Preparation and Gas Chromatographic Separation of Copper(II), Nickel(II), Palladium(II) and Vanadium(IV) Oxide Chelates of dl- and meso-Bis (pivaloylacetone) Stilbenediimine

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Summary: The copper(II), nickel(II) and palladium(II) chelates of bis-(pivaloylacetone)meso-stilbenediimine(meso-H_2PA_2S) and copper(II), nickel(II), palladium(II) and vanadium(IV) oxide chelates of bis-(pivaloylacetone) dl-stilbenediimine(dl- H_2PA_2S) were prepared and characterised using IR, ^{1}H-NMR and mass spectroscopic techniques. Spectrophotometric studies, TGA and DTA of metal complexes were also carried out. The complexes are sufficiently volatile and thermally stable and elute easily on GLC columns with linear calibration range within 125-3760 ng and detection limits within 2.8-19 ng of metal ion. Separations between copper, nickel, palladium and vanadium oxide chelates have been achieved, but some overlapping between copper and nickel complexes is obtained. A mixture of metal complexes of meso-and dl-isomers could also be resolved.

Introduction

β-Diketone pivaloylacetone (5,5-dimethylhexan-2,4-dione) and β-ketoamine Schiff base, bis-(pivaloylacetone)ethylenediimine[N,N'-ethylene bis(5,5- dimethyl-4-oxohexan-2-imine)] (H_2PA_2en), have proved useful as gas chromatographic reagents for certain metal ions [1-4]. Recently unsymmetrical tetradentate ligand (Pivaloylacetone) (trifl -uoroacetyl-acetone)ethylenediimine has been reported for the simultaneous determination of copper and nickel [5]. Thus the reagent bis)pivaloy-lace -tone)*meso*-stilbenediimine(*meso*H_2PA_2S) and bis-(pivaloylacetone)dl-stilbenediimine(dl-H_2PA_2S) and their copper(II), nickel(II), palladium (II) and vanadium(IV) oxide chelates have been prepared to investigate the effect of phenyl group substitution at bridge position in H_2PA_2en on the thermal stability and GLC elution of their metal complexes.

Experimental

Preparation of Reagents

Bis(pivaloylacetone)meso-stilbenediimine(meso-N,N'-stilbene bis(5,5'-dimethyl-4-oxohexane-2-imine](meso-H_2PA_2S).

Solution of *meso*-stilbenediamine (0.01M) in ethanol was added to pivaloylacetone (.02M) and the mixture was refluxed for 1 hr. The mixture was cooled and precipitate filtered and recrystallized from acetone.

Bis(pivaloylacetone)dl-stilbenediimine[dl-N,N'-stilbene bis(5,5-dimethyl-4-oxohexan-2-imine)] (dl-H_2PA_2S

An ice cold solution of *dl*-stilbenediamine 0.01M in ethanol was slowly added to pivaloylacetone (0.02M) with constant shaking. The reaction mixture was kept cool for 2 days. The precipitate was filtered, washed with n-hexane and recrystallised twice from cyclohexane.

Preparation of Bis(pivaloylacetone)dl-stilbenediimine copper(II) (dl-PA_2SCu), Bis(pivaloylacetone)dl-stilbenediimine nickel(II) (dl-PA_2SNi), Bis(pivaloylacetone)meso-stilbenediimine copper(II) (meso-PA_2Scu) and Bis(pivaloylacetone)meso- stilbenediimine nickel(II) (meso-PA_2-SNi)

Equimolar solutions of copper(II) acetate and nickel(II) acetate in methanol was added to the solution of *meso*-H_2PA_2S and dl- H_2PA_2S in methanol. The mixture was refluxed for 1 hr. and was concentrated. After cooling, the precipitate was filtered and recrystallized from methanol.

Preparation of Bis(pivaloylacetone)dl-stilbenediimine palladium(II) (dl-PA_2SPd) and Bis(pivaloylacetone) meso- stilbe nediimine palladium(II) (meso-PA_2SPd)

Palladium(II) chloride (0.176 g) was heated with benzonitrile (0.4 ml) for 2 hr and palladium benzonitrile complex formed was diluted with benzene (3 ml), and was added to meso-H_2PA_2S or dl-H_2PA_2S (0.46 g) in benzene. The contents were refluxed overnight and most of the benzene was distilled off. The residue was dried in vacuum desicator (70 mm Hg) and was extracted with n-hexane, containing a few drops of ethanol. Finally the palladium complexes were recrystallized from n-hexane.

