

Preparation, Characterisation and Chromatographic Studies of Copper(II), Nickel(II) and Oxovanadium(IV) Complexes of New Tetradentate Ketoamine Schiff Bases

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Summary: The copper(II), nickel(II) and vanadium(IV) complexes of bis(acetylmesityl oxide)-ethylenediimine (H₂AM₂en), bis(acetylmesityl oxide) propylenediimine (H₂AM₂pn), bis(acetylmesityl oxide) dl-stilbenediimine (dl-H₂AM₂S) and bis(acetylmesityloxi)meso-stilbenediimine (meso-H₂AM₂S) have been prepared and characterized using elemental analysis, IR, UV, ¹H-NMR and mass spectroscopic techniques. The metal complexes were found insufficiently volatile for quantitative GC, and their nickel and copper complexes could only be eluted with detection limits at sub μg levels.

However the copper, nickel and oxovanadium complexes are separated on a HPLC column Zorbax ODS (2.50 x 4.6 mm) with an ODS guard column. Complexes being eluted with 10% water in methanol, with detection limits at ng levels. Detection was achieved using a UV detector at 260 nm.

Relative elution of nickel, copper and vanadium complexes on HPLC and GC columns indicated parallel results, with a decrease in retention with methyl substitution and an increase due to phenyl substitution at the bridge position.

Introduction

Tetradentate ketoamines have been investigated as complexing reagents, gas chromatographic reagents and high performance liquid chromatographic reagents, using both normal and reversed phase modes, mostly for copper, nickel, palladium, vanadium, platinum, cobalt and iron [1-3]. Arising from the studies a number of reagents have been recommended for the separation of copper, nickel and vanadium [4-5]; copper, nickel and cobalt [6], copper, nickel and palladium [7-9] and copper, nickel, palladium and vanadium [10].

The metal complexes of bis(isovalerylaceto)ne) ethylenediimine (H₂IVA₂en) possessed appropriate volatility and thermal stability for the gas chromatographic separation of copper, nickel, palladium and vanadium [10]. The reagents bis(acetylmesityloxi) ethylenediimine (H₂AM₂en), bis(acetylmesityloxi)propylenediimine (H₂AM₂Pn), bis(acetylmesityloxi) dl-stilbenediimine, dl-H₂AM₂S) and bis(acetylmesityl oxide) meso-stilbenediimine (meso-H₂AM₂S) related to H₂IVA₂en, but containing double bonds in alkyl groups (Fig. 1) have been prepared to examine the effects of the double bond on the thermal stability, volatility and gas chromatographic elution of copper, nickel and

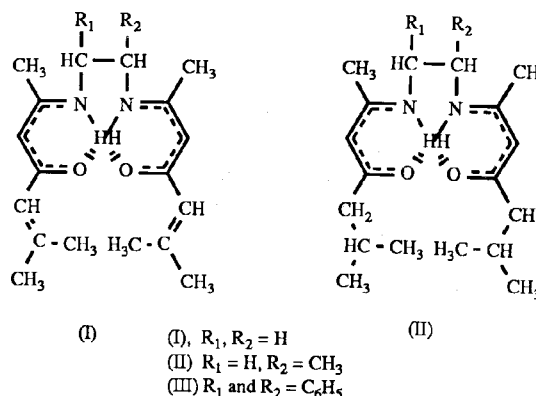


Fig.1: Structural diagrams (I.I). Bis(acetylmesityloxi)ethylenediimine-(II.I) (isovalerylaceto)ethylenediimine.

oxovanadium complexes and upon their possible separation using HPLC.

Results and Discussion

The β-diketone acetylmesityl oxide was prepared following a general procedure of Belcher *et al* [14]. The reagents and their copper and nickel

complexes were prepared by a simple synthetic route, the oxovanadium(IV) complexes were prepared by a ligand exchange method, following a similar procedure as reported by Martin and Ramaish [15]. The mass spectra of the reagents H₂AM₂en, H₂AM₂pn, dl-H₂AM₂S and meso-H₂AM₂S indicated molecular ion peaks at m/e 304, 318, 456 and 456 respectively with relative intensities within the range 0.05-1.7%. All the reagents indicated loss of -R groups, corresponding to m/e 55 (isobutene) and the reagents H₂AM₂en and H₂AM₂pn also showed loss of -RCO; loss of corresponding groups from dl-H₂AM₂S and meso-H₂AM₂S was not observed probably because of the ease of the breakage of C-C bond at bridge position. It is therefore suggested that the condensation has occurred at the carbonyl group adjacent to -CH₃. The main fragmentation pathway involved the breakage of the C-C bond at the bridge position as expected [16,17].

The IR spectra of the reagents indicate one to two bands of weak to medium intensity in the range 3300-3100 cm⁻¹ and a strong and broad band with centre around 1610-1580 cm⁻¹ these were considered as due to hydrogen bonded NH and -C=O respectively. The bands are not visible in the copper, nickel and oxo-vanadium complexes due to chelation. A band observed within the range 1655-1630 cm⁻¹ in the spectra of the reagents and their metal complexes is assigned to the C=C vibration in isobutene. A strong band observed in the spectra of oxovanadium complexes at 980-990 cm⁻¹ may be due to the V=O stretching vibration [18]. Bands

observed within the range 505-520 cm⁻¹ and 580-595 cm⁻¹ in the spectra of metal complexes could be due to M-ligand vibrations.

