

Chromatographic Separations of Copper(II), Nickel(II) and Palladium(II) Chelates of Tetradentate Schiff Bases Derived from 5-Methylhexane-2,4-dione and 1,1,1-Trifluoro-5-methylhexane-2,4-dione

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Summary: The copper(II), nickel(II) and palladium(II) chelates of the ligands bis(isopropanoyl-acetone)-ethylenediimine (H₂PA₂en) bis(trifluoroisopropanoyl-acetone)ethylenediimine (H₂F₃PA₂en) and bis(trifluoroisopropanoylacetone)propylenediimine (H₂F₃PA₂pn) were prepared. The results of our thermoanalytical studies indicated that the complexes were sufficiently volatile and could elute from the gas chromatographic columns. Adequate separation of palladium from copper and nickel complexes of H₂PA₂en were obtained on a gas chromatographic column (3m x 3mm) packed with OV101, 3% on Chromosorb WHP 80-100 mesh size. However, complete separation between copper, nickel and palladium complexes was achieved on HPLC column (200 x 4.6 mm) Si 100, 5 μ . The complexes were eluted with binary or ternary mixtures of chloroform, 1,2-dichloroethane and n-hexane. The detection by UV of each of the metal chelate was obtained at the ng levels.

Introduction

The tetradentate Schiff base ligands are unique complexing reagents, because of their selective reactions towards a limited number of metal ions, copper(II), nickel(II), cobalt(II), palladium(II), oxovanadium(IV) and iron(II) [1-3]. The neutral and monomeric complexes of copper(II), nickel(II), palladium(II) and oxovanadium(IV) are sufficiently volatile and thermally stable at high temperatures and elute from the gas chromatographic (GC) columns at normal conditions (below 300°C). Therefore quantitative separations for simultaneous determinations of metal ions at trace levels are possible [4-7]. The reagents are also interesting for high performance liquid chromatographic (HPLC) separation and determination of metal ions, because of the ease of separation of their metal complexes on normal as well as reversed phase HPLC column [7-9]. It was therefore considered useful to prepare the copper, nickel and palladium chelates of the ligands bis(isopropanoylacetone)ethylenediimine (H₂PA₂en), bis(trifluoroisopropanoylacetone)ethylenediimine (H₂F₃PA₂en) and bis(trifluoroisopropanoylacetone)propylenediimine (H₂F₃PA₂pn), derived from the β -diketones 5-methylhexane-2,4-dione and 1,1,1-trifluoro-5-methylhexane-2,4-dione to investigate their potentials for the separation of metal ions using GC and HPLC.

Results and Discussion

The results of elemental analysis (Table 1 and Fig. 1) agree with the expected values. TGA of copper, nickel and palladium chelates of H₂PA₂en (Fig. 2) indicate the loss of 90%, 93% and 95% weight in the temperature ranges of 190-310°C, 190-310°C and 220-370°C, with maximum rate of loss at 280°C, 290°C and 360°C for PA₂enCu, PA₂enNi and PA₂enpd, respectively. This data indicates that copper complex is more volatile than corresponding nickel and palladium complexes.

The copper, nickel and palladium complexes of H₂F₃PA₂en lose 97% weight between 220-270°C, 220-380°C and 175-380°C respectively. The metal complexes of the fluorinated ligand H₂F₃PA₂en are slightly more thermally stable and leave less residue (3%) than corresponding nonfluorinated ligand H₂PA₂en, which leave a 5-10% residue. But in the case of the copper and nickel chelates of the fluorinated ligand H₂F₃PA₂en a loss in weight occurs at higher temperature (220-380°C) than with the nonfluorinated ligand H₂PA₂en (190-310°C). It is therefore suggested that the copper and nickel complexes of nonfluorinated ligand H₂PA₂en are more volatile than the fluorinated ligand H₂F₃PA₂en. Similar results have been reported by Belcher *et al.* [12] and Uden *et al.* [13] with

