

Preparation Characterisation and Light Absorption Spectrophotometry of Copper(II) and Nickel(II) Complexes of Some Fluorinated Tetradentate Ketoamine Schiff Bases

M.Y.KHUHAWAR AND A.G. BHATTI

Institute of Chemistry, University of Sind, Jamshoro (Sind), Pakistan.

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Summary: Copper(II) and nickel(II) complexes of tetradentate ketoamine Schiff bases bis(trifluoroacetylmesityloxiide) ethylenediimine ($H_2F_3AM_{2en}$), bis(trifluoroacetylmesityloxiide) propylenediimine ($H_2F_3AM_{2pn}$), bis (trifluoroacetylmesityloxiide) d-stilbenediimine (dl- $H_2F_3AM_{2S}$) and bis(trifluoroacetylmesityloxiide) meso-stilbenediimine (meso- $H_2F_3AM_{2S}$) are prepared and IR, 1H -NMR and mass spectra of the reagents are recorded. Ultraviolet and visible spectra of the reagents and metal complexes are recorded in methanol, acetone, chloroform and n-hexane and possible assignment of the different bands is suggested.

Introduction

A number of investigations has been carried out on the metal chelates of tetradentate Schiff bases like bis(acetylacetone) ethylenediimine, bis (trifluoroacetylacetone)-ethylenediimine, bis(salicylaldehyde)ethylenediimine and related ligands, including their electronic spectra [1-7]. In the present work the alkyl group (isobutene) containing double bond has been introduced together with CF_3 to investigate their effects on the electronic spectra of copper(II) and nickel(II) chelates.

Experimental

Preparation of the reagents

Bis(trifluoroacetylmesityloxiide)ethylenediimine ($H_2F_3AM_{2en}$), Bis(trifluoroacetylmesityloxiide)propylenediimine ($H_2F_3AM_{2pn}$), Bis(trifluoroacetylmesityloxiide)dl-stilbenediimine (dl- $H_2F_3AM_{2S}$) and Bis (trifluoroacetylmesityloxiide)meso-stilbenediimine (meso-p- $H_2F_3AM_{2S}$).

Cooled solution of ethylenediimine or propylenediimine (0.01 mole) was slowly added to the ice cooled solution of trifluoroacetylmesityloxiide (0.02 mole) in ethanol, whereas dry ether solution of meso-or dl-stilbenediimine (0.01mole) was mixed with trifluoroacetylmesityloxiide (0.02 mole) at room temperature. The mixture was left each time at room temperature for 24 hours and the precipitate so obtained was washed with dry ether and recrystallised from n-hexane or ethanol. Results of micro- analysis are

summarized in Table-1. MS (rel.intensity %) of $H_2F_3AM_{2en}$ showed M^+ at m/z 422(22) and fragment peaks at 397(54), 343(6), 315(6), 219(30), 207(20), 206(94), 194(100), 150(26), 136(64), 122(58), 108(38). IR cm^{-1} (KBr) 3210(s), 3100(m), 1670(s), 1600(bs), 1530(s). $H_2F_3AM_{2pn}$, MS (rel.intensity %) M^+ at m/z 426 (5) and fragment peaks at m/z 411 (6), 357(0.9), 233(10), 221(18). IR (KBr) cm^{-1} 3210(m), 3100(w), 1600(bs), 1535(m), 1520(w), 1470(m). dl- $H_2F_3AM_{2S}$. MS (rel.intensity) M^+ at m/z 564(0.02) and fragment peaks at 545(0.9), 495(0.04), 440(0.015), 372(0.085), 283(24), 282(100), 268(18), 178(8), 91(17). IR(KBr) cm^{-1} 3220(w), 1665(s), 1600(s), 1565(w), 1550(w), 1530(w), 1500(m), meso- $H_2F_3AM_{2S}$. MS (rel.intensity) M^+ at m/z 564 (0.02) and fragment peaks at 545(0.8), 495(0.22), 441(0.02), 440(0.17), 413(0.01), 372(0.18), 283(24), 282(100), 268(18), 267(5), 178(8), 91(9). IR(KBr) cm^{-1} 3200(w), 3125(w), 1660(w), 1595(s), 1520(s).

