Chromatographic studies of Oxovanadium(IV), Palladium(II), Copper(II) and Nickel(II) Chelates of some Fluorinated Tetradentate Schiff Bases

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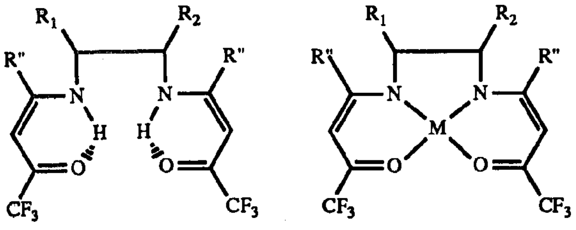
Summary: The oxovanadium(IV) complex of N,N-ethylenebis(1,1,1-trifluoro-6-methyl-5-hepten-2-oneimine) ($H_2F_3AM_2en$), palladium(II) complex of N,N-1,2-propylene-bis (1,1,1-trifluoro-6-methyl-5-hepten-2-oneimine) ($H_2F_3AM_2pn$) and oxovanadium(IV) and palladium(II) complexes of dl-N,N-stilbenebis(1,1,1-trifluoro-6-methyl-5-hepten-2-oneimine-(dl-$H_2F_3AM_2S$) are prepared. Separation of the complexes together with their copper and nickel complexes are attempted by gas chromatography (GC) and reversed phase high performance liquid chromatography (HPLC). Copper, oxovanadium and palladium or nickel, oxovanadium and palladium complexes of dl-$H_2F_3AM_2S$ are separated by GC. On the other hand, copper, nickel and palladium or copper, nickel and oxovanadium complexes are separated by reversed phase HPLC with Zorbax ODS column. The detection limits of F_3AM_2enVO, dl-F_3AM_2SVO and F_3AM_2pnPd are 10 ng, 5 ng and 10 nm, respectively.

Introduction

A reasonable GC elution and easy separation on adsorption HPLC of copper and nickel complexes of N,N'-ethylene-bis(1,1,1-trifluoro-6-me thyl-5-hepten-2-oneimine), [bis(trifluoroacetyl mesityloxide) ethylenediimine] ($H_2F_3AM_2en$); N,N'-1,2-propylene bis(1,1,1-trifluoro-6-methyl-5-hepten-2-oneimine), [bis(trifluoroacetylmesityloxide]-propylenediimine ($H_2F_3AM_2pn$); dl-N,N'- stilbene bis(1,1,1-trifluoro-6-methyl-5-hepten-2-oneimine, [bis(trifluo roacetylmesityl oxide) meso-stilbenediimine (meso-$H_2F_3AM_2S$) have recently been reported [1]. Oxo vanadium and palladium chelates of $H_2F_3AM_2en$, $H_2F_3AM_2pn$ and dl-$H_2F_3AM_2S$ were prepared (Fig. 1) and separations of the metal chelates together with their copper and nickel chelates were attempted by using GC and HPLC.



R" = Isobutene, R_1 & R_2 = H
R" = Isobutene, R_1 = H, R_2 = CH_3
R" = Isobutene, R_1 & R_2 = C_6H_5
M = Cu, Ni, Pd, VO

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

Results and Discussion

The palladium and oxovanadium complexes are easily prepared in good purity and results of elemental analysis agree with the expected values. The IR spectra of oxovanadium complexes indicate a band within 985-990 cm^{-1} which could be assigned V = O stretching vibrations [5]. The bands observed at 360, 410, 520-540 cm^{-1} of weak to medium intensity in the spectra of palladium and oxovanadium, but not in the spectra of their corresponding reagents, could be assigned to metal ligand vibrations. The spectrophotometric studies of oxovanadium chelate in chloroform indicate a band in visible region due to d-d transition and a series of high intensity bands in UV region due to intra ligand π-π^* transitions ideally suited for HPLC detection by spectrophotometry.

TG of F_3AM_2pnPd and dl-F_3AM_2SVO indicate a rapid loss of 80% and 73% in temperature range 190-360 and 240-440°C with maximum rate of loss at 300°C and 320°C respectively. However under similar conditions F_3AM_2enVO indicates rapid loss of only 50% in temperature range 190-430°C (Fig. 2). DTA of F_3AM_2enVO and dl-F_3AM_2SVO indicate melting endotherm at 190°C and 128°C respectively. The complexes indicate a series of vaporisation/decomposition exotherms, but exotherms observed between 400-500°C could be assigned to decomposition exotherms of nonvolatile residue (Fig. 3).

