

High Performance Liquid Chromatographic Separation of Copper (II), Nickel(II) Palladium (II) and Oxovanadium (IV) Complexes of Tetradentate Schiff Bases Derived from Stilbenediamines

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Summary: The nickel(II), palladium (II) and oxovanadium (IV) chelates of bis(acetyl-pivalyl-methane)meso-stilbenediimine(meso-H₂APM₂S), copper(II), nickel(II), palladium(II) and oxovanadium(IV) chelates of bis(acetyl-pivalylmethane)dl-stilbenediimine (dl-H₂APM₂S), bis-(isovalerylacetone)meso-stilbenediimine (meso-H₂I₂V₂S) and bis(isovalerylacetone)dl-stilbene-diimine (dl-H₂I₂V₂S) have been separated on reversed phase HPLC columns (250 x 4 mm) packed with Hypersil ODS 5 μ and (150 x 3.9 mm) Nova Pak C-18 with guard ODS column. The copper, nickel, palladium and oxovanadium chelates of dl-H₂I₂V₂S are also separated on normal phase HPLC column (250 x 4 mm) packed with lirosorb Si, 100 5 μ . The detection is achieved using variable wavelength UV detector. The linear calibration range is observed at ng levels and detection limits at sub ng levels of metal chelates. Finally the effect of methyl and phenyl group substitution on the relative elution of copper, nickel and palladium chelates on Nova Pak C-18 column has been examined and evaluated.

Introduction

High performance liquid chromatography (HPLC) has been extensively used for the separation, identification and determination of complex mixtures of organic compounds. HPLC could equally be used for the separation and identification of inorganic compounds. The use of HPLC for inorganic determination have been reviewed [1-3]. Metal chelates are the convenient species to be determined by HPLC, because of their close resemblance to organic compounds. The most commonly used chelating reagents for the HPLC separation of metals as metal chelates are different dialkyldithiocarbamates [4-7], dithiozones [8], oxines [9], β -diketones [10,11] and Schiff bases [12-14]. Tetradentate Schiff bases are more interesting because they form neutral and highly stable metal chelate compounds with copper(II), nickel(II), palladium(II) and oxovanadium (IV). The complexes indicate high values of molar absorptivity in UV region ideally suited for UV detection after necessary separation on HPLC [15]. In the present work the separation of copper, nickel palladium and oxovanadium chelates of bis-(isovalerylacetone) meso-stilbenediimine (meso-H₂I₂V₂S) bis(isovalerylacetone) dl-stilbenediimine (dl-H₂I₂V₂S) bis-(acetyl-pivalylmethane) meso-stilbenediimine(meso-H₂APM₂S) bis(acetyl-pivalylmethane)dl-stilbenediamine (dl-H₂APM₂S) (Fig. 1)

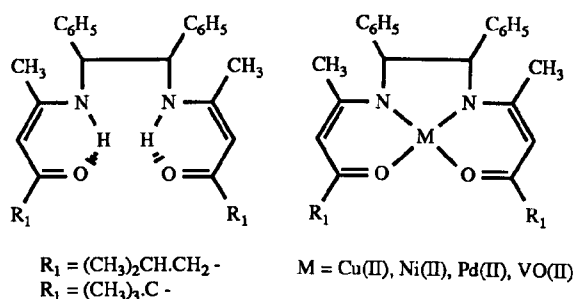


Fig. 1: Structural diagrams of reagents and metal chelates.

derived from dl-stilbenediimine and meso-stilbenediamine and β -diketones isovalerylacetone (6-methylheptane-2,4-dione) and acetyl-pivalylmethane (5,5-dimethylhexane-2,4-dione) have been examined for their separation using normal as well as reversed phase HPLC columns.

Results and Discussion

The elemental analysis of palladium and oxovanadium complexes of the reagents dl-H₂I₂V₂S and meso-H₂I₂V₂S agreed reasonably to the expected values. The results of ¹H-NMR are as

could be expected from the structure of palladium chelates and relates closely as reported for nickel chelates [16]. The IR of the oxovanadium chelates indicate a strong band at 990 cm^{-1} which could be assigned to V=O stretching vibrations [20]. Two to three bands of weak to medium intensity are observed in the spectra of the metal chelates within $525\text{--}430\text{ cm}^{-1}$, but not in the free ligand vibrations. These bands could be assigned to metal-ligand vibrations. The spectrophotometric studies of metal chelates [15] (Table 1) indicate high values of molar absorptivity in UV region ($> 10^4$) which are ideally suited for spectrophotometric detection.

