

Short Communication

Gas and liquid chromatographic studies of copper(II), nickel(II), palladium(II) and oxovanadium(IV) chelates of some fluorinated ketoamine Schiff bases

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(First received August 24th, 1992; revised manuscript received February 26th, 1993)

ABSTRACT

The copper(II), nickel(II), palladium(II) and oxovanadium(IV) chelates of N,N'-ethylenebis(1,1,1-trifluoro-6-methyl-2-oxoheptan-4-imine) (H_2TFIVA_{2en}) and N,N'-1,2-propylenebis(1,1,1-trifluoro-6-methyl-2-oxoheptan-4-imine) (H_2TFIVA_{2pn}) were eluted from gas chromatographic columns, but their copper and nickel chelates could not be resolved. The detection limits were found to be 4–40 ng for each metal chelate. The copper, nickel, palladium and oxovanadium chelates were separated on reserved-phase HPLC columns, Nova Pak C_{18} (150×3.9 mm) and Microsorb C_{18} (150×4.6 mm). Elution was obtained with a binary mixture of methanol–water or a ternary mixture of methanol–acetonitrile–water. Detection was achieved using a UV detector. Linear calibrations were obtained over the range 10–1200 ng and detection limits were 0.4–4.0 ng for the metal chelates.

INTRODUCTION

Metal chelates appear to be convenient species for the determination of metals by gas chromatography (GC) and high-performance liquid chromatography (HPLC). A number of complexing reagents for GC and HPLC of metals as metal chelate compounds have been suggested [1,2]. The most commonly used complexing reagents are β -diketones, β -thioketones, bi- and tetradentate ketoamine Schiff bases [3,4], dialkyl dithiophosphates, dialkyl dithiocarbamates and oxines [5,6]. Tetradentate ketoamine Schiff

bases are interesting because they form neutral and volatile metal chelates with copper(II), nickel(II), palladium(II), platinum(II) and oxovanadium(IV). They also have high molar absorptivities in the ultraviolet region [7,8]. The introduction of a trifluoromethyl group adjacent to carbonyl has a favourable effect on the thermal stability and volatility of metal chelates [1]. Therefore, in the present work, two new fluorinated tetradentate ligands, N,N'-ethylenebis(1,1,1-trifluoro-6-methyl-2-oxoheptan-4-imine) [bis(trifluoroisovalerylacetone) ethylenediimine] (H_2TFIVA_{2en}) and N,N'-1,2-propylenebis(1,1,1-trifluoro-6-oxoheptan-4-imine) [bis(trifluoroisovalerylacetone)propylenediimine] (H_2TFIVA_{2pn}), have been examined for their possible use for GC and HPLC separation of copper, nickel, palladium and oxovanadium.

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EXPERIMENTAL

The reagents H_2TFIVA_2en and H_2TFIVA_2pn were prepared by condensation of 1,1,1-trifluoro-6-methyl-heptane-2,4-dione with ethylenediamine or 1,2-propylenediamine in 2:1 molar ratio. The copper and nickel chelates were prepared by heating together equimolar solutions of reagent and copper(II) acetate or nickel(II) acetate. Palladium(II) chelates were prepared by refluxing together reagent solution and palladium–benzocnitrile adduct in benzene. The oxovanadium chelates were prepared by the ligand-exchange method [9,13].

Elemental microanalyses were carried out by Elemental Micro Analysis, Devon, UK. Mass spectrometry of the reagents was performed at the HEJ Research Institute of Chemistry, University of Karachi, Pakistan. Spectrometric studies were carried out using an Hitachi 220 spectrophotometer.

Thermogravimetry (TG) and differential thermal analysis (DTA) of metal chelates were recorded on a Shimadzu TG 30 thermal analyser, with a heating rate of $15^\circ C/min$ and nitrogen flow-rate of $50\text{ cm}^3/min$ and samples of 5–12 mg.

A Hitachi 163 gas chromatograph equipped with a flame ionization detector and a Hitachi 056 recorder was used. Stainless-steel columns ($2\text{ m} \times 3\text{ mm}$ and $3\text{ m} \times 3\text{ mm}$) packed with OV-101 (3%) or OV-17 (3%) on Chromosorb W HP, 80–100 mesh, and Dexil GC 400 (2%) on Uniport HP, 60–80 mesh, were used.

A Model 3700 gas chromatograph equipped with a flame ionization detector (Varian Instruments) and a DB-5 (methyl phenyl silicon) column (J. and W. Scientific) ($30\text{ m} \times 0.25\text{ mm}$ I.D., film thickness $0.25\text{ }\mu\text{m}$) were used.

A Hitachi 655A liquid chromatograph connected to a variable-wavelength UV monitor, a Rheodyne 7125 injector and a Hitachi 561 recorder was used. Nova Pak C_{18} ($150\text{ mm} \times 3.9\text{ mm}$ I.D.) (Waters) and Microsorb ($150\text{ mm} \times 4.6\text{ mm}$ I.D.) (Hewlett Packard) columns were used.

