Preparation, Thermogravimetric and Gas-Chromatographic Studies of Copper(II) and Nickel(II) Complexes of Some New Ketoamine Schiff Bases

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Summary: New ligands meso- and dl-bis(ethanoylacetone)-stilbenediimine meso- and dl-bis(n-propanoylactone)-stilbenediimine and their copper and nickel complexes have been prepared. The reagents and their metal complexes have been characterized using IR, UV, visible and mass spectroscopic techniques. The coloured copper and nickel complexes are studied spectrophotometrically and their DTA, TGA curves are recorded. The metal complexes particularly of dl-isomer indicate reasonable thermal stabilities, the metal complexes are eluted on OV101 on chromosorb column using GLC euqipped with flame ionization detector and detection limits are found in ng range of metal ions.

Introduction

Tetradentate ketoamine Schiff bases find higher promise for the analysis of the divalent transition metal ions involving gas chromatographic procedures over β-diketones [1-5]. Bis- β-diketonates are generally solvated with lower thermal stabilities at working temperatures with loss of sensitivities [6,7]. Recently phenyl groups have been substituted at the bridge position in bis(acetylacetone) ethylenediimine [10] and bis (trifluoro-acetylacetone) ethylenediimine and the copper and nickel complexes of the resulting Schiff bases, maintain thermal stabilitiies and indicate lower detection limits of metal ions gas chromatographyically owing to increase in molecular weight due to phenyl substitution.

In the present work, a few more phenyl substituted ligands at bridge position have been prepared to investigate the effect of increase of alkyl-chain on thermal stability and gas chromatographic behvaiour of metal complexes.

Experimental

Preparation of Reagents

Bis(ethanoylacetone)meso-stilbenediimine (meso-H_2EA_2S)) and Bis(n-propanoylacetone) meso-stilbenediimine (meso-H_2nPA_2S)

To the ethanoylacetone (4.5 g, 0.04M) or n-propanoylactone (5.2 g, 0.04M), was added ethanolic solution of freshly prepared meso-stilbenediamine (4.2 g, 0.02M). The mixture was refluxed for 1hr and left overnight at room temperature. The precipitate was washed with n-hexane and recrystallised from ethanol.

Bis(ethanoylacetone)dl-stilbenediimine (dl-H_2EA_2S) and Bis(n-propanoylacetone)dl-stilbenediimine(dl-H_2nPA_2S)

To the ice cold ethanolic solution of ethanoylacetone (4.46g, 0.04M) or n-propanoylacetone (5.2g, 0.04M) was added dl-stilbenediamine (4.2 g 0.02M) in ethanol. The mixture was cooled at 0°C for 24 hours and diluted with n-hexane. The precipitate was filtered and recrystallized from cyclohexane.

Metal Complexes

To the ethanolic solution of ligands, was added equimolar solution of copper

Table-1

Name of the compound	Molecular Formula	M.P	%yield	%Expected C	H	N	% Found C	H	N
1. Bis(ethanoylacetone(dl-stilbenediimine.	$C_{26}H_{32}N_2O_2$	183	68	77.22	7.92	6.93	77.26	8.51	6.94
2. Bis(ethanoylacetone) meso-stilbenediimine.	$C_{26}H_{32}N_2O_2$	185	86	77.22	7.92	6.93	77.46	8.74	6.87
3. Bis(n-propanoylacetone)dl-stilbenediimine.	$C_{28}H_{36}N_2O_2$	170	72	77.77	8.33	6.48	77.61	8.39	6.42
4. Bis(n-propanoylacetone)meso-stilbenediimine.	$C_{28}H_{36}N_2O_2$	165	80	77.77	8.33	6.48	77.88	8.51	6.42
5. Bis(ethanoylacetone)dl-stilbenediimine copper(II).	$C_{26}H_{30}N_2O_2Cu$	218	70	67.01	6.44	6.01	67.15	6.47	6.00
6. Bis(ethanoxylacetone)dl-stilbenediimine nickel(II)	$C_{26}H_{30}N_2O_2Ni$	252	70	68.01	6.10	6.10	67.83	6.57	6.07
7. Bis (ethanoylacetone)meso-stilbenediimine copper (II)	$C_{26}H_{30}N_2O_2Cu$	220	50	67.01	6.44	6.01	66.78	6.48	6.02
8. Bis(ethanoylacetone)meso-stilbendiimine nickel(II)	$C_{26}H_{30}N_2O_2Ni$	138	60	68.01	6.10	6.10	67.99	6.49	5.97
9. Bis(n-propanoylacetone)dl-stilbenediimine copper(II)	$C_{28}N_{34}N_2O_2Cu$	172	65	68.07	6.88	5.67	67.63	7.03	5.66
10. Bis(n-propanoylacetone)dl-stilbenediimien nickel(II)	$C_{28}H_{34}N_2O_2Ni$	201	65	68.75	6.95	5.73	68.74	7.11	5.72
11. Bis (n-propanoylacetone)meso-stilbenediimine copper(II)	$C_{28}H_{34}N_2O_2Cu$	140	68	68.07	6.88	6.67	68.28	7.14	5.79
12. Bis(n-propanoylacetone)meso-stilbenediimine nickel (II).	$C_{28}H_{34}N_2O_2Ni$	150	40	68.75	6.95	5.73	68.81	6.93	5.74