Table 1: Results of elemental microanalyses

Sr. No.	Name of the Compound	Molecular formula	Melting point °C	Calculated %			Found %		
				C	H	N	C	H	N
1.	H ₂ F ₃ PA ₂ en	C ₁₆ H ₂₂ N ₂ O ₂ F ₆	171	49.48	5.67	7.21	49.51	5.68	7.40
2.	H ₂ F ₃ PA ₂ Pn	C ₁₇ H ₂₄ N ₂ O ₂ F ₆	205	50.74	5.97	6.96	50.69	5.84	7.05
3.	PA ₂ enPd	C ₁₆ H ₂₆ N ₂ O ₂ Pd	220	49.74	7.25	7.25	49.98	6.69	7.22
4.	F ₃ PA ₂ enCu	C ₁₆ H ₂₀ N ₂ O ₂ F ₆ Cu	190	42.76	4.89	6.23	43.16	4.78	6.37
5.	F ₃ PA ₂ enNi	C ₁₆ H ₂₀ N ₂ O ₂ F ₆ Ni	210	43.17	4.95	6.36	43.16	4.60	6.28
6.	F ₃ PA ₂ enPd	C ₁₆ H ₂₀ N ₂ O ₂ F ₆ Pd	240	39.02	4.47	5.69	38.87	4.09	5.61
7.	F ₃ PA ₂ PnCu	C ₁₇ H ₂₂ N ₂ O ₂ F ₆ Cu	170	43.87	5.16	6.02	42.69	4.39	5.67
8.	F ₃ PA ₂ PnNi	C ₁₇ H ₂₂ N ₂ O ₂ F ₆ Ni	160	44.27	5.20	6.07	45.25	4.80	6.05
9.	F ₃ PA ₂ PnPd	C ₁₇ H ₂₂ N ₂ O ₂ F ₆ Pd	240	40.15	4.72	5.51	39.27	3.06	5.42

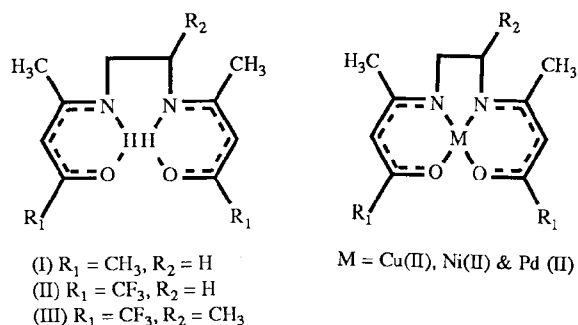
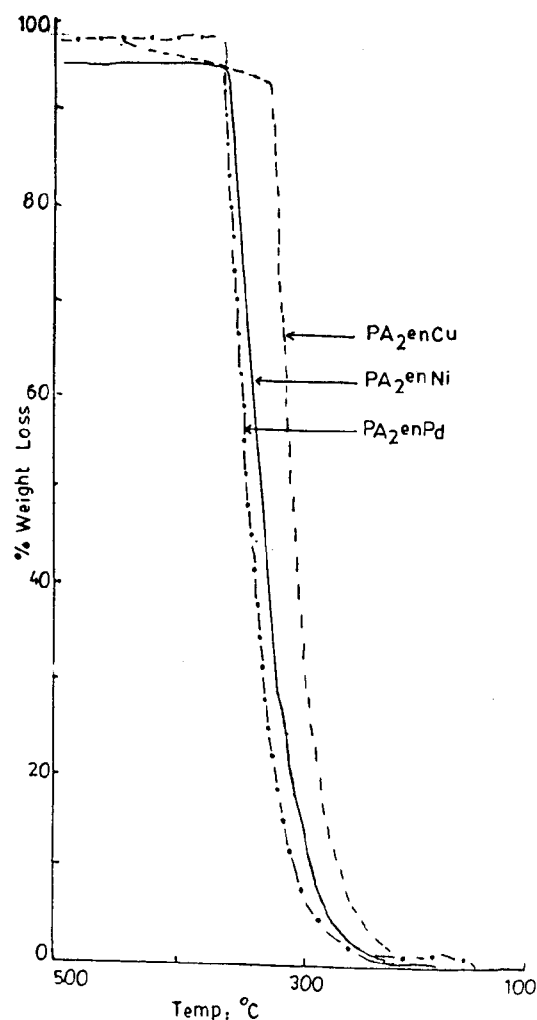


Fig. 1: Structural diagrams of reagent and their metal chelates.

fluorinated and nonfluorinated complexes of related compounds.