Table 1: Spectrophotometric data of palladium(II) and oxovanadium(IV) chelates

Compound	Solvent	$\lambda\text{-max}$ ($\epsilon\text{-mole}^{-1}\text{cm}^{-1}$)
1. dl-IVA ₂ SPd	Methanol	208(26600), 269(28000), 345(10400).
2. meso-IVA ₂ SPd	Methanol	210(7300), 271(25380) 336(3360), 408(566)
3. dl-IVA ₂ SVO	Methanol	215(14600), 250(6100), 322 (13000), 355 (sh) (4800), 440 (139), 560(100), 640(117).
4. meso-IVA ₂ SVO	Methanol	207(28100), 268(17300), 325 (19400), 365(sh) (3600), 440 (630), 448(104), 567 (52), 653(58).

To evaluate the chromatographic behaviour for the phenyl substituted ligands, the reversed phase mode of HPLC was used to obtain the separation goal of metal complexes. When a mixture of copper(II), nickel(II), palladium(II) and oxovanadium(IV) complexes of reagent meso-H₂IVA₂S was injected on the column (250 x 4 mm) packed with Hypersil ODS, the complexes easily eluted with a binary mixture of methanol:water to give symmetrical peaks, but an optimal separation was achieved with ternary mixture of methanol:acetonitrile:water (75:15:10) and UV detection at 330 nm. Under these conditions, a partial separation between palladium(II), nickel(II) and copper(II) was achieved (Fig. 2A). An attempt was made to separate the mixture by increasing the percentage of water, but a broadening and peak tailing was observed without improvement in the results. However a mixture of oxovanadium, palladium and copper complexes showed an improved separation between palladium and copper ($R_s = 1.05$) using same solvent system (Fig. 2B). The same Hypersil ODS column was also tried for the separation of

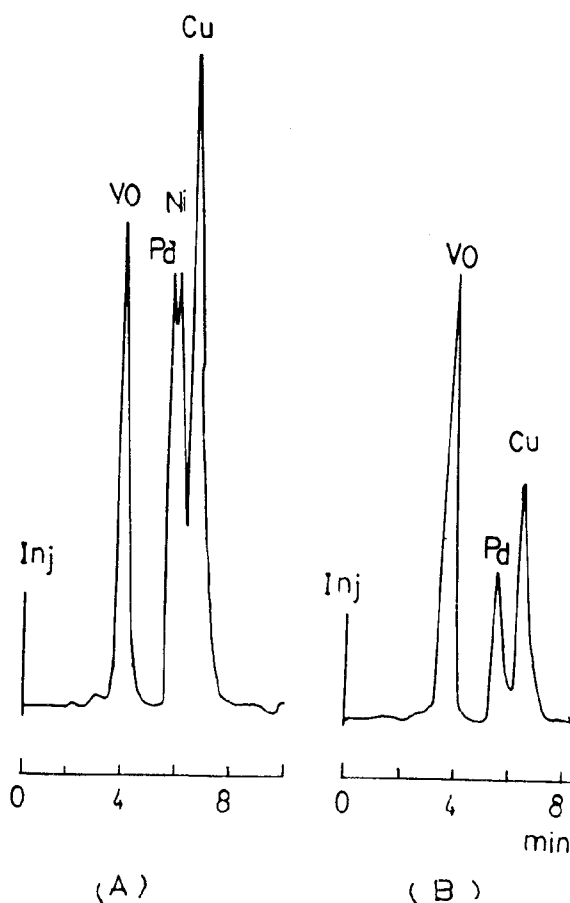


Fig. 2: HPLC separation of (A) VO, Pd, Ni and Cu (B) VO, Pd, Cu complexes of meso-H₂IVA₂S on column (450 x 4 mm) packed with Hypersil ODS 5 μ .