Fig. 2: TG curves of palladium and oxovanadium chelates (I) F_3AM_2pnPd (2) F_3AM_2enVO and (3) dl-F_3AM_2SVO at a heating rate 15°C/min and N_2 flow rate 50 cm^3/min.

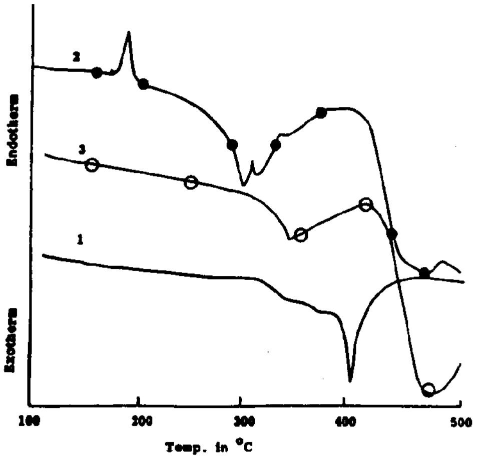


Fig. 3: DTA of palladium and oxovanadium chelate (1) F_3AM_2pnPd (2) F_3AM_2enVO (3) dl-F_3AM_2SVO at a heating rate 15°C/min and nitrogen flow rate 50 cm^3/min.

The separation of oxovanadium and palladium complexes of $H_2F_3AM_2en$, $H_2F_3AM_2pn$, and dl-$H_2F_3AM_2S$ together with their copper and nickel chelates were attempted with different GC columns. Unfortunately copper, nickel and oxovanadium complexes of $H_2F_3AM_2en$ and copper, nickel and palladium complexes of $H_2F_3AM_2pn$ could not be separated. On the other hand copper, oxovanadium and palladium or nickel, oxovanadium and palladium complexes of dl-$H_2F_3AM_2S$ were completely separated on OV17 column (Fig. 4). However, copper and nickel complexes of the same ligand were not separated. The retention times of copper, nickel, oxovanadium and palladium complexes of dl-$H_2F_3AM_2S$ were 14.61, 14.61 and 18.41, 25.33 min respectively.

In order to demonstrate the usefulness of GC for the separation of reagents and their metal chelates, using packed columns, the separation of reagents and their metal complexes of four fluorinated ligands $H_2F_3AM_2en$, $H_2F_3AM_2pn$, dl-$H_2F_3AM_2S$ and meso-$H_2F_3AM_2S$ were examined on column (3 m x 3 mm) packed with OV 17, 3% on Chromosorb WHP 30-100 mesh size. Fig. 5 shows complete separation of eight components, with elution in sequence (1) dl-$H_2F_3AM_2S$, (2) $H_2F_3AM_2pn$ (3) F_3AM_2enVo (4) F_3AM_2pnPd, (5) dl-F_3AM_2SNi (6) dl-F_3AM_2SVO, (7) meso-F_3AM_2SNi and (8) dl-F_3AM_2SPd (Fig. 5).

The calibration curves of palladium and oxovanadium complexes measured as average peak height versus amount of complex injected were linear at μg level of a complex (1-24 μg). The detection limits of F_3AM_2enVO, F_3AM_2pnPd, dl-F_3AM_2SVO and dl-F_3AM_2SPd measured as three time of background noise were 60 ng, 120 ng, 120 ng, and 160 ng respectively.

Complete separation of copper and nickel complexes of $H_2F_3AM_2en$, $H_2F_3AM_2pn$, dl-$H_2F_3AM_2S$, and meso-$H_2F_3AM_2S$ by adsorption HPLC has been reported [1], but the dominant separation mode in modern HPLC is reversed phase. It was therefore the copper, nickel and oxovanadium or copper, nickel and palladium complexes $H_2F_3AM_2en$, dl-$H_2F_3AM_2S$ and $H_2F_3AM_2pn$ were tried by reversed phase HPLC with Zorbax ODS column. The oxovanadium, cop-