When a methyl group is introduced in H₂F₃PA₂pn at bridge position to form ligand H₂F₃PA₂en, its copper, nickel and palladium complexes, indicate a similar thermal stability, with loss in weight of 95-98% as that of H₂F₃PA₂en, but loss in weight in its copper and nickel complexes occur at slightly lower temperature (210- 360°C) than (H₂F₃PA₂en) (220-380°C). It is therefore suggested that introduction of methyl group at bridge position improve the volatility of copper and nickel complexes.

DTA of metal complexes of H₂PA₂en, H₂F₃PA₂en and H₂F₃PA₂pn indicate endotherms, corresponding to their melting points, followed by a series of vaporization/decomposition endotherms and exotherms (Fig. 3).

Fig. 2: TGA of copper(II), nickel(II) and palladium(II) chelates of H₂PA₂en at a heating rate 15°C/min and nitrogen flow rate 50 cm³/min.

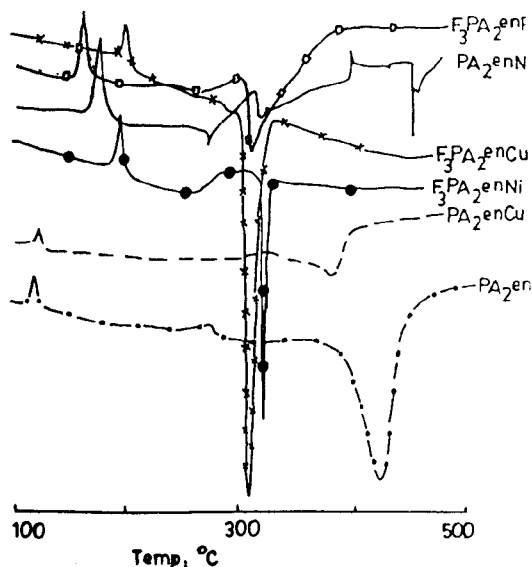


Fig. 3: DTA curves of copper(II), nickel(II) and palladium(II) chelates of H_2PA_2en and $H_2F_3PA_2en$.

Thus the thermo-analytical studies indicate that the complexes are sufficiently stable for gas chromatographic elution of metal chelates. All the metal complexes easily eluted on the GC columns between 220-265°C, injection port 240-270°C and nitrogen flow rate of 30 cm³/min., giving symmetrical peaks with base line return. When attempt was made for the separation of copper, nickel and palladium chelates of fluorinated ligands $H_2F_3PA_2en$ and $H_2F_3PA_2pn$, the separation of palladium from copper and nickel was easily achieved (Fig. 4) on the GC columns (2m x 3mm) or (3m x 3mm) packed with OV101, 3% or OV17, 3% on Chromosorb WHP 80-100 mesh size and Dexil GC 400, 2% on Uniport HP 60-80 mesh size, but without any separation between copper and nickel complexes of the same ligand. The temperature of column, injection port and nitrogen flow rate was changed without much success in the resolution of the copper and nickel complexes. However, some partial separation between copper and nickel complexes of H_2PA_2en was obtained with the retention time of 5-50, 6-40 and 9-40 min for PA_2enCu , PA_2enNi and PA_2enPd , respectively with resolution of 0.88 between copper and nickel (Fig. 5).

The linear calibration curves of all the complexes were found within 1-7 μg of a complex, and

