrolyte^[19]. This may be due to the fact that only one chloride ion may be outside the coordinate zone as well as one of the two ligands is coordinated to Ni(II) in its deprotonated form. Analytical results given in the Table1 for the monochloro salt would fit either



And



Previous works by Dutta and Ray^[3] and Dutta and Manihar^[10] on Ni(II) complexes of 1-amidino-O-alkylurea and 1-phenylamidino-O-alkylurea have shown that the basis are all obtained in the anhydro form than having no water of constitution or crystallization whatsoever. Moreover the conductivity

is very low for hydroxide nitrate formation. In fact, in dimethylsulfoxide(DMSO), they have behaved as uni-univalent electrolytes. Similarly in our cases, the bis dichloro complexes, $[\text{Ni}(\text{Bu}^n\text{AMeUH})_2]\text{Cl}_2$ and $[\text{Ni}(\text{Bu}^i\text{AMeUH})_2]\text{Cl}_2$ behave as uni-univalent electrolyte in DMF. Taking all these into consideration we prefer the formulation as $[\text{Ni}(\text{Bu}^n\text{AMeUH})(\text{Bu}^n\text{AMeU})]\text{Cl}$ or $[\text{Ni}(\text{Bu}^i\text{AMeUH})(\text{Bu}^i\text{AMeU})]\text{Cl}$. Generally the conductance values of nitrate Ni(II) complexes are higher than those dichloroNi(II) complexes indicating that nitrate complexes are more ionic.

C. IR Spectra

The IR spectral data of the bis(ligand)Ni(II) complexes show the absence of the nitrile band^[19-21]. Instead the complexes new bands characteristics of C-O-C stretch at ca 1250cm^{-1} ^[22,23]. The band attributed to the butylamine(azomethine) $\nu(\text{C}=\text{N})$ vibration exhibits down shifting ($\Delta \sim 30 - 50\text{cm}^{-1}$) in the spectra of the bis(ligand)Ni(II) complexes showing that azomethine nitrogen(C=N) is coordinated to the metal ion^[24-28]. Further the result of the shifting of band of C=N indicates that the “order” of the N=N bond, which might be expected to change on coordination through the C-O-C moiety^[29]. The fragment N=C-O-C of the imino ether group more delocalized in the complexes and the bond order of the =C-O- group is raised^[29]. Appearance of band at ca $410-470\text{cm}^{-1}$ region due to $\nu(\text{Ni}-\text{N})$ ^[20,23-32], further substantiated the

participation of azomethine(C=N) group in complexation. A very strong absorption band at ca 1380cm^{-1} ^[33,34] indicates that the nitrate present in the bis(ligand)Ni(II) complexes is ionic which is again supported by conductivity evidence (Table II). The IR spectra do not exhibit any band in the 1700cm^{-1} ^[22,29,35] area avoiding the guanylurea structure, VII ($\text{C}_4\text{H}_9\text{-NH-C(=NH)-NH-C(=O)-NHCH}_3$).

Thus, Ni(II) promoted addition of alcohols and is giving structure, 1-n-butylamidino-O-methylurea(I) and 1-iso-butylamidino-O-methylurea(II). Therefore, the possible structure(VII) ($n\text{-C}_4\text{H}_9\text{-NH-C(=NH)-NH-C(=O)-NHCH}_3$) and VIII (iso- $\text{C}_4\text{H}_9\text{-NH-C(=NH)-NH-C(=O)-NHCH}_3$) of 1-n-butylamidino-O-methylurea and 1-iso-butylamidino-O-methylurea are rejected by IR evidence.

