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Thermoanalytical and chromatographic studies of copper(II), nickel(II) and oxovanadium(IV) complexes of tetradentate Schiff bases derived from β-diketones and 2,3-diaminopentane

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ABSTRACT

Differential thermal analysis and thermogravimetric analysis of copper(II) and nickel(II) complexes of [4,4′-(1-ethyl-2-methyl-1,2-ethanediyl)dinitrilo]bis(1,1,1-trifluoro-2-pentanone) [bis(trifluoroacetylacetone)ethylmethylethylenediimine]($H_2F_3A_2EMen$) and [4,4′-(1-ethyl-2-methyl-1,2-ethanediyl)dinitrilo]-bis(1,1,1-trifluoro-6-methyl-5-hepten-2-one) [bis(trifluoroacetylmesityl oxide)ethylmethylethylenediimine] ($H_2F_3AM_2EMen$) and copper(II), nickel(II) and oxovanadium(IV) complexes of [4,4′-(1-ethyl-2-methyl-1,2-ethanediyl)dinitrilo]bis(2-pentanone) [bis(acetylacetone)ethylmethylethylenediimine] (H_2A_2EMen) were carried out and losses in weight between 78 and 100% occurred at temperatures up to 300°C. The copper, nickel and oxovanadium complexes of H_2A_2EMen are adequately separated by gas chromatographic (GC) columns, but the copper and nickel complexes of $H_2F_3A_2EMen$ and $H_2F_3AM_2EMen$ could not be resolved. The copper and nickel complexes of $H_2F_3A_2EMen$ and $H_2F_3AM_2EMen$ and the copper, nickel and oxovanadium complexes of H_2A_2EMen were separated on normal- and reversed-phase high-performance liquid chromatographic (HPLC) columns. The elution of copper and nickel complexes on GC and HPLC columns was compared in order to evaluate the effects of substituents on elution.

INTRODUCTION

Tetradentate Schiff bases have proved to be promising reagents for the gas chromatographic (GC) and high-performance liquid chromatographic (HPLC) separation of copper and nickel [1–6], copper, nickel and palladium [7–9], copper, nickel and cobalt [10,11], copper, nickel and oxovanadium [12–14] and copper, nickel, palladium and oxovanadium [15,16] as metal chelate compounds. The reagents react with a limited number of metal ions quantitatively at all concentrations. Therefore, in this work the copper(II) and nickel(II) complexes of [4,4′-(1-ethyl-2-methyl-1,2-ethanediyl)dinitrilo]bis(1,1,1-trifluoro-2-pentanone) [bis(trifluoroacetylacetone)ethylmethylethylenediimine] ($H_2F_3A_2EMen$) and [4,4′-(1-ethyl-2-methyl-1,2-ethanediyl)dinitrilo]bis(1,1,1-trifluoro-6-methyl-5-hepten-2-one) [bis(trifluoroacetylmesityl oxide)ethylmethylethylenediimine] ($H_2F_3AM_2EMen$) and copper(II), nickel(II) and oxovanadium(IV) complexes of [4,4′-(1-ethyl-2-methyl-1,2-ethanediyl)dinitrilo]bis(2-

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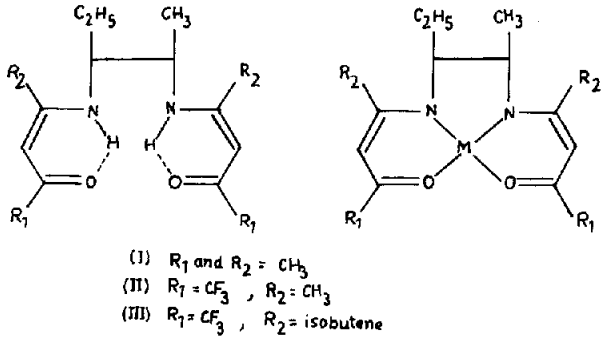

Fig. 1. Structures of reagents and metal chelates. The metal (M) is Ni(II), Cu(II) or VO(IV).

pentanone) [bis(acetylacetone)ethylmethylethylenediimine] (H_2A_2EMen) (Fig. 1) were examined on GC and HPLC columns for their possible separations and to examine the effect of substituents on their relative elution.