The results of ¹H-NMR are as expected from the structure of reagents and metal complexes (Table 2). The reagents indicate two to three doublets due to methyl groups in isobutene at δ 1.82-2.14 ppm. These doublets shifted to δ 1.7-2.07 in nickel complexes due to the restriction of the free rotation about C-C bond at bridge position and a fixed configuration. The signal observed at δ 11.20-12.07 ppm due to NH protons in the spectra of the reagents disappeared in the spectra of the metal chelates as expected [19]. The protons in -CH and -CH₂ groups present at the bridge position indicated a similar pattern as has been reported for bis(trifluoroacetylmesityl oxide) ethylenediimine and related compounds [20].

The spectrophotometric studies of the reagents and their metal complexes in chloroform was carried out to examine different transitions in the UV and visible region and evaluate them for spectrophotometric determinations (Table 3). The nickel complexes indicate a symmetrical band at 568-580 nm (ε = 139- 320 l.mole.⁻¹ cm⁻¹), similar to that observed in bis(acetylaceton)dl-stil-benediimine, and this has been assigned to a square planar configuration [21]. The copper complexes of H₂AM₂pn and dl-H₂AM₂S also show symmetrical bands at 548 nm and 545 nm respectively (Fig. 2), characteristic of square planar complexes, but AM₂enCu shows a band at 547 nm and a shoulder

Table 1: Results of micro analyses of reagents and metal chelates.

Name of Compound	Molecular formula	Melting point °C	% Calculated			% Found		
			C	H	N	C	H	N
meso-H ₂ AM ₂ S	C ₃₀ H ₃₆ N ₂ O ₂	194	78.95	7.89	6.14	78.40	8.16	6.28
meso-AM ₂ SCu	C ₃₀ H ₃₄ N ₂ O ₂ Cu	250	69.55	6.56	5.41	69.46	6.72	5.47
meso-AM ₂ SNi	C ₃₀ H ₃₄ N ₂ O ₂ Ni	225	70.21	6.63	5.46	70.55	6.80	5.27
meso-AM ₂ SVO	C ₃₀ H ₃₄ N ₂ O ₂ VO	278	68.97	6.51	5.36	69.11	6.41	5.16
dl-H ₂ AM ₂ S	C ₃₀ H ₃₆ N ₂ O ₂	128	78.95	7.89	6.14	78.48	8.01	6.10
dl-AM ₂ SCu	C ₃₀ H ₃₄ N ₂ O ₂ Cu	274	69.55	6.56	5.41	69.50	6.72	5.50
dl-AM ₂ SNi	C ₃₀ H ₃₄ N ₂ O ₂ Ni	253	70.21	6.63	5.46	70.45	6.70	5.40
H ₂ AM ₂ en	C ₁₈ H ₂₈ N ₂ O ₂	170	71.05	9.21	9.21	69.92	9.36	9.30
AM ₂ enNi	C ₁₈ H ₂₆ H ₂ O ₂ Ni	255	59.88	7.20	7.76	59.70	7.38	8.0
AM ₂ enCu	C ₁₈ H ₂₆ N ₂ O ₂ Cu	252	59.06	7.11	7.65	59.18	6.98	7.50
AM ₂ enVO	C ₁₈ H ₂₆ N ₂ O ₂ VO	250	58.39	7.02	7.56	58.86	7.12	7.58
H ₂ AM ₂ pn	C ₁₉ H ₃₀ N ₂ O ₂	102	71.69	9.43	8.80	71.80	9.40	8.76
AM ₂ pnNi	C ₁₉ H ₂₈ N ₂ O ₂ Ni	172	60.84	7.47	7.47	6.43	7.48	7.46
AM ₂ pnCu	C ₁₉ H ₂₈ N ₂ O ₂ Cu	183	60.05	7.37	7.37	60.45	7.33	7.40
AM ₂ pnVO	C ₁₉ H ₂₈ N ₂ O ₂ VO	233	59.38	7.29	7.29	58.85	7.20	7.17

Table 2: $^1\text{H-NMR}$ data of the reagents and their nickel complexes in CDCl_3 in δ ppm with possible assignments.

Compound	-CH ₃ group	= CH isobutene	-CH and -CH ₂ bridge	= CH	-NH	others - C ₆ H ₅ bridge
H ₂ AM ₂ en	1.8145(d) 2.142(d) 1.8917(s) 1.9088(s)	5.7805(m)	3.340(m) 3.42(m)	4.943 4.468	11.204	-
AM ₂ enNi	1.7043(d) 1.9847(d) 1.5465(s) 1.8556(s)	5.003(m)	2.9812(s)	4.8847(s)	-	-
H ₂ AM ₂ pn	1.8078(d) 2.1307(d) 2.1410(d) 1.873(s) 1.8843(s)	5.7722(m)	3.27(m) 3.712(m)	4.8867(s) 4.9155(s)	11.017(d) 11.296(t)	-
dl-H ₂ AM ₂ S	1.823(d) 2.187(d) 1.8863(s)	5.8048(m)	4.7446(s)	4.9607(s)	12.07(d)	6.975(m) 7.144(m) 7.158(m)
dl-NH ₂ SNi	1.7368(d) 2.0781(d) 1.502(s) 1.508(s)	5.5175(m)	4.1434(s)	4.8312(s) 4.8464(s)	-	7.3236(m) 7.476(m) 8.2805(m)
meso-AM ₂ SNi	1.7332(d) 2.0739 1.5351(s) 1.5391(s)	5.5175(m)	4.1434(s)	4.8657(s)	-	7.0175(s)

