

GLC and HPLC Studies of Copper(II) Nickel(II) Palladium(II) and Vanadium(IV) Complexes of Bis(Salicylaldehyde)Tetramethylethylenediimine

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Summary: The copper, nickel, palladium and vanadium complexes of tetradentate ligand bis(salicylaldehyde)tetramethylethylenediimine (H_2SA_2Ten) are prepared and their DTA and TGA are recorded. Nickel complex indicates reasonable volatility and thermal stability with loss in weight upto 98.7%, but copper, palladium and vanadium complexes leave significant residue behind with loss in weight in the range from room temperature to $500^\circ C$. The metal complexes elute on GLC column (6' x 0.085) packed with OV101, 3% on Chromosorb WHP 80-100 size with detection limits at sub μg level of metal complexes and complete separation palladium from copper, nickel and vanadium complexes.

The spectrophotometric studies of metal complexes indicate reasonable sensitivity within UV region and their adsorption HPLC column (250 x 4 mm) packed with Licrosorb Si100, 5μ , connected with UV detector demonstrated complexes. The complexes were eluted isocratically with binary mixture of chloroform 1,2-di-chloroethane and detection limits were found at sub ng levels of metal complexes.

The reagent has been applied for the determination of nickel in nickel-aluminium alloy using both GLC and adsorption HPLC. The result agree to each other and the expected value.

Introduction

Thermal stability and volatility have remained a limiting factor for the successful gas-liquid chromatography (GLC) of tetradentate salicylal-diimine chelate [1]. However GLC of copper, nickel and zinc chelates of bidentate salicylal-diimine have been reported [2]. High Performance Liquid

Chromatography (HPLC) which is not limited by the thermal stability, has proved promising and separation of copper and nickel complexes of tetradentate ligand bis(salicylaldehyde) ethylene-diimine (H_2SA_2en) on silica 10μ and copper, nickel and palladium complexes of $H_2SA_2 en$ on bonded

octadecyl substrate as reversed phase HPLC have been reported [3,4]. Recently copper and nickel complexes of meso and dl-bis(salicylaldehyde)stilbene diimine have been reported on adsorption HPLC [5].

Averill and Broman have prepared the ligand bis(salicylaldehyde)-tetramethylethylenediimine (H₂SA Ten) and its cobalt complex to study the polarographic behaviour of its cobalt(III) chelate [6]. In the present work the ligand H₂SA₂ Ten containing maximum number of methyl groups at bridge position has been examined for the elution of its metal complexes on GLC column and for the separation of copper, nickel, palladium and vanadium complexes on adsorption HPLC.

Experimental

The reagent H₂SA₂ Ten was prepared as reported by Averill and Broman [6].

Preparation of Metal Complexes

The copper, nickel oxovanadium complexes were prepared by refluxing equimolar solution of the reagent (0.01 M, 0.33 g) in methanol with copper (II) acetate (0.001 M, 0.02 g), nickel (II) acetate (0.001 M, 0.25 g) and vanadium (IV) sulphate (0.001 M, 0.25 g) in methanol for 30 min. The reaction mixture was quickly filtered, concentrated and cooled. Precipitate obtained was recrystallized from ethanol or methanol. Palladium complex was prepared by refluxing reagent (0.001 M, 0.33 g) in benzene and palladium - benzonitrile complex in benzene for 24 hrs. The palladium benzonitrile complex was prepared by heating together palladium(II) chloride (0.001 M, 0.18 g) and benzonitrile (0.5 cm³) for 2 hr. The reaction mixture was filtered and most of the solvent was distilled off. The residue was dissolved in n-hexane and precipitate obtained was recrystallized from n-hexane.

Elemental micro analysis (Table-1) was carried out by Elemental Micro-Analysis Ltd., U.K. Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) was recorded on Shimadzu TG 30 Thermal Analyser at a heating rate of 15°C/min and nitrogen flow rate of 50 cm³/min. Hitachi 163 Gas Chromatograph with FID detector system and recorded 056 was used. Column (6' x 0.0185") packed with OV101, and OV17, 3% on Chromosorb WHP 80-100 mesh size (Altech Assoc.) were used during the study.

Hitachi 655A Liquid Chromatograph connected with variable wavelength UV monitor, Rheodyne 7125 injector and recorder 561 were used. Column (250 x 4 mm) packed with Licrosorb Si100, 5μ and (200 x 4.6 mm) Si, 100, 5μ (Helwett and Packard) were used for adsorption HPLC.

Quantitative Determinations

Solutions

The stock solutions of nickel(II), copper(II) and oxovanadium(IV) containing 1 mg/ml were prepared in water from NiCl₂·6H₂O, CuCl₂·2H₂O and VOSO₄·3H₂O.

