

Preparation and Spectroscopic Studies of Copper(II), Nickel(II), Palladium(II) and Oxovanadium(IV) Chelates of Fluorinated Schiff Bases

M.Y. KHUHAWAR AND ALTAF I. SOOMRO
Institute of Chemistry, University of Sindh, Jamshoro, Pakistan

(Received 25th February, 1994, revised 4th December, 1994)

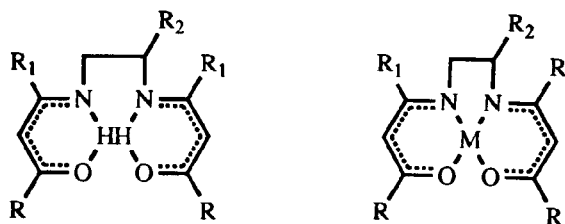
Summary: The copper(II), nickel(II) palladium(II) and oxovanadium(IV) chelates of two tetradentate Schiff bases, *N,N'*-ethylene bis(1,1,1-trifluoro-6-methyl-2-oxoheptan-4-imine) (H_2TFIVA_{2en}) and 1,2-propylenebis(1,1,1-trifluoro-6-methyl-2-oxoheptan-4-imine) (H_2TFIVA_{2pn}) have been prepared. The reagents and their metal chelates have been characterized using infrared, mass, 1H -NMR and UV/Vis spectrophotometry. The structures have been assigned to ligand and their metal chelates.

Introduction

The tetradentate β -ketoamine Schiff bases are interesting complexing reagents, because of their selective reactions towards a limited number of metal ions copper(II), nickel(II), palladium(II), platinum(II) oxovanadium(IV) and cobalt(II). The metal chelates are somewhat coloured and volatile. The reactions of the reagents towards metal ions are also quantitative [1-5]. A number of the reagents and their metal chelates have been reported and their structures have been assigned [2,3]. Recent interests in metal chelates of Schiff bases have increased because of their possible use as stationary phases for gas chromatography and as mobile phase additives in high performance liquid chromatographic separations [6-7]. In the present work two fluorosubstituted ligands and their metal chelates have been synthesized and their structure have been assigned with the aid of spectroscopic techniques.

Results and Discussion

The preparation of the reagents and their metal chelates did not encounter much difficulty. The results of element micro-analyses corresponded closely to the expected values (Fig. 1) (Table -1). The mass spectra of the reagent H_2TFIVA_{2pn} indicates the molecular ion peak M^+ (relative intensity %) at m/e 430 (4.5). The fragmentation pattern of the reagent involves the loss of $-CF_3$ with peak at m/e 361 (1.25). This is followed by the loss of fragment corresponding to $C_7H_{11}NO$ at m/e 236 (4). The major fragmentation path way involves the cleavage of the carbon-carbon bridge with the base peak at m/e 222 (100)



I = R-CF₃; R₁-(CH₃)₂CH; R₂-H
 II = R-CF₃; R₁-(CH₃)₂CH; R₂-CH₃
 M = Cu; Ni; Pd; VO

Fig. 1: Structural diagram of reagents and their metal chelates.

and at m/e 208(40). The loss of fragment corresponding to C_4H_8 from the base peak results in the observation of peak at m/e 166 (15.8). The reagent H_2TFIVA_{2en} shows a similar fragmentation pattern as observed in H_2TFIVA_{2pn} with molecular ion peak M^+ at m/e 415 (4.5) and peaks at m/e 347 (2.9) and 319 (0.75) corresponding to the loss of $-CF_3$ and $COCF_3$ respectively. This supports that $-CF_3$ groups are attached to carbonyl carbon in ligand structure. The reagent also shows diagnostic peaks at m/e 97 (19.5) and 69(47) corresponding to $-COCF_3$ and $+CF_3$ groups and confirms the assignment that $-CF_3$ are adjacent to carbonyl groups.