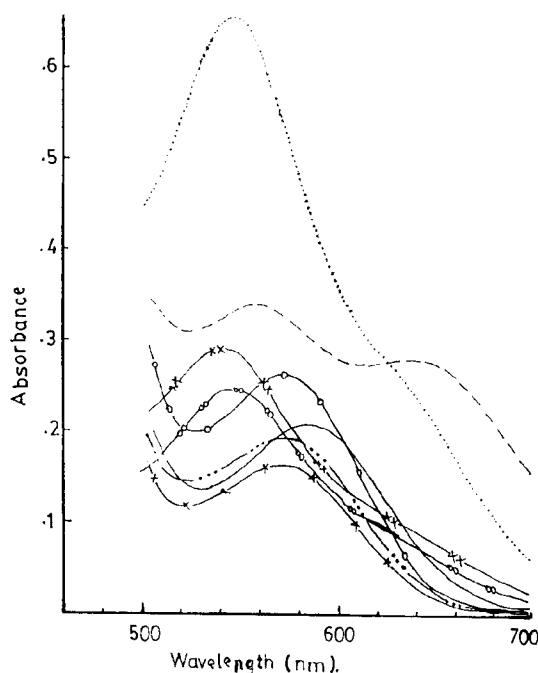


Fig. 2: Absorption spectra of copper(II) and nickel(II) chelates in chloroform within 500-700 nm indicating d-d transition.

meso-AM₂SNi -----
 meso-AM₂SCu -----
 dl-AM₂SNi ---x---x---
 dl-AM₂SCu ---xx---xx

AM₂pnNi —○—○—
 AM₂pnCu —□—□—
 AM₂enNi - - - - -
 AM₂enCu - - - - -

at 640 nm, and meso-AM₂SCu shows bands at 558 nm and 640 nm. Kenatomi *et al* [21] and Martell *et al* [22] have observed similar bands in bis(acetylaceton)cyclohexanedimine and have suggested a distorted square planar configuration. It is therefore considered that AM₂enCu and meso-AM₂SCu may have distorted square planer configuration.

The oxovanadium complex AM₂enVO shows four bands within 640-450 nm as has been reported by Pasini and Gullotti [18] in five coordinate square pyramidal vanadium complexes of bis(acetylaceton)ethylenedimine and related compounds, due to d-d transitions in d¹ system of oxovanadium(IV) complexes. However AM₂pnVO and meso-AM₂SVO show one and two bands within the region due to d-d transition.

The nickel complexes shows one to three charge transfer bands within the range 455-385 nm ($\epsilon = 2700-10000$), but the corresponding band in copper complexes of H₂AM₂en, H₂AM₂pn and dl-H₂AM₂S is visible as a shoulder at 380-385 nm ($\epsilon = 11000-13000$) and in vanadium complexes of H₂AM₂en, as a shoulder at 395-405 nm (6600-9900). The reagents and their metal complexes show a number of high intensity bands at 370-250 nm due to intraligand $\pi-\pi^*$ transitions (Table 3).

Table 3: Spectrophotometric data of reagents and their metals.

Compound	complexes in chloroform λ -max nm ($\epsilon = 1.\text{mole}^{-1} \text{cm}^{-1}$)
H ₂ AM ₂ en	350(24000), 295(26000), 250(sh) (13000)
AM ₂ enCu	640(sh) (87), 547(240), 380(sh) (12000), 345 (33000). 335(sh) (30000), 29 (sh) (13000), 245 (29000)
AM ₂ enNi	575(140) 455(sh) (2700), 410(3200), 385 (6600), 335(sh) (11000), 295 (23000), 255 (25000).
AM ₂ enVO	635(81), 550(sh) (160), 505(230), 478 (sh) (230), 395(sh) (9600), 355 (35000), 250 (21000).
H ₂ AM ₂ Pn	365(sh) (3200), 358 (4200), 350 (16000).
AM ₂ PnCu	548(290), 380(sh) (13000), 345(38000), 335(sh) (34000), 292 (sh) (14000), 246 (33000).
AM ₂ pnNi	568 (150), 450 (sh) (3500), 408 (10000), 386 (sh) (8300), 339 (sh) (12000), 295 (29000), 253 (sh) (32000) 240 (36000).
AM ₂ pnVO	636 (100), 395 (sh) (9900), 353 (37000), 248 (21000).
dl-H ₂ AM ₂ S	345 (37000), 250 (20000).
dl-AM ₂ SCu	545(230), 385(sh) (11000), 350 (78000), 338 (sh) (24000), 320 (19000), 252 (23000).
dl-AM ₂ SNi	570 (130), 450 (sh) (3100), 410 (7800), 336 (13000), 298 (21000), 243 (29000).
meso-H ₂ AM ₂ S	350(35000), 250 (12000).
meso-AM ₂ SCu	640(220), 558 (270), 348 (36000), 300 (sh) (13000), 254 (30000).
meso-AM ₂ SNi	580 (320), 410 (9800), 340 (sh) (12000), 290 (22000), 255 (sh) (24000), 244 (25000).
meso-AM ₂ SVO	640 (sh) (88), 565 (sh) (125), 405 (sh) (6700), 362 (40000) 348 (sh) (33000), 259 (40000), 245 (38000).

