

# Preparation and some Studies of Copper(II) and Nickel(II) Complexes of New Tetradentate Schiff Bases Derived from $\beta$ -Diaminopentane

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**Summary:** The copper(II) and nickel(II) complexes of new tetradentate ligands bis (acetylaceton)ethylmethylethylenediimine ( $H_2AA_2EMen$ ), bis(trifluoroacetylaceton)ethylmethylethylenediimine ( $H_2F_3AA_2EMen$ ) and bis(trifluoroacetylmesityloxy)ethylmethylethylenediimine ( $H_2F_3AM_2EMen$ ) have been prepared and characterized using IR  $^1H$ -NMR and mass spectroscopic techniques. The reagents and metal complexes have been examined spectrophotometrically and the effects of complexation, solvent and fluorosubstitution on the absorptiometric properties have been reported.

## Introduction

Simple inorganic metal chelates are becoming important, because of their resemblance to biological systems as oxygen carriers [1,2]. For instance iron(II) complexes of porphyrins [3] and cobalt(II) complexes of Schiff bases [1,4], porphyrins and phthalocyanines [5] have widely been studied as oxygen carrier. The tetradentate ketoamine Schiff bases are also thus of some interest.

A number of studies has been made on bis-(acetylaceton)ethylenediimine and related compounds to determine the structural features of the ligands and their metal complexes [6-9]. In the present work three tetradentate ligands have been pre-

pared by the condensation of appropriate  $\beta$ -diketone with 2,3-diaminopentane. The spectrophotometric studies have been carried out to understand the structural features of the reagents and their copper and nickel complexes.

## Results and Discussion

The reagents  $H_2AA_2EMen$ ,  $H_2F_3AA_2EMen$  and  $H_2F_3AM_2EMen$  and their copper(II) and nickel(II) chelates are easily prepared in a pure state and the elemental analysis closely corresponded expected values (Table 1). The IR of the reagents indicate one to two weak bands within  $3300-3100\text{ cm}^{-1}$

Table 1: Elemental microanalysis of reagent and their metal complexes

Compound	Mol. Formula	M.P. °C	Expected %			Found %		
			C	H	N	C	H	N
H <sub>2</sub> AA <sub>2</sub> EMen	C <sub>15</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub>	164	67.92	9.43	10.56	67.43	9.70	10.36
AA <sub>2</sub> EMenCu	C <sub>15</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> Cu	117.4	54.93	7.32	8.54	54.34	7.11	8.34
AA <sub>2</sub> EMeNi	C <sub>15</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> Ni	147.2	55.78	7.43	8.67	55.53	7.25	8.52
H <sub>2</sub> F <sub>3</sub> AA <sub>2</sub> EMenNi	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> F <sub>6</sub>	208	47.87	5.87	7.44	48.28	5.29	7.42
F <sub>3</sub> AA <sub>2</sub> EMenCu	C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> F <sub>6</sub> C	164.	42.13	4.57	6.39	42.38	4.72	6.75
F <sub>3</sub> AA <sub>2</sub> EMenNi	C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> F <sub>6</sub> Ni	175	41.50	4.62	6.47	40.97	3.99	6.22
H <sub>2</sub> F <sub>3</sub> AM <sub>2</sub> EMen	C <sub>21</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> F <sub>6</sub>	158	55.53	6.16	6.16	55.41	5.33	5.74
F <sub>3</sub> AM <sub>2</sub> EMenCu	C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> F <sub>6</sub> Cu	155	48.90	5.04	5.43	48.80	5.08	5.70
F <sub>3</sub> AM <sub>2</sub> EMenNi	C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> F <sub>6</sub> Ni	161	49.15	5.09	5.48	49.27	4.77	5.59

and a broad and strong band within 1630-1580 cm<sup>-1</sup> due to hydrogen bonded NH and C=O groups respectively. Both of the bands are not visible in copper and nickel complexes. It is therefore suggested that dianion of the ligands is involved in complexation with coordination with C=O groups.