Elution: Methanol:acetonitrile:water (75:15:10). Flow rate 0.5 cm³/min. Detection UV at 330 nm.

copper, nickel, palladium and oxovanadium chelates of dl-H₂APM₂S using ternary mixture of methanol:acetonitrile: water (75:10:15) as eluent, with a flow rate of 0.7 cm³/min and UV detection at 330 nm. An adequate separation between vanadium, palladium and nickel was achieved while the nickel and copper complexes failed to resolve completely (Fig. 3).

When Nova Pak C-18 column was used for the separation of oxovanadium, palladium and nickel complexes of the reagent meso-H₂APM₂S and the chelates were isocratically eluted with binary mixture of methanol:water (87.5:12.5) using flow rate of 0.8 cm³/min, the complexes were easily

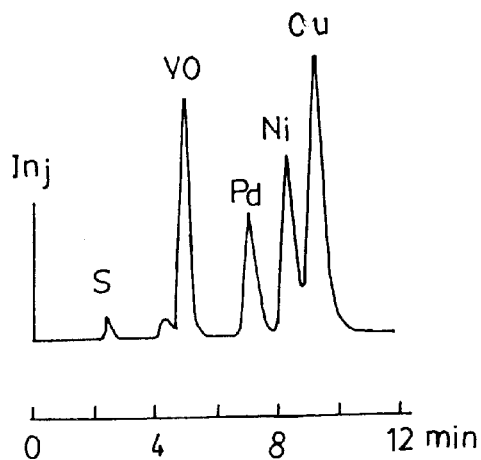


Fig. 3: HPLC separation of VO, Pd, Ni and Cu complexes of dl- H_2IVA_2S on column (450 x 4 mm) packed with Hypersil ODS, 5μ .

Elution: Methanol:acetonitrile:water (75:15:10). Flow rate $0.7\text{ cm}^3/\text{min}$. Detection UV at 300 nm.

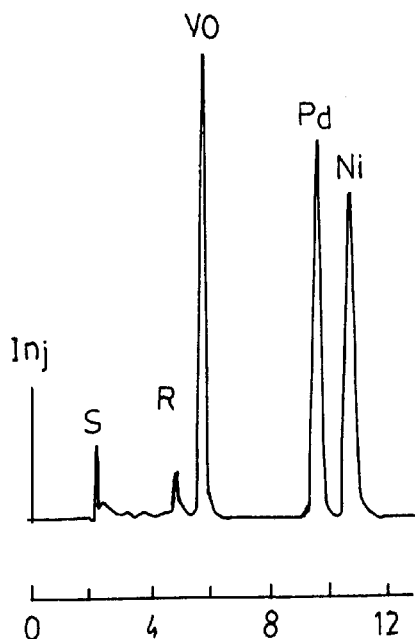


Fig. 4: HPLC separation of VO, Pd, Ni chelates of meso- H_2APM_2S on column Nova Pak C-18 (150 x 3.9 mm). Elution with methanol:water:(87.5:12.5). Flow rate $0.8\text{ cm}^3/\text{min}$. Detection UV at 254 nm.

separated. Detection was obtained with UV detector fixed at 254 nm (Fig. 4). Similarly a mixture of the copper, nickel, palladium and vanadium chelates of dl- H_2IVA_2S on Nova Pak C-18 column, separated with ternary mixture of methanol:acetonitrile:water (73:10:17) with $0.8\text{ cm}^3/\text{min}$ flow rate and 330 nm wavelength fixed at UV detection (Fig. 5).

The copper, nickel, palladium and oxovanadium chelates of dl- H_2IVA_2S were also examined on normal phase column (250 x 4 mm) packed with lirosorb Si 100, 5μ . An optimum separation was achieved when complexes were eluted with binary mixture of 12% chloroform in n-hexane, adjusting the flow rate at $1\text{ cm}^3/\text{min}$ at 310 nm UV detection (Fig. 6).

Comparing the figures 5 and 6, it is observed that reversed phase column Nova Pak C-18 indicate a better resolution between copper, nickel, palladium and oxovanadium complexes as compared to normal phase column packed with lirosorb Si 100, 5μ . However the order of elution on reversed phase column was the elution of oxovanadium, palladium, nickel and copper as compared to palladium, nickel, copper and oxovanadium observed on normal phase column.