The observation of these bands at slightly different positions and intensities in metal complexes as compared to the reagents may be attributed to coordination as more planar metal chelates.

The values of molar absorptivities in visible region generally suggest that metal chelates are insensitive for spectrophotometric determination, except for nickel complexes which have a reasonable values of molar absorptivity. DTA and TGA of the metal complexes were recorded to evaluate the reagents for GC separations of metal complexes. The results (Fig. 3 and 4) indicate that nickel complexes are somewhat volatile with rapid loss in weight of 78-85% upto 400°C, but the copper complexes show rapid loss in weight of 50-70% within the same temperature range. TG of AM₂enVO indicates that the complex is even less volatile and thermally stable with a rapid loss of 50% by 350°C. DTA shows a melting endotherm., followed by a series of exotherms and endotherms due to vaporization/decomposition. A fairly large exotherm observed at 400-500°C has been assigned to decomposition because of nonvolatile residue (Fig. 5A and B).

The thermal analysis of metal complexes did not suggest adequate thermal stability and volatility for their effective use for the gas chromatographic separation of metal complexes, however they were examined for possible elution on a stainless steel

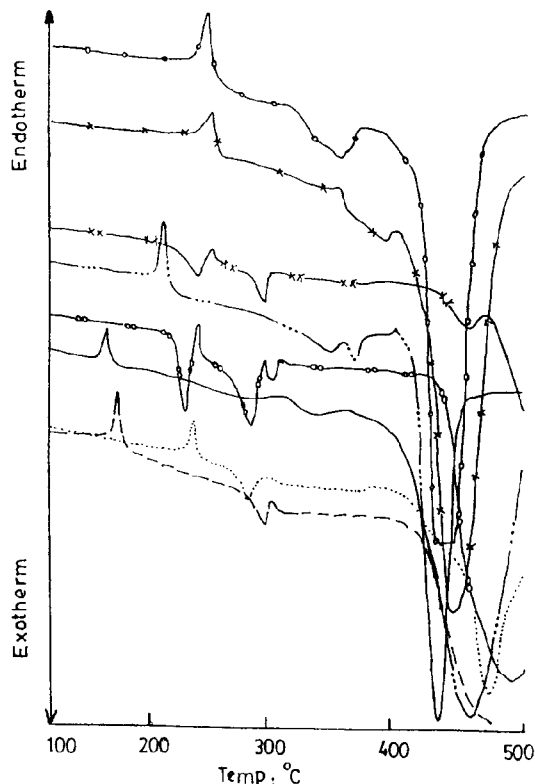


Fig.3: DTA of copper and nickel chelates at a heating rate of 15°C/min and nitrogen flow rate 50 cm³/min.

AM ₂ PnNi	—	dl-AM ₂ SNi	-x-x-
AM ₂ pnCu	----	dl-AM ₂ SCu	-x-x-x-
AM ₂ enNi	-o-o-	meso-AM ₂ SNi
AM ₂ enCu	-oo-oo-	meso-AM ₂ SCu	-----

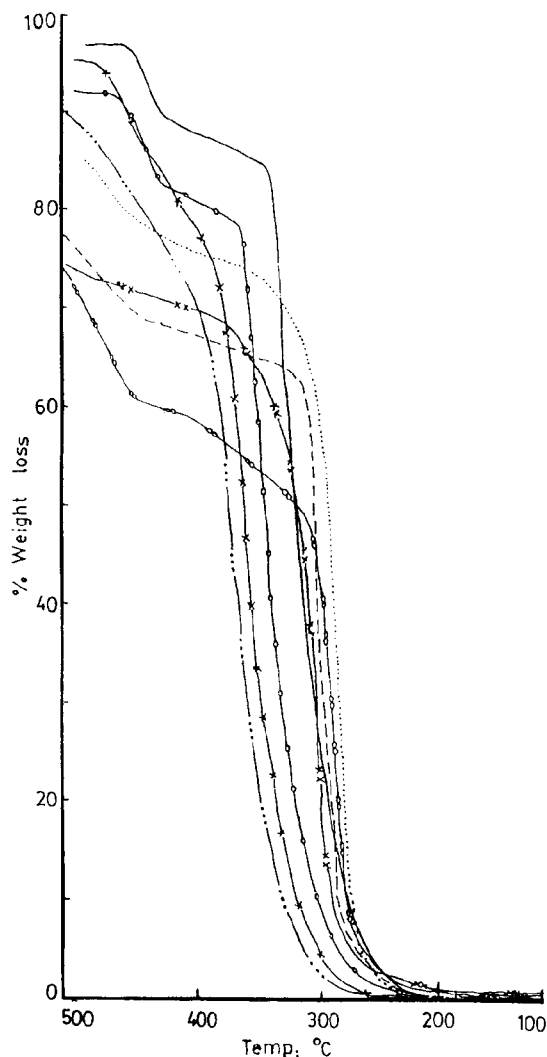


Fig.4: TGA of copper and nickel chelates at same conditions and indicated by same lines as fig. 3.