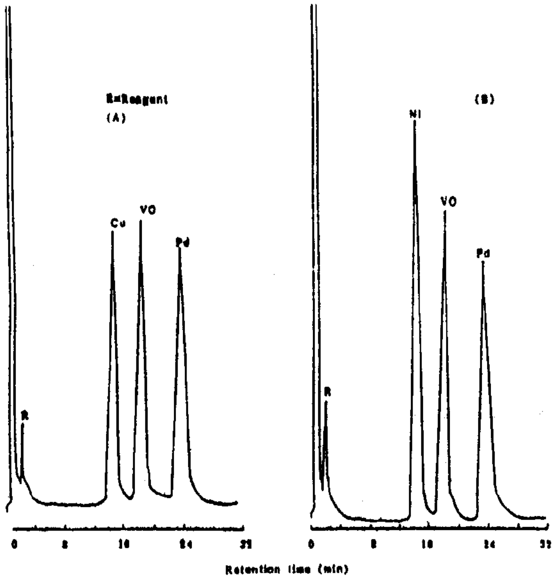


Fig. 4: GC separation of (A) Cu, VO and Pd (B) Ni, VO and Pd chelates of dl-$H_2F_3AM_2S$. Column (3m x 3mm) packed with OV17, 3% on Chromosorb WHP 80-100 mesh size, column temperature 270°C, injection port 290°C and nitrogen flow rate 30 cm^3/min.

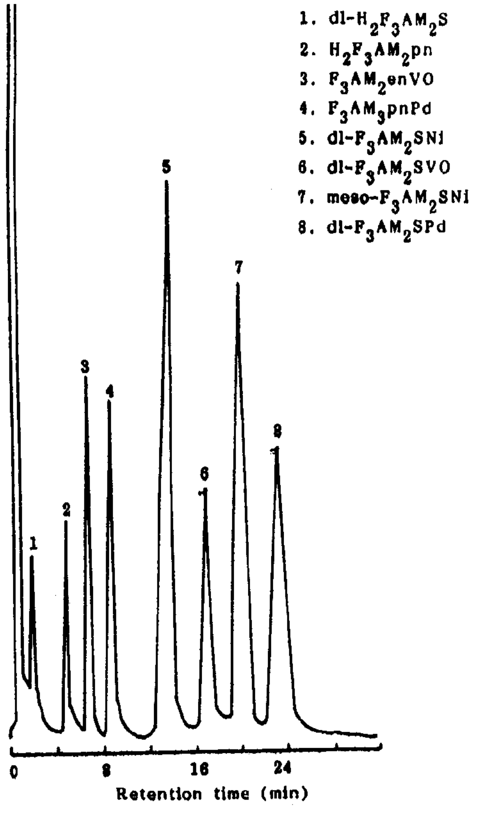


Fig. 5: GC separation of reagents and their metal chelates (1) dl-$H_2F_3AM_2S$ (2) $H_2F_3AM_2pn$ (3) F_3AM_3enVO (4) F_3AM_2pnPd (5) dl- F_3AM_2SNi (6) dl-F_3AM_2SVO (7) meso-F_3AM_2SNi (8) dl-F_3AM_2SPd. Column (3m x 3mm) packed with OV17, 3% on Chromosorb WHP-100 mesh size. Column temperature 280°C, injection port 290°C and nitrogen flow rate 30 cm^3/min.

per and nickel complexes of $H_2F_3AM_2en$ and dl-$H_2F_3AM_2S$ (Fig. 6) and palladium, copper and nickel complexes of $H_2F_3AM_2Pn$ (Fig. 7) were separated with a binary mixture of 20% water in methanol.

The effect of the presence of reagent on the separation of metal complexes was also checked, and it was found that the reagent dl- $H_2F_3AM_2S$ eluted just after the solvent and $H_2F_3AM_2en$ after its oxovanadium complex, but before copper and nickel complexes without affecting the separation of metal chelates. However, the reagent $H_2F_3AM_2pn$ under similar conditions interferred the responses of its metal chelates.

The linear calibration curves of oxovanadium and palladium complexes were obtained under optimum separation conditions at μg levels of a complex injected (0.5-5μg) (Fig. 8). The approximate detection limits for F_3AM_2enVO, dl-F_3AM_2SVO and F_3AM_2pnPd were 10 ng, 5 ng and 10 ng respectively, corresponding to 1.4 VO, 0.54 ng VO and 2 ng Pd.

Experimental

Preparation of palladium complexes

Palladium(II) chloride (0.088 g) and benzonitrite (0.5 cm^3) were refluxed for 2 hrs and the mixture was diluted with benzene (5 cm^3). The reagent $H_2F_3AM_2en$ (0.22 g) or dl-$H_2F_3AM_2S$ (0.28 g) dissolved in benzene was added to palladium-benzonitrile adduct and the mixture was refluxed for 24 hrs. The solution was filtered and the benzene from filtrate was distilled off and remaining solvent was evaporated under vacuum desicator. The residue was dissolved in n-hexane containing a few drops of ethanol. The precipitate obtained was recrystallised from n-hexane. F_3AM_2pnPd, calculated for $C_{19}H_{22}N_2O_2F_6Pd$, expected %, C=43.01, H=4.15, N=5.28; found %, C=43.21, H=4.22, N=5.30, dl-F_3AM_2SPd, m.p = 250°C, calculated for $C_{30}H_{28}N_2O_2F_6Pd$, expected % C=53.89, H=4.19, N=4.19; found % C=53.76, H=4.30, N=4.25. IR (KBr) cm^{-1} F_3AM_2pnPd, 520(w), 560 (vw), 1420 (s) 1520(s), 1606(s), 1635(w), dl-F_3AM_2SPd, 360(wb), 520(wb), 1305(vs), 1510(vs), 1600(vs), 1650 (w).