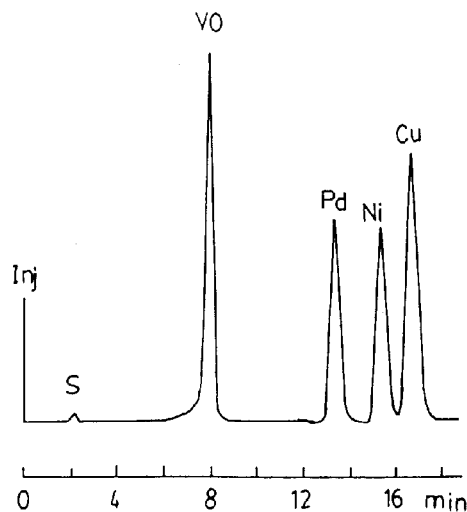


Fig. 5: HPLC separation of VO, Pd, Ni and Cu chelates of dl- H_2IVA_2S on Nova Pak C-18 with guard ODS column.

Elution: Methanol:acetonitrile:water (73:10:17), with flow rate $0.8\text{ cm}^3/\text{min}$. Detection UV at 330 nm.

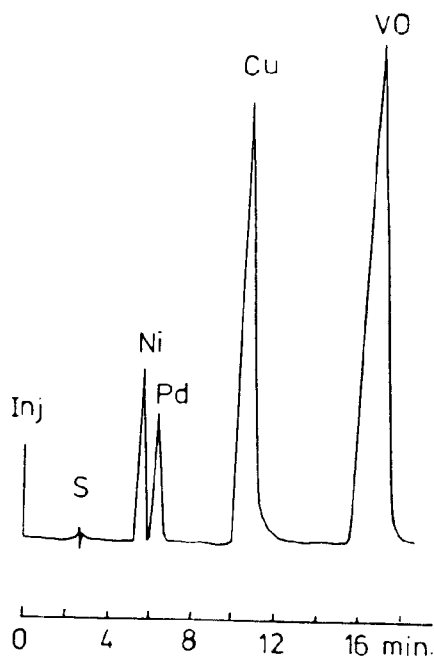


Fig. 6: HPLC separation of Ni, Pd, Cu, VO chelates of dl-H₂IVA₂S on column (250 x 4 mm) packed with lichrosorb Si, 100, 5 μ (1) Ni, (2) Pd (3) Cu (4) VO.

Elution: Chloroform:n-hexane (12:88). Flow rate 1 cm³/min. Detection UV at 310 nm.

Quantitative response of the detector at the optimized conditions of separation was examined for all the complexes. Injecting different amounts of complexes gave linear calibration curves by plotting average peak height of two to three injections versus the amount of complex injected. Linear calibrations were obtained in the range of 20-1000 ng of each of the complex, corresponding to 1.94-188 ng of metal ion (Fig. 7). The detection limits measured as thrice the background noise was found within 0.16-10 ng of metal chelate, corresponding to 15.5-1341 pg of metal ion.

In order to examine the effect of methyl and phenyl groups substitution at the bridge position on the relative elution of metal chelates, the copper, nickel or palladium complexes of the ligands H₂IVA₂en, H₂IVA₂pn, dl-H₂IVA₂S and meso-H₂IVA₂S were mixed together and injected on the column Nova Pak C-18. The conditions of their separations were optimized. The copper complexes were eluted with ternary mixture of methanol:acetonitrile:water (75:15:10) with a flow rate of 0.6 cm³/min and UV detection at 330 nm (Fig. 8). The