acetate or nickel acetate in ethanol. The mixture was refluxed for 1 hr and cooled at room temperature. The precipitate was filtered and recrystallized from ethanol. The results of micro-analysis are summarized in Table-1

Ethanoylacetone and n-propanoylacetone were prepared by claisen condensation [12]. Meso-stilbenediamine [13] and dl-stilbenediamine [14] were prepared by reported methods. Elemental micro-analysis TG and DTA were carried out by Elemental Micro Analysis Ltd. U.K. DTA and TGA were carried out with about 10 mg of each sample at the heating rate of 15°C/min in flowing nitrogen atmosphere at the rate of 20 cm^3/min. Spectrophotometeric studies of the reagents and metal complexes in chloroform were carried on Hitachi 220 spectrophotometer. IR spectra in KBr were recorded on Unicam SP-1025 IR spectrophotometer in the range of 3800-650 cm^{-1}. Mass spectra of the reagents were recorded from HEJ Research Institute of Chemistry, University of Karachi. Hitachi 163 Gas Chromatograph equipped with flame ionization detector was used throughout the study. Stainless steel column 2mx3mm packed with OV101, 3% and OV1, 3% on chromosorb WHP 80-100 mesh size were used throughout the study.

Results and Discussion

The reagents are easy to prepare by heating together the ethanolic solution of two moles of ß-diketone and one mole of stilbenenediamine. However in case of dl isomer the reactions has to be carried out below 5°C and required longer reaction time. The elemental micro analysis of the metal complexes indicate that dianoin of the reagents are involved in complexation. The IR of the ligands and their metal complexes requires little discussion and show similar pattern observed with reported compounds [11,15]. The mass spectra of meso and dl isomer of n-H_2nPA_2S and H_2EA_2S indicate similar mass spectral pattern with molecular ion peaks of relatively low intensity at m/e 432 and 404 respectively and confirm the ease of the fragmentation of the compounds. The fragmentation of the reagents H_2nPA_2S and H_2EA_2S shows a similar [16] pattern (Table II) with initial loss of fragments at m/e 43 and 29 corresponding to n-propyl and ethyl radicals, followed by losses of m/e 83 corresponding to C_4H_5NO and m/e 90 for C_7H_6 to give base peaks (100%) at m/e 216 and 202 as half of the molecular ion peaks [3].

The results of spectrophotometric studies of copper (II) nicke(II) complexes and reagents (table III) indicate that the values of molar absorptivities for copper and nickel complexes at wavelength of maximum absorbances between 540-580 nm are relatively low for quantitative determinations of metal ions. The yellow colour of nickel complexes at their λ_{max} between 360-380 nm is relatively more sensitive and obeys the Beer's law, but the reagents also show a little absorbance in the region, and is affected at high reagents concentration. The colour of the complexes does not show any change in absorbance of their chloroform solutions upto four days and does not show sign of decomposition when kept as solid atleast for 2 months.

