Gas Chromatographic Studies of Palladium(II) and Vanadium(IV) oxide Complexes of Meso-And DL- Bis(acetylacetone)stilbenediimine and Meso-And DL- Bis(trifluoroacetylacetone)stilbenediimine

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Summary: The palladium and vanadium(IV) oxide complexes of bis(acetylacetone)-meso-stilbenediimine (meso-H_2AA_2S), bis(acetylacetone)dl-stilbenediimine (dl-H_2AA_2S), bis(trifluoroacetylacetone)meso-stilbenediimine(meso-$H_2F_2AA_2S$) and bis(trifluoroacetylacetone)dl-stilbene -diimine(dl-$H_2F_3AA_2S$) have been prepared, and their DTA and TGA indicate that the complexes are somewhat volatile. The complexes eluted from the stainless steel gas chromatographic column (2 m x 3 mm) and (3 m x 3 mm) packed with OV101, 3% on Chromosorb 80-100 mesh size and Dexil 400 GC, 2% on Uniport HP 60-80. The linear calibration ranges were within 0.5-20 μg and detection limits were within 10-250 ng of metal complexes at the optimized conditions of separation. The relative elution of the metal complexes on nonpolar column indicated that introduction of phenyl groups increases and trifluoromethyl group decreases on column retention of the metal complexes.

Introduction

The gas chromatography (GC) of metal chelates have remained limited by the volatility and thermal stability of metal chelates. The ligands used for successful gas chromatographic elution and separation of metals as metal chelates involve mostly β-diketones, β-thioketones, bis and tetradentate β-ketoamines, dialkyldithiocarbamates, dialkyldithiophosphates and prophyrins as complexing re agent [2]. The tetradentate ketoamine Schiff bases have proved useful gas chromatographic reagents for copper (II), nickel(II), palladium(II) and vana dium (IV) oxide complexes [3-5]. Recently gas chro -matographic elution of copper(II) and nickel(II) complexes of meso- and dl-bis(acetylace- tone)-stilbenediimine (meso-H_2AA_2S) and (dl-H_2AA_2S) and meso-and dl-bis(tri-fluoro-acetylacetone)stilbe -nediimine (meso-$H_2F_3AA_2S$ and dl-HF_3 AA_2S, have been reported [6,7]. In the present work the elution and separation of palladium and vanadium oxide complexes of meso-H_2AA_2S, dl-H_2 AA_2S, meso-$H_2F_3AA_2S$ and dl-$H_2F_3AA_2S$ toge- ther with their copper and nickel complexes have been examined on GC columns and the effects of substituents on the comparative elution have been determined.

Experimental

The copper(II) and nickel(II) complexes of bis(acetylacetone)meso-stilbenediimine(meso-H_2A A_2S),bisacetylacetone)dl-stilbenediimine(dl-H_2 AA_2S),bis(trifluoroacetylacetone)meso-stilbenedii mine (meso $H_2F_3AA_2S$) and bis (trifluoroacctylace -tone) dl-stilbenediimine (dl-$H_2F_3AA_2S$) were prepared as reported earlier [6-8]. The vana dium (IV) oxide complexes of dl-H_2AA_2S and meso-H_2 AA_2S were prepared as reported by Pasini and Gullotti [9]. The vanadium (IV) oxide complex of dl-$H_2F_3AA_2S$ was prepared by ligand exchange method, following general procedure of Martin and Ramish [10].

The palladium complexes were prepared by refluxing together (8-12 hr) equimolar solution of the reagent and palladium-benzonitrile complex in benzene. The solvent was removed and the complex was repeatedly extracted in n-hexane at 50-60 ^{o}C. The extracts were concentrated and cooled. The precipitates obtained were recrystallized from n-hexane or ethanol.

Elemental micro analysis (Table-1) was carried ou by Elemental Micro-Analysis Ltd., U.K. TG

and DTA of palladium and vanadium(IV) oxide complexes were recorded on Shimadzu TG 30 Thermal Analyser at a heating rate of 15°C/min and nitrogen flow rate of 50 cm^3/min.