Preparation of Metal Complexes

Equimolar solution of copper(II) acetate or nickel(II) acetate in methanol was added to the solution of the reagents in ethanol. The mixture was refluxed for 30 minutes and was concentrated and cooled. The precipitate was filtered and copper and nickel complexes of $H_2F_3AM_{2en}$ and $H_2F_3AM_{2pn}$ were recrystallised from n-hexane and dl- $H_2F_3AM_{2S}$ and meso- $H_2F_3AM_{2S}$ from ethanol. $F_3AM_{2en}Cu$, IR(Nujol) cm^{-1} 1665(m), 1605(s), 1530(s), $F_3AM_{2en}Ni$, IR(Nujol) cm^{-1} 1657(m),

Table 1: Elemental micro-analysis of reagents and their metal complexes

Compound	Mol. Formula	MP ^o C	% Expected			% Found		
			C	H	N	C	H	N
H ₂ F ₃ AM ₂ en	C ₁₈ H ₂₂ N ₂ O ₂ F ₆	176	52.42	5.33	6.79	52.42	6.10	6.82
H ₂ AM ₂ enCu	C ₁₈ H ₂₀ N ₂ O ₂ F ₆ Cu	184	45.61	4.22	5.91	45.72	4.19	5.77
F ₃ AM ₂ enNi	C ₁₈ H ₂₀ N ₂ O ₂ F ₆ Ni	185	46.09	4.26	5.97	46.32	4.26	5.53
H ₂ F ₃ AM ₂ pn	C ₁₉ H ₂₄ N ₂ O ₂ F ₆	171	53.52	5.63	6.57	53.77	5.74	6.21
F ₃ AM ₂ pnCu	C ₁₉ H ₂₂ N ₂ O ₂ F ₆ Cu	240	46.29	5.68	5.68	46.95	4.42	5.76
F ₃ AM ₂ pnNi	C ₁₉ H ₂₂ N ₂ O ₂ F ₆ Ni	252	47.25	4.51	5.74	47.75	4.67	5.88
H ₂ F ₃ AM ₂ S	C ₃₀ H ₃₀ N ₂ O ₂ F ₆	183	63.82	5.31	4.94	63.98	5.67	4.87
dl-F ₃ AM ₂ SCu	C ₃₀ H ₂₈ N ₂ O ₂ F ₆ Cu	190	57.55	4.46	4.47	57.56	4.53	4.51
dl-F ₃ AM ₂ en	C ₃₀ H ₂₈ N ₂ O ₂ F ₆ Ni	200	58.06	4.51	4.51	58.19	4.68	4.57
meso-H ₂ F ₃ AM ₂ S	C ₃₀ H ₃₀ N ₂ O ₂ F ₆	205	63.82	5.31	4.96	63.74	5.82	4.91
meso-F ₃ AM ₂ SNi	C ₃₀ H ₂₈ N ₂ O ₂ F ₆ Ni	190	58.06	4.51	4.51	58.08	4.90	4.25
meso-F ₃ AM ₂ SCu	C ₃₀ H ₂₈ N ₂ O ₂ F ₆ Cu	185	57.60	4.48	4.48	57.39	4.88	4.62

1605(s), 1520(s). F₃SAM₂pnCu, IR(Nujol) cm⁻¹ 1660(s), 1610(s), 1530(s), 1515(w). F₃AM₂pnNi. IR(Nujol)cm⁻¹ 1662 (s), 1610(s), 1525(s), dl-F₃AM₂S Cu, IR(KBr) cm⁻¹ 1660(m), 1600(s), 1510(s), 1480(s), 510(m), 430(w). meso-F₃AM₂S Ni. IR (KBr) cm⁻¹ 1660(m), 1600(s), 1510(s), meso-F₃AM₂SCu, IR (KBr) cm⁻¹ 1660(m), 1602(s), 1500(s), 1475(s), 512(m), 432(w). mso-F₃AM₂SNi, IR (KBr) cm⁻¹ 1662(m), 1605(s), 1505(s), 1478(s), 515(w), 430 (w).