The results of DTA and TGA of the nickel and copper complexes in table IV and fig. (I) to (IV) indicate that dl-n-PA_2SNi, dl-EA_2SNi and meso-n-PA_2SNi lose weight in the range of

Table-II Mass spectral assignment for the ligands

Assignment	dl-H_EA2S	meso-H_2EA_2S	dl-H_2PA_2S	meso-H_2nPA_2S
$[M]^+$	404(1.0)	404(2.7)	432(0.9)	432(1.8)
$[M - R]^+$	375(4.5)	475(4.9)	389(3.6)	389(5.0)
$[M - A]^+$	292(1.8)	292(2.7)	306(2.2)	306(2.7)
$[M - B]^+$	203(22)	203(23)	217 (45.5)	217(62)
$[M - B - H]^+$	202(100)	202(100)	216(100)	216(100)
$[M - B - R]^+$	174)(98)	174(81)	174(65.5)	174(74)
$[M - B - RCO]^+$	146(98)	146(99)	146(100)	146(100).
$[M - B - A]^+$	91(64.5)	91(67.3)	91(100)	91(100)

Relative intensitites are shown in parenthesis. A = R CO CH: $C(CH_3)NH$, and B = R CO.CH: $C(CH_3)N$ (CHC_6H_5).

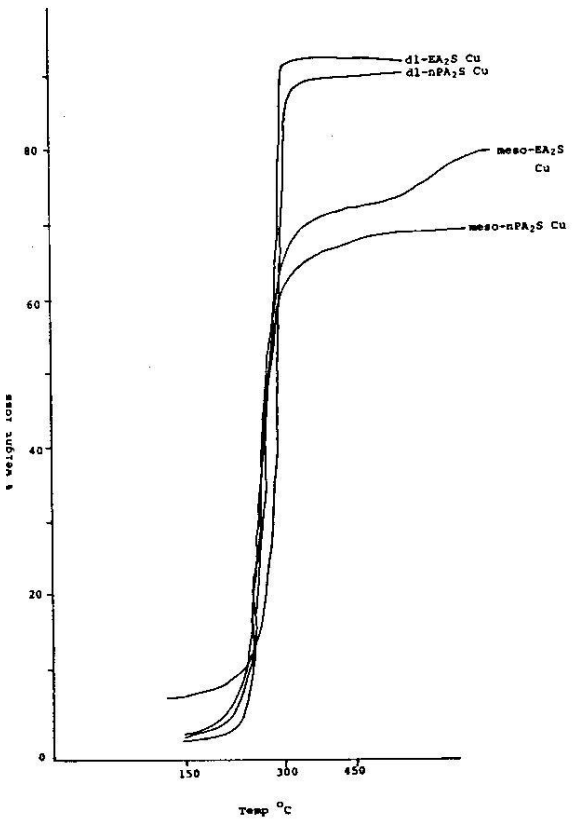

Fig.1: TGA Curves Copper Complexes.

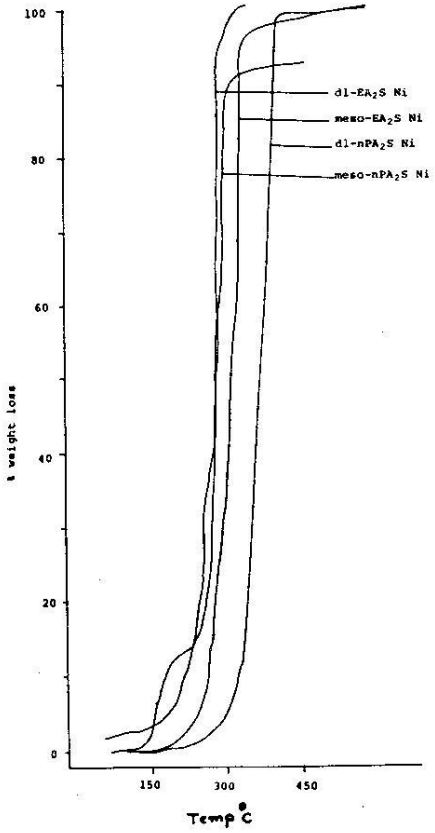

Fig.2: TGA Curves of Nickel Complexes.