The band observed at 1610 cm<sup>-1</sup> in H<sub>2</sub>AA<sub>2</sub>EMen due to hydrogen bonded C=O group shifts to 1625 cm<sup>-1</sup> because of -CF<sub>3</sub> substitution in H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen adjacent to the carbonyl group. The reagent H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen and its copper and nickel complexes indicate a band within 1660-65 cm<sup>-1</sup> due to the presence of C=C groups in isobutene. The metal ligand vibrations are observed at 440-55, 460-65 and 490 cm<sup>-1</sup> in nickel and copper complexes. The mass spectra of the reagents indicate molecular ion peaks at m/z 266, 374 and 454 for H<sub>2</sub>AA<sub>2</sub>EMen, H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen respectively, with relative intensity within 0.02-2%. The reagents H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen lose fragments, corresponding to -CF<sub>3</sub> group to give the peaks at m/z 305 and 385 respectively. The reagents H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen also give fragment peak at m/z 97 corresponding to -COCF<sub>3</sub> and supports that -CF<sub>3</sub> is attached with carbonyl group and condensation has occurred on C=O group attached to non-fluorinated groups.

The results of <sup>1</sup>H-NMR of the reagents and their metal complexes are summarized in (Table-2). The results are as expected from structure (Fig. 1). The reagents and their nickel complexes indicate two to four signals within δ 1.6-2.00 corresponding to the number of methyl groups present in the compounds. It may be noted that the signals shift to lower value in nickel complex as compared to the corresponding signal in their respective reagents (Table 2) due to a fixed configuration in nickel complexes. The reagents indicate two multiplets

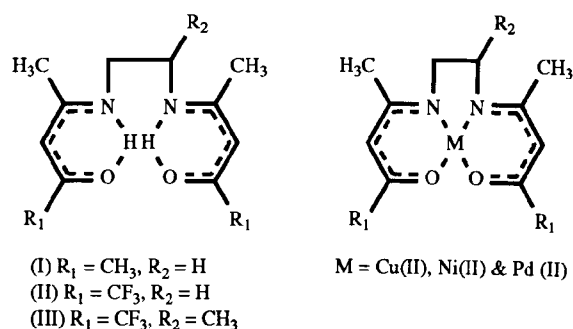


Fig.1: Structural formula of the ligand and metal complexes.

within 3.24-3.69 ppm due to two-CH groups at bridge position, which change into two quadruplets within δ 2.56-3.09 in each nickel complex. The reagents and their metal complexes indicate two singlets, corresponding to two =CH protons within δ 4.8-5.4 ppm. The reagents H<sub>2</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen indicate a doublets, but H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen has a triplet within δ 11.0-11.3 ppm due to NH protons. A similar signals are not visible in nickel complexes and supports that a dianion of the ligands are involved in complexation.

The results of spectrophotometric studies of the reagents H<sub>2</sub>AA<sub>2</sub>EMen, H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen, and their copper and nickel complexes in chloroform, methanol, n-hexane, and acetone (Table 3) indicate that all the reagents show a similar pattern in UV region, but different from their copper and nickel chelates. The reagents in methanol and n-hexane indicate one to two bands with 199-210 nm due to π-π\* transitions in C=N and C=C chromophores [13]. The reagent H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen also indicate a band within 253-60 nm in chloroform, methanol and n-hexane due to the presence of an additional C=C group in isobutene.