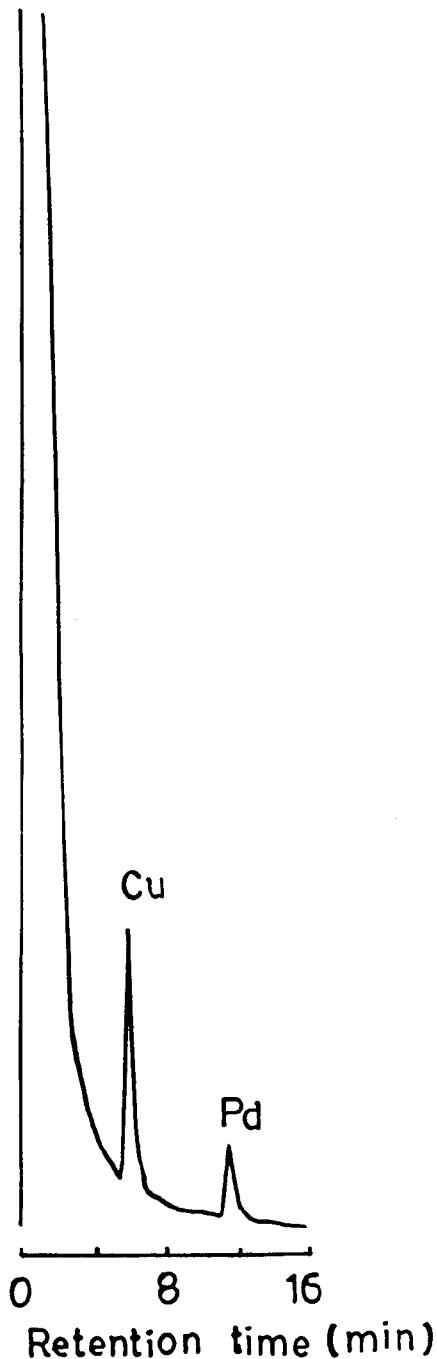


Fig. 4: GC separation of copper(II) and palladium(II) chelates of $H_2F_3PA_2pn$ on column (2m x 3 mm) packed with OV17, 3% on chromosorb WHP 80-100 mesh size, temperature column 270°C injection port 280°C and nitrogen flow rate 30 cm³/min.

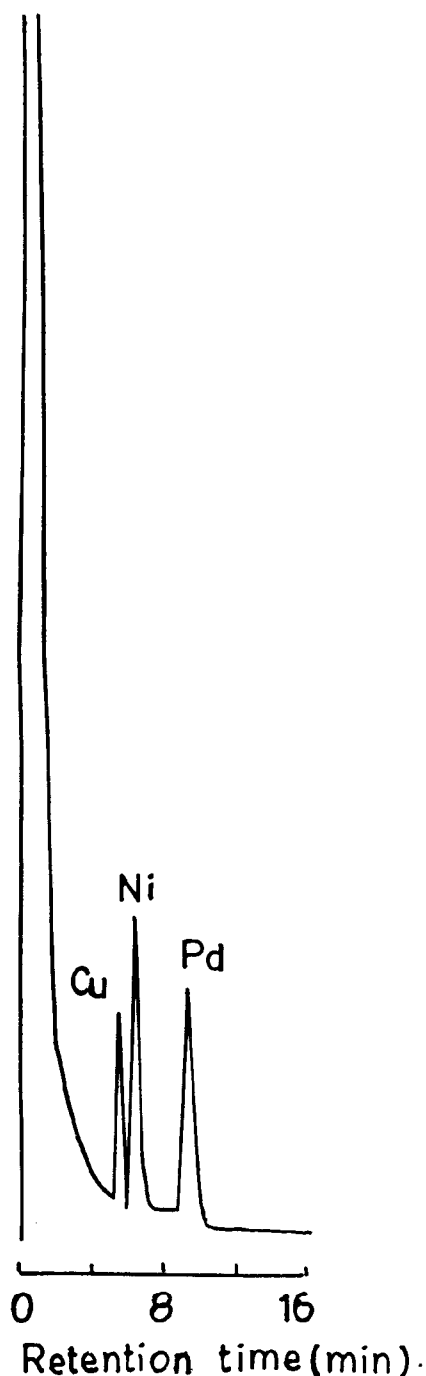


Fig. 5: GC separation of copper(II), nickel(II) and palladium(II) chelates of H_2PA_{2en} . Column (3m x 3mm) packed with OV101, 3% on chromosorb WHP 80-100 mesh size temperature column $250^\circ C$, injection port $270^\circ C$ and nitrogen flow rate $30\text{ cm}^3/\text{min}$.

approximate detection limit between 50-100 ng for each complex.

The complexes easily eluted from the GC columns to give the symmetrical peaks, but incomplete or no separation between copper and nickel complexes led to investigate normal phase HPLC for their possible separations. The spectrophotometric studies of all the metal chelates were carried out to select suitable wavelength for the UV detection of metal chelates. The results of spectrophotometric studies in chloroform are summarized in Table 2. The complexes indicate a number of high intensity $\pi-\pi^*$ transitions in UV region, which could be used for the spectrophotometric detection of metal complexes.