RESULTS AND DISCUSSION

The results of elemental microanalyses corresponded to the expected values. The mass and

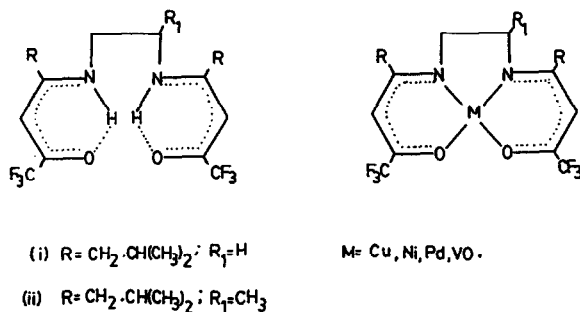


Fig. 1. Structural diagram of reagents and metal chelates.

infrared spectra agreed with the structure of ligands and metal chelates assigned (Fig. 1) [13].

TG and DTA of metal chelates were performed to check their volatility and thermal stability. The results of thermoanalytical studies (Fig. 2) show that rapid and single-stage weight loss of copper, nickel and palladium chelates of H_2TFIVA_2pn within 92–100% occurred in the temperature range $205\text{--}365^\circ C$. However, the oxovanadium chelate lost mass in three stages. A major loss of 59% occurred between 225 and $350^\circ C$, with a maximum rate of loss at $310^\circ C$. A secondary loss of 16% occurred by $405^\circ C$ and a total loss of 84% by $500^\circ C$.

The copper, nickel, palladium and oxovanadium chelates of H_2TFIVA_2en and H_2TFIVA_2pn were investigated on different packed columns, but a better peak shape with baseline return was observed on the $3\text{ m} \times 3\text{ mm}$ column packed with Dexil GC 400 (2%) on Uniport HP, 60–80 mesh size. When separation of copper, nickel, oxovanadium and palladium chelates of H_2TFIVA_2en was attempted, copper, nickel and oxovanadium co-eluted and only palladium could be separated. Similarly, the palladium chelate of H_2TFIVA_2pn was completely separated from the copper, nickel and oxovanadium chelates, and partial separation of oxovanadium from copper and nickel was obtained, but no separation of copper and nickel chelates was observed (Fig. 3). For the separation of copper and nickel, a DB-5 ($30\text{ mm} \times 0.25\text{ mm}$) capillary column was also tried, but without any success.

The response of the flame ionization detector using a packed column was compared with the amount of the complex injected; calibration curves were obtained by plotting average peak

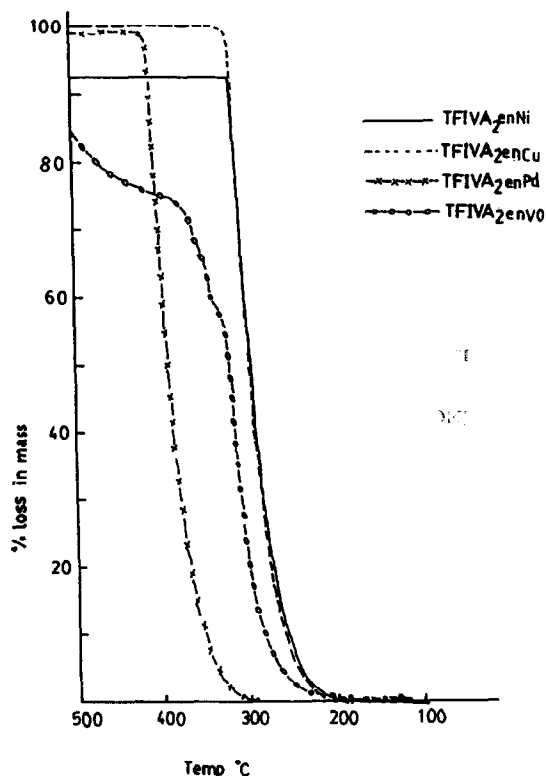


Fig. 2. TG of metal chelates at a heating rate 15°C/min and nitrogen flow-rate 50 cm³/min.

height ($n = 3$) versus amount of complex injected and were found to be linear in the range 1–8 μg . The detection limit measured as three times the background noise was found to be 4–40 ng of metal chelates, corresponding to 0.5–5 ng of a metal ion, and compare favourably with related compounds [4,8,10].

The metal chelates had reasonable thermal stability and volatility on elution from GC columns, but failed to separate adequately. It was therefore decided to examine the reagents for HPLC separation of their metal chelates. HPLC was combined with variable UV detection.