1H -NMR of the reagent H_2TFIVA_{2en} indicates a broad singlet at δ 11.36 ppm due to NH proton, but it disappears in its nickel and palladium chelates. A multiplet observed at δ 3.624 ppm in

Table-1: Results of elemental micro analyses

Compound	Molecular formula	M.P. °C	% Expected			% Found		
			C	H	N	C	H	N
1. H ₂ TFIVA ₂ en	C ₁₈ H ₂₆ N ₂ O ₂ F ₆	180	51.92	6.25	6.73	52.44	6.24	6.65
2. TFIVA ₂ enCu	C ₁₈ H ₂₄ N ₂ O ₂ F ₆ Cu	173	45.21	5.02	5.86	45.81	4.81	5.44
3. TFIVA ₂ enNi	C ₁₈ H ₂₄ N ₂ O ₂ F ₆ Ni	176	45.69	5.08	5.92	45.31	5.03	5.84
4. TFIVA ₂ enPd	C ₁₈ H ₂₄ N ₂ O ₂ F ₆ Pd	196	41.53	4.62	5.38	41.33	4.59	5.26
5. TFIVA ₂ enVO	C ₁₉ H ₂₄ N ₂ O ₂ F ₆ V	159	44.91	5.02	5.81	44.91	5.08	5.80
6. H ₂ TFIVA ₂ pn	C ₁₉ H ₂₂ N ₂ O ₂ F ₆	194	53.02	6.55	6.55	52.52	6.54	6.41
7. TFIVA ₂ pnCu	C ₁₉ H ₂₂ N ₂ O ₂ F ₆ Cu	120	46.39	5.33	5.69	45.92	5.40	5.62
8. TFIVA ₂ pnNi	C ₁₉ H ₂₂ N ₂ O ₂ F ₆ Ni	147	46.85	5.38	5.75	47.56	5.44	5.75
9. TFIVA ₂ pnPd	C ₁₉ H ₂₂ N ₂ O ₂ F ₆ Pd	183	42.67	4.90	5.24	42.04	4.78	5.10
10. TFIVA ₂ pnVO	C ₁₉ H ₂₂ N ₂ O ₂ F ₆ V	190	46.06	5.29	5.65	45.25	5.26	5.49

the spectrum of the reagent changed into singlet at δ 3.09 and 3.54 ppm in nickel and palladium chelates respectively. These support that a dianion of the ligands is involved in complexation. It may be noted that the singlet observed in the nickel chelates at δ 3.09 ppm is at lower values than multiplet in the spectrum of the reagent at δ 3.62 ppm but its palladium complex absorbs at δ 3.54 ppm at a comparable position as that of reagent. It may be due to the fixed configuration and small size of nickel(II), the δ ppm shifts to lower value in nickel complex, but as the size of metal in palladium(II) increases, the palladium complex absorbs at a comparable position as that of the reagent. A similar effect has been observed on the doublet present in the spectra of the reagent and its nickel and palladium chelates due to methyl groups. The reagent indicates a doublet at δ 0.985 ppm, corresponding to the number of methyl groups, shifts to a doublet at δ 0.94 and 0.97 ppm in its nickel and palladium chelates respectively [8]. A singlet observed at δ 5.35, 5.39 and 5.37 ppm in the spectra of H₂TFIVA₂en and its nickel and palladium chelates respectively due to =CH protons, are less affected due to complexation.

In the infra red (IR) of the reagents and metal chelates in the region 1700-1300 cm⁻¹ show many absorption bands of strong to medium intensity, which are important in diagnosing the compounds. The first band in reagents at 1615 cm⁻¹ could be due to hydrogen bonded C=O group, followed by at 1590 cm⁻¹ owing to C=C groups. The first band is absent in metal chelates and second shifts +10-25 cm⁻¹ positively in metal chelates. The reagents and their metal chelates show a strong band within 1190-1140 cm⁻¹ which could be assigned to C-F stretching vibrations. The IR of oxovanadium complexes have been

extensively studied [10]. In the present work comparing the IR spectra of oxovanadium complexes with the spectra of the corresponding copper(II), nickel(II) palladium(II), and the free ligand in 1020-940 cm⁻¹ region, it was possible to identify band in TFIVA₂pnVO and TFIVA₂enVO at 1000 cm⁻¹ and 940 cm⁻¹ respectively. Finally weak to medium intensity bands appear at 530, 510 and 490 cm⁻¹ in metal chelates and could be assigned to metal ligand vibrations [9].

Molecular absorption in ultraviolet (UV) and visible region of the spectrum of the reagent and metal chelates is dependent on the electronic structure and the nature of bonding in the compounds. The first band in reagent H₂TFIVA₂pn and H₂TFIVA₂en is observed at 200 nm (ϵ 41000 l mole⁻¹ cm⁻¹) and 210 nm (ϵ = 14000) respectively. The reagent H₂TFIVA₂pn shows a shoulder at 228 nm (ϵ = 3200) and a band at 272 nm (ϵ = 8900) and H₂TFIVA₂en indicates a band at 273 nm (ϵ = 31500). The bands are thought to arise from π - π^* transitions from C=C and C=N groups, but the bands observed around 270 nm might have originated from π - π^* transitions in -C=C-C=O chromophore [31,11].