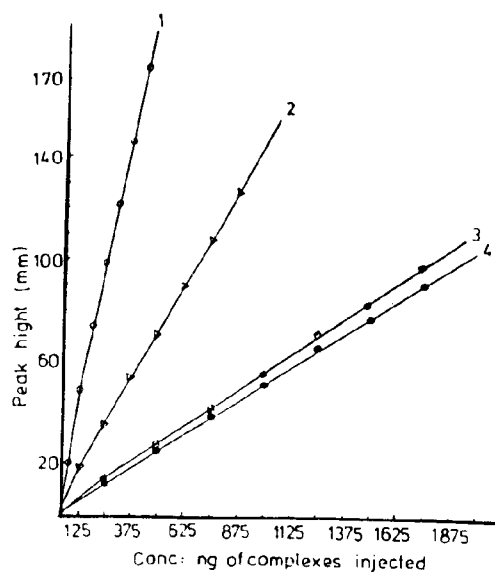


Fig.7: Linear calibration curves (1) VO (2) Cu (3) Pd (4) Ni chelates dl-H₂IVA₂S conditions same as Fig. 5.

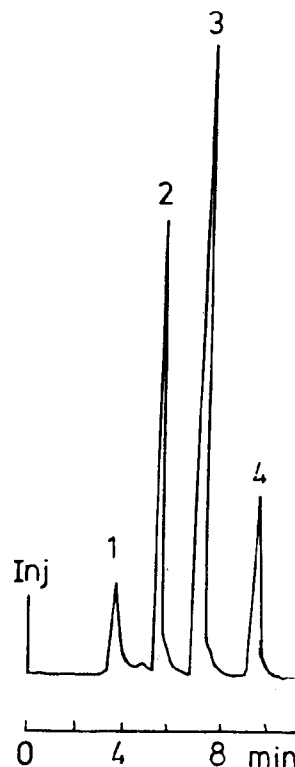


Fig. 8: Comparative HPLC elution (1) IVA₂pnCu (2) IVA₂enCu (3) dl-IVA₂SCu (4) meso-IVA₂SCu. on Nova Pak C-18 column.

Elution: Methanol:acetonitrile:water (75:15:10). Flow rate 0.7 cm³/min. Detection UV at 330 nm.

nickel complexes were separated when eluted with acetonitrile:water (92:8) with a flow rate of $0.6 \text{ cm}^3/\text{min}$ and UV detection at 330 nm (Fig. 9). Similarly optimal separation between the palladium chelates were obtained when eluted with methanol:acetonitrile:water (75:15:10) with a flow rate of $0.6 \text{ cm}^3/\text{min}$ and UV detection at 320 nm (Fig. 10). A similar order of elution was obtained with a elution of metal chelates of $\text{H}_2\text{IVA}_2\text{pn}$ first, followed by $\text{H}_2\text{IVA}_2\text{en}$, dl- $\text{H}_2\text{IVA}_2\text{S}$ and meso- $\text{H}_2\text{IVA}_2\text{S}$. However the palladium chelates $\text{H}_2\text{IVA}_2\text{pn}$, and $\text{H}_2\text{IVA}_2\text{en}$, co-eluted.

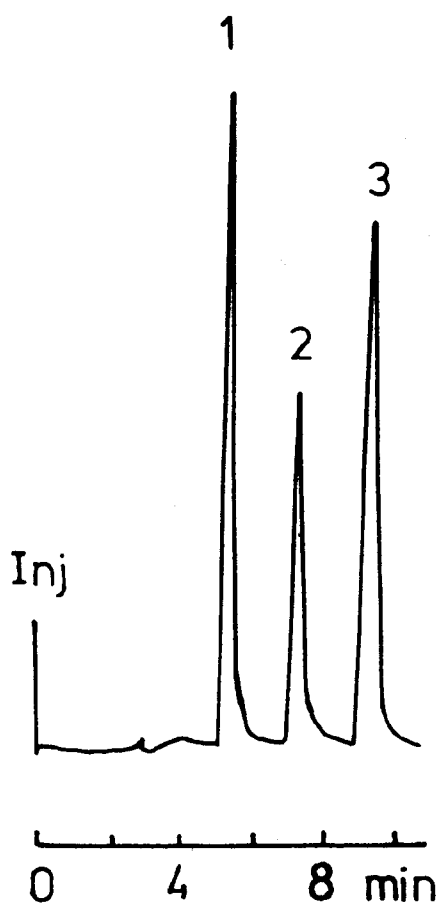


Fig. 9: Comparative HPLC elution (1) IVA_2pnNi (2) IVA_2enNi (3) dl- IVA_2SNi (4) meso- IVA_2SNi on Nova Pak C-18 column.