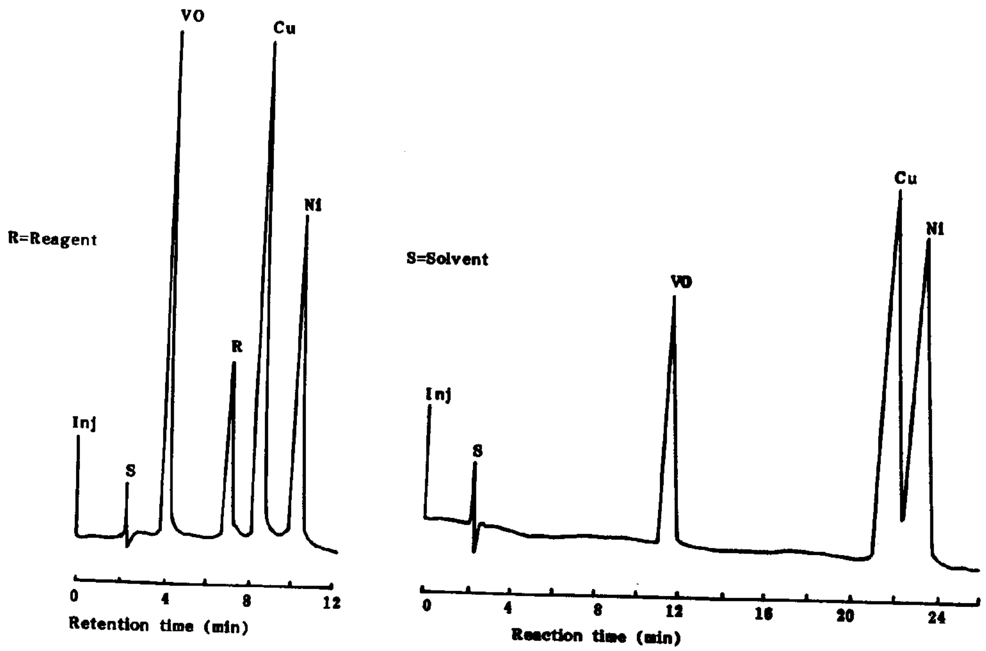


Fig. 6: HPLC separation of VO, Cu and Ni complexes of (A) $H_2F_3AM_2en$ (B) dl-$H_2F_3AM_2S$. Column (250 x 4.6 mm) Zorbax ODS with guard ODS column. Eluent methanol:water (80:20), flow rate 1 cm^3/min. UV detection at 310 nm.

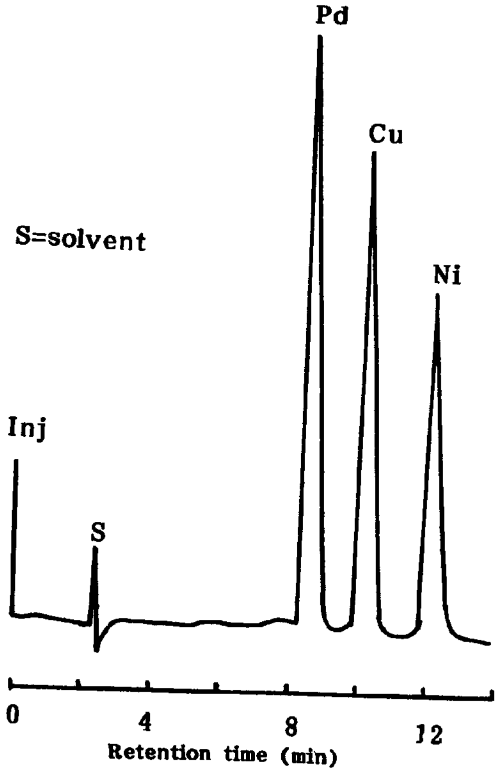


Fig. 7: HPLC separation of Pd, Cu, Ni complexes of $H_2F_3AM_2pn$ on Zorbax ODS column. Eluent methanol:water (80:20) flow rate 1 cm^3/min and UV detector at 310 nm.