Buffer solutions in the pH range 5-9.5 from acetic acid-sodium acetate (1M) and sodium bicarbonate - sodium carbonate (0.5 M) pairs. The pH of the solutions was measured with WPA CD-620 Digital pH meter with glass electrode containing internal reference electrode.

Reagent solution (0.2 - 0.75 % w/v) was prepared in ethanol.

Analytical Procedure

An aliquot of solution (1-2 cm³) containing (0-200 μg) copper, nickel or both in a mixture was transferred to well stoppered tube (10 cm³), fol-

Table-1: Results of Elemental Micro - Analysis

Compound	Mol. Formula	M.P.	% Expected			% Found		
			C	H	N	C	H	N
H ₂ SA ₂ Ten	C ₂₀ H ₂₂ N ₂ O ₂	130°C	74.04	7.40	8.64	74.00	7.44	8.83
CuSA ₂ Ten	C ₂₀ H ₂₂ N ₂ O ₂ Cu	300°C	62.25	5.78	7.26	62.09	5.77	6.98
NiSA ₂ Ten	C ₂₀ H ₂₂ N ₂ O ₂ Ni	353°C	63.04	5.77	7.35	62.98	5.84	7.11
VOSA ₂ Ten	C ₂₀ H ₂₂ N ₂ O ₂ VO	347°C	61.69	5.65	7.19	61.52	5.24	6.78
PdSA ₂ Ten	C ₂₀ H ₂₂ N ₂ O ₂ Pd	336°C	55.89	5.89	6.51	55.69	5.34	6.55

lowed by bicarbonate buffer pH 8 (2 cm^3), ethanol (2 cm^3), and reagent solution (0.2 - 0.75 % w/v) (0.5 cm^3) in ethanol. The contents were heated on water bath for 30 min. and allowed to cool. Toluene (1 cm^3) was added and contents were mixed on mechanical shaker for 15 min. The layers were allowed to separate and extract ($1-5 \mu\text{l}$) was injected on GLC or HPLC column at the optimized conditions.

Analysis of sample for nickel

Nickel-aluminium alloy (0.2 g) (BDH) was added a mixture of hydro chloric acid - nitric acid (3:1) (5 cm^3) and heated gently on hot plate to near dryness. Hydrochloric acid (10 cm^3) was added and again heated to near dryness. Water was added and volume was adjusted to 100 cm^3 . Solution (10 cm^3) was again diluted to 100 cm^3 and solution (0.1 - 0.5 cm^3) was transferred to well stoppered tube (10 cm^3) and volume adjusted to 2 cm^3 . The nickel was extracted in toluene following analytical procedure. The amount of nickel in sample was determined on GLC and HPLC at the optimized conditions. The amount of nickel in sample was evaluated from standard calibration curve prepared from known amounts of nickel.

Results and Discussion

The metal complexes are easily prepared and the elemental microanalysis corresponds to metal-ligand (1:1). TGA of metal complexes indicated that loss in weight started in temperature range $230-300^\circ\text{C}$ with rapid loss of 69-98.7% upto 55°C . The maximum rate of loss occurred with $314-410^\circ\text{C}$ (Fig. 1). The vanadium complex indicate rapid loss of 69% by 460°C secondary loss upto 75% by 500°C . Copper complex leaves maximum residue, followed by vanadium and palladium. Nickel complex leaves minimum residue behind and has maximum thermal stability among the series. DTA of metal complexes indicate melting endotherm, followed by series exotherm corresponding vaporization/decomposition and a fairly large exotherm within temperature $460-500^\circ\text{C}$ due to the decomposition of residue at high temperature (Fig. 2).

High temperature required for the volatilization of metal complexes led to select stainless steel column ($6' \times 0.0185''$) packed with OV101, 3% on Chromosorb 80-100 mesh size to check the possible