Table 2:  $^1\text{H-NMR}$  spectra of the reagent and nickel complexes in d ppm with possible assignments

Compound	-CH <sub>3</sub> group	-CH bridge	= CH	NH	Others (methyl and ethyl group at bridge position)
H <sub>2</sub> AA <sub>2</sub> EMen	1.8384(s) 1.8541(s) 1.9702(s) 1.9803(s)	3.2425(m)	4.8784(s) 4.8976(s)	11.012(d)	0.9474(T), (CH <sub>3</sub> of ethyl) 1.2521(d), (CH <sub>3</sub> ), 1.450 (m) (CH <sub>2</sub> )
AA <sub>2</sub> EMenNi	1.823(s) 1.829(s) 1.8477(s) 1.8595(s)	2.5655 (q) 2.9661(q)	4.8201(s) 4.8439(s)		0.8779(T) (CH <sub>3</sub> of ethyl) 1.249(d) (CH <sub>3</sub> ), 1.676 (m) (CH <sub>2</sub> )
H <sub>2</sub> F <sub>3</sub> AA <sub>2</sub> EMen	2.0018(s) 2.0067(s)	3.4489(m) 3.6803(m)	5.2841(s) 5.3097(s)	11.309(d)	1.0094(T) (CH <sub>3</sub> of ethyl) 1.3793(d) (CH <sub>3</sub> ) 1.8885 (m) (CH <sub>2</sub> ) 0.9277 (T) (CH <sub>3</sub> of ethyl)
F <sub>3</sub> AA <sub>2</sub> EMenNi	1.9827(s) 1.9857(s)	2.7163(q) 3.0917(q)	5.3833(s) 5.4145(s)		1.3159(d) (CH <sub>3</sub> ) 1.8618(m) (CH <sub>2</sub> ) 0.9501(T) (CH <sub>3</sub> of ethyl)
H <sub>2</sub> F <sub>3</sub> AM <sub>2</sub> EMen	1.7735(T) 1.8808(d)	3.4821(m) 3.6928(m)	5.2478(s) 5.2667(s)	11.096(T)	1.3019(d) (CH <sub>3</sub> ) 1.5114(m) (CH <sub>2</sub> ) 5.673 of = CH of isobutene
F <sub>3</sub> AM <sub>2</sub> EMenNi	1.669(s) 1.789(d) 1.8012(d)	2.719(q) 3.0959(q)	5.3572(s) 5.388(s)	-	0.8250(d) (CH <sub>3</sub> ), 1.2145(d) (CH <sub>3</sub> ), 1.5266 (m) (CH <sub>2</sub> ), 6.4005 of = CH of isobutene.

Table 3: Spectrophotometric data of the reagent and their copper(II) and nickel(II) complexes in different solvents  $\lambda_{\text{max}}$  nm ( $\epsilon = 1.\text{mole}^{-1}\text{cm}^{-1}$ )