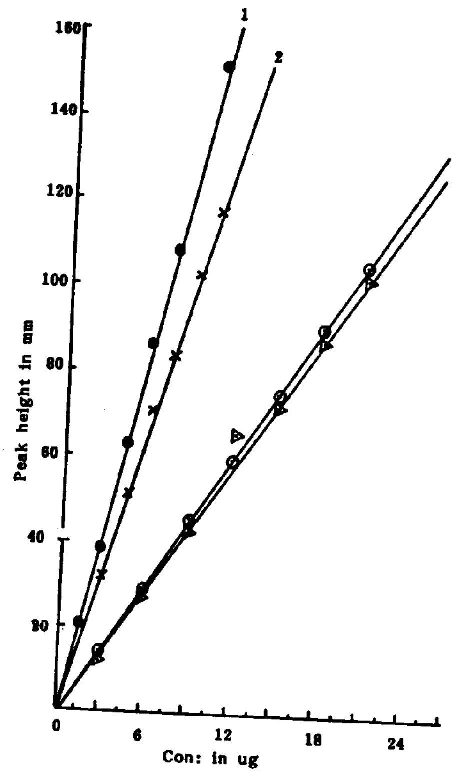


Fig. 8: Linear calibration of (1) dl-F_3AM_3SVO (2) dl-F_3AM_2SPd (3) F_3AM_2PnPd and (4) F_3AM_2enVO. Conditions same as Fig. 6.

Preparation of oxovanadium(IV) complexes

The oxovanadium complexes were conveniently prepared by ligand exchange method, following a general procedure of Martin and Ramish [2] as under:

Bis(acetylacetone)oxovanadium(IV) (0.13 g) and $H_2F_3AM_2en$ (0.23 g) or dl-$H_2F_3AM_2S$ (0.28 g) were placed together in 10 cm^3 round bottom flask connected to high vacuum pump, the mixture was heated between 220-30°C at 3 mm Hg for 2 hr. The contents were washed with dry ether and recrystallized from n-hexane or benzene. F_3AM_2enVO, m.p. = 190°C, calculated for $C_{18}H_{20}N_2O_2F_6VO$, expected % C = 59.9, H = 5.50, N = 7.71; found % C = 59.41, H = 5.32, N = 7.80, dl-F_3AM_2SVO, m.p. = 128°C calculated for $C_{30}H_{28}N_2O_2F_6VO$, expected % C = 57.23, H = 4.45, N = 4.45; found % C = 57.30, H = 4.50, N = 4.39. IR (KBr) cm^{-1}, F_3AM_2enVO, 410(w), 460(w), 525(m), 990(m), 1245(m), 1525(w), 1545(s), 1615(s), 1655(w), dl-F_3AM_2SVO, 360(w), 540 (w), 985(m), 1300(mb), 1500(s), 1600(s), 1640(s). UV and visible, chloroform λ-max nm (ε = 1. mole^{-1} cm^{-1}), F_3AM_2enVO, 560(sh) (23), 355 (sh) (1500), 320(5300), 282 (sh) (10000), 275 (11000), 242 (21000), dl- F_3AM_2SVO, 614(112), 355 (sh) (6800), 322 (24000), 285 (sh) (15000), 240 (13000).

The reagents and their copper and nickel complexes were prepared as reported [3]. Bis(acetylacetone) oxovanadium(IV) complex was prepared as reported [4].

Elemental analysis was carried out by Elemental Micro-Analysis Ltd. U.K. The IR spectra of the compounds were measured with Perkin Elmer 1430 IR spectrophotometer. Spectrophotometric studies were carried out with Hitachi 220 Spectrophotometer. DTA and TGA of metal chelates were carried out with Shimadzu TG 30 Thermal Analyzer at a heating rate of 15°C min and nitrogen flow rate of 30 cm^3/min.

Hitachi 163 gas chromatograph, connected with FID detection system and recorder 056 was used. Stainless steel column (2m x 3 mm) or (3m x 3mm) packed with OV17, 3% or OV101, 3% on Chromosorb WHP 80-100 mesh size were used.

Shimadzu LC-5 liquid chromatograph, connected with spectrophotometric detector SPD-2A, LC injector SIL-1A and Chromatograph C-RIB was used. Zorbax ODS column (250 x 4.66 mm) and guard ODS column were used for separation by reversed phase HPLC.

References

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