Preparation of Bis(pivaloylacetone)dl-stilbenediimine vanadium(IV) oxide (dl-PA_2SVO)

Bis (acetylacetone) vanadium(IV) oxide (0.2g) and *dl*-H_2PA_2S (0.54 g) were heated in a microdistillation apparatus connected to vacuum pump at 230-240°C at a pressure of 8 mm Hg for 3 hr. The reaction mixture was washed with dry ether and residue was dissolved in n-hexane-ethanol and recrystallised from n-hexane.

Elemental micro-analysis (Table 1) and DTA and TG of the copper and nickel complexes were recorded by Elemental Micro-Analysis Ltd. U.K. DTA and TG was recorded at a heating rate of 15°C/min and nitrogen flow of 20 cm^3/min. DTA and TG of palladium complexes were recorded on Shimatzu TG 30 Thermal Analyser at a heating rate of 15°C/min and nitrogen flow rate of 50 cm^3/min. TG and DTA of vanadium complex was recorded by Department of Chemistry, Quaid-e-Azam University, Islamabad at a heating rate of 10°C/min and nitrogen flow rate of 40 cm^3/min. IR spectra in range of 4000-250 cm^{-1} was recorded in KBr on Hitachi 260-50. Mass spectra on Finnigan MAT 1125 and ^{1}H-NMR on Bruker AM 300 in $CDCl_3$ were recorded at HEJ Research Institute of Chemistry, University of Karachi. Spectrophotometric studies were carried out on Hitachi 220 Spectrophotometer.

Hitachi 163 Gas Chromatograph equipped with flame ionization detector and recorder 056 were used throughout the study. Stainless steel columns (2m x 3 mm) packed with OV101, 3%, OV1, 3% and OV17, 3% on chromosorb WHP 80-100 mesh size were used.

Results and Discussion

The reagents and their copper and nickel complexes are easily prepared by simple synthetic routine [14]. The palladium complexes are prepared by refluxing together the palladium- benzonitrile complex and reagent in benzene [9]. The vanadium complex is prepared by chelate exchange method [10]. The reagents and metal complexes indicate IR spectral pattern similar to the related compounds [11,12]. ^{1}H-NMR spectra of *meso*-H_2PA_2S and *dl*- H_2PA_2S indicated a multiplet at δ 11.81 and 11.91 ppm respectively due to NH....O, which disappeared in their nickel and palladium complexes. A multiplet at δ 4.65 and 4.16 ppm in *meso*-H_2PA_2S and *dl*-H_2PA_2S due to bridge CH changed into singlet at 4.65 and 4.64 ppm nickel chelates and δ 4.91 and 4.63 ppm in palladium chelates, respectively (Table-2). This data supports that the ligand exist predominately in ketoamine form (Fig. 1) and dianion of the ligand is involved

Table-1: Elemental Micro Analysis

Compound	M.P.	Molecular Formula	% Expected C	H	N	% Found C	H	N	% Yield
dl-H_2PA_2S	153	$C_{30}H_{40}N_2O_2$	78.26	8.69	6.08	78.25	8.64	6.11	61
meso-H_2PA_2S	211	$C_{30}H_{40}N_2O_2$	78.26	8.69	6.08	78.09	8.84	6.24	70
dl-PA_2SCu	165	$C_{30}H_{38}N_2OCu$	69.02	7.28	5.36	68.87	7.47	5.39	50
dl-PA_2SNi	215	$C_{38}H_{38}N_2O_2Ni$	69.6	7.35	5.41	69.16	7.46	5.39	50
meso-PA_2SCu	205	$C_{30}H_{38}N_2O_2Cu$	69.02	7.28	5.36	69.16	7.46	5.39	75
meso-PA_2SNi	220	$C_{30}H_{38}N_2O_2Ni$	69.6	7.35	5.41	69.43	7.53	5.46	60
dl-PA_2SPd	233	$C_{30}H_{38}N_2O_2Pd$	63.82	6.73	4.96	63.64	6.89	5.05	60
dl-PA_2SVO	169	$C_{30}H_{38}N_2O_2VO$	68.57	7.23	5.03	68.32	7.21	5.88	75
meso-PA_2SPd	267	$C_{30}H_{38}N_2O_2Pd$	63.82	6.73	4.96	63.34	6.06	4.56	60

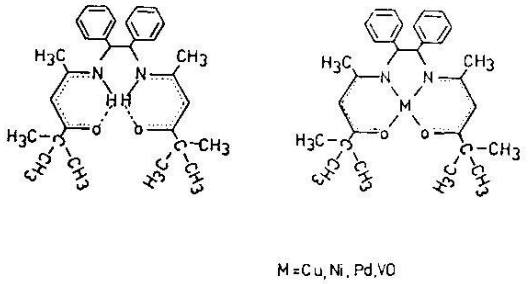

Fig.1: Structural diagrams of reagent and metal complexes.

