Gas Chromatographic Separation of Copper(II), Nickel(II) and Palladium(II) Complexes of Meso-and DL-Bis (Isopropanoylacetone)Stilbenediimine

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Summary: Copper(II), nickel(II) and palladium(II) complexes of bis(isopropanoylacetone)dl-stilbenediimine(dl-H_2PA_2S) and nickel(II) and palladium(II) complexes of bis(isopropanoylacetone)meso-stilbenediimine(meso-H_2PA_2S) are prepared for their possible use for gas chromatographic separation of copper, nickel and palladium. The reagents and metal complexes are characterized using IR, UV, ^{1}HNMR and mass spectroscopic techniques. The metal complexes are somewhat volatile as evident from their DTA and TG curves and complete separation between nickel and palladium of both ligands is achieved, but incomplete separation is demonstrated between copper and nickel complexes. Linear calibration range and detection limits of the complexes are determined.

Introduction

A useful gas chromatographic separation of copper, nickel, palladium and vanadium have been achieved using tetradentate ketoamine shiff bases [1-5]. Thus two new ligands bis(isopropanoylacetone)dl-stilbenediimine(dl-H_2PA_2S) and bis(isopropanoylacetone) meso-stilbenediimine (meso-H_2PA_2S) for their possible use as gas chromatographic reagents for copper, nickel and palladium have been prepared.

Experimental

Preparation of the Reagents:

Bis(isopropanoylacetone)dl-stilbenediimine(dl-H_2PA_2S) and Bis(isopropanoylacetone)meso-stilbenediimine(meso-H_2PA_2S).

Isopropanoylacetone (0.04 mole) and meso-and dl-stilbenediamine (0.02 mole) dissolved in ethanol was refluxed for 30 min. and most of the ethanol was distilled off. The residue was cooled overnight and the precipitate so obtained was recrystallised from ethanol. dl-H_2PA_2S, m.p. = 117°C, MS (m/z (rel. intensity %) 432 (M^+ 0.1), 389 (0.5), 309 (0.2), 261 (0.5), 217 (33), 216 (100), 172 (24), 146 (12), 91 (32); ^{1}H NMR ($CDCl_3$) δ in ppm 1.07(d) 1.5Hz, 1.38(d) 1.5Hz, (4-CH_3), 1.86(s) (2-CH_3), 2.45(m) (CH-isopropyl), 4.67(m) (-CH bridge), 4.995(s) (=CH), 11.79(d) 4.9Hz (NH), 6.94(m), 7.14(m) (-C_5H_5). IR (KBr cm^{-1}) 3450(m), 1640(w), 1607(s), 1577(s), 1495(m), 1380(w), 1360(w), Anal. Calcd. for $C_{28}H_{26}N_2O_2$) % C=77.77, H=8.33, N=6.48; found % C=77.73, H=8.17, N=6.31 meso-H_2PA_2S m.p. = 203°C, MS (rel. intensity %) 432 (M^+,1.0), 389 (9.0), 306 (1.0), 262 (0.5), 217 (22), 216 (100), 174 (12.0), 146 (9.5), 91 (30); ^{1}H NMR ($CDCl_3$) in ppm δ 1.078(d) 6.8Hz (4-CH_3) 1.534(s),

($2-CH_3$), 2.393(m) (-CH isopropyl), 4.695(m) (-CH bridge), 4.838 (=CH), 11.637(d) 6.9Hz (-NH), 7.299(s) ($-C_6H_5$). IR (KBr, cm^{-1}), 3360(w), 1645(w), 1610(s), 1570(s), 1490(s), 1430(m) 1380(m), 1360(m). Anal. Calcd. for $C_{28}H_{36}N_2O_2$ % C=77.77, H=8.33, N=6.48; found % C=76.89, H=8.76, N=6.59.