Table 2: Spectrophotometric data of reagents and their metal chelates in chloroform

Compound	$\lambda\text{-max}$ ($\epsilon\text{-l.mol}^{-1}\text{cm}^{-1}$)
(1) H_2PA_{2en}	321(27700)
(2) $PA_{2en}Cu$	242(6600), 313 (18100), 313 (18100), 372 (750), 545(214)
(3) $PA_{2en}Ni$	245(25100), 269(9600), 313(3500), 376(6200), 560(110).
(4) $PA_{2en}Pd$	241(3400), 347(8040)
(5) $H_2F_3PA_{2en}$	326(27500), 335(29500)
(6) $F_3PA_{2en}Cu$	242(7720), 275 (7270), 308 (13450), 380 (440), 550 (106).
(7) $F_3PA_{2en}Ni$	243(18770), 270(11750), 305 (4080) 368(2940) (sh), 383 (3050), 576(82).
(8) $H_2F_3PA_{2Pn}Cu$	325(30000), 335(32000)
(9) F_3PA_{2Pn}	277(52600), 304(37400), 555 (83).
(10) $F_3PA_{2Pn}Ni$	245(16100), 273 (11600), 322 (10400), 355(10200), 362 (3700), 384 (3680) 560 (61)
(11) $F_3PA_{2Pn}Pd$	272(24000), 348 (11000).

The separation of copper, nickel and palladium complexes was carried out on column (200 x 4.6 mm) Si, 100, 5μ . The detection was achieved using a UV detector fixed at 298 nm. The complexes eluted as symmetrical peaks, with a binary mixture of chloroform: n-hexane. The copper, nickel and palladium complexes of $H_2F_3PA_{2pn}$ separated completely when eluted with a binary mixture of 20% chloroform in n-hexane, with elution of nickel, followed by copper and palladium (Fig. 6a). The retention volumes calculated for nickel, copper and palladium were 8.8, 11.68 and 13.36 cm^3 using flow rate of $1.6\text{ cm}^3/\text{min}$. The separation between copper, nickel and palladium

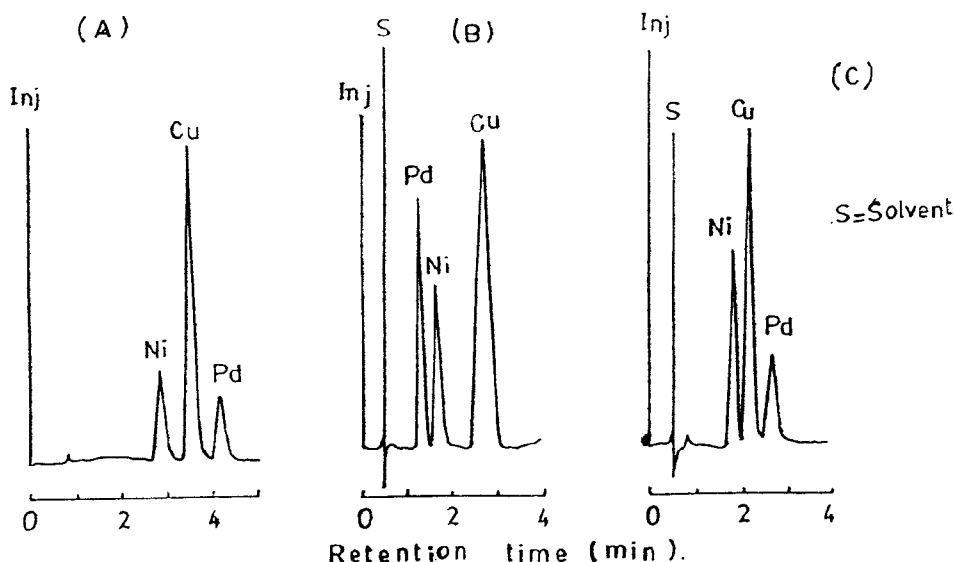


Fig. 6: HPLC separation of copper, nickel and palladium chelates of (A) $H_2F_3PA_2pn$ (B) $H_2F_3PA_2en$ (C) H_2PA_2en . Column (200x4.6 mm) Si, 100 μ . Eluent (A) Chloroform: n-hexane (20:80), flow rate 1.6 cm^3/min (B) 1,2-dichloroethane: n-hexane (52:48), flow rate 2.5 cm^3/min . (C) Chloroform:1,2-dichloroethane: n-hexane (10.3:6.9:72.7) flow rate 2.5 cm^3/min . Detection UV at 298 nm.