Elution: Methanol: water (92:8). Flow rate $0.6 \text{ cm}^3/\text{min}$. Detection UV at 330 nm.

On examining the separation of copper, nickel and palladium complexes of the ligands on reversed phase HPLC column Nova Pak C-18 it becomes clear that the metal complexes of ligands

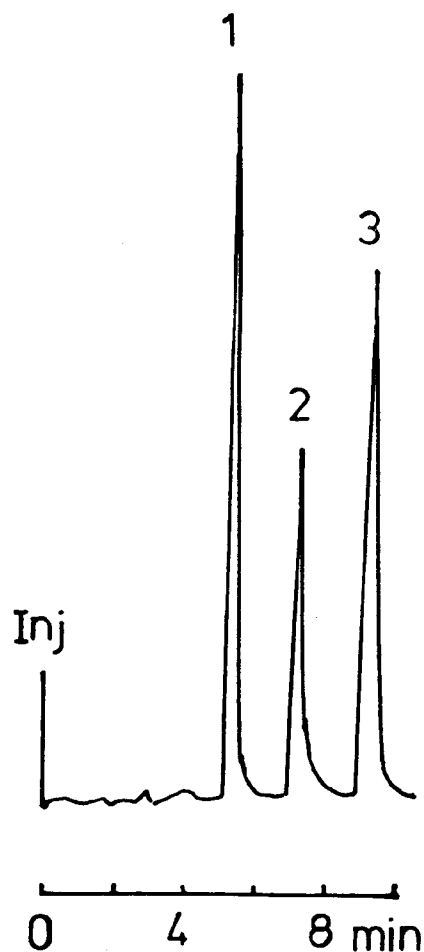


Fig. 10: Comparative HPLC elution (1) $\text{IVA}_2\text{pnPd} + \text{IVA}_2\text{enPd}$ (2) dl- IVA_2SPd (3) meso- IVA_2SPd on Nova Pak C-18 column.

Elution: Methanol:acetonitrile:water (75:15:10). Flow rate $0.6 \text{ cm}^3/\text{min}$. Detection UV at 320 nm.

derived from ethylenediamine and propylenediamine elute first as compared to ligand derived from meso-stilbenediamine and dl-stilbenediamine and containing phenyl groups at bridge position irrespective of the strength of the eluent. The copper and nickel complexes with the ligand $\text{H}_2\text{IVA}_2\text{pn}$ substituted with a methyl group at bridge position elute before the unsubstituted ligand at bridge position $\text{H}_2\text{IVA}_2\text{en}$. A similar order of elution has been reported on GC of copper and nickel chelates [21].

It may be concluded that the metal complexes of ligands derived from ethylenediamine and propylenediamine could be eluted with more polar solvent than ligands substituted with phenyl groups

at bridge position and derived from dl-stilbenediamine and meso-stilbenediamine on reversed phase column.

Experimental

The copper and nickel complexes of the ligands dl-H₂IVA₂S and meso-H₂IVA₂S, copper, nickel and palladium chelates of ligands bis(isovalerylaceton)ethylenediimine (H₂IVA₂en) and bis(isovalerylaceton)propylenediimine (H₂IVA₂pn) and copper, nickel, palladium and oxovanadium chelates of dl-H₂APM₂S and meso-H₂APM₂ were prepared as reported [16-18]. The palladium and oxovanadium complexes of reagent dl-H₂IVA₂S and meso-H₂IVA₂S were prepared as under. The palladium complexes were prepared using general procedure of Belcher et al [19] and oxovanadium chelate by ligand exchange method [20].