Compound	n-hexane	Methanol	Chloroform	Acetone
H <sub>2</sub> AA <sub>2</sub> EMen	199(5700), 210 (sh) (4300) 308(32000)	206(6600), 309(sh) (43000) 322 (47000)	310 (sh) (54000), 320 (58000)	327 (25000)
AA <sub>2</sub> EMeNi(II)	560(61), 380(8000), 360(7100), 315 (sh) (6400), 305(sh) (6800), 273 (20000), 240(35000), 210(sh) (27000).	555 (48), 368 (5200), 352(sh) (5300), 270 (13000), 235(25000), 210(sh) (2000)	560 (63) 375 (7100) 359(6900), 311(sh) 5700), 273 (17000), 243(24000)	560(60), 375(8000), 355(7600).
AA <sub>2</sub> EMenCu(II)	553(180), 340(sh) 7900), 313(27000), 278(11000), 255(sh) (10000), 232(16000), 205(17000).	542(140), 330(sh) (8300), 307(22000), 278 (sh) (11000), 232(17000), 207(15000),	545(200), 338(sh) (9700), 310(30000), 275(15000), 243(18000).	550(200), 331(10000)
H <sub>2</sub> F <sub>3</sub> AA <sub>2</sub> EMen	330(sh) (19000), 320(19000) 202(25000)	330 (sh) (32000), 322(32000), 207(6100).	333(31000) 331(33000).	
F <sub>3</sub> AA <sub>2</sub> EMenNi(II)	565(36), 390(5800), 365(sh) (5500), 312 (6900), 273(16000), 245(sh) (18000), 228(39000), 202(35000)	560(44), 380(4400), 358(sh) (4500), 312 (4800), 268(14000), 243(sh) (16000) 225(36000), 205(sh) (20000)	565(46), 388(3300), 360(3400), 313(3700), 272(12000), 243(13000).	565(48), 380(4400), 358(4300), 315(sh), (3000).
F <sub>3</sub> AA <sub>2</sub> EMenCu(II)	558(140), 340(sh) (5400), 310(19000), 293(sh) (11000), 273(9400), 233(18000), 204(26000).	558(77), 328(sh) (4400), 302(13000), 268(sh) (7000), 228(11000), 208(13000)	555(150), 337(sh) (4300), 307(18000), 272(91000), 240(80000).	558(100), 331(3800)
H <sub>2</sub> F <sub>3</sub> AM <sub>2</sub> EMen	338(30000), 253(15000), 201(51000)	340(28000), 260(13000), 207 (sh) (6800).	342(44000), 258(19000)	340(31000)
F <sub>3</sub> AM <sub>2</sub> EMenNi(II)	565(68), 400(5900), 370(sh) (4700), 320(8700), 280(19000), 245(sh) (3800), 230(13000),	560(51), 390(4700), 365(sh) (4300), 317(7900), 275(sh) (27000) 227(37000), 207(3500),	565(74), 390(4600), 383(sh) (3900), 320(7000), 280(sh), (16000), 245(27000), 202(44000).	560(62), 390(5300) 370(sh) (4900), 335 (6600)
F <sub>3</sub> AM <sub>2</sub> EMenCu(II)	558(220), 345(sh) (11000), 320(26000), 250 (sh) (23000), 202(29000)	560(140), 340 (sh) 8800), 230(sh) (22000), 207(28000)	555 (190), 345 (sh) (10000), 315(27000), 268(28000), 245(sh) (23000)	558(170), 335 (10000)

Reagent H<sub>2</sub>AA<sub>2</sub>EMen in chloroform and methanol indicates two bands at 310 and 320 nm and 322 and 309 nm respectively. H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen also indicates two bands in chloroform, methanol and n-hexane at 325 and 333 nm, 322 and 330 nm and 320 and 330 nm respectively. The reagent

H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen indicates a single band at 342, 340 and 338 nm in chloroform, methanol and n-hexane respectively. However all the three reagents H<sub>2</sub>AA<sub>2</sub>EMen, H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen in acetone indicate a single band at 327, 331 and 340 nm respectively (Fig. 2). The