The copper, nickel, palladium and oxovanadium complexes of $\text{H}_2\text{TFIVA}_2\text{en}$ eluted easily with a binary mixture of methanol and water on a Nova-Pak C₁₈ column, but optimal separation of copper, nickel, palladium and oxovanadium was obtained when complexes were isocratically eluted with a ternary mixture of methanol–ac-

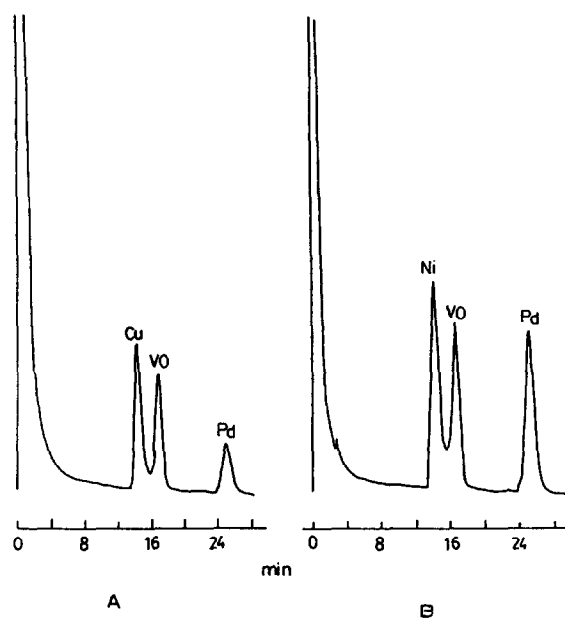


Fig. 3. GC separation of (A) copper, oxovanadium and palladium and (B) nickel, oxovanadium and palladium chelates of $\text{H}_2\text{TFIVA}_2\text{en}$ on a column (3 m \times 3 mm) packed with Dexil GC 400 (2%) on Uniport HP, 60–80 mesh size. Column temperature, 260°C, with programmed rise in temperature of 0.5°C/min up to 280°C; injection port temperature, 290°C; nitrogen flow-rate, 30 cm³/min.

etonitrile–water (65:7:28, v/v/v) (Fig. 4). The order of elution was oxovanadium, copper, palladium and nickel, and retention volumes were 7.36, 26.21, 33.70 and 35.46 cm³, respectively. It should be noted that resolution between palladium and nickel complexes at optimized conditions of separation was only 1.03.

The elution and separation of metal chelates

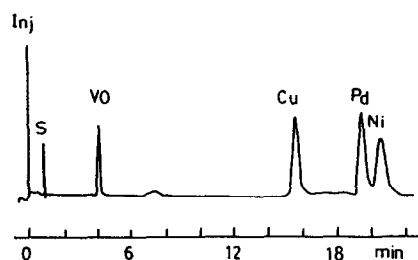


Fig. 4. HPLC separation of oxovanadium, copper, palladium and nickel chelates of $\text{H}_2\text{TFIVA}_2\text{en}$ on a Nova Pak C₁₈ (150 \times 3.9 mm) column. Elution: methanol–acetonitrile–water (65:7:28, v/v/v), flow-rate 1.7 cm³/min. Detection UV at 300 nm.

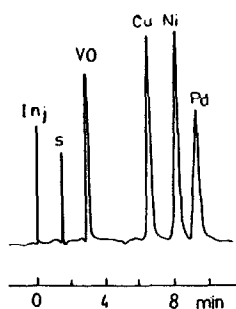


Fig. 5. HPLC separation of oxovanadium, copper, nickel and palladium chelates of H_2TFIVA_2pn on a Microsorb C_{18} (150×4.6 mm) column. Elution: water–methanol (15:85). Flow-rate $1\text{ cm}^3/\text{min}$. Detection: UV at 260 nm.

of H_2TFIVA_2pn were investigated on a Microsorb C_{18} column. Complete separation of oxovanadium, copper, nickel and palladium was obtained when the complexes were eluted isocratically with a binary mixture of 15% water in methanol (Fig. 5). The order of elution observed was oxovanadium, copper, nickel and palladium, and retention volumes were 2.92, 6.5, 8.1 and 9.34 cm^3 , respectively.

The linear calibration ranges at optimized conditions of separation were also checked and were found to be in the range 10–1200 ng of metal chelates. The detection limits were found to be 0.4–4.0 ng of metal chelates, corresponding to 44–764 pg of metal ions. Thus an improvement in detection limits has been observed as compared with related compounds [10–12].

CONCLUSIONS

The metal chelates are volatile and on elution from GC columns only complete separation of

palladium from copper, nickel and oxovanadium is achieved. Calibration curves are linear at the microgram level and detection limits are 4–40 ng of metal chelate. Reversed-phase HPLC with UV detection not only provided ease of separation, but also resulted in considerable improvement in the detection limits to 0.4–4.0 ng of metal chelates. The separation of copper, nickel, palladium and oxovanadium chelates of H_2TFIVA_2pn on a Microsorb C_{18} column within 10 min may be considered as highly promising for the quantitative determination using pre-column derivatization as reported for related compounds [10–12].

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