EXPERIMENTAL

The reagents H_2A_2EMen, $H_2F_3A_2EMen$ and $H_2F_3AM_2EMen$ and their copper and nickel complexes were prepared as reported [17]. The reagents were prepared by condensation of acetylacetone (0.01 *M*), trifluoroacetylacetone (0.01 *M*) or trifluoroacetylmesityl oxide (1,1,1-trifluoro-6-methyl-5-hepten-2,4-dione) with 2,3-diaminopentane (0.005 *M*) in ethanol and chloroform as solvent. The copper and nickel complexes were prepared by refluxing together an equimolar solution of reagent (0.001 *M*) and nickel acetate or copper acetate (0.001 *M*) in methanol. The results of elemental analysis agreed with the expected values and the mass spectra of the reagents indicated the molecular ion peak corresponding to the expected molecular weight.

Preparation of oxovanadium complex of [4,4'-(1-ethyl-2-methyl-1,2-ethanediyl)-dinitrilo]bis(2-pentanone) [bis(acetylacetone)ethylmethylethylenediimine] (H_2A_2EMen)

The oxovanadium (IV) complex of H_2A_2EMen is conveniently prepared by a ligand-exchange method [18]. An equimolar amount of the reagent H_2A_2EMen (0.133 g, 0.0005 *M*) and bis(acetylacetone)oxovanadium(IV) (0.13 g, 0.0005 *M*) were placed together in a 10-cm^3 round-bottomed flask connected to a high-vacuum pump. The mixture was heated and maintained within the range 220–230°C for 2 h at 3 mmHg. The residue was washed with diethyl ether and recrystallized from *n*-hexane, m.p. 195°C. Calculated for $C_{15}H_{24}N_2O_3V$, C 55.22, H 7.23, N 8.43%; found, C 54.34, H 6.54, N 9.03%. IR (KBr), cm^{-1}: 1580(s), 1510(sb), 1400(s), 990(vs). UV–visible spectra (methanol), λ_{max}, nm (molar absorptivity ε, $l\,mol^{-1}\,cm^{-1}$, in parentheses): 630 (522), 546 (46), 433 (67), 355 (4100), 315 (16 000), 240 (sh) (8000), 208 (16 000).

Bis(acetylacetone)oxovanadium(IV) was prepared as reported [19]. Elemental analysis was carried out by Elemental Micro-Analysis, UK. IR and spectrophoto-

metric studies were carried out on a Perkin-Elmer Model 1430 IR spectrophotometer using potassium bromide discs and a Hitachi Model 220 spectrophotometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of metal complexes were carried out on Shimadzu TG 30 and DTA 30 thermal analysers at the Department of Chemistry, Quaid-e-Azam University, Islamabad, at heating rates of 10 and 15°C min^{-1} for TGA and DTA, respectively, and a nitrogen flow-rate of 40 cm^3 min^{-1}. DTA and TGA were carried out between room temperature and 500°C with 5–12-mg samples in aluminium cups against alumina as a reference material.

A Hitachi Model 163 gas chromatograph equipped with a flame ionization detector and a Model 056 recorder was used. Stainless-steel columns (6 ft. × 0.085 in. I.D. and 3 m × 3 mm I.D. packed with 3% OV-101 and 3% OV-17 on Chromosorb W HP (80–100 mesh) were used.

A Hitachi Model 655A liquid chromatograph equipped with a variable-wavelength UV detector, a Rheodyne Model 7125 injector and a Model 561 recorder and a Shimadzu LC-5 liquid chromatograph equipped with an SPD-2A spectrophotometric detector, a SIL-1A LC injector and a Chromatopac C-RIB were used. A stainless-steel column (250 mm × 4 mm I.D.) was packed with LiChrosorb Si 100 (5 μm) (Merck) as reported earlier [5] and a Zorbax ODS (5 μm) column (250 mm × 4.6 mm I.D.) DuPont with an ODS guard column obtained from a commercial source were used.

Solutions of 1 mg cm^{-3} for GC and normal- and reversed-phase HPLC were prepared with acetone, chloroform and methanol respectively. Samples of 1–5 μl was injected for GC and HPLC separations. Calibration graphs were constructed by plotting average peak height *versus* amount of complex injected.

RESULTS AND DISCUSSION

The IR spectrum of the oxovanadium complex shows the expected pattern and a band is observed at 990 cm^{-1} due to V=O stretching vibrations. A spectrophotometric study of the oxovanadium complex in methanol indicated three bands in the visible region due to d–d transitions in the d^1 system of oxovanadium(IV). The complex also shows fairly high molar absorptivities in the UV region, ideally suited for HPLC separations with UV detection.