complexes of $H_2F_3PA_2en$ was achieved when complexes were eluted isocratically with 52% 1,2-dichloroethane in n-hexane, with slight different order of elution. The palladium eluted first, followed by a nickel and copper complexes (Fig. 6b). The observed retention volumes were 5.87, 7.75 and 11.25 cm^3 using flow rate of 2.5 cm^3/min . for palladium, nickel and copper complexes respectively. However the optimum separation between copper, nickel and palladium complexes of H_2PA_2en (Fig. 6c) was obtained when complexes were eluted with a ternary mixture of n-hexane:chloroform 1,2-dichloroethane (82.7:10.3: 6.9), with a elution of nickel, followed by copper and palladium, as observed with the metal complexes of $H_2F_3PA_2pn$. The calculated retention volumes were 8.25, 10.37 and 12.87 cm^3 using flow rate of 2.5 cm^3/min for nickel, copper and palladium chelates, respectively.

The response of the detector was checked by injecting different amounts of each of the complex at the optimized conditions of separation, and average peak height of at least two injections was measured. The linear calibrations were obtained within 0.2-8 μ g of each of the complex. The detection limits measured at least three times the background noise was found to be within 4-20 ng of a complex, corresponding to 0.7-5 ng of metal ion.

Finally in order to examine the effect of phenyl and methyl groups substitution at bridge position and trifluoromethyl group in the ligand, on the elution of copper and nickel complexes on adsorption HPLC column, the copper or nickel complexes of the ligands bis(isopropanoylacetone) dl-stilbenediimine (dl- H_2PA_2S), bis(trifluoroisopropanoyl-acetone meso-stilbenediimine (meso- $H_2F_3PA_2S$), bis(trifluoroisopropanoylacetone dl-stilbenediimine dl- $H_2F_3PA_2S$ H_2PA_2pn , $H_2F_3PA_2en$ were mixed together and injected on the column (200 x 4.6 mm) Si, 100, 5μ . Complete separation of nickel and copper complexes were achieved, when the complexes were eluted with a binary mixture of 20% chloroform in n-hexane, using a flow rate of 1 cm^3/min . The detection was achieved using UV detector fixed at 298 nm. The order of elution for nickel complexes were [1] dl- H_2PA_2S [2] meso- $H_2F_3PA_2S$ [3] H_2PA_2en (4) $H_2F_3PA_2pn$ [5] $H_2F_3PA_2en$. The order of elution for copper complexes were also similar with elution of the complexes of the reagents in the sequence [1] dl- $H_2F_3PA_2S$ [2] dl- $H_2F_3PA_2S$ [3] H_2PA_2en [4] $H_2F_3PA_2pn$ [5] $H_2F_3PA_2en$.

The order of elution for both copper and nickel complexes on adsorption HPLC column (Fig. 7) indicates that the metal complexes of the

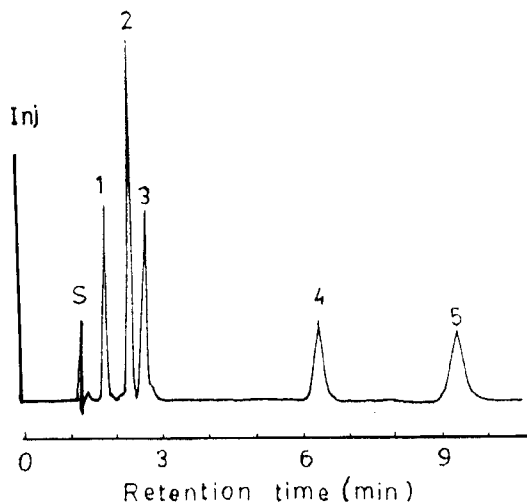


Fig. 7: Comparative elution of copper complexes of (1) dl-H₂PA₂S (2) dl-H₂F₃PA₂S (3) H₂PA₂dn (4) H₂PA₂pn (5) H₂F₃PA₂en. Column (200 x 4.6 mm) Si 100, 5 μ . Eluent chloroform:n-hexane (20:80). Flow rate 1 cm³/min. Detection UV at 298 nm.