gas chromatographic column (6 x 0.085" 1D) packed with 3% OV101 on Chromosorb WHP 80-100 mesh size. The column temperature range was 240-260°C injection port 260-270°C and nitrogen flow rate 30-45 cm³/min. It was observed that oxovanadium complexes failed to elute on the column. Similarly the copper complex meso-AM₂SCu failed to elute and that of AM₂enCu eluted only at sub mg range with poor sensitivity. All the nickel complexes and copper complexes of H₂AM₂pn and dl-H₂AM₂S eluted from the column to give symmetrical peaks with a linear calibration range within 2-24 μg of each complexes and detection limits within the range 0.3-0.8 μg of complex.

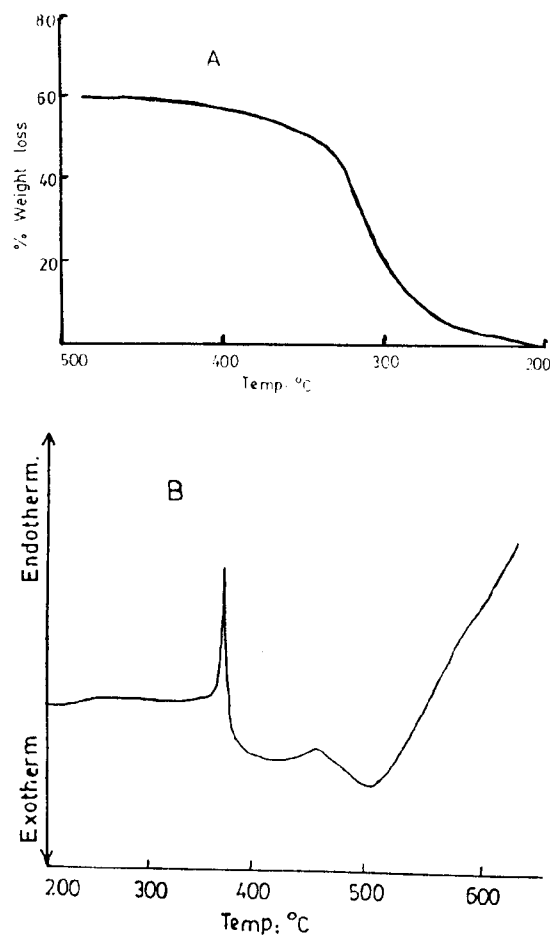


Fig. 5: (A) TGA (B) DTA of AM₂enVO at heating rate (A) 10°C/min (B) 15°C/min. nitrogen flow rate 40 cm³/min.

When an attempt was made to resolve the copper and nickel complexes of H₂AM₂pn and dl-H₂AM₂S they failed to resolve adequately with only a partial separation between copper and nickel complexes of H₂AM₂pn. The effect of methyl and phenyl group substitution at the bridge position in the ligand H₂AM₂en was examined with respect to the relative elution of nickel and copper complexes. It was observed (Fig. 6 A & B) that methyl group substitution decreased and phenyl group substitution increased retention of both copper and nickel complexes, such behaviour has been observed for related compounds [9].

The poor separation of metal complexes on GC led to the examination of reversed phase HPLC on a Zorbax ODS column (250 x 4.6 mm) with an