The β-diketone, trifluoroacetylmesityloxiide (1,1,1-trifluoro-6-methyl-5-hepten-2,4-dione) was prepared by the condensation of mesityloxiide (4-methyl-3-pentene-2-one) with trifluoroethyl acetate following the general procedure of Belcher et al. [8]. Stilbenediamines were prepared following reported procedures [9,10].

Elemental micro analysis was carried out by Elemental Micro Analysis Ltd., UK. IR(KBr) were recorded on Hitachi 260-30 IR spectrophotometer in the range 4000-250 cm⁻¹ and in nujol on Unicam SP 1025 IR Spectrophotometer. Mass spectra of the reagents on Finnigan MAT 1125 and ¹H NMR on Bruker AM 300 were carried out at H.E.J. Research Institute of Chemistry, University of Karachi. Spectrophotometric studies were carried out on Hitachi 220 spectrophotometer.

Results and Discussion

The reagents are easy to prepare by a simple synthetic routine. The mass spectra of the reagents show molecular ion peak at m/z corresponding to their expected molecular weight, but the relative intensity of the M⁺ decreases with substitution at ethylene bridge and is found to be lowest in phenyl substituted ligands dl-H₂F₃AM₂S and meso-H₂F₃AM₂S. The reagents indicate a peak at m/z corresponding to the loss of -CF₃ group and the reagent H₂F₃AM₂ en also show a peak due to the loss of -COCF₃, but a similar peak could not be identified in the spectra of H₂F₃AM₂pn, dl-H₂F₃AM₂S and meso-H₂F₃AM₂S, may be due to the ease of breakage of C-C bond of ethylene group due to methyl or phenyl group substitution at bridge position. Thus it may be suggested that the -CF₃ group is near to the carbonyl group. The mass spectra of reagents follow a similar pattern as has been observed with the related compounds by Belcher et al [11] and Lindoy [12] with the base peak (100%) due to the breakage of ethylene bridge, except H₂F₃AM₂en which shows base peak at m/z 194 owing to the breakage of the C-N bond adjacent to ethylene bridge.

The IR of the reagents indicate one to two bands near 3200 cm⁻¹ due to the NH group, but the

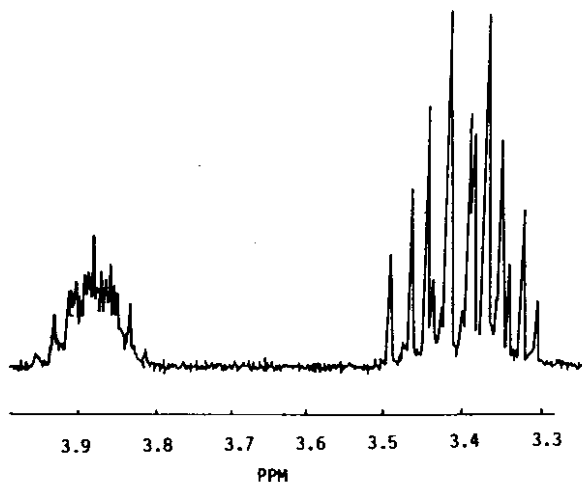
relative intensity of the band considerably decreases and the bands are just visible in *dl*-H₂F₃AM₂S and *meso*-H₂F₃AM₂S due to the phenyl groups substitution at bridge position. The bands disappear in copper and nickel complexes as expected [13]. A band observed in the spectra of the reagents and metal complexes within the range of 1655-70 cm⁻¹ is assigned to C=C of the alkyl (isobutene) group. A similar pattern here is also observed as with the related compounds [13-15].