Preparation of Copper and Nickel Complexes:

Equimolar solution of copper(II) acetate or nickel(II) acetate dissolved in methanol was added to the solution of meso-H_2PA_2S and dl-H_2PA_2S in methanol and refluxed for 30 min. The solution was concentrated and cooled. Precipitates obtained was recrystallized from methanol. dl.PA_2S.Cu, m.p.=195°C, IR (KBr, cm^{-1}) 1575(s), 1520(s), 1505(s), 1475(s), 1400(w), 1375(w), 1360(w), 600(m), 480(m). Anal. Calcd. for $C_{28}H_{34}N_2O_2$, % C=68.15, H=6.89, N=5.67; found % C=67.88, H=6.67, N=5.57. dl-PA_2SNi. m.p. = 228°C; ^{1}H NMR ($CDCl_3$) in ppm , 1.078(d) 6.8Hz ($4-CH_3$), 1.52(s) ($2-CH_3$), 2.38(m) (CH-isopropyl) 4.166(s) (-CH bridge), 4.888(s) (=CH), 7.38(m) & 8.24(m) ($-C_6H_5$). IR (KBr cm^{-1}) 1570(s), 1515(s), 1410(w), 1375(w), 1360(w), 600(m), 490(m). Calcd. for $C_{28}H_{34}N_2O_2$, % C=68.85, H=6.96, N=5.73; found, % C=68.39, H=6.69, N=5.67. meso-PA_2SNi, m.p. = 140°C, IR (KBr cm^{-1}), 1565(s), 1530(s), 1510(s), 1500(s), 1420(s), 1380(w), 1360(w), 500(s), Calcd. for $C_{28}H_{34}N_2O_2$.Ni % C=68.85, H=6.96, N=5.73; found, % C=68.39, H=6.69, N=5.67.

Preparation of Palladium(II)-Complexes:

Palladium(II) chloride (0.1g) was heated with benzonitrile (0.2ml) for 2 hrs and dissolved in benzene (5-10ml). The mixture was added dl-H_2PA_2S or meso-PS_2S (0.43g) in benzene and refluxed for 24 hrs. The solution was filtered and benzene was removed. The residue was diluted with n-hexane. The precipitate so obtained was recrystallised from ethanol dl-PA_2SPd, m.p.= 290°C, ^{1}H NMR ($CDCl_3$) in ppm δ 1.159(d) 6.8Hz ($4-CH_3$), 1.52(s), ($2-CH_3$), 2.572(m), (-CH isopropyl), 4.632(s) (-CH bridge), 4.831 (=CH), 7.257(m), 7.380(m), 7.804(m), ($-C_6H_5$). IR (Nujol, cm^{-1}), 1575(s), 1555(s), 1505(s), 1415(m), 1378(w), 1360(w). Calcd. for $C_{28}H_{34}N_2O_2Pd$, C=62.68, H=6.34, N=5.22; found 62.31, H=6.44, N=5.29. meso-PA_2SPd, m.p.=242°C, IR (Nujol, cm^{-1}) 1610(s), 1575(s), 1500(s), 1470(s). Calcd. for $C_{28}H_{34}N_2O_2Pd$, % C=62.68, H=6.34, N=5.22; found % C=63.52, H=6.52, N=5.51.

Isopropaoylacetone was prepared followig general procedure of Belcher et al. [6] and dl and meso-stilbenediamine were prepared by reported procedures [7,8].

Elemental analysis was carried out by Elemental Micro Analysis Ltd, U.K. IR spectra was recorded on Hitachi 260-30 and Unicam SP-1025 IR Spectrophotometers using KBr & Nujol mull techniques. Mass spectra of the reagents on Finnigan Mat 1125 Mass Spectrometer and ^{1}H NMR of Palladium complex on Bruker AM 300 NMR Spectrometer in $CDCl_3$ were recorded by HEJ Research Institute of Chemistry, University of Karachi. ^{1}H NMR of the reagents and nickel complex were recorded on Jeol FX 100 at PINSTECH Islamabad. The absorptiometric data was recorded on Hitachi 220 Spectrophotometer. DTA and TGA of metal complexes were carried out on Shimatzu TG-30 Thermal Analyser using sample of 5-10 mg at heating rate of 15°C and nitrogen flow rate of $50cm^3$. Hitachi 163 Gas Chromatograph equipped with flame ionization detector was used. Stainless steel column (2mx3mm) packed with OV101, 3% and (6'x.085 ID) packed with OV17, 3% on Chromosorb 80-100 (Attach Assoc.) was used throughout the study.

