

Separation of Copper(II), Nickel(III), Palladium (II) and Vanadium (IV) Oxide Complexes of Bis(isovalerylacetone)ethylenediimine Using Solvent Extraction and Gas Chromatography

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Summary: The copper(II), nickel(II) palladium (II) and vanadium (IV) oxide complexes of bis(isovalerylacetone)ethylenediimine (H_2IVA_2en) are prepared and eluted on OV101 and OV 17, 3% on Chromosorb 80-100 GC columns and separation between copper, nickel, palladium and vanadium is achieved. The reagent has been examined for the extraction of the metal ions in cyclohexane and the efficacy of the reagent for analytical utility is investigated with regards to gas chromatographic behaviour. Detection limits and calibration range of metal ions are reported.

Introduction

There are a number of applications of GLC to inorganic chemistry over many years [1-4]. The tetradentate β -ketoamines form coloured metal complexes with favourable features in terms of thermal stability and have proved useful gas chromatographic reagents for copper(II) nickel (II), palladium (II) and vanadium (IV) oxide metal ions [5-9]. Lindoy and his co-workers have recorded magnetic moments 1H -NMR, ^{13}C NMR, mass, UV and visible spectra of the reagent H_2IVA_2en and its copper and nickel complexes [10]. They have suggested a stereochemical form of ligand with planar metal chelates. In the present work palladium(II) and vanadium(IV) oxide complexes together with copper(II) and nickel(II) complexes of H_2IVA_2en have been considered for their possible use for the gas chromatographic determination of metal ions.

Experimental

The reagent H_2IVA_2en and its copper and nickel complexes were prepared by the method of Lindoy *et. al.* [10]. Elemental micro-analysis were carried out by Elemental Micro-Analysis Ltd., U.K.

Bis(isovalerylacetone)ethylenediimine (H_2IVA_2en), calculated for $C_{18}H_{32}N_2O_2$, %, C = 70.13, H = 10.38, N = 9.09; found %, C = 70.03, H = 10.38, N = 9.15.

Bis(isovalerylacetone)ethylenediimine nickel(II) ($Ni.IVA_2en$). Calculated for $C_{18}H_{30}N_2O_2Ni$, %, C = 59.23, H = 8.22, N = 7.67; found, %, C = 59.06, H = 8.28, N = 7.78

Bis(isovalerylacetone) ethylenediimine copper (II) ($CuIVA_2en$). Calculated for $C_{18}H_{30}N_2O_2Cu$, %, C = 58.45, H = 8.11, N = 7.51; found, %, C = 58.59, H = 8.20, N = 7.55.

The palladium complex was prepared following general procedure of Belcher *et. al.* [11] and vanadium complex using ligand exchange method of Martin *et al* [12] as under:

Bis(isovalerylacetone)ethylenediimine palladium (II) (PdIVA₂en)

Palladium(II) chloride (0.1 g) was heated together with benzonitrile (0.2 - 0.5 ml) for 2 hr. The benzonitrile palladium complex formed was dissolved in benzene (10 ml). To this was then added equimolar amount of the reagent in benzene. The mixture was refluxed for 6 hr. and filtered while hot. Most of the solvent was removed from the filtrate and the residue was extracted several times with n-hexane. The extracts were concentrated and cooled. The precipitate obtained was recrystallized from n-hexane m.p. 209°C. Calculated for $C_{18}H_{30}N_2O_2Pd$ %, C = 52.4, H = 7.28, N = 6.76; found, %, C = 52.47, H = 7.53, N = 6.87.

Bis(isovalerylacetone)ethylenediimine vanadium (IV) oxide: (VOIVA₂en)

Bis-acetylacetone vanadium(IV) oxide complex (0.011 mole) and H_2IVA_2en (0.01 mole) were mixed together and heated at 220-240°C at 0.2 mm pressure Hg for 2 hr to distill off the released acetylacetone. The residue was dissolved in n-

hexane and precipitate obtained was recrystallized from n-hexane m.p. = 124°C. Calculated for C₁₈H₃₀N₂O₃V, % C=57.90, H=8.04, N=7.50; found, % C=57.90, H=8.08, N=7.02.

All the spectrophotometric studies were carried out with Hitachi 220 Spectrophotometer.

The dried chelates were sublimated at reduced pressure in a sublimating apparatus, immersed in oil bath and the sublimate was collected on cold finger.

TG and DSC of copper and nickel chelates were recorded by Elemental Micro-Analysis Ltd., U.K., at a heating rate of 15°C/min TG and 15°C/min DSC in flowing nitrogen atmosphere at a rate of 20-25 cm³/min. TG and DTA of palladium and vanadium complexes were recorded at a heating rate of 15°C/min and nitrogen flow rate of 50 cm³/min on Shimadzu TG 30 Thermal Analyser.

Hitachi 163 Gas Chromatograph equipped with flame ionization detector and stainless steel column 2m x 3mm and 3m x 3mm packed with OV101, OV1, OV17, 3% on Chromosorb WHP 80-100 mesh size (Altech Associate) were used.

Conventional buffer solutions (2 M) in pH range 1-10 and bicarbonate buffer (0.2 M) at pH 8-9 were used.

Extraction Procedures

To aqueous sample (1-3 ml) containing 0-300 µg of copper, nickel or palladium (0.2-1.5 mg) was added 2 ml of bicarbonate buffer (pH 8), 1 ml of ethanol, 1 g of potassium bromide and 3 ml of 1-1.5% W/V reagent in cyclohexane. The solution was warmed to 45- 50°C for 5-10 min and was shaken on mechanical shaker for 50 min. The layers were allowed to separate and 1-5 µl of the extract was injected onto the gas chromatographic column (2m x 3mm) packed with OV101, 3% on Chromosorb 80-100 mesh size at 250°C, injection port 26°C and nitrogen flow rate 20 cm³/min. The amount of metal ion was determined by comparing the peak area with the calibration curve.