In order to determine the volatility and thermal stability of metal chelates to assess their possible elution and separation on GC columns, DTA and TGA of the metal chelates were studied. The TGA results (Fig. 2) indicate that nickel complexes are more thermally stable and lose more weight, in the range 94–100%, between 150 and 285°C than copper and oxovanadium complexes, which lose 83–96% and 78% weight between 130 and 310°C and 170 and 285°C, respectively. The copper and nickel complexes of fluorinated ligands are more thermally stable and lose more weight, in the range 94–100%, than corresponding copper and nickel complexes of the non-fluorinated ligand H_2A_2EMen, which lose 83–94% weight within a similar temperature range. DTA (Fig. 3) shows mostly a melting endotherm, followed by vaporization/decomposition endotherms and exotherms, but exotherms observed above 300°C could be assigned to decomposition exotherms of non-volatile residues.

The complexes were examined on different GC columns to assess the elution and possible separation of metal complexes and it was observed that the metal com-

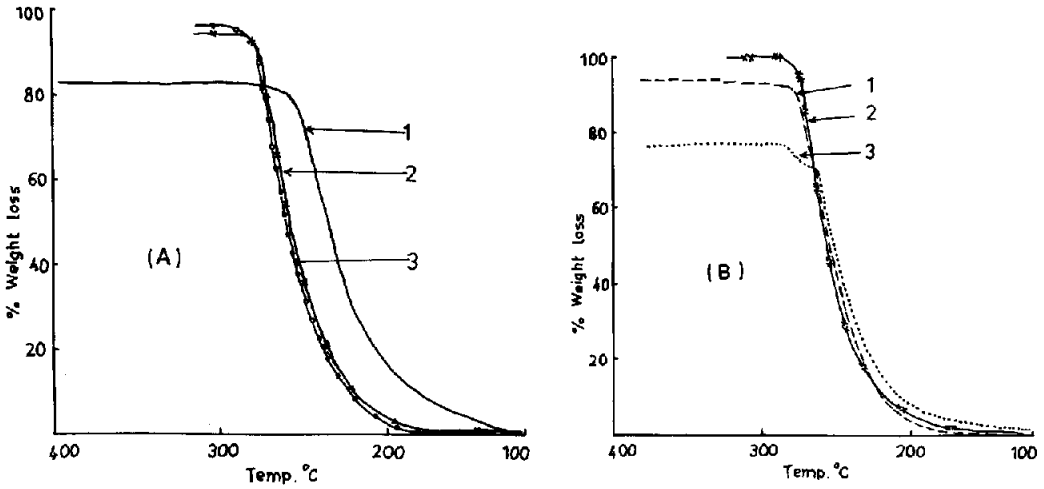

Fig. 2. (A) TGA of copper(II) complexes at a heating rate of 10°C min^{-1} and a nitrogen flow-rate of 40 cm^3 min^{-1}. 1, $A_2EMenCu$; 2, $F_3A_2EMenCu$; 3, $F_3AM_2EMenCu$. (B) TGA of nickel and oxovanadium complexes at a heating rate of 10°C min^{-1} and a nitrogen flow-rate 40 cm^3 min^{-1}. 1, $A_2EMenNi$; 2, $F_3A_2EMenNi$; 3, $A_2EMenVO$.

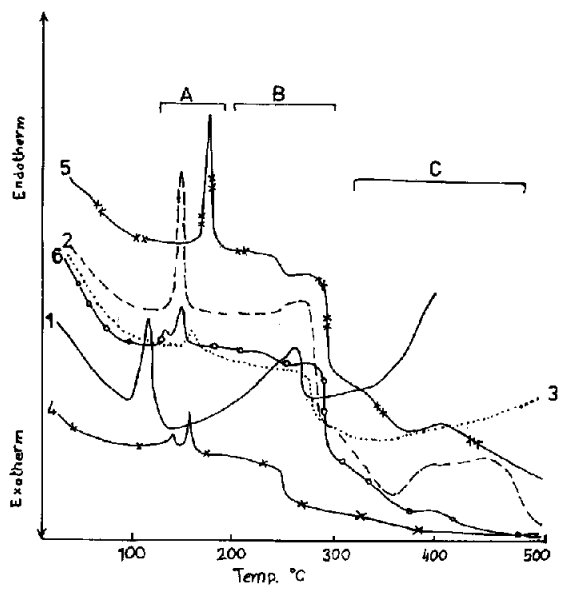

Fig. 3. DTA of metal complexes at a heating rate of 15°C min^{-1} and a nitrogen flow-rate 40 cm^3 min^{-1}. 1 = $A_2EMenCu$; 2 = $A_2EMenNi$; 3 = $A_2EMenVO$; 4 = $F_3A_2EMenCu$; 5 = $F_3A_2EMenNi$; 6 = $F_3AM_2EMenCu$. (A) Melting endotherms; (B) vaporization/decomposition endotherms and exotherms; (C) decomposition exotherm of non-volatile residue.