The results of ¹H-NMR are summarized in Table-II. The reagents shows two doublets each corresponding to 6H atom in the range of δ 1.42-1.89 ppm with J within 1.4Hz due to long range coupling in isobutene, except H₂F₃AM₂pn which shows a triplet corresponding to 6H and two doublets, each corresponding to 3H due to asymmetric methyl substitution at bridge position. The δ value in H₂F₃AM₂en (1.8-1.89) shifts to lower side in

meso-H₂F₃AM₂S (1.4- 1.75) due to the diamagnetic shielding effects of phenyl group. The nickel complexes also show two doublets each corresponding to 6H at slightly shifted position within δ 1.05-1.79 ppm, except H₂F₃AM₂pn which shows four doublets each corresponding to 3H in the same region due to a fixed configuration in metal complexes and methyl group substitution at bridge position. The reagents H₂F₃AM₂en, *dl*-H₂F₃AM₂S and *meso*-H₂F₃AM₂S indicate a multiplet within δ 3.5-4.9 ppm due to CH₂- or CH- groups at bridge position, of the similar shape as has been observed with related compounds [14,16]. The multiplet changes into singlet within δ 3.0-4.9 ppm in nickel complexes as expected [17]. But the reagent H₂F₃AM₂pn shows a complex multiplet centered around δ 3.89 ppm and two close multiplets at δ 3.44 and 3.37 ppm each corresponding to 1 H (Fig. 1). The first multiplet has been assigned to CH and two to CH₂ at bridge position. It has been suggested

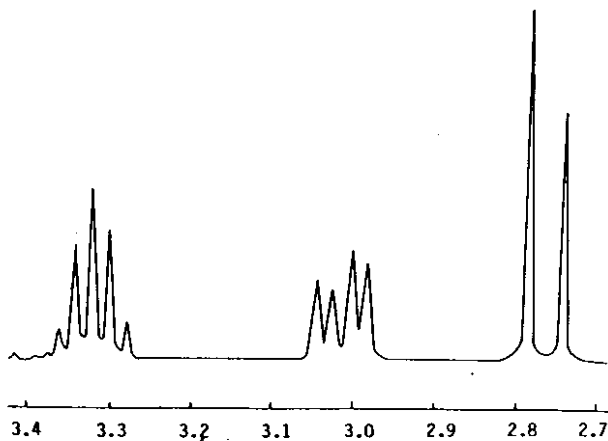
Table 2: ¹H-NMR spectra of the reagents and nickel complexes in δppm with possible assignment

Compound	-CH ₃ groups of isobutene	= CH of isobutene	CH and CH ₂ of bridge	= CH	NH	Others
H ₂ F ₃ AM ₂ en	1.803(d),1.29Hz 1.892(d),1.38Hz	5.7135(t),1.32Hz	3.531(m)	5.32(s)	11.04(b)	-
F ₃ AM ₂ enNi	1.672(d),1.08Hz 1.792(d),1.32Hz	5.5558(d),1.11Hz 5.6843(t),1.26Hz	3.0126(s) 3.371(m)	5.399(s) 5.2811(s)	- 10.98(d),9.3Hz	- 1.30125(d)
H ₂ F ₃ AM ₂ pn	1.7917(t),1.05Hz 1.8795(d),1.38Hz 1.8939(d),0.99Hz	5.6843(t),1.26Hz 5.7082(t),1.1Hz	3.371(m) 3.44(m) 3.894(m)	5.2811(s) 5.3085(s)	10.98(d),9.3Hz 11.103(b)	1.30125(d) 6.63Hz(-CH ₃ bridge)
F ₃ AM ₂ pnNi	1.6531(d),0.96Hz 1.6752(d),0.99Hz 1.7861(d),1.26Hz 1.7988(d),1.29Hz	5.5326(s) 5.6528(t),1.26Hz	2.76(d),13.11Hz 3.0124(m) 3.3192(m)	5.3691(s) 5.4012(s)	-	1.2466(d) 6.48Hz(-CH ₃ bridge)
<i>dl</i> -H ₂ F ₃ AM ₂ S	1.6726(d),0.93Hz 1.8745(d),1.41Hz	5.6971(t),1.29Hz	4.8544(m)	5.3332(s)	11.835(d), 6.9Hz	6.95(m),7.251 (-C ₆ H ₅ bridge)
<i>dl</i> -F ₃ AM ₂ SNi	1.0547(d),0.93Hz 1.5379(d),1.2Hz	5.1776(t),1.23Hz	4.2786(s)	5.3620(s)	-	7.356(m),7.494(m) 8.174(m),(-C ₆ H ₅ bridge)
<i>meso</i> -H ₂ F ₃ AM ₂ S	1.4258(d),1.2Hz 1.7521(d),1.35Hz	5.2729(t) 1.23Hz	4.8239(m)	5.1436(s)	11.7085(d) 6.9Hz	7.21(m),7.24(m) 7.33(m) for C ₆ H ₅ at bridge
<i>meso</i> -F ₃ AM ₂ SNi	1.3752(d),0.91Hz 1.3957(d),1.02Hz	5.1642(t)	4.926(s)	5.3591(s)	-	7.0429(m) (C ₆ H ₅ at bridge)