Results and Discussion

The preparation of the both the reagets and metal complexes did not encounter any difficulty. However the reaction of copper(II) acetate with meso-H_2PA_2S developed a dark colour, but the elemental micro-analysis of the product did not agree to meso-PA_2S.Cu. Moreover when the product was injected to a gas chromatograph under the conditions optimized for metal complexes of the same ligand it failed to elute. Thus further work for the characterization of the product was abandoned. The IR of the reagents and their metal complexes follow similar pattern as has been observed by the related compound [9,10]. The mass

Table-I: Qualitative Absorptiometric Data of the Reagents and their Metal Complexes.

Reagent	Metal Ion	Solvent	Colour	λ max nm	ε-mole^{-1}cm^{-1}
Bis(isopropanoylacetone)meso-stilbenediimine.	-	Chloroform	Colourless	318 242	34263 332
	Ni(II)	Chloroform	Redish brown	570 359 249	184 7564 24934
	Pd(II)	Acetone	Yellow	350 328	8442 711336
Bis(isopropanoylacetone)dl-stilbenediimine.	-	Acetone	Colourless	328 214	17550 2127
	Ni(II)	Acetone	Redish brown	564 378 359 214	80 6647 6207 2518
	Cu(II)	Acetone	Purple	548 330 211	277 5238
	Pu(II)	Acetone	Yellow	350 215	16776 5735

spectra show molecular ion peak at m/z 432 with a low relative intensity and a base peak at the half of the molecular ion peak at m/z 216 and agree with similar pattern observed by Belcher et al. [11] and Lindoy et al. [12] with similar ligands.

^{1}H NMR of the reagents, nickel and palladium complexes indicate that the reagents predominately exist in ketoamine form where multiplet at δ 4.6 ppm owing to bridge CH changes into singlet around δ 4.16-4.63 and doublet around δ 11.63-11.79ppm because of -NH disappear in metal complexes and confirm that dianion of the ligand is involved in the metal complexes. The methyl signal in dl-H_2PA_2S (δ 1.89ppm) moves downward in meso-H_2PA_2S (δ 1.53ppm) and dl-PA_2S.Ni (δ 1.52ppm) due to greater diamagnetic shielding of methyl groups with π cloud in phenyl ring in meso-isomer and restricting the rotation about the single bond C-C and fixed configuration in nickel complexes. The methyl group signal in dl-PA_2S.Pd (δ 1.64ppm) moves upward as compared to the dl-PA_2SNi due to difference in ionic size of metal ions. The effect is also noticeable on the bridge -CH signal where δ 4.67ppm in dl-H_2PA_2S. Ni move significantly downfield to δ 4.166 ppm in dl-PA_2S.Ni as compared to δ 4.632 ppm in dl-PA_2S.Pd due to the difference in ionic sizes of metal ions.

The spectrophotometric studies of the reagents was carried out in chloroform and acetone solution (table I). The copper and nickel complexes show a band within 570-548nm due to d-d transitions with molar absorptivity in the range of 80-480 mole^{-1} cm^{-1}. The nickel and palladium complexes indicate charge transfer band within 350-378nm, which is fairly sensitive with molar absorptivity in the range of 6.6×10^3 to 1.6×10^4 and obey the Beers law at their respective wavelength of maximum absorbance, but the reagent also absorb at the wavelength, particularly when present in large excess.