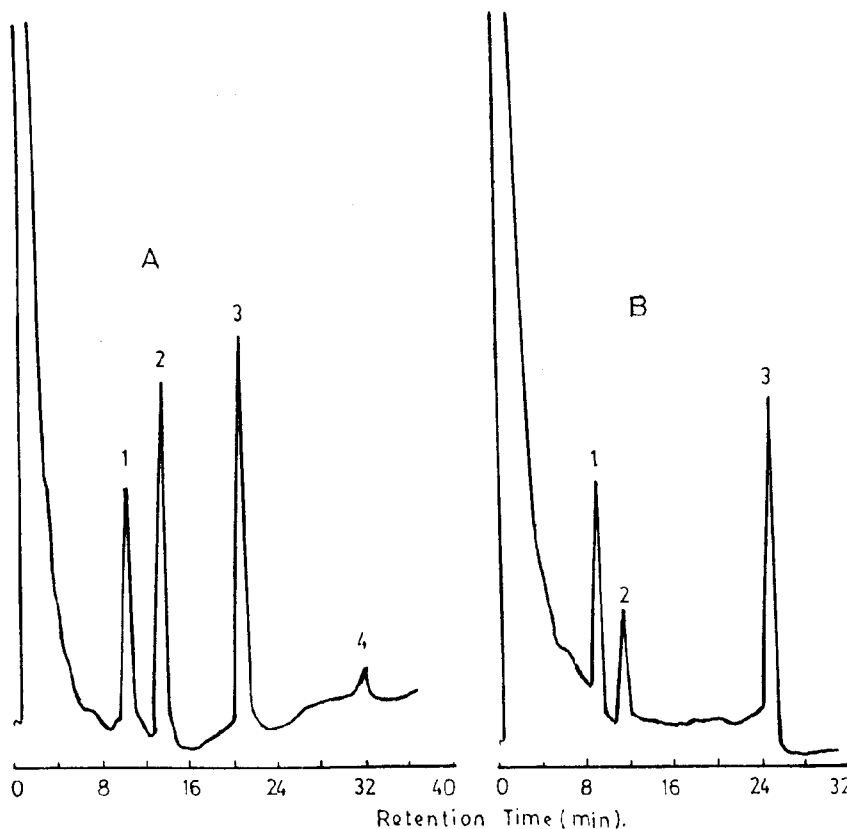


Fig.6: Comparative elution of (A) nickel complexes (B) copper complexes of (1) H₂AM₂Pn (2) H₂AM₂en (3) dl-H₂AM₂S (4) meso-H₂AM₂S Column (6' x 0.085" I.D) packed with OV101, 3% on Chromosorb WHP 80-100 mesh size nitrogen flow rate 40 cm³/min. temperatures column (A) 235°C after 9-50 min. programmed rise in temperature 2°C/min. upto 270°C (B) 235°C, rise in temp 1°C for 11-18 min and 2°C/min upto 260°C.

ODS guard column for the separation of copper, nickel and oxovanadium complexes. When the complexes were injected and were eluted with 10% water in methanol, good peak shape was obtained for each complex. When the separation of copper, nickel and oxovanadium complexes of H₂AM₂en, H₂AM₂pn and meso-H₂AM₂S and the copper and nickel complexes of dl-H₂AM₂S were examined, elution of oxovanadium occurred first, followed by nickel and copper complexes (Fig. 7 A,B,C and D). The effect of the presence of the reagent on the separation of metal complexes was also examined, it being found that the reagent separated adequately from copper, nickel and oxovanadium complexes of dl-H₂AM₂en, meso-H₂AM₂S and copper and nickel complexes of dl-H₂AM₂S, but there was some overlapping between H₂AM₂pn and its oxovanadium complexes.

The response of the UV detector at 260 nm was checked by simultaneous calibration of copper, nickel and oxovanadium complexes of H₂AM₂en, H₂AM₂pn and meso-H₂AM₂S and copper and nickel complexes of dl-H₂AM₂S. Linear calibration curves were obtained in the range of 0.5-5 µg of a complex and detection limits were 5-20 ng of a complex corresponding to 0.6-2.0 ng of a metal ion.

Finally the effect of methyl and phenyl substitution on the relative elution of copper, nickel and oxovanadium complexes was investigated on a Zorbax ODS column (250 x 4.6 mm) with ODS guard column. The complexes being eluted with 10% water in methanol. The order of elution for copper and nickel complexes was (1) H₂AM₂pn (2) H₂AM₂en (3) dl-H₂AM₂S (4) meso-H₂AM₂S as was observed in GC. However for oxovanadium