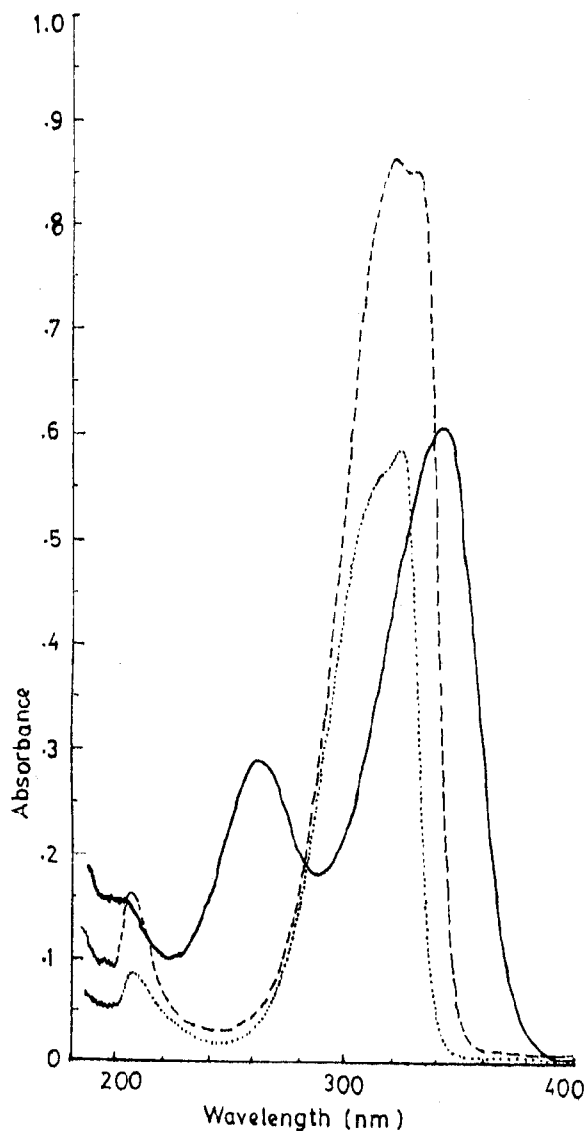


Fig. 2: Absorption spectra of the reagents in methanol.

1. H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen —————
2. H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen - - - - -
3. H<sub>2</sub>AA<sub>2</sub>EMen .....

bands can be assigned to  $\pi-\pi^*$  transitions in  $C=C-C=O$  chromophore. Martell et al [13] and Gluotti et al [14] have reported the presence of two bands in bis(acetylacetonate)-ethylenediamine and related compounds in chloroform and methanol due to the different relative arrangements of two conjugated systems arising from the rotation about ethylene bridge. Same explanation may be considered as valid for the reagents H<sub>2</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen, but the reagent H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen

contains extended conjugated double bond system due to the presence of isobutene, which is probably restricting the different arrangements in which it can exist and the observation of a single band in the region. A similar observations have been reported with related compounds [12]. The observation of a single band in acetone may be due to the better coordination of the solvent. It may be noted that there is a bathochromatic shift in  $\lambda$ -max in all the solvents as we move from H<sub>2</sub>AA<sub>2</sub>EMen to H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen due to the substitution of electron withdrawing  $-CF_3$  in H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen, and  $-CF_3$  and isobutene in H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen.

Absorption spectra of copper and nickel complexes in methanol and n-hexane indicate a band within 205-210 nm, as has been observed in the spectra of the ligands. The copper and nickel complexes indicate two bands in chloroform within 240-34 nm and 268-80 nm, in methanol within 225-35 nm and 266-78 nm and in n-hexane within 228-40 nm and 273-80 nm (Fig. 3). The first band is due to  $\pi-\pi^*$  transitions in conjugated  $C=N$  and  $C=C$ , but the second might have origin due to  $\pi-\pi^*$  transitions in  $C=C-C=O$  chromophore [9]. The difference of the absorption bands from those of the reagents may be due to better delocalization of electron density in more planar metal complexes. However these bands are not visible in acetone solution. The next band of strong absorption intensity in copper complexes is observed 302-320 nm range of  $1.3 \times 10^4$  l.mole<sup>-1</sup>cm<sup>-1</sup>. The band in nickel complexes of H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen, and H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub>EMen in chloroform, methanol, n-hexane and H<sub>2</sub>AA<sub>2</sub>EMen in n-hexane is visible within 313-20 nm ( $\epsilon = 3.7-8.7 \times 10^3$ ). The band may be assigned to  $\pi-\pi^*$  in  $C=C-C=O$  as for reagents. It may be noted that the values of molar absorptivity for nickel complexes are much lower as compared to the corresponding copper complexes and it is observed that in methanol the band shifts to lower wavelength (Table 3) as compared to chloroform and n-hexane, due to possible hydrogen bonding in methanol.