A band of strong intensity appears in reagent H₂TFIVA₂en and H₂TFIVA₂pn at 336 nm (ϵ = 64500) and 335 (ϵ = 43300). The molar absorptivity values suggest that the bands arise from electronic transition π - π^* involving conjugated C=C and C=O chromophore in hydrogen bonded chelate rings [3].

The copper(II) and nickel(II) chelates in UV region show a similar pattern (Table 2) as has been observed for related compounds [3,11,12]. In visible region nickel chelates indicate two bands

Table-2: Spectrophotometric data of reagents and their metal chelates in methanol.

Compound	
1. $H_2TFIVA_{2,en}$	210(104000), 273(316000), 336(64480)
2. $H_2TFIVA_{2,pn}$	200(sh)(41100), 228(sh) (31570), 272 (88730), 335 (43300).
3. $TFIVA_{2,en}Cu$	209(29600), 231(26600), 270(33200), 300 (34700), 322 (sh) (6400), 570 (132).
4. $TFIVA_{2,pn}Cu$	233 (14400), 271 (16500), 303 (21400), 382 (sh) (651), 565 (112).
5. $TFIVA_{2,en}Ni$	226(31800), 245(sh) (13700), 270 (11800), 310 (4800), 358 (3150), 383 (2840), 460 (sh) (289), 570 (79).
6. $TFIVA_{2,pn}Ni$	226(47800), 244 (sh) (23500), 267 (15800), 310 (5700), 360 (4580), 380 (4290), 430 (400) 560 (126).
7. $TFIVA_{2,en}Pd$	213(27000), 253 (9900), 340 (6708)
8. $TFIVA_{2,pn}Pd$	216(99800), 290(sh) (29000), 334 (13800) 415 (sh) (451).
9. $TFIVA_{2,en}VO$	209(21000), 308(1097), 530(76), 720(50)
10. $TFIVA_{2,pn}VO$	215(6300), 310(14200), 537(66), 715 (39)

within 358-383 nm and a shoulder within 430-460 nm. The bands may be assigned to charge transfer involving both nickel atom and the reagent. Similar bands do not appear in copper chelates, but a shoulder in $TFIVA_{2,pn}Cu$ appears at 382 nm ($\epsilon=650$) which might have an origin from charge transfer band [13].

The electronic spectra of copper and nickel chelates show an absorption of weak intensity between 560-70 nm. The band arise from d orbitals of nickel and copper chelates and have square planar structure exhibiting single absorption band. This is in agreement with the findings of Kanatomi *et al.* [12].

The palladium chelates $TFIVA_{2,en}Pd$ and $TFIVA_{2,pn}Pd$ indicate two bands in UV region due to intraligand $\pi - \pi^*$ transition, but characteristic band $TFIVA_{2,en}Pd$ indicates at 340 nm ($\epsilon =6770$) and $TFIVA_{2,pn}Pd$ at 334 nm ($\epsilon =13800$) and a shoulder at 415 nm ($\epsilon =451$). Since these bands appear close to the charge transfer bands observed in nickel chelates. Therefore they might arise from charge transfer transitions.

The oxovanadium chelates also show two bands in UV region due to intra ligand $\pi-\pi^*$ transitions, but charge transfer bands as observed in nickel and palladium chelates are not visible in oxovanadium chelates, may be they are masked by intra ligand excitations. Two characteristic bands of low intensity are observed within 530-720 nm ($\epsilon =40- 80$) which may be due to d-d transitions of d^1 oxovanadium(IV) system [15,16].

Experimental

Preparation of N,N-ethylenebis(1,1,1-trifluoro-6-methyl-2-oxoheptan-4-imine)[Bis(trifluoro-isovaleryl-acetone) ethylenediimine] ($H_2TFIVA_{2,en}$).

To the ice cooled solution of 1,1,1-trifluoro-6-methyl-heptane-2,4-dione(4.5 cm³, 0.025 mole) in ethanol (10 ml) was added cooled 1,2-diaminoethane (0.8 ml, 0.012 mole). The mixture was refluxed on water bath for 15 min. and the contents were left at -10°C for 24 hrs. The solid mass was separated, washed with petroleum ether (40-60°C) and recrystallized from methanol.