Fig. 1: $^1\text{H-NMR}$ of $\text{H}_2\text{F}_3\text{AM}_2\text{pn}$ in CDCl_3

that the two hydrogens of CH_2 group have resulted into axial and equatorial hydrogens because of being adjacent to asymmetric centre. The effect is also noticed in its nickel complex, where axial hydrogen shows a doublet at δ 2.76 ppm and equatorial and unsymmetrical quartet at δ 3.01 ppm. The CH at asymmetrical centre indicates a multiplet at δ 3.32 ppm (Fig. 2). The reagents dl- $\text{H}_2\text{F}_3\text{AM}_2\text{S}$ and meso- $\text{H}_2\text{F}_3\text{AM}_2\text{S}$ indicate a doublet within δ 11.7-11.87 ppm corresponding to NH protons as compared to δ 11.04 ppm in $\text{H}_2\text{F}_3\text{AM}_2\text{en}$. Thus the NH bands shift down field in the former ligands due to phenyl groups substitution. But the ligand $\text{H}_2\text{F}_3\text{AM}_2\text{pn}$ shows a doublet at δ 10.98 and a broad band at δ 11.1 ppm each corresponding to one NH hydrogen. However the bands corresponding to NH hydrogens disappear in nickel complexes as expected [17].

The spectrophotometric studies of the reagents and metal complexes were carried out in n-hexane, chloroform, methanol and acetone (Table-III). All the reagents in n-hexane, and meso- $\text{H}_2\text{F}_3\text{AM}_2\text{S}$ and dl- $\text{H}_2\text{F}_3\text{AM}_2\text{S}$ in methanol show a band at 205 nm ($\epsilon = 1.2\text{-}2.4 \times 10^4 \text{ l.mole}^{-1}\text{cm}^{-1}$). This band is followed by a band at 258 ± 2 nm ($\epsilon = 0.81\text{-}1.4 \times 10^4$) in n-hexane, chloroform and methanol in all the reagents because of $\pi\text{-}\pi^*$ transitions in C-N, C=C and benzenoid rings [1,6,7]: These bands are found absent in acetone, may be because of masking of the transitions due to interaction of lone pair of the solvent with the π electrons of the reagents.

Fig. 2: $^1\text{H-NMR}$ of $\text{F}_3\text{AM}_2\text{pnNi}$ in CDCl_3

The next band of strong intensity in the reagents appears at 340-43nm ($\epsilon = 2.7\text{-}3.1 \times 10^4$) in chloroform, 338-40nm ($\epsilon = 2.7\text{-}3.2 \times 10^4$) in acetone and n-hexane and 335-38 nm ($\epsilon = 2.2\text{-}3.2 \times 10^4$) in methanol due to $\pi\text{-}\pi^*$ transition in $\text{C}=\text{C}-\text{C}=\text{O}$ chromophore. It may be noted that a single band is observed in the region in all the solvents, as compared to two bands for the same chromophoric group in the related ligands due to different arrangements of the rotation about the ethylene bridge [1,3,14]. It may be that the extended conjugated system because of double bond in alkyl radical is restricting the different arrangements and it changes into a band.

