Comparative Gas Chromatographic Elution of Copper and Nickel Complexes of some Fluorinated Tetradentate Ketoamines

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Summary: Copper(II) and nickel(II) complexes of new tetradentate Schiff base bis(trifluoroacetylacetone)phenylethylenediimine (TFA_2PE) have been prepared and characterized using IR, ^{1}H-NMR and mass spectroscopic techniques. The metal complexes are studied spectrophotometrically and their thermal stabilities are checked using TG and DTA. The complexes, together with the copper and nickel complexes of bis(trifluoroacetylacetone)ethylenediimine (TFA_2en), bis(trifluoroacetylacetone)propylenediimine (TFA_2Pn), bis(trifluoroacetylacetone)dl-stilbenediimine (dl-TFA_2S) and bis-(trifluoroacetylacetone)meso-stilbenediimine (meso-TFA_2S) have been eluted on gas chromatographic columns with OV101, OV-17 and Dexil 400 GC and the effect of methyl and phenyl groups substitution on the elution of the copper and nickel complexes is established. The methyl group substitution is decreasing the retention time and phenyl group substitution at bridge position is increasing the retention times of both copper and nickel complexes, but the complexes maintain characteristic stability and elutes as symmetrical peaks.

Introduction

The fluorinated ligands bis(trifluoroacetylacetone)ethylenediimine (TFA_2en) and bis(trifluoroacetylacetone)propylenediimine (TFA_2Pn) have been extensively studied as gas chromatographic reagents for copper, nickel and palladium [1-5]. Recently Khuhawar has reported the thermal stability and gas chromatographic elution of copper and nickel complexes of meso-and dl-bis(trifluoroacetylacetone)stilbenediimine(meso-TFA_2S., dl-TFA_2S) [6]. In the presence work copper and nickel complexes of TFA_2PE have been prepared and characterized and their GLC elution have been compared with existing similar fluorinated ligands.

Experimental

Elemental micro-analysis was carried out by Elemental Micro-Analysis Ltd., U.K. ^{1}H-NMR spectrum was recorded on Jeol FX100 in $CDCl_3$ at PINSTECH, Islamabad. Mass spectrum was recorded by HEJ Research Institute of Chemistry, University of Karachi.

Spectrophotometric studies were carried out on Hitachi 220-Spectrophotometer, and IR on Hitachi 230-10 IR

Spectrophotometer in the range of 4000-250 cm^{-1} using KBr technique. TG and DTA was carried out on Shimadzu TG 30 Thermal Analyser using heating rate of 15°C/min between 25-500°C and nitrogen flow rate of 50 cm^3/min.

GC was carried out on Hitachi 163 Gas Chromatograph equipped with flame ionization detector. Stainless steel columns 2mx3mm packed with OV101, 3%, OV17, 3% and OV17 + QF_1, 1.5 + 1.95% on Chromosorb WHP 80-100 mesh size and 3mx3mm column packed with Dexil 400 GC, 2%, on Uniport HP 60-80 mesh size were used.

Preparation of the Reagents

The reagents and copper and nickel complexes of bis(trifluoroacetylacetone)ethylenediimine(TFA_2en), bis (trifluoroacetylacetone)-propylenediimine(TFA_2Pn), bis(trifluoroacetylacetone)dl-stilbenediimine(dl-TFA_2S) and bis(trifluoroacetylacetone) meso-stilbenediimine (meso-TFA_2S) were prepared by the reported methods [1,2,6]. 1-Phenylethylenediamine dihydrochloride was prepared by the reduction of phenylglyoxime using procedure reported by Bernth and Larsen [7].

Bis(trifluoroacetylacetone)phenylethylenediimine(TFA_2PE).