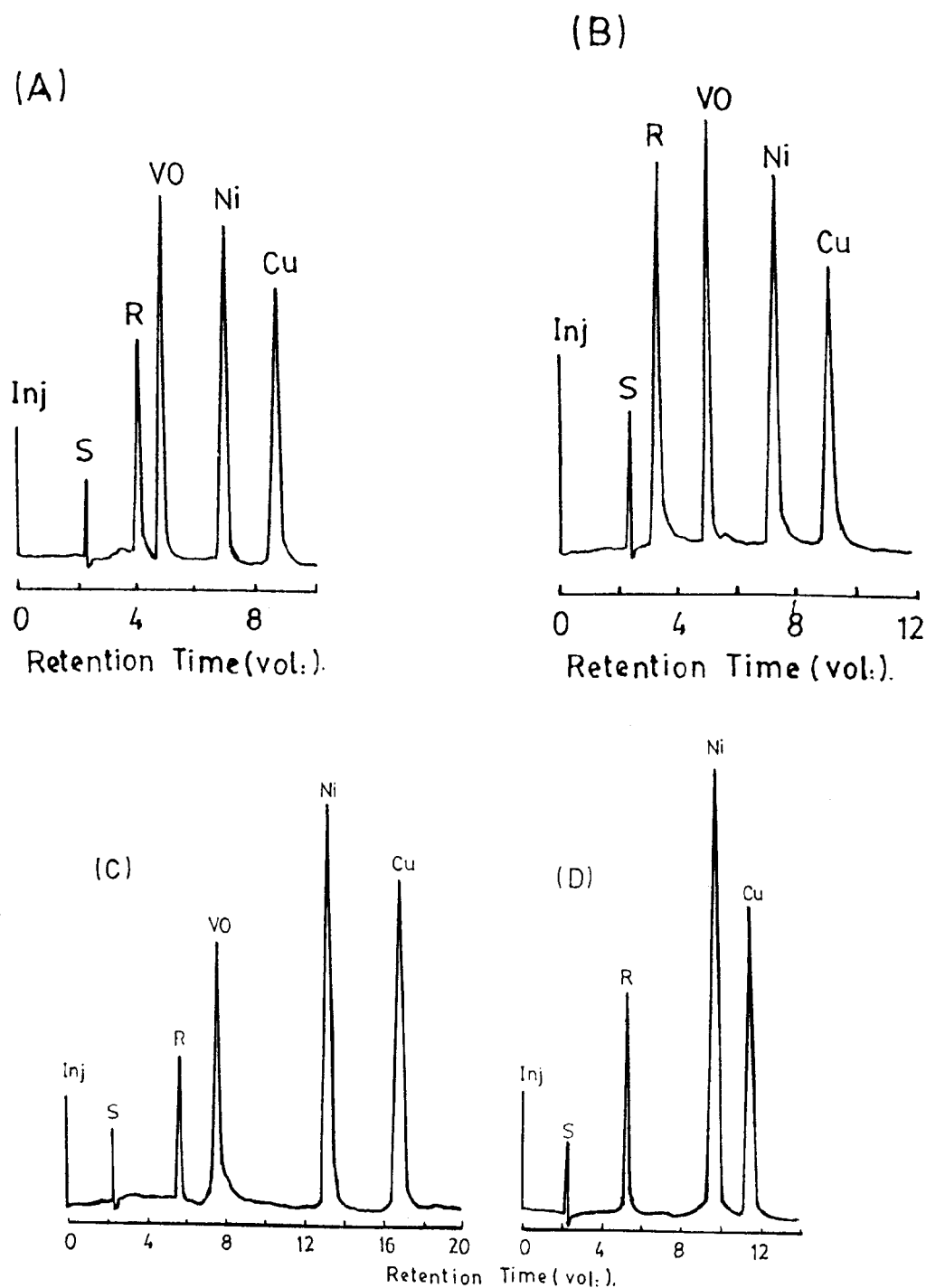


Fig.7: Reversed phase HPLC separation of reagent, oxovanadium, nickel and copper complexes of ligands (A) H₂AM₂pn (B) H₂AM₂en (C) meso-H₂AM₂S and (D) Separation of Reagent, nickel and copper complexes of dl-H₂AM₂S. Column (250 x 4.6 mm) Zorbax ODS with guard column ODS. Eluent 10% water in methanol. Flow rate 1 cm³/min. Detection UV fixed at 260 nm.

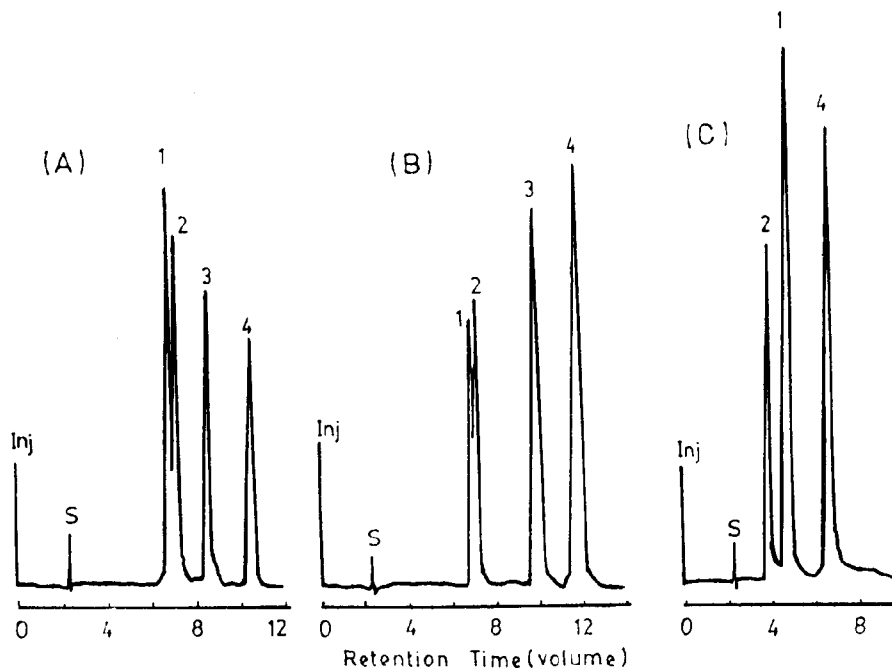


Fig.8: Comparative HPLC elution of (A) Copper (B) Nickel (C) oxovanadium, complexes of ligands (1) H_2AM_2Pn (2) H_2AM_2en (3) $dl-H_2AM_2S$ (4) $meso-H_2AM_2S$. Column (250 x 4.6 mm) Zorbax ODS with guard column ODS.

Eluent (A). Water: acetonitrile: methanol (7:3:90). (B and C) 10% water in methanol. Flow rate $1\text{ cm}^3/\text{min}$. Detection UV at 260 nm.

complexes the order was slightly different, being (1) H_2AM_2en (2) H_2AM_2pn (3) $meso-H_2AM_2S$ (Fig. 8. A, B and C). It is here suggested as for GC that the methyl group substitution decrease and phenyl substitution increase retention of copper and nickel complexes. It may also be noted that copper and nickel complexes of the ligand $meso-H_2AM_2S$ containing the phenyl group at bridge position axial-equatorial position are retained on GC and HPLC columns longer than $dl-H_2AM_2S$ which has corresponding phenyl groups at diaxial positions.