Hitachi 163 Gas Chromatograph connected with FID detection system and recorder 056 was used. Stainless steel column (2 m x 3 mm) and (3 m x 3 mm) packed with OV101, 3% or OV17, 3% on Chromosorb 80-100 mesh size and (3 m x 3 mm) Dexil 400 GC, 2% on Uniport HP 60-80 mesh size was used.

Results and Discussion

The palladium and vanadium complexes are easily prepared and the results of elemental analysis correspond to the expected value. The results of TG of palladium complexes (Fig. 1) indicated rapid loss of 65-97% in weight upto 370°C. The palladium complexes of fluorinated ligands dl-$H_2F_3AA_2S$ and meso-$H_2F_3AA_2S$ have less residue and hence are more thermal stable and volatile as compared to nonfluorinated ligands dl-H_2AA_2S and meso-H_2AA_2S. Similarly, palladium complexes of dl-$H_2F_3AA_2S$ and dl-H_2AA_2S show higher percent weight loss as compared to the corresponding meso- isomers (meso-$H_2F_3AA_2S$ and meso-H_2AA_2S). TG of dl-AA_2SVO and dl- F_3AA_2SVO indicate rapid loss of 81%, followed by secondary loss upto 500°C. Fluoro substitution in vanadium complex dl-F_3AA_2SVO also imparts higher percent weight loss as compared to unsubstituted complex dl- AA_2SVO. DTA of the metal complexes show melting endotherms, followed by vaporisation/decomposition exotherms (Fig.2).

The palladium(II) and vanadium(IV) oxide complexes are somewhat volatile as reflected from their TG curves. The complexes were therefore examined on a GC column. The complexes meso-AA_2SVO and meso-AA_2SPd were difficult to elute from GC columns and failed to give single peaks, but a series of peaks was observed which may be due to decomposition products. The palladium complex meso- F_3AA_2SPd eluted from the GC columns in temperature range within 260-90°C and nitrogen flow rate of 30 cm^3/min. The separation of the palladium complex from meso-F_3AA_3SCu and meso- F_3AA_2SNi was easily achieved, but the separation between the copper and nickel complexes on OV101 and OV17 could not be obtained

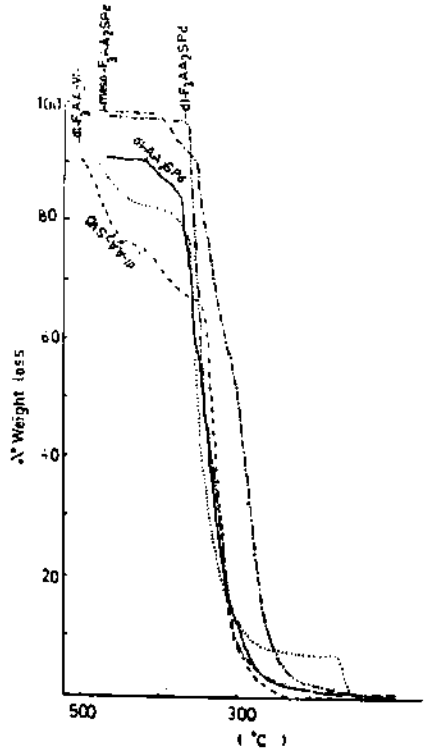

Fig.1: TG of Pd(II) and V(IV)O complexes at a heating rate of 15°C/min and nitrogen flow rate of 50 cm^3/min.

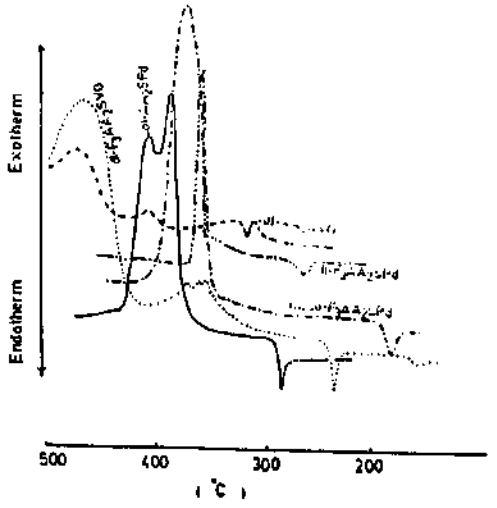

Fig.2: DTA of metal complexes at a heating rate of 15°C/min and nitrogen flow rate of 50 cm^3/min.