The copper complexes indicate a band at 210-11 nm in acetone, 205-7nm in n-hexane and meso- $\text{F}_3\text{AM}_2\text{Cu}$ and dl- $\text{F}_3\text{AM}_2\text{S}$ Cu in methanol at 205 nm and 220nm respectively. The band in chloroform is not visible due to low transparency of the solvent in the region. Similarly meso- $\text{F}_3\text{AM}_2\text{S}$ Ni, dl- $\text{F}_3\text{AM}_2\text{S}$ Ni in n-hexane and methanol and $\text{F}_3\text{AM}_2\text{pnNi}$ in methanol absorb within 207-10 nm. The copper complexes show two bands within 240-45nm and 267-70nm in chloroform, two bands in 228-255 and 265-75 nm in methanol and one to two bands within 225 nm and 238-70 nm in n-hexane. Similarly nickel complexes indicate one to two bands within 244-80 nm and 275-80nm in chloroform, two to three bands within 218-255 nm and 278 nm in methanol and one to three bands within 228-280 nm in n-hexane, but the cor-

Table 3: Spectrophotometric data of the reagent and their copper(II) and nickel(II) complexes in different solvents λ_{\max} nm (ϵ l.mole⁻¹ cm⁻¹)

Compound	n-Hexane	Methanol	Chloroform	Acetone
H ₂ F ₃ AM ₂ en	338(30000),255(11000) 205(12000)	338(27000). 260(10000)	342(28000). 257(11000)	338(27000)
F ₃ AM ₂ enCu	560(160),315(17000). 260(17000),225(15000) 207(17000)	565(180),310(22000) 265(24000) 230(sh)(4756)	558(165),315(17000) 268(18000) 240(sh)(5669)	558(157),327(23000) 210(4000)
F ₃ AM ₂ enNi	565(140),390(3400) 365(3200),315(5300) 278(12000),245(26000) 228(25000)	565(90),390(5000) 365(5000),315(8900) 278(17000),245(2800) 230(sh)(18590)	565(68),392 (2900),368(2700). 318(5100),278(11500) 248(20000)	568(83),388(14000) 363(13000) 335(14000)
H ₂ F ₃ AM ₂ pn	338(22000),258(9000) 205(10000)	338(27000) 260(100000)	242(27000) 259(9300)	338(27000)
F ₃ AM ₂ pnCu	560(200),315(21000) 260(20000),225(18000) 207(20000)	565(180),310(22000) 265(23000) 245(sh)(17053)	555(180),315(20000) 268(22000) 242(sh)(14396)	553(308),327(22000) 210(3900)
F ₃ AM ₂ pnNi	560(62),395(3500) 368(2900),315(5400) 278(12000),245(24000) 228(25000),210(sh)(32854)	565(81),390(4900) 368(4900),315(8100) 278(16000). 225(34000)	565(62),390(4100) 388(3800),318(7400) 275(8254) 245(14339)	565(40),388(9100) 365(8700),335(11000)
dl-H ₂ F ₃ AM ₂ S	338(18000),260(6200) 205(18000)	335(26000),260(11000) 205(19000)	340(31000) 260(14000)	338(23900)
dl-F ₃ AM ₂ SCu	550(210),315(24000) 270(22000),207(45000)	550(200),315(26000) 268(23000) 255(23587),220(34011)	558(168),318(19500) 270(16200) 244(12044)	558(180),327(30000) 211(5600)
dl-F ₃ AM ₂ SNi	565(73),390(5000) 365(4500),315(7200) 280(17000),208(17000)	560(75),390(7400) 368(7200),315(2300) 278(24000),255(17544) 210(33619)	565(66),392(4420) 370(3890),314(5900) 280(15000) 244(20800)	568(83),390(10300) 370(9200),335(9400)
meso-H ₂ F ₃ AM ₂ S	340(31000),258(10000) 205(24000)	338(32000),260(11000) 205(22000)	343(29000),258(8100)	340(31100)
meso-F ₃ AM ₂ SCu	640(sh)(60),560(90). 320(14000),238(8600) 225(12000),205(35000)	640(sh), (50),580(75) 315(2000),275(18000) 228(19000),205(33000)	640(sh)(62),558(105). 322(20200) 267(1800) 244(17000)	640(sh)(80) 575(180),327(30000) 211(5600)
meso-F ₃ AM ₂ SNi	580(140),390(4500) 370(4500),315(6800) 205(41000)	580(150),390(4300) 365(4800),245(24000) 218(35000),207(38000)	582(133),385(1900) 330(4600),244(10600)	579(179),385(9200) 370(9500) 335(10700)