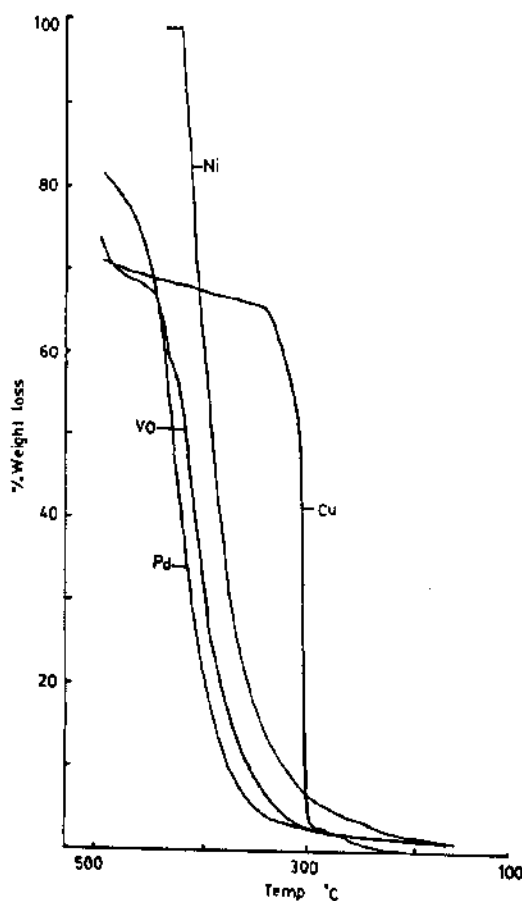


Fig.1: TGA of metal complexes of $\text{H}_2\text{SA Ter}$ at a heating rate of $15^\circ\text{C}/\text{min}$ and nitrogen flow rate of $50 \text{ cm}^3/\text{min}$.

elution of the complexes. The complexes eluted as fairly symmetrical peaks at a column temperature 290°C injection port 295°C and nitrogen flow rate $45 \text{ cm}^3/\text{min}$, with retention times of 6-48, 7-12, 8-48 and 12-24 min for copper, nickel vanadium and palladium complexes respectively. Thus the separation of palladium from copper, nickel and vanadium (Fig. 3) could easily be obtained, but without separation between copper, nickel and vanadium complexes.

In order to check the response of the detector with the amount of complex injected, different amounts of complexes were injected and average peak area of at least two injections were measured and linear calibration curves were obtained in the range of $1-6 \mu\text{g}$ of complexes. The detection limits

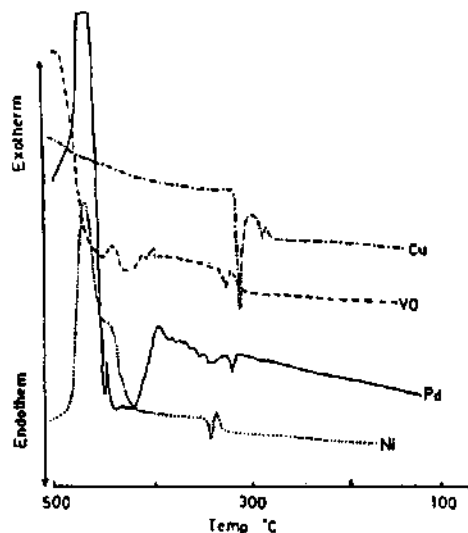


Fig.2: DTA of metal complexes of H_2SATen at a heating rate of $15^\circ C/min$ and nitrogen flow rate of $50 cm^3/min$.

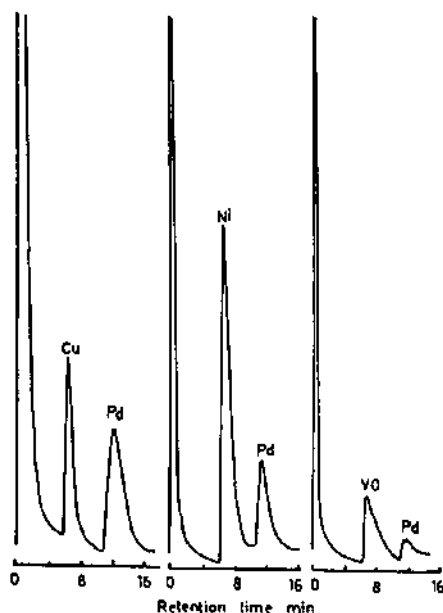


Fig.3: Gas Chromatographic Separation (A) Cu & Pd (B) Ni & Pd (C) VO & Pd on stainless steel column ($6' \times 0.085''$) packed with 3% OV101 on Chromosorb WHP 80-100 column temp. $290^\circ C$, injection port $290^\circ C$ and nitrogen flow rate $45 cm^3/min$.

measured as thrice the background noise were $0.4 \mu g$ of nickel, palladium and vanadium complexes and $0.6 \mu g$ of copper complex.

The preliminary gas chromatographic studies on stainless steel column ($6' \times 0.085''$) packed with OV101, 3% on Chromosorb WHP 80-100 mesh size indicated the elution of its nickel complex as a symmetrical peak, with some separation from the reagent peak. It was therefore the reagent bis-(salicylaldehyde) tetramethylethylenediamine was investigated for the determination of nickel gas chromatographically after necessary complexation in aqueous phase, followed by extraction of nickel complex in organic phase.