Preparation of palladium (II) chelates

Palladium(II) chloride (0.09 g) was refluxed with benzonitrile (0.2 cm³) forming a palladium benzonitrile complex which was diluted with 4 cm³ of benzene. The ligands dl-H₂IVA₂S or meso-H₂IVA₂S was added slowly and the reaction mixture was refluxed for 12 hrs. Distillation of the solvent followed and the remaining evaporating by vacuum desiccator gave yellow fine crystals which were purified by recrystallization from n-hexane with small addition of absolute ethanol. dl-IVA₂SPd, m.p. 270°C, C₃₀H₃₈N₂O₂Pd requires % C=63.82, H=6.73, N=4.96; found % C=63.47, H=5.85, N=5.06 ¹H-NMR (CDCl₃) δ ppm 0.926(d), 0.9469(d), 1.597(s), 1.625(s) -CH₃; 2.1367(m) -CH isovaleryl; 4.6354(s) -CH bridge; 4.7932(s), =CH and 7.259(m), 7.2836(m), 7.308(m), 7.3761(m), 7.386(t), 7.410(m), 7.8044(m) C₆H₅. IR (KBr) cm⁻¹ 1580(s), 1555(w), 1505(s), 525(m), 430(w), meso-IVA₂SPd, m.p. = 213°C, C₃₀H₃₈N₂O₂Pd requires % C=63.83, H=6.74, N=4.96; found % C=64.8, H=6.83, N=5.10. ¹H-NMR (CDCl₃) δ ppm, 0.921(s), 0.9417(d), 1.5536(s), 1.8124(s) -CH₃; 2.1286(m) -CH isovaleryl; 4.7887(s), -CH bridge 5.0603(s) = CH and 6.996(m) -C₆H₅. IR (KBr) cm⁻¹ 1570(s), 1510(vs), 490(w), 460(w).

Preparation of oxovanadium(IV) chelates

The reagents dl-H₂IVA₂S or meso-H₂IVA₂S (1.1 g) and bis (2,4-pentanedione) oxovanadium

(IV) (0.54 g) were heated together for 3 hr at 220-250°C in a micro-distillation apparatus (0.2 Torr). During the first 20 min most of the 2,4-pentanedione distilled off. The product was washed with dry ether and recrystallized from n-hexane dl-IVA₂SVO, m.p. = 236°C, C₃₀H₃₈N₂O₃V requires % C=68.57, H=7.23, N=5.33, found % C=68.53, H=7.39, N=5.86. IR (KBr) cm⁻¹, 1560(s), 1515(s), 1470(w), 990(s), 525(m), 500(w), 430(w); meso-IVA₂SVO m.p. = 247°C, C₃₀H₃₈N₂O₃V required % C=68.57, H=7.23, N=5.33, found % C=68.53, H=7.39, N=5.86, IR (KBr) cm⁻¹, 1575(vs), 1510(vs), 1480(m), 980(vs), 500(m), 465(w), 430(w).

Elemental micro analysis were carried out by Elemental Micro-Analysis Ltd. U.K. IR of the compounds in KBr were recorded on Perkin Elmer 1430. ¹H-NMR of palladium chelates were recorded on Bruker AM 300 NMR spectrometer in CDCl₃ containing TMS as internal standard at HEJ Research Institute of Chemistry, University of Karachi. Spectrophotometric studies were carried out on Hitachi 220. HPLC studies were carried out on Hitachi 655A liquid chromatograph connected with variable wavelength UV monitor, Rheodyne 7125 injector and Hitachi recorder 561.

Columns (250 x 4 mm) were packed with Hypersil ODS, 5μ and Licrosorb Si 100 as reported earlier [13]. Column (150 x 3.9 mm) Nova Pak C-18 with guard ODS column (Waters) was obtained from commercial source.

Conclusion

HPLC separation of the metal chelates of four ligands dl-H₂APM₂S, meso-H₂APM₂S, dl-H₂IVA₂S and meso-H₂IVA₂S have been examined. The copper, nickel, palladium and oxovanadium complexes of dl-H₂IVA₂S separated completely on Nova Pak C-18 with guard ODS column and Licrosorb Si 100, 5μ column. The detection limits of copper, nickel, palladium and oxovanadium chelates of dl-H₂IVA₂S on normal phase column were 0.16, 0.4, 0.4 and 0.16 ng respectively.

The relative elution of copper, nickel and palladium chelates on Nova Pak C-18 with guard ODS column indicated that substitution of phenyl groups increased the retention time of metal chelates as compared to unsubstituted ligand on reversed phase column.

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