as has been reported earlier [6]. The separation of Copper(II), nickel(II), palladium(II) and vanadium (IV)oxide complexes of dl-$H_2F_3AA_2S$ was ex-

amined on different columns and complete separation between nickel, vanadium, palladium, and copper, vanadium and palladium was achieved on stainless steel column (3 m x 3 mm) packed with Dexil 400 GC, 2% on Uniport HP 60-80 at temperatures column 280°C, injection port 290 and nitrogen flow rate 30 cm^3/min (Fig. 3A). However, the separation between copper and nickel complexes was again not obtained as reported earlier [6]. Similarly, the separation between copper (II), nickel(II), palladium(II) and vanadium (IV) oxide complexes of dl-H_2AA_2S was examined on GC column and on optimum separation between copper, nickel, vanadium and palladium complexes was achieved, when the complexes were eluted on stainless steel column (3 m x 3 mm) packed with OV101, 3% on Chromosorb 80-100mesh size at a column temperature 250°C with programmed rise in temperature 1°C/min upto 270°C injection port 280°C and nitrogen flow rate 30 cm^3/min (Fig. 3b).

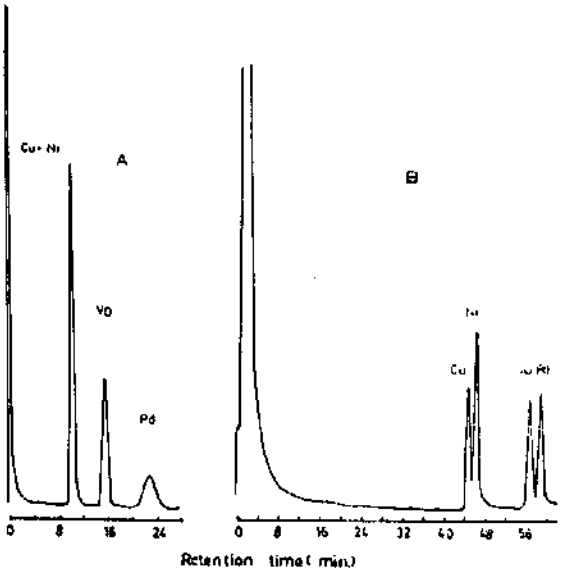

Fig.3: Gas chromatographic separation (A) Cu(II), Ni(II), V(IV)O and Pd(II) complexes of dl-$H_2F_3AA_2S$ on column (3 m x 3 mm) packed with Dexil GC 400, 2% on Uniport HP 60-80, temperature column 280, injection port 290, N_2 flow rate 30 cm^3/min. (B) Separation of Cu(II), Ni(II), V(IV)O and Pd(II), complexes of dl-H_2AA_2S on column (3 m x 3mm) packed with OV101, 3% on Chromosorb WHP 80- 100 at temperature column 250°C with programmed rise in temp 1°C/min upto 270°C, injection port 280°C, N_2 flow rate 30 cm^3/min.

The linear calibration ranges of palladium and vanadium oxide complexes were determined by injecting different amounts of the complexes at the optimized conditions of separation and average peak of at least two injections was measured. They were within 5- 20 μg meso-F_3AA_2SPd, 1-6 μg dl-AA_2SPd, 0.5-3.0 μg dl-F_3AA_2SPd, 2-6 μg AA_2SVO and 0.5-5.6, μg dl-F_3AA_2SVO. The detection limits measured at least three times the background noise were 50 ng meso-F_3AA_2SPd, 50 ng dl-AA_2SPd, 10ng, dl- F_3AA_2SPd, 100 ng dl-AA_2SVO and 10 ng dl-F_3AA_2SVO.