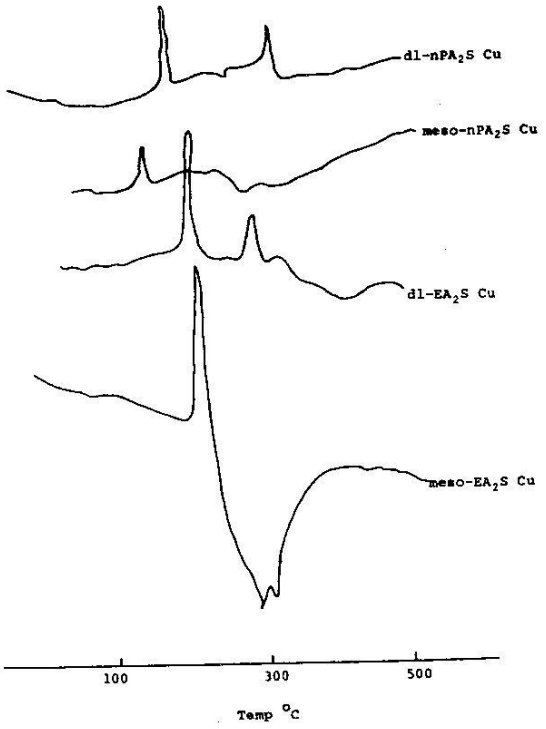

Fig.3 DTA of Copper Complexes.

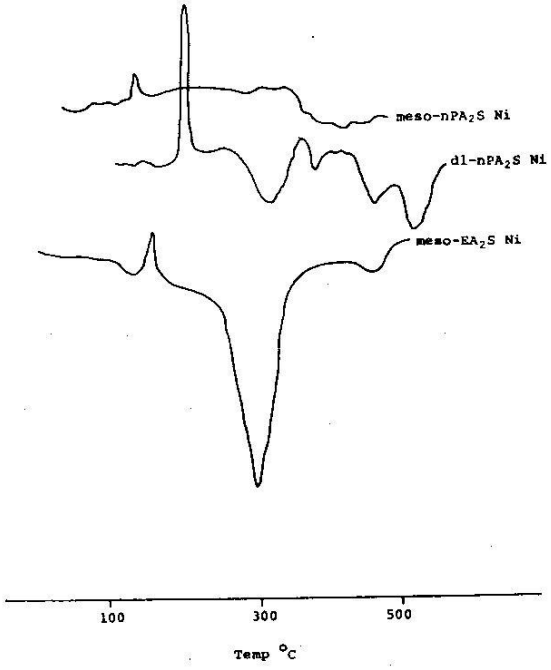

Fig.4: DTA of Nickel Complexes.

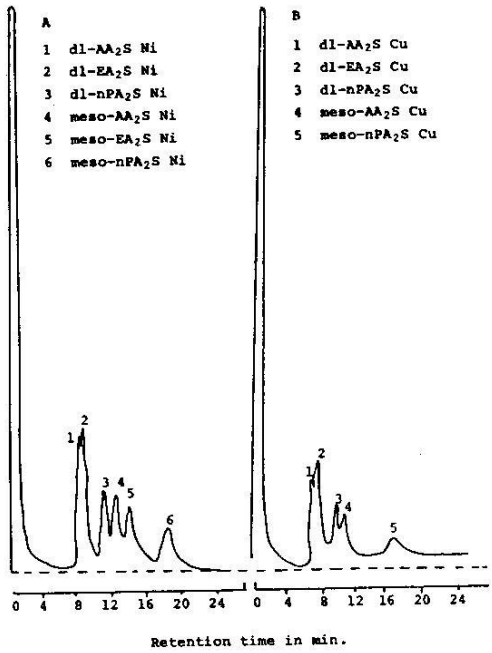

Fig.5: Gas Chromatographic order to elution of (a) Nickel Complexes (B) Copper Complexes of meso and dl ketoamines. on stainless steel Column 2mx3mm packed with 3% OV-101 on Chromosorb WHP 80/100 mesh size. Column temp: 250°C, Nitrogen flow rate 30 cm^3/min.