Tabl-2: ^{1}H NMR Spectral assignment in d ppm for the ligands and their Nickel, Palladium complexes.

Compound	-CH$_3$	-CH bridge	=CH-	-CH---O	bridge C$_6$H$_5$	t-butyl group
dl-H$_2$PA$_2$S	1.92(s)	4.64(m)	5.14(s)	11.92(b)	7.01(m)	1.14(s)
dl-PA$_2$SNi	1.52(s)	4.16(s)	4.07(s)		7.26(s) 4.40(m) 8.17(m)	1.11(s)
dl-PA$_2$SPd	1.53(s) 1.65(s)	4.63(s)	4.393(s)		7.82(m) 7.38(m) 7.35(m) 7.40(m)	1.21(m)
meso-H$_2$PA$_2$S	1.50(s)	4.65(m)	4.95(s)	11.81(m)	7.31(s)	1.11(s)
meso-PA$_2$SNi	1.55(s)	4.65(s)	4.98(s)		7.02(m) 7.26(s) 7.52(s)	1.09(s)
meso-PA$_2$SPd	1.54(s) 1.62(s)	4.91(s)	5.05(s)		6.99(m) 7.25(m)	1.19(m)

into complexation [16,12]. The reagents and their nickel complexes indicate a peak corresponding to six hydrogens in the range of δ 1.92-1.52 ppm, but their palladium complexes show two peaks each corresponding to three protons in the same region. These may be assigned to the two methyl groups adjacent to the azomethine groups. The tertiary butyl groups attached near to the carbonyl groups absorb within δ 1.09-1.21 ppm.

The mass spectra of the reagents *meso*-H_2P_2S and *dl*-H_2PA_2S indicate molecular ion peak at m/z 460 (rel.intensity) (0.9-1.0%), followed by main fragment peaks at m/z 403(8-10%), 320 (3-4%), 231(22%) and 230 (100%), corresponding to subsequent loss of C_4H_9, C_4H_5NO, C_5H_7 and H from molecular ion peak. Other main fragment peaks are at m/z 146 and 91.

The results of spectrophotometric studies in visible region of metal complexes in chloroform and methanol (Table-3) indicate that the copper and nickel compelxes absorb within 560 $\pm$ 15 nm (ε 80-240) due to d-d transition [11], but *meso*-PA_2SCu

Table-3: Spectral Data of the Metal Complexes in Visible region

Compound	Solvent	λmax. nm(ε-1.mole^{-1} cm^{-1})
meso-PA$_2$SCu	CHCl$_3$	635(160), 555(240), 390(sh) (1700)
meso-PA$_2$SNi	"	574(220), 378(6400), 362(7200).
dl-PA$_2$SCu	"	545(110), 380(sh), (330)
dl-PA$_2$SNi	"	
meso-PA$_2$SPd	Methanol	407(835), 358(4510).
dl-PA$_2$SPd	"	348 (11760).
dl-PA$_2$SVO	"	650(92), 570(73), 430(140).

shows an additional bands at 635 (ε 160) and has been assigned to d-d transition due to distortion from square planar configuration owing to steric hindrance between methyl groups on azomethine and equatorial phenyl groups [13,14]. The vanadium complexes shows three bands in visible region at 650 nm, 570 nm and 430 nm with molar absorptivity within 73-140 mole^{-1} cm^{-1} due to d-d transition in d^1 of vanadium(IV) oxide system [15].

The nickel and palladium complexes indicate one to two charge transfer bands within 380-340 nm (ε = 4500 - 11800) [13], but within this region reagents also absorb, when present in excess and interfere in spectrophotometric determination of metal ions. However the colour of the complexes is highly stable and does not show any change in absorbance upto a week.

The spectrophotometric studies made only possible insensitive spectrophotometric determination of metal ions. Thus the thermal stability of the metal complexes was examined to evaluate their suitability for their use as gas chromatographic reagents for metal analysis. TG of metal complexes indicates that *meso*-PA_2SCu decomposes relatively to larger extent, may be due to having a distorted square planar structure, but square planar meso-PA_2SNi, *meso*-PA_2SPd, *dl*-PA_2SCu, *dl*-PA_2SNi, *dl*-PA_2SPd; and dl-PA_2SVO are somewhat volatile, with loss in weight within 94-100% in temperature range 160-320°C.