The nickel complexes show two charge transfer bands between 352-70 nm and 368-400 nm ( $\epsilon = 3.3-8.0 \times 10^3$ ) in chloroform, methanol and acetone solvents. The nickel complex of H<sub>2</sub>AA<sub>2</sub>EMen absorbs at 359 nm ( $\epsilon = 6.9 \times 10^3$ ) and 375 nm ( $\epsilon = 7.1 \times 10^3$ ) and in methanol at 352 ( $\epsilon = 5.3 \times 10^3$ ) in n-

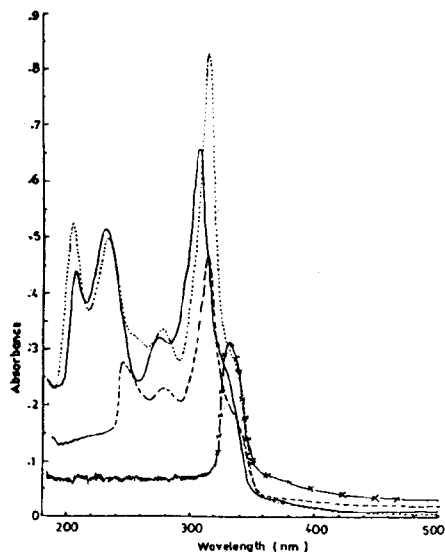


Fig. 3: Absorption spectra of copper complexes of H<sub>2</sub>AA<sub>2</sub>EMen in various solvents.

- 1. Methanol —————
- 2. Chloroform - - - - -
- 3. n-hexane .....
- 4. Acetone - x - x - x - x - x - x -

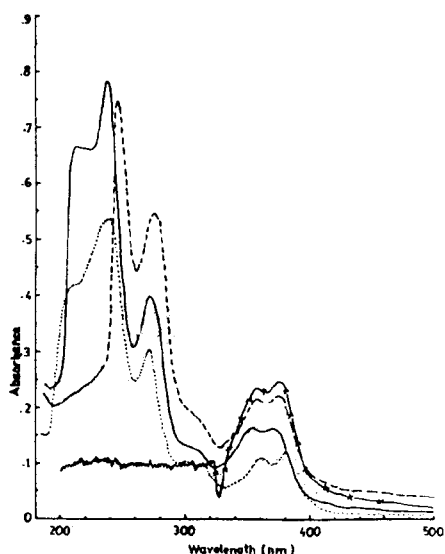


Fig.4: Absorption spectra of nickel complexes of H<sub>2</sub>AA<sub>2</sub>EMen in various solvents.

- 1. Methanol —————
- 2. Chloroform - - - - -
- 3. n-hexane .....
- 4. Acetone - x - x - x - x - x - x -

hexane at 360 nm ( $\epsilon$  7.1x10<sup>3</sup>) and 380 nm ( $\epsilon$  8.0 x 10<sup>3</sup>), and 368 nm ( $\epsilon$  5.2 x 10<sup>3</sup>) (Fig. 4). Thus a hypsochromatic shift with decrease in molar absorptivity in both the bands has occurred in methanol due to hydrogen bonding.

The nickel complex of H<sub>2</sub>AA<sub>2</sub>EMen absorbs maximally at 375, 368, 380 and 375 nm in chloroform, methanol, n-hexane and acetone respectively as compared to the nickel complex of H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen, which absorbs at 388, 380, 390 and 380 nm in same solvent system respectively. Thus a bathochromatic shift of 5-13 nm has occurred due to the substitution of trifluoromethyl group in H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen in place of methyl in H<sub>2</sub>AA<sub>2</sub>EMen. Similar bands in copper complexes could not be identified, however a shoulder within 328-345 nm in chloroform, methanol and n-hexane is visible in each of the complex, which could be assigned as charge transfer band [15].

A band is visible in all the copper and nickel complexes in all the solvents within 542-62 nm ( $\epsilon$ =44-220) due to d-d transition (Fig. 5). The bands observed are symmetrical in all the solvents and characteristic of square planer complexes, as has been reported with related compounds [7,17].