Preparation of N,N'-1,2-Propylenebis(1,1,1-trifluoro-6-methyl-2-oxoheptan-2,4-imine) [Bis (trifluoroisovaleryacetone) propylenediimine] ($H_2TFIVA_{2,pn}$).

To the ice cooled ethanolic solution of 1,1,1-trifluoro-6-methyl-heptane-2,4-dione (4.5 ml, 0.025 mole) was added cooled 1,2-diaminopropane (1.02 ml, 0.012 mole) slowly. The contents were then warmed at 50°C for 15 min. and left at -10°C for 12 hrs. The solid mass separated from yellow liquid was washed with *n*-hexane. The product was recrystallized from methanol.

Preparation of Copper(II) and Nickel(II) Chelates

An ethanolic solution of reagent (0.001 mole) was refluxed with methanolic solution of copper(II) acetate (0.001 mole) or nickel(II) acetate (0.001 mole) for 30 min. The solution was concentrated to about half the volume and cooled at -10°C overnight. The precipitate was filtered and recrystallized from *n*-hexane.

Preparation of Palladium(II) Chelates

Palladium(II) chloride (0.0005 mole) and benzonitrile (0.2 ml) refluxed together and palladium benzonitrile adduct formed was diluted with benzene (4 ml). The ligand (0.0005 mole) in benzene was slowly added and the reaction mixture was refluxed for 12 hrs. The benzene was removed by distillation and remaining solvent was evaporated by vacuum desicator. The palladium complex was extracted by *n*-hexane. The yellow product was recrystallized from *n*-hexane.

Preparation of oxovanadium complex

Solid reagent (0.005 mole) and bis(pentane-2,4-dionato)oxovanadium (0.005 mole) were mixed

and heated together at 140-150°C for 1 hr. The product was washed with ether and recrystallized from *n*-hexane.

The elemental micro-analysis were carried out by Elemental Micro-Analysis Ltd. Deven, U.K. Mass spectra of the reagents and ¹H-NMR of reagents, nickel and palladium chelates were recorded at HEJ Research Institute of Chemistry, University of Karachi. IR of the compounds were recorded on Perkin-Elmer 1430 IR spectrophotometer using KBr pellet technique in the range of 4000-200 cm⁻¹. Spectrophotometric studies were carried out on Hitachi 220 spectrophotometer.

Acknowledgement

Pakistan Science Foundation Islamabad acknowledged for financially supporting the project.

References

1. P.C. Uden and D.E. Henderson, *Analyst* **102**, 889 (1977).
2. P.C. Uden, *J. Chromatogr.*, **313**, 3 (1984).
3. M.Y. Khuhawar and A.G.M. Vasandani, *J. Chem. Soc. Pak.*, **10**, 213 (1988).
4. S. Dilli, A.M. Maitra and E. Patsalides, *Inorg. Chem.*, **21**, 2832 (1982).
5. A. Khaliq, W.I. Stephen, D.E. Henderson and P.C. Uden, *Anal. Chim. Acta*, **101**, 117 (1978).
6. J. Muslowska and G. Bazylak, *Collect. Czech. Chem. Commun.*, **54**, 1530 (1989).
7. G. Bazylak, *Analyst*, **117**, 1429 (1992).
8. M.Y. Khuhawar and A.K. Talpur, *J. Chem. Soc. Pak.*, **12**, 236 (1990).
9. K. Ueno and A.E. Martell, *J. Phys. Chem.*, **59**, 998 (1955).
10. K. Ramaiah and D.F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 1663 (1965).
11. B. Bosnish, *J. Am. Chem. Soc.*, **90**, 627 (1968).
12. R.S. Downing and F.L. Urbuch, *J. Am. Chem. Soc.*, **91**, 5977 (1966).
13. A.C. Braithwaite, F.E. Wright and T.N. Walters, *J. Inorg. Nucl. Chem.*, **37**, 1669 (1975).
14. H. Kanatomi, I. Murase and A.E. Martell, *J. Inorg. Nucl. Chem.*, **38**, 1465 (1976).
15. A. Pasini and M. Gullotti, *J. Coord. Chem.*, **3**, 319 (1974).
16. L.J. Boucher, E.C. Tynan, T.F. Yen, *Inorg. Chem.*, **7**, 2665 (1968).