Meso-PA_2SCu shows loss in weight by 160°C and 83% loss by 280°C and 87% upto 600°C, with maximum rate of loss by 231°C. DTA shows melting endotherm at 240°C, followed by a large exotherm between 300-600°C (Fig. 2). The loss in

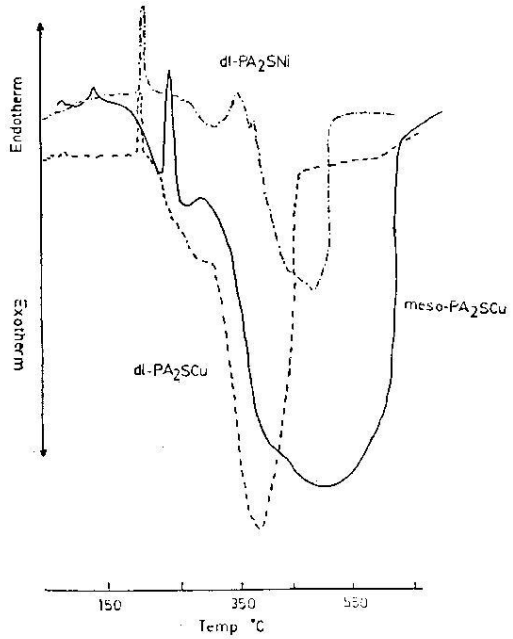

Fig.2: DTA curves of copper and nickel chelates at a heating of 15°C/min and nitrogen flow rate of 20 cm^3/min.

weight of *meso*-PA_2SNi starts by 205°C and complete loss by 300°C, with maximum rate by 248°C. DTA shows melting endotherm at 215°C, followed by a complex endotherm between 450-550°C *meso*-PA_2SPd shows loss in weight by 230°C and loss of 94% by 390°C, with maximum rate at 320°C. DTA shows melting endotherm at 195°C and exotherm at 370°C. The loss in weight of *dl*-PA_2SCu starts by 181°C and 96% loss by 320°C, with maximum rate by 280°C. DTA shows melting endotherm at 215°C, followed by complex loss exotherms upto 484°C with maximum at 370°C *dl*-PA_2SNi loses weight by 205°C, with maximum rate of loss by 310°C, leaving 4% yellow colour residue upto 500°C. DTA shows melting endotherm at 223 and complex loss exotherms at 341 and 530°C *dl*-PA_2SPd loses weight by 210°C and complete loss by 350°C, with maximum rate at 320°C. DTA shows melting endotherm at 210°C, followed by exotherm at 335°C. The loss in weight of *dl*-PA_2SVO starts by 210°C and complete loss by 320°C, with maximum rate of loss at 270°C. DTA shows endotherms at 185°C and 210°C, followed by exotherm at 485°C.

High temperature required for the volatilization of the metal complexes led to select stainless steel columns (2mx3mm) and (3mx3mm) packed

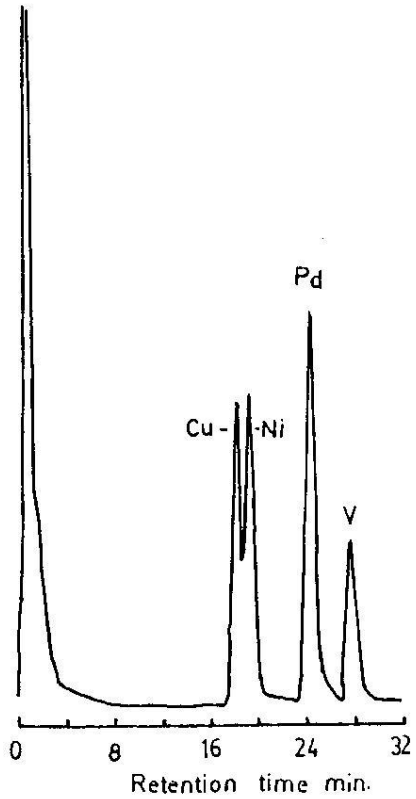

Fig.3: Chromatographic separation of Cu(II), Ni(II), Pd(II) and V(IV)O complexes of dl-H_2PA_2S on column (2m x 3mm) packed with OV101, 3% on Chromosorb WHP-100 mesh size at column temperature of 230°C with progammed rise in temperature of 1°C/min upto 260°C, injection port 270 and nitrogen flow rate of 30 cm^3/min.

with OV101, OV1, OV17, 3% on Chromosorb WHP 80-100 mesh size. The metal complexes eluted on OV101, 3% on Chromosorb 80-100 as symmetrical peaks within temperatures, column 240-270°C, injection port 250-275°C and nitrogen flow rate 30 cm^3/min. However *meso*-PA_2SCu indicated slight disturbed base line, probably due to on column decomposition of complex.