90-100% at high temperature, but their DTA curves indicates an endotherm corresponding to the melting of the complexes followed by the exotherms indicative of the partial decomposition of the complexes. Similarly dl-n-PA_2S Cu and dl-EA_2Cu show loss of weight of 90-92% by 330-60°C and their DTA curves indicate sharp endotherms for melting point of the complexes, followed by sharp vaporization endotherm and a few exotherms for certain decomposition of the complexes. The complexes meso-n-PA_2SCu, meso EA_2S Cu and meso-EA_2Ni show 68% , 79% and 97% loss in weight, but DTA of meso-n-PA_2Cu, meso-EA_2S Cu, meso-EA_2SNi complexes show large

Table-III: Quantitative Spectrophotometic studies of ligands and metal complexes.

Name of the compound	Colour	max nm	mole^{-1} cm^{-1}	Calibration range
Bis (ethanoylactone)-dl-stilbenediimine		312 240	32497 7928	
Bis(Ethanoylacetone) dl-stilbenediimine.Ni(II)	Yellow	560 375 360 270 247	75 6694 6234 11532 19740	Obeys Beer's law in the range 8 to 80 µg of complex corresponding to 1.019 to 10.19 µg/ml of Nickel, at 375 nm.
Bis(Ethanoylacetone) dl-stilbenediimine. Cu(II)	Blue	540 347 259	280 3226 1643	Obyes Beer's law in the range 320 to 2560 µg of complex corresponding to 43.67 ug to 349.40 µg/ml of Cu(II) at 540 nm.
Bis(ethanoylacetone)meso-stilbenediiamine		320 241 220	36082 4192 3295	
Bis(ethanoylacetone)meso stilbenediamine. Ni(II)	Dark yellow	575 380 362 249	145 6032 6968 19191	Beer's law obeyed in the range 8 to 80 µg complex corresponding to 1.019 to 10.91 g/ml of nickel at 362 nm.
Bis(ethanoylacetone)meso-stilbenediimine. Cu(II)	Blue	550 380 352	282 1643 3609	Beer's law objeyed in the range 320 to 2560 µg of complex corresponding to 41.19 to 329.6 µ g/ml of the Cu. at 550 nm.
Bis(n-propanoylacetone)dl-stilbenediimine.		320 220	25440 3915	

Table-III Cont...

Name of the Compound	Colour	max nm	mole^{-1} cm^{-1}	Calibration range
Table-III cont.				
Bis(n-propanoylacetone)-dl-stilbenediimine.Ni(II)	Yellow	560 378 358 275 247	70 6689 6170 15750.39 22399	Beer's law obeyed in the range 8 to 80 µg/ of the complex corresponding to 0.961 to 9.16 g/ml of nickel at 378 nm.
Bis(n-propanoylacetone)-dl-stilbendiimine. Cu(II)	Blue	540 349 260	200 5465 1730	Beer's law obeyed in the range 320 to 2560 µg of the complex coresponding to 4.19 to 329.6 µg/ml of Cu at 540 nm.
Bis(n-propanoylacetone)-meso-stilbenediimine		320 220	32940 4212	
Bis(n-propanoylacetone)-meso-stilbenediamine. Ni(II)	Dark Yellow	570 362 360 250	239 9484 9438 25428	Obeys Beer's law in the range 8 to 80 µg of the complex, corresponding to 0.961 to 9.61 µg/ml of Nickel at 362 nm.
Bis(n-propanoylacetone)-meso-stilbenediimine.Cu(II).	Blue	555 640 258 349	239 174 1710 3814	Obeys Beer's law in the range 320 to 2560 µg of the complex corresponding to 41.19 to 329.6 g/ml of the Cu. at 555 nm.

Table-IV: TG and DTA Studies of Copper(II) and Nickel(II) Complexes.