In order to find out optimum pH, solvent and reagent concentration for the quantitative extraction of nickel (II), exactly $1 cm^3$ of 100 ppm solution of nickel was transferred to well stoppered tube ($10 cm^3$), followed by particular buffer solution ($2 cm^3$) in pH range 6-9, ethanol ($2 cm^3$) and reagent solution (0.75 % w/v) ($0.5 - 1.0 cm^3$) in ethanol. The mixture warmed on water bath for 5-30 min was allowed to cool. The contents were shaken on mechanical shaker for 15-30 min. The organic layer was separated and extract ($1-5 \mu l$) was injected on column ($6' \times 0.085''$) packed with OV101, 3% on Chromosorb WHP 80-100 mesh size at column temperature $270^\circ C$, injection port $280^\circ C$ and nitrogen flow rate $30 cm^3/min$. It was observed that the quantitative transfer of nickel complex from aqueous to organic phase was not quantitative in cyclohexane. In case of chloroform reagent was also extracted and interfered to the response of nickel complex. The toluene proved a better choice for the extraction of nickel complex from aqueous solution. The concentration of reagent solution ($0.5 cm^3$ of 0.75% w/v) proved adequate for complexation. The complexation and extraction of nickel complex in toluene was fairly constant between pH 7-8.5 and bicarbonate buffer pH 8 covered pH range satisfactory and restricted the extraction of reagent in toluene.

In order to examine the linear calibration range for the extraction and determination of nickel GLC, different amounts of nickel were taken and nickel extracted using extraction procedures. Extract ($2 \mu l$) was injected at the optimized conditions

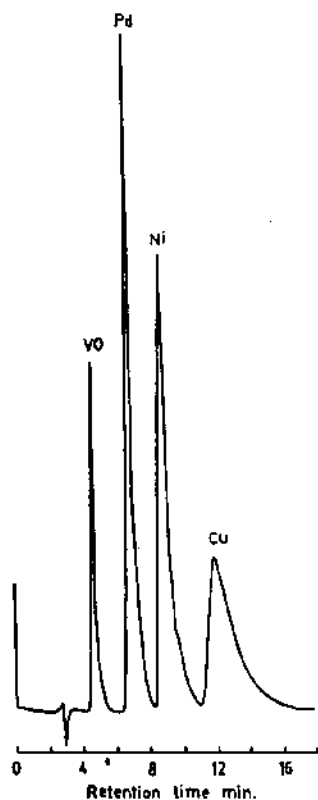


Fig.4: HPLC Separation of Cu, Ni, Pd and VO on column (250 x 4 mm) packed with Licrosorb Si 100, 5 μ . Eluent 1,2- dichloroethane, flow rate 0.9 cm³/min. detection UV at 260 nm.

of GC. Straight line calibration curves was obtained by plotting average peak height versus amount of nickel in solution, within 20-200 μ g of nickel (Fig. 5). The amount of nickel in nickel - aluminium alloy determined from the standard calibration curve. The amount of nickel was found 51.5% (present 50% approx.). The results agree closely to the expected value.

The complex eluted on GLC column, and indicated a reasonable accuracy for the analysis of nickel, but lack separation between copper, nickel and vanadium chelates, led to investigate absorption HPLC, using column (250 x 4 mm) packed with Licrosorb Si 100, 5 μ for the possible separation of copper, nickel, palladium and vanadium complex.

The spectrophotometric studies of the metal complexes (Table-2) indicated that complexes have reasonably high values of molar absorptivity in UV

Table-2: Spectrophotometric Data of Ligand and its complexes in 1,2-dichloroethane

Compound	λ_{max} (E.mole ⁻¹ cm ⁻¹)
H ₂ SAzTen	339 (406), 278 (7090), 262 (81600), 227 (577000).
CuSAzTen	556(565), 367 (16810), 267 (55750), 239 (76410)
NiSAzTen	545(166), 418(6570), 349(8014), 329(8319), 250(62820)
VOSAzTen	598(863), 363(19810), 277(98690), 247(107600),
PdSAzTen	414(26070), 322(26820), 237 (17740).

region and UV detector for the present investigation was thus selected. The values of molar absorptivities at 260 nm fixed for present investigation in 1,2- dichloroethane were 50900, 47970, 102820 and 98690 l.mole cm³ for copper, nickel palladium and vanadium complexes respectively. The complexes eluted as symmetrical peaks with chloroform, but complete separation between vanadium, palladium, nickel and copper complexes was obtained by isocratic elution with 1,2-dichloroethane. The retention volumes of vanadium, palladium, nickel and copper complexes were 3.9, 5.8, 7.7 and 10.6 cm³ using flow rate of 0.9 cm³/min. (Fig. 4).