When a mixture of copper, palladium and vanadium, or nickel, palladium and vanadium complexes of dl-H_2PA_2S was injected on the column, complete separations between copper, palladium and vanadium; and nickel palladium and vanadium complexes were obtained. However when a mixture of copper, nickel, palladium and vanadium complex of *dl*-H_2PA_2S was injected a partial separation between copper and nickel was obtained. An optimum separation between copper, nickel,

Table-4: Quantitative Gas Chromatographic Data of Copper(II), Nickel(II), Palladium(II), and Vanadium(IV) Chelates on Stainless Steel Column (2m x 3mm) packed with OV-101, 3%, on Chromosorb WHP 80-100 mesh Size.

Name of the chelate	Column temp. °C	Injection port °C	N_2 flow rate ml/min	Retention time in sec.	Calibration range (Attenuation Settings)	Detection Limit (Attenuation Settings)
dl-PA_2SCu	245	255	30	480	125-625 μg of chelate corresponding to 15-76 ng of copper (10x16).	25 ng of chelate corresponding to 3 ng of copper (1x4).
dl-PA_2SNi	255	565	30	420	125-625ng chelate corresponding to 14-71 ng of nickel (10x32).	25ng of chelate corresponding to 2.8 ng of Nickel (1x4).
dl-PA_2SPd	270	275	30	520	1-8μg of chelates corresponding to 168-1503 ng of palladium(II) 10^2x16)	60 ug of chelate corresponding to 11.3 ng of of palladium(II) (10x4)
dl-PA_2SVO	280	285	30	450	1-8ug of chelate corresponding to 97-777 ng of Vanadium (10_2x16)	50 ng of chelate corresponding to 4.8 ng of vanadium(10x8).
meso-PA_2SCu		260	270	28	540 corresponding to 112.6-901 ng of copper (10^2x16)	1-8 ng of complex 150 ng of chelate corresponding to 18 ng of copper (1 X 2)
meso-PA_2SNi	270	280	27	550	0.5-5ng of corresponding to 57-570 ng of nickel(10^2x16).	50 ng of chelate corresponding to 5 ng of nickel (1x8)
meso-PA_2SPd		275	275	30	788 chelate corresponding to 940-3759 ng of palladium (10^2X8)	5-20 μg of 100 ng of chelate correspond ing to 18.8 ng of palladium (10x4).

palladium and vanadium complexes of *dl*-H_2PA_2S on stainless steel column (2m3mm) packed with OV101, 3% on Chromosorb 80-100 was obtained, when mixture was injected at a column temperature 230°C, with programmed rise in temperature of 1°C/min, upto 260°C, injection port 270°C, and nitrogen flow rate of 30 cm^3/min (Fig. 3), with retention times of 18-30, 19-30, 24-35 and 28-0 min, for copper, nickel, palladium and vanadium complexes respectively.

Similarly when a mixture of copper nickel and palladium complexes of meso-H_2PA_2S was injected on GLC columns, complete separation of palladium from copper and nickel was obtained, but a partial separation between copper and nickel was here also achieved (Fig. 4). The metal complexes of *meso*-isomer takes longer elution time than the corresponding *dl*-isomer on similar conditions (Table-4). Thus metal complexes of *dl*-and meso-isomers could also be separated.

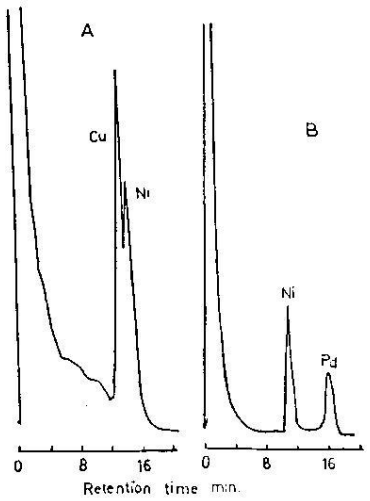

Fig. 4: Chromatographic separation of (A) copper and nickel(B) Nickel and palladium complexes of meso-H_2PA_2S on column (2mx3mm) packed with OV 101, 3%, on Chromosorb WHP 80-100 mesh size at a nitrogen flow rate of 30 cm^3/min. (A) Column temperature 250°C, injection port 260°C (B) Column temperature 270°C, injection port 275°C.

In order to check the quantitative elution of complex and the response of the detector with the amount of complex injected, average peak heights of at least two injections were measured and linear calibration curves were obtained in the range corresponding to 14-570 ng nickel, 15-900 ng copper, 18-3760 ng palladium and 97-780 ng vanadium. The detection limits measured as thrice the background noice were in the range of 3-18 ng copper, 3-5 ng nickel, 11-19 ng palladium and 5 ng vanadium(Table4).

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