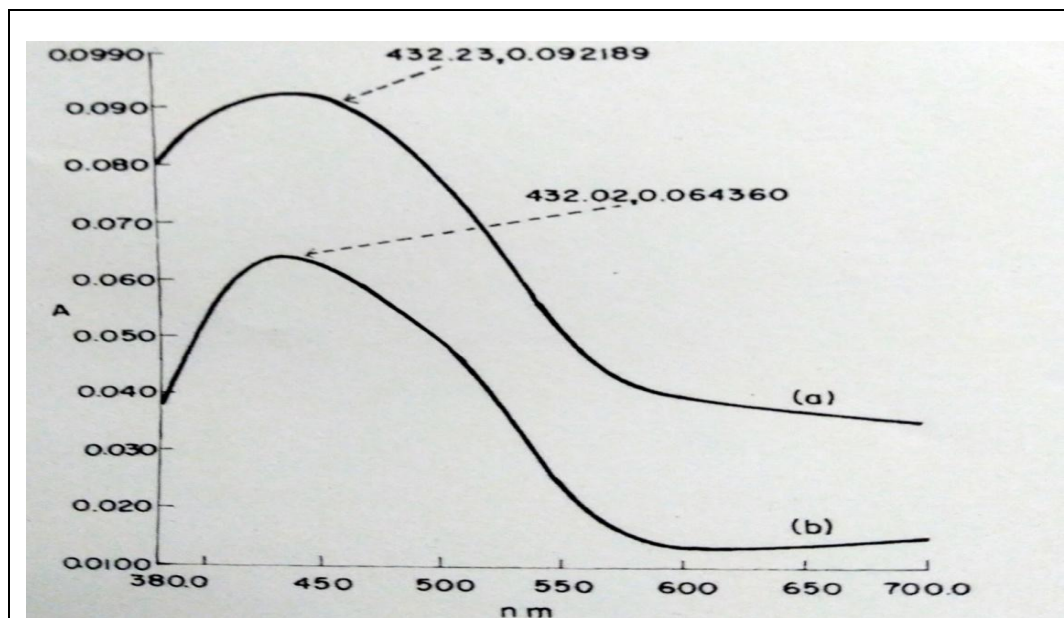


Fig. I: Electronic spectra of $[\text{Ni}(\text{Bu}^n\text{AMeUH})_2]\text{Cl}_2$ in (a) MeOH and (b) DMF

D. Electronic Spectra

The electronic spectra of the four complexes are taken in MeOH and DMF media. The electronic spectra of Complex 1 is shown in figure

I. The spectral data of the complexes are given in the Table III.

Table III: Electronic spectral data of Ni(II) complexes in MeOH and DMF

Complex	Solvent	$\bar{\nu}(\text{cm}^{-1})$	ϵ
1.([Ni(Bu ⁿ AMeUH) ₂]Cl ₂)	MeOH	23135	46.09
	DMF	23147	32.16
		19113sh	22.75
2.([Ni(Bu ⁿ AMeUH) ₂](NO ₃) ₂)	MeOH	21834	29.92
	DMF	23612	43.38
		19613sh	22.75
3.([Ni(Bu ^l AMeUH) ₂]Cl ₂)	MeOH	22123	46.06
	DMF	22147	38.86
		19791sh	28.75
4.([Ni(Bu ⁿ AMeUH) ₂](NO ₃) ₂)	MeOH	22228	43.94
	DMF	23100	52.09
		19856sh	40.18

By comparing the band positions of these complexes in two different solvents (MeOH and DMF), it is cleared that there is blue shift in the DMF solution (Table III). But in the case of dichloro bis(ligand) complex and bis(ligand)nitrate complex, there is a change in band positions towards the shorter wavelength (blue shift) i.e. larger wave number ($\bar{\nu}$). The diamagnetic nature and band positions of these complexes are regarded as a diagnostic nature and band positions of these complexes in DMF solution as compared to that in MeOH (Table III), unlike that observed in square planer ethylene biguanide Ni(II)^[36]. This blue shift may be attributed to the taking part of the axial ligation of the DMF molecule in solution.

IV. CONCLUSION

Ni(II)chloride and Ni(II)nitrate promote the alcohol addition when react with n-butyl dicyandiamide and iso-butyl dicyandiamide. But it can't add higher alcohol because of the steric hindrance between one alkyl group (n-butyl or iso-butyl) and bulky group of the second ligand in a square planer around Ni(II) ions. The diamagnetic natures and their strong absorption band at ca 23100cm⁻¹ including shoulder at ca 19600cm⁻¹ in DMF strong support to a square planer geometry. The complexes show ¹A_{2g} → ¹A_{1g}(d_{xy} → d_{x²-y²) and ¹B_{1g} → ¹A_{2g}(d_{x²-y² → d_{xy}) transitions respectively.}}

The energy order of d-orbital in a square planer environment is $E_{dz^2} < E_{d_{xz}, d_{yz}} < E_{d_{xy}} < E_{d_{x^2-y^2}}$. In the visible region all Ni(II) complexes exhibit two bands in the region 19613-19856cm⁻¹ (shoulder) and a second band (23100-23612cm⁻¹) whose molar absorptivity lies between 22.75 to 46.09. These may be considered as due to ¹A_{2g} → ¹A_{1g}(d_{xy} → d_{x²-y²) and ¹B_{1g} → ¹A_{2g}(d_{x²-y² → d_{xy}) transitions respectively is expected for square planer Ni(II) complexes^[37,39]. On the basis of magnetic moment and spectral evidence, square planer configurations are suggested for all the isolated Ni(II) complexes with [NiN₄] chromophore.}}

From the conductance data, the bis dichloro complexes are uni-univalent electrolyte in DMF solution. Hence, only one chloride ion is outside the coordination zone. Generally the conductance value of nitrate Ni(II) complexes are higher than those of dichloro Ni(II) complexes indicating that nitrate complexes are more ionic. The IR spectral data show that there is Ni-N band at 440-450cm⁻¹. Therefore, from the above experimental results Ni(II) compounds promote alcohol addition and the corresponding complexes formed possess square planer with [NiN₄] chromophore and diamagnetic.

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