The DTA and TG of the metal complexes (table 2) (Fig. 1) indicate

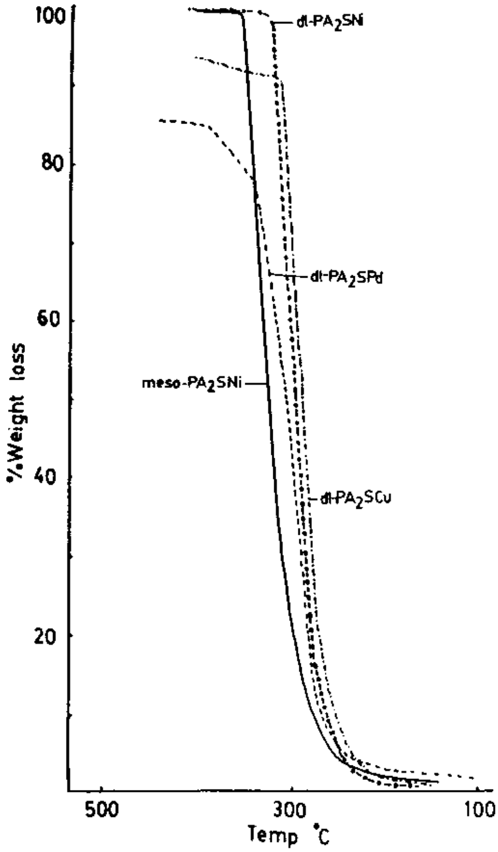

Fig.1: TGA of metal complexes.

that the loss in weight in nickel complexes is almost quantitative upto 330°C, but the copper and palladium complexes leave certain residue in the range of 7-15%. The palladium complexes show a large exotherm at high temperatures, due to the certain decomposition of metal complexes (Fig.02).

The results of TG indicated that the metal complexes were some what volatile and their possible use for the

Table-II: Thermogravimetric Studies of Metal Chelates.

Complexing Reagents	Metal Chelates Copper	Metal Chelates Nickel	Metal Chelates Palladium
Bis(isopropanoyl-acetone)meso-stilbenediimine.		10.8 mg sample T.G. loss in weight starts by 240°C and loss of 98% at 370°C with maximum rate by 320°C leaving 2% residue.	10 mg sample T.G. loss in weight starts from 260°C and loss of 86% by 385°C with maximum rate 330°C leaving 14% residue.
		D.T.A. shows melting endotherm at 137°C and endotherm at 362°C, complex loss exotherm by 432°C.	D.T.A. shows melting endotherm at 285°C and endotherm at 300°C, strongly exotherm by 370°C.
Bis(isopropanoyl-acetone)dl-stil-benediimine.	5 mg sample T.G. loss in weight starts by 230°C and loss of 93% by 330°C with maximum rate by 295°C leaving 7% residue.	13.2 mg sample T.G. loss in weight starts by 240°C and loss of 100% by 330°C with maximum rate by 330°C.	10 mg sample T.G. loss in weight starts by 260°C and loss of 85% by 285°C with maximum rate 340°C leaving 15% residue.
	D.T.A. shows melting endotherm at 188°C and endotherm at 315°C, complex loss endotherm by 330°C.	D.T.A. shows melting endo-therm at 245°C, endo-therm at 323°C and complex-endotherm by 347°C.	D.T.A. shows melting endotherm at 215°C and strong endotherm by 480°C.

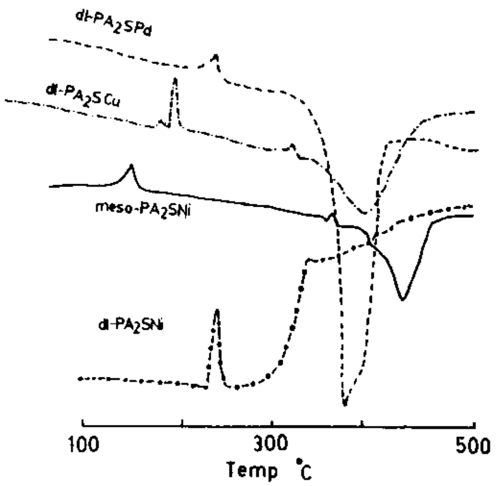

Fig.2: DTA of metal complexes.