plexes were eluted at column temperatures of 220–250°C. Attemps were made to separate the copper and nickel complexes of $H_2F_3A_2EMen$ and $H_2F_3AM_2EMen$, but no separation was obtained on the columns tested. However, there was an adequate separation of the reagent from the complexes. The detection limits, measured as three times background noise, on the 6 ft. × 0.085 in. I.D. column packed with 3% OV-101 on Chromosorb W HP (80–100 mesh) were 15–30 ng for the complex.

Similarly, when copper, nickel and oxovanadium complexes of H_2A_2EMen were investigated for their separation and the conditions were optimized, a complete separation between the copper, nickel and oxovanadium complexes was obtained on the 3 m × 3 mm I.D. column packed with 3% OV-17 on Chromosorb W HP (80–100 mesh) at a column temperature of 250°C, with retention times of 11.2, 13.7 and 24.4 min for the copper, nickel and oxovanadium complexes, respectively (Fig. 4). When an excess of the reagent was added to the metal complex solution and the mixture was injected under the optimized separation conditions, no interference by the reagent on the separation of copper, nickel and oxovanadium was observed. Linear calibration graphs for copper, nickel and oxovanadium complexes were obtained at microgram

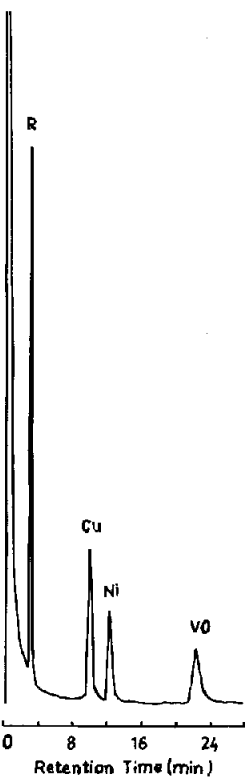

Fig. 4. GC separation of H_2A_2EMen and its Cu, Ni and VO complexes on a stainless-steel column (3 m × 3 mm I.D.) packed with 3% OV-17 on Chromosorb W HP (80–100 mesh). Column temperature, 250°C; injection port temperature, 270°C; nitrogen flow-rate, 30 cm^3 min^{-1}.

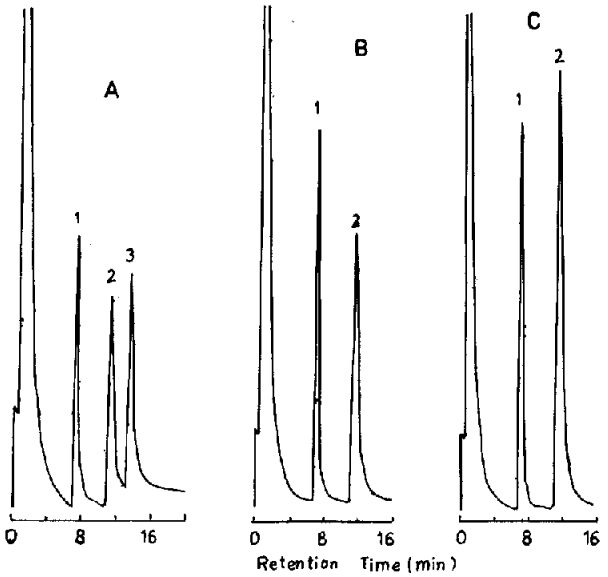

Fig. 5. Relative GC elution of (A) (1) $F_3A_2EMenNi$, (2) $F_3AM_2EMenNi$ and (3) $A_2EMenNi$; (B) (1) $F_3A_2EMenCu$ and (2) $A_2EMenCu$; (C) (1) $F_3A_2EMenCu$ and (2) $F_3AM_2EMenCu$. Column, 3 m × 3 mm I.D., 3% OV-17 on Chromosorb W HP (80–100 mesh). Column temperature, 250°C; injection port temperature, 270°C; nitrogen flow-rate, 30 cm^3 min^{-1}.

levels of the complexes injected with detection limits of 50, 40 and 50 ng of copper, nickel and oxovanadium complexes, respectively.