Phenylethylenediamine dihydrochloride (0.01mole) dissolved in water was neutralized with ammonia. The extract of the diamine in chloroform was dried over anhydrous sodium sulphate and added to the solution of trifluoroacetylacetone (0.02mole) in ethanol. The mixture was refluxed for 30 minute and the solution was concentrated to about 4-5 ml and remaining solvent was removed at room temperature at reduced pressure. The solid so obtained was recrystallized twice from ethanol m.p. 140°C. MS, (m/e (rel intensity) 408 (M^+, 0.22), 389 (0.27), 339 (1), 243 (36), 242 (100); ^{1}H-NMR ($CDCl_3$) 2.044 and 2.068 (2-CH_3), 3.55 (d) (-CH_2 bridge), 3.95 (m) (-CH bridge), 5.34 and 5.37 (2, =CH-), 7.26 (C_6H_5) 11.24 (2-NH). IR (KBr cm^{-1}) 3200(w), 3125(w) 1620(bs) 1580 (m) 1460m)., Anal. Calcd. for $C_{18}H_{18}N_2O_2F_6$:C, 52.92; H, 4.41; N, 6.86; Found C, 53.14; H, 5.00; N, 7.00.

Metal Complexes

Equimolar solution of copper(II) acetate or nickel(II) acetate dissolved in methanol was added to solution of TFA_2PE in methanol. The mixture was refluxed for 30 minutes and was concentrated and cooled. The precipitate was filtered and recrystallised twice from methanol. TFA_2PE Cu, m.p. 200°C. IR (KBr cm^{-1}) 1627(s), 1585 (w), 1545(s), 1485(s) 660(w), 470(m), Anal.Cacld. $C_{18}H_{16}N_2O_2F_6Cu$: C, 46.00; H, 3.40; N, 5.96; Found C, 46.26; H, 3.50; N, 6.03. TFA_2PE. Ni m.p. 230 IR (KBr cm^{-1}) 1620(s), 1530(s), 1480(s), 620(m), 480(m). $C_{18}H_{16}N_2O_2F_6Ni$: C, 46.48; H, 3.44; N, 6.02; Found C, 46.64; H, 3.04; N, 5.97.

Results and Discussion

The IR spectra of the reagent TFA_2PE and its copper and nickel complexes are identical to these reported for related compounds [6]. The mass

Table-1: Spectrophotometric Data of TFA_2PE and its Copper and Nickel Complexes in Acetone.

Metal ion	λ_{max} nm	ε $mole^{-1}cm^{-1}$
-	332	$1.9x10^4$
	211	$4.1x10^3$
Cu(II)	560	140
	326	$4.4x10^3$
	212	$4.8x10^3$
Ni(II)	562	64
	377	$1.9x10^3$
	333	$1.16x10^4$
	211	$2.6x10^3$

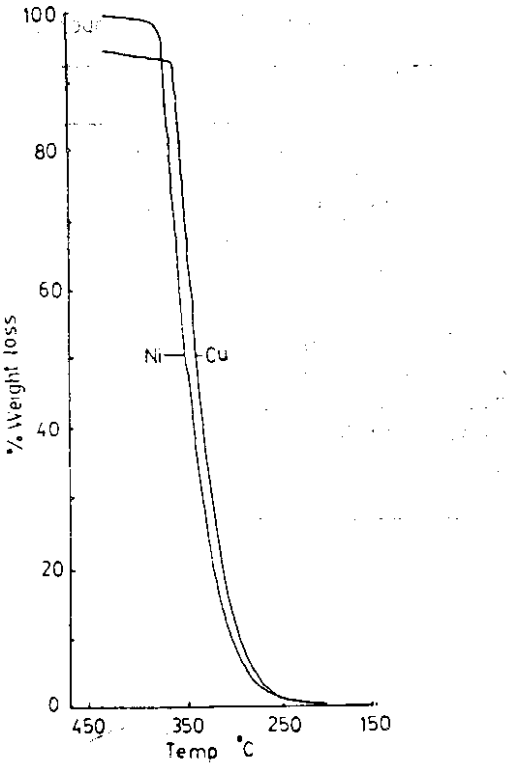

Fig.1: TG of Copper(II) and Nickel(II) complexes of TFA_2PE at a heating rate of 15°C/min and N_2 flow rate of 50°C cm^3/min.