gas chromatographic separation and quantitative determination was investigated by injecting the acetone solution of the metal complexes on the OV101 and OV17, 3% on Chromosorb 80-100 mesh size column. The temperature of column and injection port and nitrogen flow rate was varied and complete separation between nickel and palladium, and copper and palladium was easily achieved each time at column temperature of 270-80°C and injection port 280-90°C and nitrogen flow rate of 30 cm^3/min within 24 mins. (Fig. 03). However when a mixture of copper (II), nickel (II) and palladium (II) complexes of dl-PA_2S was injected on OV17 column at a temperature of 280°C, injection port 290°C and nitrogen flow rate of 30 cm^3/min, a partial separation between copper and nickel complexes was achieved (Fig.04).

Table-III: Quantitative Gas Chromatographic Data of Metal Compounds at Nitrogen Flow Rate of 30ml/min.

Reagent	Metal Ion	Retention time in min.	Nitrogen Flow rate ml/min.	Column temp °C	Injection port temp °C	Column used	Ketoamine calibration Range	Detection Limits.
Bis(isopropanoylacetone)-meso-stilbene-diimine.	Ni(II)	9-14	30	280	290	OV-101 3% on Chromosorb.	0.5 to 3.5 µg of the complex correspon-ding to 60-423ng of the Ni(II).	0.1µg corr-esponding 6 ng of Ni(II)
Bis(isopropanoylacetone)-meso-stilbene-diimine.	Pd(II)	15-15	30	290	295	OV17 3% on Chromosorb	2 to 9µg of the complex correspond-ing to 398-1789ng of the Pd(II).	1µg of the complex corresponding 199ng of Pd(II)
Bis(isopropanoylacetone)-dl-stilbene-diimine.	Cu(II)	4-05	30	270	280	OV-101 3% on Chromo-sorb.	1 to 5 µg of the complex corresponding to 129-643ng of the Cu(II).	0.1 µg of complex corresponding 26ng of Cu(II).
Bis(isopropanoylacetone)-dl-stilbene-diimine.	Ni(II)	4-10	30	270	280	OV-101 3% Chromosorb.	1 to 4 µg of the complex corresponding to 121-484 ng of Ni(II).	0.2 µg of complex correspond-ing 12 ng of Ni(II).
Bis(isopropanoylacetone)-dl-stilbene-diimine.	PDII)	14-15	30	280	290	OV-17 3% on Chromosorb.	1 to 16 µg of the complex corresponding to 199-1185	.02 µg of the complex corresponding 4 ng of Pd

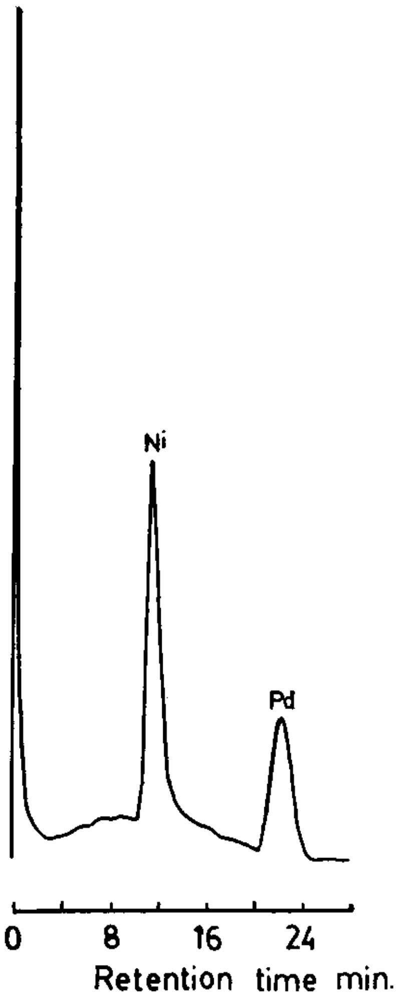

Fig.3: Separation of Nickel and Palladium complexes of meso-H_2PA_2S. Column 6'x0.0185" ID packed with OV17 on 3% on Chromosorb WHP 80-100, column temperature 280°C, injection port 290, Nitrogen flow rate 30 Cm^3/min.