ligands derived from stilbenediamine containing phenyl groups at bridge position elute first, followed by those derived from propylenediamine and ethylenediamine. Thus the metal complexes of ligand substituted with phenyl group could be eluted with a less polar solvent, followed by methyl as compared to the unsubstituted ligand.

Experimental

The reagent bis(isopropanoylacetone)ethylenediamine-(H₂PA₂en) and its copper and nickel complexes were prepared as reported by Lindoy *et al.* [3]. The copper and nickel complexes of ligands bis(isopropanoylacetone)dl-stilbenediamine(dl-H₂

PA₂S), bis(trifluoroisopropanoylacetone)dl-stilbenediamine(dl-H₂F₃PA₂S), bis(trifluoroisopropanoylacetone)meso-stilbenediamine(meso-H₂F₃PA₂S) were prepared as reported earlier [10,11].

Preparation of Bis(trifluoroisopropanoylacetone)ethylenediamine (H₂F₃PA₂) and Bis(trifluoroisopropanoylacetone)propylenediamine (H₂F₃PA₂pn)

Ethylenediamine (0.01M, 0.6 g) or propylenediamine (0.01M, 0.74g) dissolved in ethanol was cooled in ice bath. To this cold trifluo-

roisopropanoylacetone (1,1,1-trifluoro-5-methylhexane-2,4-dione) (0.02M, 3.64g) was added dropwise with stirring. The solution was then warmed on water bath for 15 min and was left over night at -5°C. A white crystalline precipitate formed was filtered and recrystallized from methanol.

Preparation of copper and nickel chelates

Copper(II) acetate (0.001M, 0.2g) or nickel(II) acetate (0.001M, 0.25g) dissolved in methanol was added to the reagent solution of H₂F₃PA₂en (0.001M, 0.39 g) or H₂F₃PA₂pn (0.001M, 0.40g) in methanol. The mixture was refluxed for 30 min and solvent was distilled off. The residue was cooled to room temperature. The metal complexes were filtered and recrystallized from methanol.

Preparation of palladium complexes

Palladium (II) chloride (0.18 mg) was heated with benzonitrile, (0.5 cm³) for 2 hr. The palladium benzonitrile complex formed was diluted with benzene (4 cm³). Reagent, H₂PA₂en (0.28 g), H₂F₃PA₂en (0.39 g) or H₂F₃PA₂pn (0.40 g) dissolved in benzene was added to the palladium benzonitrile complex. The mixture was refluxed overnight and was filtered. Most of the solvent was distilled off and remaining solvent was evaporated at reduced pressure at room temperature. The residue was dissolved in n-hexane and the isolated precipitates were recrystallized from n-hexane.

The elemental microanalysis (Table 1) were carried out by Elemental Micro Analysis Ltd, U.K. Spectrophotometric studies within 700-185 nm were carried out on Hitachi 220 spectrophotometer.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of metal complexes were carried out on Shimadzu TG-30 Thermal analyser using sample of 5-14 mg at a heating rate of 15°C/min and nitrogen flow rate of 50 cm³/min. The gas chromatography (GC) was carried out on a Hitachi 163 gas chromatograph connected to flame ionization detector (FID) and recorder 056. Columns (3m x 3mm and 2m x 3mm) packed with OV, 101, 3% or OV 17, 3% on Chromosorb WHP 80-100 mesh size or Dexil 400 GC, 2% on Uniport HP 60-80 mesh size were used.

HPLC studies were carried out on a Hitachi 655 A liquid chromatograph, connected with vari-

able wavelength UV monitor, Rheodyne injector 7125 and recorder 561. Column (200 x 4.6 mm) Si, 100 $5\mu\text{h}$ (Hewlett Packard) was used.

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