In order to determine the effects of substituents on the GC elution of copper and nickel complexes, mixtures of copper and nickel complexes of all three reagents were injected onto the 3 m × 3 mm I.D. column packed with 3% OV-17 on Chromosorb W HP (80–100 mesh) at a column temperature of 250°C, injection port temperature 270 °C and nitrogen flow-rate 30 cm^3 min^{-1}. Complete separations between all three nickel complexes and separation of the copper complex of $H_2F_3A_2EMen$ from those of H_2A_2EMen and $H_2F_3AM_2EMen$ were obtained (Fig. 5). It is concluded from the separations that CF_3 substitution decreases and alkyl (isobutene) substitution increases the retention of metal complexes.

The reagent H_2A_2EMen gave a highly promising GC separation of copper, nickel and oxovanadium complexes, but shows no separation between copper and nickel complexes of $H_2F_3A_2EMen$ and $H_2F_3AM_2EMen$. Normal- and reversed-phase HPLC were thus investigated for the separation of metal complexes, the separation of GC with flame ionization detection was compared with that of HPLC with UV detection.

When mixtures of copper and nickel complexes of $H_2F_3AM_2EMen$ and $H_2F_3A_2EMen$ were injected onto a 250 mm × 4 mm I.D. column packed with LiChrosorb Si 100 (5 μm), the complexes were easily eluted with chloroform–*n*-hexane. However, optimum separations between copper and nickel complexes of $H_2F_3AM_2EMen$ and $H_2F_3A_2EMen$ were obtained when eluted with chloroform–*n*-hexane (10:90) and chloroform–1,2-dichloroethane–*n*-hexane (15:3:82), respectively

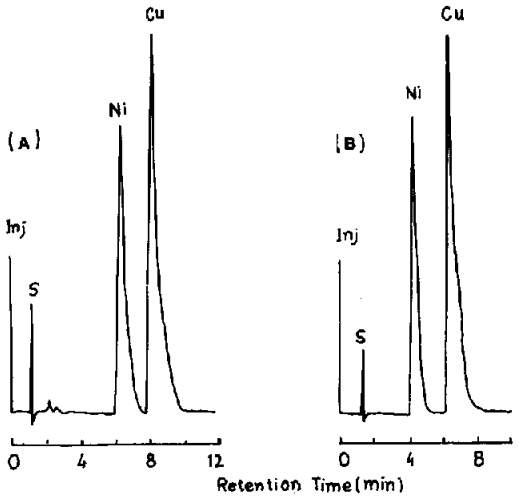

Fig. 6. HPLC separation of copper and nickel complexes of (A) $H_2F_3A_2EMen$ and (B) $H_2F_3AM_2EMen$. Column, 250 mm × 4 mm I.D., Si 100 (5 μm). (A) Eluent, chloroform–1,2-dichloroethane–*n*-hexane (15:3:82); flow-rate, 2.2 cm^3 min^{-1}; detection, UV at 295 nm. (B) Eluent, chloroform–*n*-hexane (10:90); flow-rate, 2.0 cm^3 min^{-1}; detection, UV at 300 nm.

(Fig. 6). The retention volumes of the copper and nickel complexes of $H_2F_3AM_2EMen$ were 8.56 and 12.66 cm^3 and for $H_2F_3A_2EMen$ 14.12 and 18.44 cm^3, respectively, with flow-rates of 2.0 and 2.2 cm^3 min^{-1}, respectively.

Linear calibration graphs for the copper and nickel complexes of $H_2F_3AM_2EMen$ and $H_2F_3A_2EMen$ using UV detection at 300 nm were obtained over the range 0.5–6.0 μg of complex and the detection limits were 10–15 ng of metal.

Similarly, when the copper, nickel and oxovanadium complexes of H_2A_2EMen were investigated for HPLC separation on the Zorbax ODS column, optimum sep-

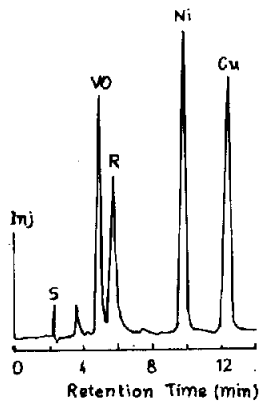

Fig. 7. HPLC separation of H_2A_2EMen and its Cu, Ni and VO complexes on a Zorbax ODS (5 μm) column. Eluent, water–methanol (25:75); flow-rate, 1 cm^3 min^{-1}; detection, UV at 260 nm.