In order to optimize the separation between copper and nickel, the programmed column temperature elution was used and a mixture of copper and nickel was injected at a column temperature of 250°C and a rise in temperature of 2°C/min upto 270°C and injection port 270°C, an optimum separation between copper and nickel with resolution factor of 0.817 was achieved.

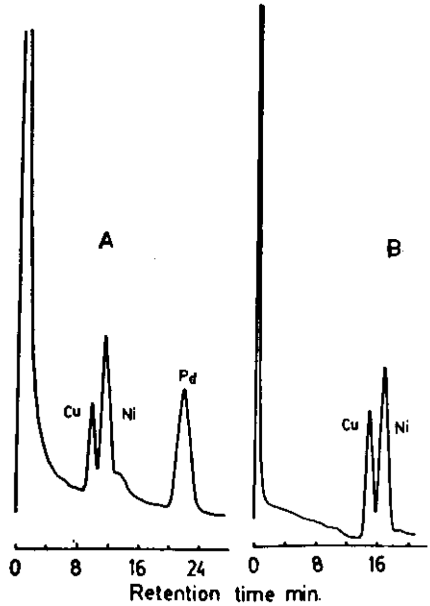

Fig.4: (A) Separation of Copper, Nickel and Palladium Complexes of dl-H_2PA_2S. Column temperature 270°C injection port 280°C.
(B) Separation of Copper and Nickel Complexes of dl-H_2PA_2S, Column temperature 250°C, programmed at a rate of 2°C/min upto 270°C. Injection port 270. Column 6'x0.0185" ID packed with OV.17, 3% on Chromosorb WHP 80-100 flow rate 30Cm^3/min.

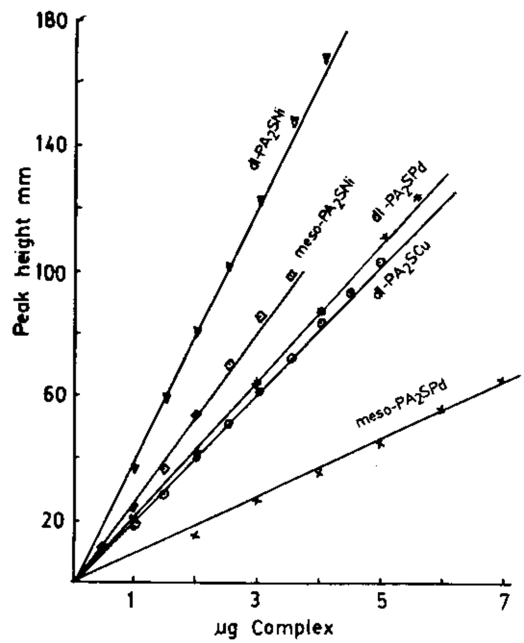

Fig.5: Linear Calibration curve of metal complexes.

In order to check if the response of the detector was linear with the amount of the complex injected, different amounts of the complex was injected and average peak height of at least two injections were measured and linear calibration curve was obtained in the range of 1-5μg, 1-4 μg and 1-6μg of copper, nickel and palladium complexes of dl-H_2PA_2S and 0.5-3.5μg and 2-9μg of nickel and palladium complexes of meso-H_2PA_2S respectively (Fig.05). Dectection limits at least thrice the background noise were found 0.1μg of copper and nickel complex of both the ligands and 0.02-1 μg for palladium complexes (table 3).

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