Reagent	Copper(II) Complex	Nickel(II) Complex
1 meso-H_2nPA$_2$S	Loss in weight starts by 180°C and 68% by 400C° and slow loss above 400, with maximum rate at 268°C	Slow loss of 3% by 170°C followed by major loss of 92% by 350°C with maximum rate at 310°C.
	DTA shows a sharp endotherm at 140°C for melting of the complex, folowed by exoth erms between 300-400°C.	DTA shows sharp melting endotherm at 150°C followed by small exotherms.
2 dl-H_2nPA$_2$S	Loss in weight starts at 226°C and 90% by 360°C and maximum rate at 305°C.	Loss starts by 181°C and single and complete loss by 360 with maximum rate at 320°C.
	DTA shows sharp melting endotherm at 178°C followed by vaporisation endotherm at 322°C.	DTA shows sharp melting endotherm at 198°C followed by multiple exotherms upto 500°C.
3 meso-H_2EA$_2$S	Loss starts by 192°C and 70% by 380°C and 79% by by 480°C with maximum rate 278°C.	Loss starts by 180°C and 97% by 315°C and complete by 500°C with maximum rate at at 279°C.
	DTA shows melting endotherm at 220°C followed by multiple exotherm till 320°C	DTA shows melting endotherm at 130°C followed by exo-therms until 310°C and 380°C.
4 dl-H_2EA$_2$S	Loss starts by 169°C and 92% by 330°C with maximum rate at 280°C.	Major loss of 94% by 300°C followed by slow loss of the remainder with maximum rate at 258°C.
	DTA shows melting endotherm at 231°C, followed by vaporization endotherm at 315°C and a few exotherms after that.	

Table-V: Gas Chromatographic Data of Copper and Nickel Complexes at column temperature of 250°C and N_2 flow rate 30 cm^3/min

Reagent	Metal ion	Retention time in sec.	Detection Limit rate cm^3/min.
1 dl-H_2EA_2	Ni	520	0.2 µg of complex, corresponding to 25 ng of nickel.
	Cu	515	0.4µg of complex, correspondong to 54 ng of nickel.
2 dl-H_2nPA_2S	Ni	640	0.2 g of complex, corresponding to 24µg of nickel
	Cu	625	0.4 µg of complex, corresponding to 51µg of copper.
3 meso-H_2EA_2S	Ni	850	0.3 µg of complex, corresponding to 32 ng of nickel
	Cu	810	0.6 µg of complex, corresponding to 81 g of Cu.
4 meso-H_2EA_2S	Ni	1100	0.3 µg of complex, corresponding to 30 µg of nickel.
	Cu	1050	0.6µ g of complex, corresponding to 77 µg of copper.

exotherms corresponding to pronounced decomposition at high temperatures. DTA of meso-n-PA_2SCu and meso-EA_2SNi was also recorded in flowing air atmosphere at the rate of 20 cm^3/min. DTA curves show unchanged melting point endotherm, followed by excessively large exotherms indicative of oxidative decompostions of the complexes.

The useful thermal analysis data was used to explore the potentials of the reagents for metal analysis involving gas chromatographic methods. Because of the high temperature required for the volatilization of the metal complexes, a number of stationary phases was tried, but stainless steel column 2mx3mm packed with OV101, 3% on chromosorb 80-100 mesh size gave reasonably good response, with fairly symmetrical peaks for the compounds eluted in the present work. But an attempt to separate copper and nickel complexes of a ligand failed and a suitable stationary phase has yet to be found to separate a mixture of copper and nickel complexes. However when a mixture of copper and nickel complexes of all the reagents is injected on the column the elution order in fig.5 indicates that metal complexes of dl-isomer elute first followed by meso isomer. It also confirms that the retention times increase with the increase in the chain lenght of the alkyl group.

In order to evaluate the potentials of reagents for metal analysis, the detection limit for each of the complexes was determined at optimized conditions. The detection limits were found in the ragne of 0.2-0.6 g of complexes, and dl isorems of both copper and nickel compelxes are found more sensitive than corresponding meso-isomer.

Finally the detection limits of the complexes are compared with detection limits of copper and nickel complexes of meso and dl-bis(acetylacetone) stilbenediimine [10] and the detection limits of the latter are in the range of 0.05-0.5 µg of complexes and show comparable sensitivity with the compounds reported in the present work.

It may therefore be concluded that no useful purpose is served in increasing the chain length of alkyl group and the favourable effect on the detection limits due to the increase in molecular weight is compensated by the steric factor intoroduced by the increase of chain length.

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