Experimental

Preparation of Acetylmesityl oxide (6-Methyl-5-hepten-2,4-dione)

Dry diethyl ether (200 ml), sodium hydride with 20% paraffin liquid (30 g) and ethanol (10 ml) were transferred to a flask containing a magnetic stirrer, fitted with a dropping funnel and condenser. The mixture was stirred for 30 min and ethyl acetate (120 ml) was added during 1 hour. Mesityl oxide (4-methyl-3-penten-2-one) (130 ml) was then

added over a period of 2 hrs. and contents were further stirred for 4 hrs. The mixture was cooled for 20 hrs. Ice cooled water (100 ml) was slowly added to the aqueous layer and the organic layer was extracted with diethyl ether. The extract was dried over anhydrous sodium sulphate and the β -diketone was distilled off at 60°C and 3 mm Hg pressure and collected.

Ethylenediamine, propylenediamine and mesityloxide (Merck) were used. Meso-stilbenediamine, dl-stilbenediamine and bis(acetylacetonate) oxovanadium(IV) were prepared by reported methods [11-13].

Preparation of Bis(acetylmesityl oxide) ethylenediamine- (H_2AM_2en), Bis(acetylmesityl oxide) propylenediamine (H_2AM_2pn)

An ice cooled solution of 1,2-diaminoethane (.005M) or 1,2-diaminopropane (.005M) in ethanol was slowly added to the cooled solution of acetylmesityl oxide (.011 M) in ethanol. The contents were mixed well and kept cool in ice for 30 min.

The mixture was left at room temperature for 12 hrs. and the solvent was evaporated in a vacuum desiccator. The oily mass obtained was dissolved in n-hexane and the solution was concentrated and kept cool for 1 week. The crystalline product formed was filtered and recrystallized from n-hexane.

Preparation of Bis(acetylmesityl oxide)dl-stilbenediamine-(dl-H₂AM₂S) and Bis(acetylmesityl oxide) meso-stilbenediamine (meso-H₂AM₂S)

Meso-stilbenediamine (0.005M) or dl-stilbenediamine (.005 M) was added to acetylmesityl oxide (.011 M) and the mixture was heated on a water bath for 30 min. The mixture solidified slowly, being left at room temperature for 12 hrs. The solid mass obtained was recrystallized twice from n-hexane or ethanol.

Preparation of Copper and Nickel Complexes

An equimolar solution of copper(II) acetate or nickel(II) acetate in methanol was slowly added to the warm solution of the reagent in ethanol. The mixture was heated for 30 min. and was concentrated and cooled at -5°C. The precipitate formed was filtered and recrystallized from n-hexane or ethanol.

Preparation of oxovanadium(IV) complexes

Bis(acetylacetone)oxovanadium(IV) (.001 M) and H₂AM₂pn or meso- H₂AM₂S (.0011 M) were heated together at a temperature maintained between 220-230°C and a pressure of 3mm Hg for 2 hrs. The residue was washed with dry ether and recrystallized from n-hexane.

Elemental micro analysis were carried out by Elemental Micro- Analysis Ltd. U.K. (Table 1). IR of the reagents and metal complexes in the range of 4000-250 cm⁻¹ were recorded on Hitachi 260-30 and Perkin Elmer 1430 spectrophotometers using KBr disc techniques. The mass spectra of the reagents and ¹H NMR were recorded at HEJ Research Institute of Chemistry, University of Karachi, on a Finnagan MAT 1125 mass spectrometer and Bruker AM 300 NMR spectrometer in CDCl₃. Spectrophotometric studies were carried out on a Hitachi 220 spectrophotometer.

DTA and TGA were recorded on a Shimadzu TG 30 thermal analyser at heating rate of 15°C/min and a nitrogen flow rate of 50 cm³/min. DTA and TG of AM₂enVO at heating rates of 15°C/min and 10°C/min respectively and a nitrogen flow rate 40 cm³/min were recorded at Quaid-e-Azam University, Islamabad.

A Hitachi 163 Gas chromatograph connected with FID detection and a recorded Model 056 was used.

A stainless steel column (6'.0x0.085" ID) packed with 3% OV101 on Chromosorb WHP 80-100 mesh size (Altech Assoc:) was used.

A Shimadzu LC-5 liquid chromatographic system with a spectrophotometric detector model SPD-2A, LC injector SIL-1A, Chromatopac C-RIB and Zorbax ODS, columns (5μ, 250 x 4.6 mm), and ODS guard column was used.

Conclusion

The reagents and metal complexes are easily prepared by synthetic routes and the analytical and spectroscopic data agree with expected values. The copper, nickel, palladium and oxovanadium complexes of the reagent bis(isovalerylacetone) ethylenediamine containing the isobutyl group adjacent to the carbonyl groups are reported [10] to show good GC elution and separation of metal complexes, but the copper nickel and oxovanadium complexes of the corresponding bis(acetylmesityl oxide)ethylenediamine, containing isobutene adjacent to carbonyl groups show poor GC characteristics. It is therefore suggested that including the double bond near to the carbonyl group decreases the thermal stability and volatility of metal complexes to produce undesirable GC characteristics. The copper and nickel complexes with square planar configuration only eluted from the GC column. However, HPLC, which is not limited by the volatility and stability of metal complexes easily separated copper, nickel and oxovanadium complexes at μg levels.

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