The response of the detector at 260 nm was also checked and linear calibration curve, passing through the origin were obtained by plotting average peak of atleast two injections against the

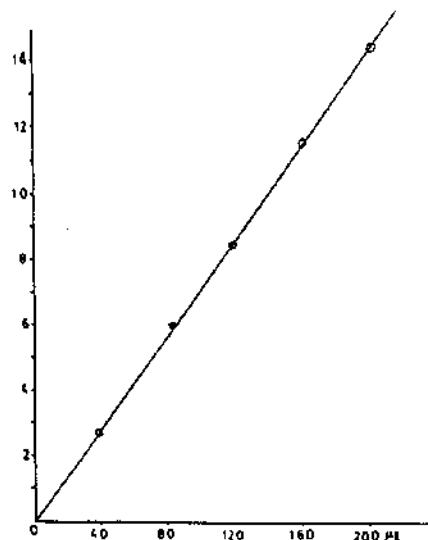


Fig. 5: Calibration curve of nickel(II) on GLC. Column (6' x 0.085") packed with OV101. 3% on Chromosorb WHP 80-100 mesh size. Temperature column 270°C, injection port 280°C and nitrogen flow rate 45 - cm³/min.

amount of complex injected and were found to be in the range of 0.8-4 μ g of copper and nickel complexes, 0.8-4.8 μ g palladium complex and 1.5-7 μ g vanadium complex. The detection limits measured as thrice the background noise, as compared to similar volume of solvent injected, were 10,10, 18, 20 pg of copper, nickel, vanadium and palladium complexes respectively.

The reagent was also examined for the determination copper and nickel using the optimized conditions of the extraction, developed for the gas chromatographic determination of nickel. Some analytical procedure was used, but here the concentration of reagent was reduced to (0.2 % w/v) (0.5 cm³). The elution and separation of copper and nickel complexes was carried out with 30% 1,2-dichloroethane in chloroform. The wavelength of the detector was fixed at 300 nm. The copper and nickel complexes easily separated on these conditions, but when the extract of copper and nickel in column was injected on the column and the response of the UV detection was measured at 260 nm, toluene also gave a response which interfered the peak of nickel. It was therefore the wavelength of UV detector was changed to 300 nm, where the toluene gave a minimum response and did not interfere the determination of nickel.

In order to examine the linear calibration range for the extraction and determination of copper and nickel on adsorption HPLC, different amounts of nickel and copper were taken and extracted using analytical procedures. Extract (2 μ l) was injected at optimized conditions, straight line calibrations, were obtained, by plotting the average peak height versus 2-20 μ g of copper or nickel in the solution. The nickel-aluminium alloy was here also analysed and amount of nickel in sample was evaluated from standard calibration curve. The amounts of nickel in sample was found 50.2% (Actual about 50%). The results agree with the expected value and obtained on GLC.

The conditions optimized for the extraction of copper and nickel were also tried for the extraction of oxovanadium, but the oxovanadium complexes failed to extract quantitatively in toluene. Chloroform was also tried for its extraction, but it was found that the extraction of oxovanadium was again not quantitative and the reagent was also extracted appreciably in chloroform and interfered the response of oxovanadium complex.

Conclusion

The metal complexes do not show thermal stability required for gas chromatographic application and leave significant amount of residue behind, except for nickel complex. But it is interesting to note that the complexes eluted on GLC column packed with OV101, 3% on Chromosorb 10-100 mesh size, with detection limits at sub μ g of complexes, as compared to bis(salicylaldehyde) ethylenediamine failed to elute on GLC column. This difference may be due to substitution of tetramethyl groups at the bridge position in the ligand H₂SA Ten, which improves the thermal stability and volatility of metal complexes and metal complexes elute on GLC column. However the separation between copper, nickel and vanadium complexes was not obtained. Nickel complex has a reasonable peak shape, was used for the determination of nickel in nickel aluminium alloy. The ease of separation copper, nickel, palladium and vanadium complexes on adsorption HPLC using isocratic elution with a binary mixture of chloroform 1,2-dichloroethane with detection limits at sub μ g levels of metal complexes using UV detector are highly encouraging for the simultaneous determination of metal ions at trace levels, based on the complexation in aqueous phase, followed by extraction in toluene and subsequent determination on adsorption HPLC. The analysis of nickel in nickel aluminium alloy agreed closely to the expected value and result obtained on GLC.

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