responding bands in both copper and nickel complexes are not observed in acetone. These bands could be assigned to $\pi-\pi^*$ transitions of C-N, C=C and benzenoid chromophore groups. The observation of these bands at different position than the reagent could be due to better delocalisation of π orbitals with extended conjugation with π orbitals of alkyl radical in more planar and symmetrical metal chelate (Fig. 3).

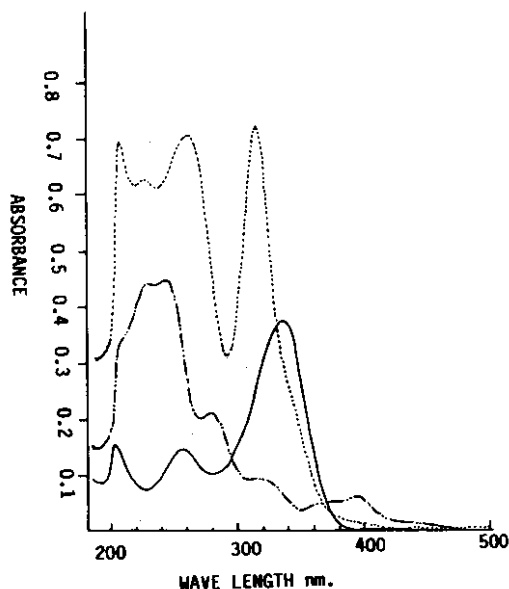


Fig. 3: Absorption spectra in n-hexane of: $H_2F_3AM_2en$; F_3AM_2enNi ; F_3AM_2enCu .

The next band in nickel and copper complexes is observed within 315-35nm, where the nickel complexes in n-hexane absorb maximally at 315 nm ($\epsilon = 3.2-7.2 \times 10^3$), but in acetone bathochromic shift to 335 nm ($\epsilon = 0.94-1.4 \times 10^4$) with increase in molar absorptivity is observed. Similarly a band observed at 315-20 nm ($\epsilon = 1.4-2.4 \times 10^4$) in copper complexes in n-hexane shifts to 327nm ($\epsilon = 2.2-3.0 \times 10^4$) with increase in molar absorptivity. The corresponding band has been observed in the spectra of the reagents at a slightly shifted position and could be assigned to $\pi-\pi$ transitions in C=C-C=O chromophore with extended double bond conjugation with alkyl radical (isobutene), as for the reagent. The increase in molar absorptivity with a bathochromic shift in acetone may be attributed to better coordination of the solvent. However it may be noted that the values of the molar absorptivity for the nickel complexes for the band are considerably lower as compared to its reagent and its copper complex.

One to two bands are observed in the spectra of the nickel complexes within 365-392 nm due to charge transfer bands as expected [3]. The values of molar absorptivities in acetone ($\epsilon = 0.9-1.4 \times 10^4$), are considerably higher than chloroform ($\epsilon = 1.9-4.4 \times 10^3$), because of the donor properties of the acetone (Fig. 4). The corresponding band in copper complexes could not be identified; but only a shoulder near 360nm in methanol is hardly visible, which might have its origin from the charge transfer from metal to ligand or ligand-metal ion [18]. Thus it may be, because of the presence of intense charge transfer band in nickel complexes, the band intensity of nickel complexes at 315-35nm is decreased.