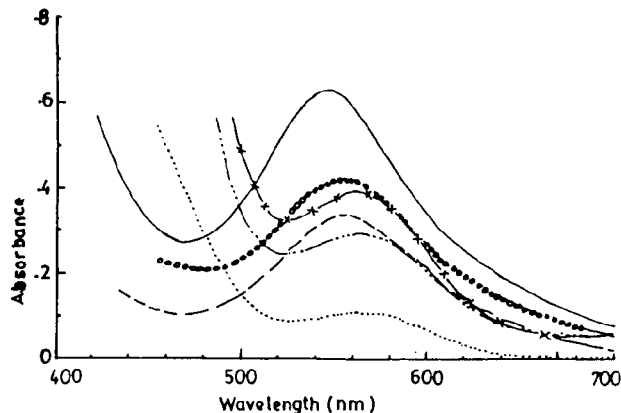


Fig. 5: Absorption spectra for d-d transition of copper and nickel complexes in chloroform within 700-450 nm.

- 1. AA<sub>2</sub>EMenCu —————
- 2. AA<sub>2</sub>EMenNi - x - x - x - x -
- 3. F<sub>3</sub>AA<sub>2</sub>EMenCu - - - - -
- 4. F<sub>3</sub>AA<sub>2</sub>EMenNi .....
- 5. F<sub>3</sub>AM<sub>2</sub>EMenCu ○○○○○○
- 6. F<sub>3</sub>AM<sub>2</sub>EMenNi - . - . - . - . - . - . -

## Experimental

### Preparation of 2,3-diaminopentane

Ethylmethylglyoxime was prepared by the reported method of Belcher *et al* [10]. The glyoxime was dissolved in ethanol and reduced to diamine with sodium metal, following a general procedure of Bernth and Larson [11]. A dark coloured product was isolated, which reacted with  $\beta$ -diketones to form tetradentate ketoamines.

*Preparation of Bis(acetylaceton)ethylmethylethylenediimine- (H<sub>2</sub>AA<sub>2</sub>EMen); Bis(trifluoroacetylaceton)ethylmethylethylenediimine(H<sub>2</sub>F<sub>3</sub>AA<sub>2</sub>EMen) and Bis(trifluoroacetylmesityloxiide) ethylmethylethylenediimine (H<sub>2</sub>F<sub>3</sub>AM<sub>2</sub> EMen).*

2,3-Diaminopentane hydrochloride (0.001 M) dissolved in water was neutralized with ammonia and the liberated diamine was extracted 3-4 times with a small portions (5 ml) of chloroform. The dried extract over anhydrous sodium sulphate was slowly added to acetylaceton, trifluoroacetylaceton or trifluoroacetylmesityloxiide (> .002 M) and the mixture was refluxed for 30 min. Most of the solvent was evaporated under vacuum desiccator and the gummy mass obtained was dissolved in n-hexane. The concentrated solution was cooled at 10°C and fine needle like crystalline products obtained were recrystallized from n-hexane twice.

### Preparation of copper(II) and nickel(II) chelates

Equimolar solution of copper(II) acetate or nickel(II) acetate dissolved in methanol was added to the refluxing solution of the reagent in ethanol. The mixture was refluxed for 30 min and concentrated and cooled. The precipitate obtained was filtered and recrystallized from methanol.

$\beta$ -Diketones acetylaceton and trifluoroacetylaceton were obtained from commercial source (Merck) and trifluoroacetylmesityl oxide (1,1,1-trifluoro-6-methylhept-5-ene-2,4-dione) was prepared by Claisen condensation as reported earlier [12]. Elemental microanalysis (Table 1) was carried out

by Elemental Micro-Analysis Ltd., U.K. IR in KBr were recorded on Perkin Elemer 1430 IR spectrophotometer within the range 4000-200 cm<sup>-1</sup>. Mass spectra of the reagents on Finnigan MAT 1125 and <sup>1</sup>H-NMR on Bruker AM-300 were recorded at HEJ Research Institute of Chemistry, University of Karachi. The spectrophotometric studies were carried out on Hitachi 220 spectrophotometer.

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