Finally, relative elution of copper(II), nickel(II), palladium(II) and vanadium(IV)oxide complexes of dl-$H_2F_3AA_2S$, meso- H_2AA_2S, meso-$H_2F_3AA_2S$, and bis(acetylacetone)ethyleneldiimine (H_2AA_2en) was examined on the column(2 m x 3 mm) packed with OV101, 3% on Chromosorb 80-100 mesh size (Fig. 4). It was observed that the metal complexes of the ligands having phenyl group substitution of the bridge position are retained for longer time than unsubstituted ligand H_2AA_2en. The metal complexes of fluoro-substituted ligands (dl-$H_2F_3AA_2S$ and meso-$H_2F_3AA_2S$) eluted on nonpolar column (OV101, 3% on Chromosorb 80-100) before the nonfluorinated ligands dl-H_2AA_2S and meso-H_2AA_2S. The results are in agreement

Table-1: Results of Microanalysis

S.No.	Compound	Molecular formula	Melting point °C	% Calculated C	H	N	% Found C	H	N
1.	Bis (trifluroacetylacetone) dl-stilbenediimine Pd(II)	$C_{24}H_{20}N_2O_2F_6Pd$	242	48.96	3.39	4.75	48.50	3.24	4.74
2.	Bis(trifluroacetylacetone) meso-stilbenediimine Pd(II)	$C_{24}H_{20}N_2O_2F_6Pd$	256	48.96	3.39	4.76	48.95	3.94	5.73
3	Bis(acetylacetone)dl-stilbenediimine Pd(II)	$C_{24}H_{26}N_2O_2Pd$	300	59.92	5.40	5.82	59.20	5.38	5.63
4	Bis(acetylacetone)meso-stilbenediimine Pd(II)	$C_{24}H_{26}N_2O_2Pd$	300	59.92	5.40	5.82	60.62	5.60	6.14
5	Bis(trifluoroacetylacetone) dl-stilbenediimine VO(IV)	$C_{24}H_{20}N_2O_2F_6VO$	242	5.36	3.63	5.09	51.87	4.09	4.89
6	Bis(acetylacetone)dl-stilbenediimine VO(IV)	$C_{24}H_{26}N_2O_2VO$	300	65.15	5.86	6.33	65.69	6.06	6.40

with the earlier work of Belcher et al [11] with related tetradentate ligands.

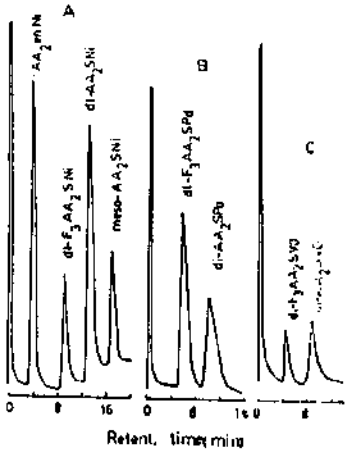

Fig.4: Relative gas chromatographic elution of metal complexes on column (2 m x 3 mm) packed with OV101, 3% on Chromosorb WHP 80- 100 N_2 flow rate of 30 cm^3/min. (A) Ni complexes at temperature 220°C with programmed rise in temp 2°C/min upto 250°C injection port 260°C (B) and (C) at column temp 260 and injection port 270°C.

References

1. P.C. Uden and D.E. Henderson, *Analyst,* **102**, 889 (1977).
2. P.C. Uden, *J.Chromatogr.*, **313**, 3 (1984).
3. R. Belcher, A. Khalique and W.I. Stephen, *Anal.Chim.Acta,* **100**, 503 (1978).
4. S. Celli and E. Patsalides, *Anal.Chim.Acta,* **128**, 109 (1981).
5. O.W. Lau and W.I. Stephen, *Anal.Chim.Acta.*, **180**, 417 (1986).
6. M.Y. Khuhawar, *J.Chem.Soc.Pak.*, **7**, 237 (1985).
7. M.Y. Khuhawar, *Arab Gulf J.Scient.Res., 4, 463 (1986).*
8. H. Kanatomi, I. Murase and A.E. Martell, *J.Inorg.Nucl.Chem.*, **38**, 1465 (1976).
9. A. Pasini and M. Gullotti, *J. Cood. Chem.*, **3**, 319 (1974).
10. D.F. Martin and K. Ramish, *J.Inorg.Nucl.Chem.*, **27**, 2027 (1965).
11. R. Belcher, K. Blessel, T. Cardwell, M. Pravica and W.I. Stephen, *J.Inorg. Nucl. Chem.*, **35**, 1127 (1973).