spectrum of the reagent shows weak molecular ion peak at m/z 408 due to easy loss of the fragments and follow major fragmentation path due to the rupture of the C-C bond at the bridge position with a base peak m/z 242 (100%) [2]. The ^1H-NMR of the reagent shows two singlets at δ 2.044 and 2.068 ppm corresponding to two methyl groups and two singlets at δ 5.34 and 5.37 ppm due to the two =CH hydrogen owing to asymmetrical phenyl substitution at bridge position. A broad unresolved band, corresponding to two hydrogen atoms, observed at 11.27 ppm, is assigned to hydrogen bonded NH.....O group. The spectrophotometric studies (Table I) indicate that copper and nickel complexes shows a weak band in visible region at 560-562 nm due to d-d transitions. The nickel complex also show a band at 377 nm with a molar absorptivity of $1.9x10^3$ 1 $mole^{-1}$ cm^{-1} due to the charge transfer band. TG and DTA of the copper and nickel complexes shows that they are somewhat volatile with loss in weight of 94-100% by the temperature 355°C (Table II).

When copper(II) and nickel(II) complexes of TFA_2PE were injected on the column with OV101,3% on Chromosorb, at a column temperature of 250°C, injection port 270°C and nitrogen flow rate of 30cm^{-3}/min, symmetrical peaks were obtained. However, when a mixture of copper and nickel complexes was injected at the optimized conditions, no separation between the two complexes was achieved. Different

Table-II: DTA and TGA of the Copper and Nickel Complexes of TFA_2^{PE}

Copper(II) Complex	Ni(II) Complex
Sample 8.2 mg, loss in weight starts at 228°C and loss of 94% by 345°C, leaves residue about 6%, maximum rate of loss by 332.	Sample 12mg. loss in weight starts at 240°C and loss of 100% by 355°C. Maximum rate of loss 320°C.
DTA show melting endotherm at 207°C, followed vaporization endotherm at 332 and exotherm at 341, 360 and 375°C.	DTA shows melting endotherm at 223°C followed by vaporization endotherm at 350°C.

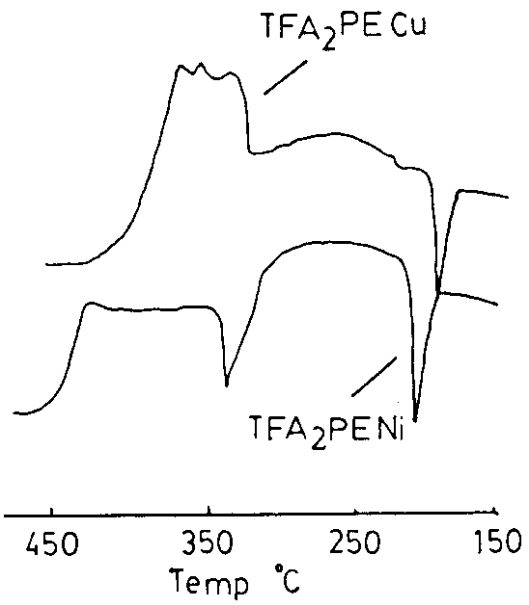

Fig.2: DTA of copper and nickel complexes.

conditions of the column temperature, nitrogen flow rate and column with OV17.3%, OV17,+QF_1, 1.5 + 1.95% on Chromosorb 80-100 and Dexil 400 GC, 2% on Uniport 60-80 did not cause much effect on the peak separation.

In order to confirm if the response of the detector was linear with the amount of the complex injected, varying amount of copper and nickel complexes were injected and average peak height of atleast two injections was measured and linear calibration curve in the range of 0.20-1.2ug of copper or nickel (complex) corresponding to 27-162 ng of copper and 25-150 ng of nickel was obtained. The detection limits atleast twice the background noice, were in the range of 40ng of copper or nickel complex, corresponding to 5.4ng of copper and 5.0ng of nickel. The detection limits of the copper and nickel complexes were compared with those of TFA_2en to evaluate the effect of phenyl substitution at the bridge position. The detection limits of copper and nickel complexes of TFA_2en were found to be 40ng complex, corresponding to 6.45 ng of copper and 6.04ng of nickel.