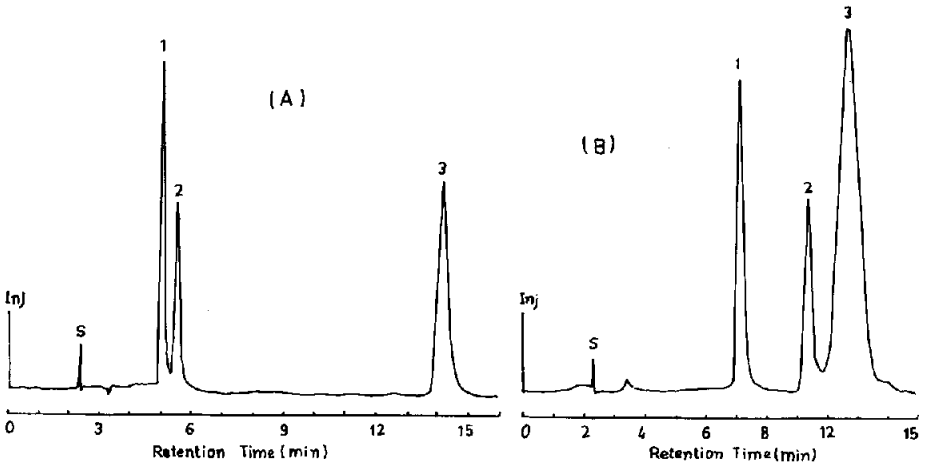

Fig. 8. (A) Relative elution of nickel complexes on a Zorbax ODS (5 μm) column. (1) $F_3A_2EMenNi$; (2) $A_2EMenNi$; (3) $F_3AM_2EMenNi$. Eluent, methanol–water (80:20); flow-rate, 1 cm^3 min^{-1}; detection, UV at 260 nm. (B) Relative elution of (1) $F_3A_2EMenCu$, (2) $A_2EMenCu$ and (3) $F_3AM_2EMenCu$ on a Zorbax ODS (5 μm) column. Eluent, methanol–water (75:25); flow-rate, 1 cm^3 min^{-1}; detection, UV at 260 nm.

aration was obtained when the complexes were eluted isocratically with methanol–water (75:25), with retention volumes of 4.93, 9.75 and 12.3 cm^3 for the oxovanadium, nickel and copper complexes, respectively, at a flow-rate of 1 cm^3 min^{-1}. The reagent solution was also added to the mixture to determine its effect on the HPLC separation of metal the complexes, and it was found that the reagent eluted with a retention volume of 5.67 cm^3 and interfered with the response for the oxovanadium complex (Fig. 7).

The response of the detector at 260 nm was checked under the optimized conditions of separation, and linear calibration graphs were obtained over the range 0.5–3.5 μg of the complex and the detection limit was 10 ng of complex.

Finally, the relative elution of the copper and nickel complexes of all the three reagents was investigated on the Zorbax ODS column. The copper or nickel complexes of the ligands were mixed, injected onto the column and eluted with methanol–water (80:20 and 75:25, respectively). Separations between the nickel and copper complexes were obtained (Fig. 8A and B), with elution of the copper and nickel complexes of $H_2F_3A_2EMen$, followed by H_2A_2EMen and $H_2F_3AM_2EMen$. The results also suggest that the CF_3 group slightly decreases and an alkyl (isobutane) group increases the retention in reversed-phase HPLC, as was observed in GC.

CONCLUSIONS

The work demonstrated the applicability of GC and HPLC for the separation of copper, nickel and oxovanadium complexes of tetradentate ketoamine Schiff bases at microgram to nanogram levels. GC provides easy separations of copper, nickel and oxovanadium complexes of H_2A_2EMen without any interference from excess of the reagent. Similar separations were also obtained by reversed-phase HPLC, with the reverse order of elution to that observed in GC, but the reagent interfered with

elution of the oxovanadium complex. The separation of copper and nickel complexed of fluorinated ligands, which was unsuccesful using GC, was easily achieved by normal-phase HPLC. HPLC with UV detection gave a greater sensitivity than GC with flame ionization.

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