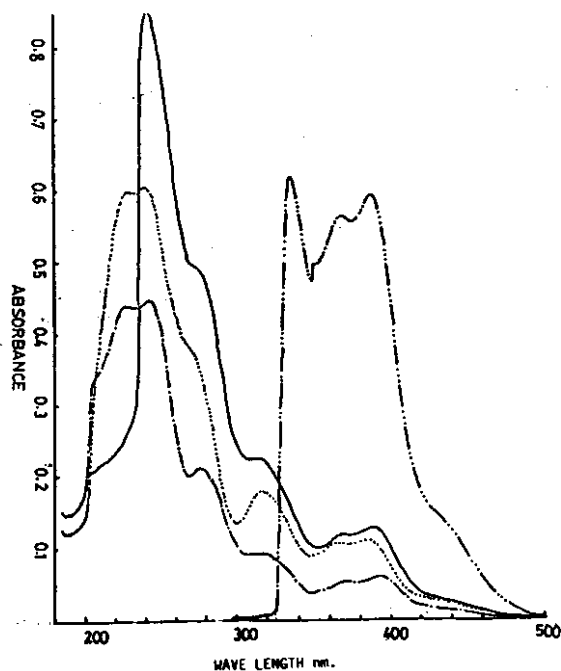


Fig. 4: Absorption spectra of F_3AM_2enNi in: chloroform _____; n-hexane _____; methanol _____; acetone _____.

The copper and nickel complexes show a band within 550-82nm with molar absorptivity within $400 \text{ l.mole}^{-1} \text{ cm}^{-1}$ due to d-d transitions. The nickel complexes show a symmetrical band, owing to the square planar configuration [1,2,15] within 560-70 nm, except a bathochromic shift of 10-20 nm is observed in the spectra of the meso- F_3AM_2SNi complex (Fig. 5). The copper complexes F_3AM_2enCu , F_3AM_2pnCu and $dl-F_3AM_2SCu$ also show a symmetrical band with spectral pattern resembling with square planar configuration observed with related compounds. However a measure of asymmetry in the spectra of meso-

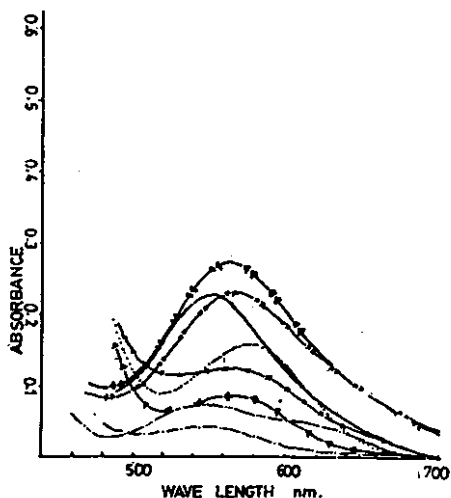


Fig. 5: Absorption spectra for d-d transition in n-hexane:
 dl- F_3AM_2SCu _____; dl- F_3AM_2SNi _____; meso-
 F_3AM_2SCu _____; meso- F_3AM_2SNi _____;
 F_3AM_2enNi x x x x F_3AM_2enCu
 xx xx F_3AM_2pnNi Δ Δ Δ Δ
 F_3AM_2pnCu ΔΔ ΔΔ

F_3AM_2SCu is observed with a shoulder of lower intensity around 640 nm. A similar observation has been reported with bis(acetylacetonemeso-stilbene)diimine copper(II) [2] and related compounds [15] and it has been suggested that a change in ligand field symmetry results from the steric hinderance between the methyl and equatorial phenyl groups. Thus the copper complex has become distorted from square planar configuration.

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