However, when a mixture of copper or nickel complexes of TFA_2Pn, TFA_2en, TFA_2PE, dl-TFA_2S, meso TFA_2S were injected on a column with OV101 or OV17(2mx3mm) at a column temperature of 210°C with a rate of increase in temperature of 2°C upto

Table-III: Comparative GC elution of copper(II) and nickel(II) complexes a nitrogen flow rate of 30 cm^3/min.

Column	Column temp	Metal Ion	TFA_2Pn	TFA_2en	TFA_2PE	dl-TFA_2S	meso-TFA_2S
OV101,3% on chromosorb WHP 80-100 (2mx3mm)	210° with rate of rise in temp 2° C/min upto 260°C	Cu	4.83	6.58	10.92	14.42	19.92
		Ni	4.92	6.58	10.75	14.50	19.75
Dexil GC 400 2% on Uniport 60-80 3mx3mm	260°C with the rate of increase of temp 2°C/min. upto 290°C	Cu	6.20	8.30	11.25	12.0	19.0
		Ni	6.20	8.35	11.17	12.0	19.00
OV-17,3% on Chromosorb WHP 80-100 2mx3mm.	Isothermal temperature of 270°C	Cu	2.00	2.83	4.92	6.50	11.66
		Ni	2.00	3.00	5.83	6.92	11.92

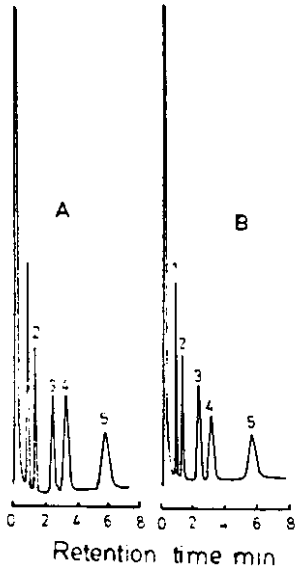

Fig.3: Chromatographic separation of (A) Nickel complexes (B) Copper complexes (1) TFA_2Pn (2) TFA_2en (3) TFA_2PE (4) dl-TFA_2S. (5) meso-TFA_2S.

Stainless steel column (2mx3mm), packed with OV17 on Chromsorb WHP 80-100, column temperature 270°C, injection port 290°C, N_2 flow rate 30 cm^3/min.

260°C, complete separation of copper or nickel complexes of all the five ligands was achieved where metal complexes of TFA_2Pn eluted first and meso-TFA_2S, the last. When the column with Dexil 400GC 2% on Uniport 60-80 (3mx3mm) was used and the complexes were injected at 260°C with a programmed rise in temperature of 2°C/min upto 290°C with a nitrogen flow rate of 30 cm^3/min, same order of elution was observed with an improved resolution between metal complexes, of TFA_2Pn & TFA_2en, but a decrease in resolution of TFA_2PE and dl-TFA_2S. Thus the liquid phase OV17 on Chromosorb proves satisfactory for the optimal separation of metal complexes of all the five ligands using isothermal or programmed temperature elution of the complex. It is reasonable to confirm from the data (Table III) that methyl group substitution at bridge position is decreasing the retention time of both copper and nickel

complexes, but the phenyl group substitution at the bridge position is increasing the retention time of both copper and nickel complexes, with the result that diphenyl-substituted ligands dl-TFA_2S and meso-TFA_2S show longer retention time, then single phenyl-substituted ligand TFA_2PE, irrespective of column and operating parameters.

Conclusion

The copper and nickel complexes of new ligand TFA_2PE could be eluted in the gas chromatographic column with detection limits comparable to TFA_2en. The copper or nickel complexes of the five flourinated ligands have been separated and the order of elution has been confirmed on different columns. The work support that the phenyl group substitution at bridge position is increasing the retention time of the metal complexes, but the complexes maintain their characteristic thermal stability and gas chromatographic elution.

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