During the study of interfering ions 1 mg of different cations and anions were added to 0.1 mg of copper or nickel solution and the amount of copper and nickel were determined using extraction

procedure. The change in peak area more than ± 5% was considered as an evidence for interfering effect. Residual copper and nickel in aqueous phase were determined by atomic absorption spectrophotometer using Hitachi 180-50.

Results and Discussion

The spectrophotometric studies of copper and nickel complexes in chloroform and vanadium and palladium complexes in acetone indicate that copper and nickel complexes absorb at 548 nm and 568 nm with molar absorptivity of 236 and 101.1 mole⁻¹ cm⁻¹ respectively. Similarly vanadium complex indicates three bands in visible region at 620 nm, 560 nm and 440 nm with molar absorptivity of 56, 65 and 2.7 x 10³ l. mole⁻¹cm⁻¹. The copper, nickel and vanadium complexes obey the Beer's law, but at mg/ml range of metal complexes at their respective λ_{max}, and indicate that the complexes are fairly stable and make possible insensitive spectrophotometric determination of metal ions. The nickel and palladium complexes also indicate bands at 375 nm and 348 nm with molar absorptivity of 6.4 x 10³ and 1.9 x 10⁴ l. mole⁻¹ cm⁻¹ respectively, but the reagent also absorb at the wavelengths and interfere in spectrophotometric determination of metal ions when present in excess.

The preliminary sublimation studies indicated that the copper and nickel complexes could be collected as purple and brown sublimates at 160-180°C at 2.5 Torr.

The thermogravimetry of copper, nickel, palladium and vanadium complexes indicate that the loss in weight in copper and nickel complexes occurs even below 200°C, but in case of palladium and vanadium complexes, loss in weight starts above 220°C (Table 1). The copper, nickel and palladium complexes indicate single and rapid loss in weight in the range of 89-95%, but vanadium complex shows primary loss in weight of only 58%, followed by secondary and tertiary loss in weight upto 94% at 500°C (Fig. 1 to 4). Thus it may be inferred that a profound decomposition occurs in vanadium complex at high temperature.

Keeping in view the high temperatures required for the volatilization of the complexes, stainless steel columns (2m x 3mm and 3m x 3mm) packed with OV101 and OV17 on Chromosorb 80-

Table: TG, DTA AND DSC OF METAL CHELATES

CuIVAzen	NiIVAzen	PdIVAzen	VOIVAzen
TG with 2.5 mg sample	Tg with 2.5 mg sample indicated	TG with 6.1 mg samples indicated	TG with 5.8 mg
indicated loss in weight by 158°C and loss of 95% upto 500°C with maximum rate of loss at 290°C, followed by a slow change in weight leaving 5% residue	loss in weight started by 181°C and major loss 89% at 315°C followed by the secondary loss of 7% by 407°C leaving behind 4% residue. Maximum rate of loss at 279°C.	loss in weight started by 225°C, and loss of 94% by 330°C with maximum rate of loss t 280°C.	sample loss in weight started by 225°C, and loss of 58% by 325°C, with maximum rate of loss at 290°C; followed by secondary loss of 25% at 395°C and loss of 94% by 500°C
DSC with 2.2 mg showed a very small phase change at 130°C due to some unknown reasons, followed by a sharp melting endotherm at 140°C. Major exotherm started by 236°C finished by 400°C with sublimation of yellow oil	DSC with 2.2 mg indicated a little phase change at 104°C may be due to loss of water vapours, followed by a very sharp melting endotherm 165°C. Major exotherm between 220-380°C with with sublimated of yellow solid.	DTA showed melting endotherm at 190°C and an exotherm at 240°C, followed by at a sharp exotherm at 330°C.	DTA showed melting followed by exotherm at 305°C, 370°C and at 305°C, 370°C and large exotherm at 460°C

100 were selected. The metal complexes were successfully eluted within column temperatures of 235-270°C, injection port 240-275°C and nitrogen flow rate of 20-30 cm³/min. Complete separations between copper, vanadium and palladium, and nickel vanadium and palladium were easily achieved using isothermal or programmed temperature elution of metal complexes. However, some overlapping of peaks of copper and nickel complexes was observed on (2m x 3mm) column (Fig. 5). An optimum separation between copper, nickel, palladium and vanadium was achieved by injecting a mixture on a column (3m x 3mm) packed with OV101, 3% on Chromosorb 80-100 at a column temperature of 250°C with programmed rise in 0.25°C/min upto 270°C, injection port 275°C and nitrogen flow rate of 30 cm³/min (Fig. 5) with retention times of 12-0, 13-35, 18-00 and 21-0 min. for copper, nickel, palladium and vanadium complexes respectively.

To check the response of detector with the amount of complex injected, known amounts of the complexes were injected at the optimized conditions and average peak area of at least two injections were measured and linear calibration curves were obtained in the range of 0.5-4.0 µg, 0.2-1.6 µg, 3.75-20 mg and 3-16 µg of copper, nickel, palladium and vanadium metal complexes respectively and detection limits measured as thrice the background noise were 0.2 µg, 0.04 µg, 1.0 µg and 1.5 µg respectively.

The results indicate that the nickel complex shows better sensitivity than copper, vanadium and palladium using FID detector system. It was considered, probable that a profound decomposition occurs in the injection port due to its high temperature. The effect of variation of the temperature of injection block in the range 240-280°C at 5°C interval was investigated when the copper complex was

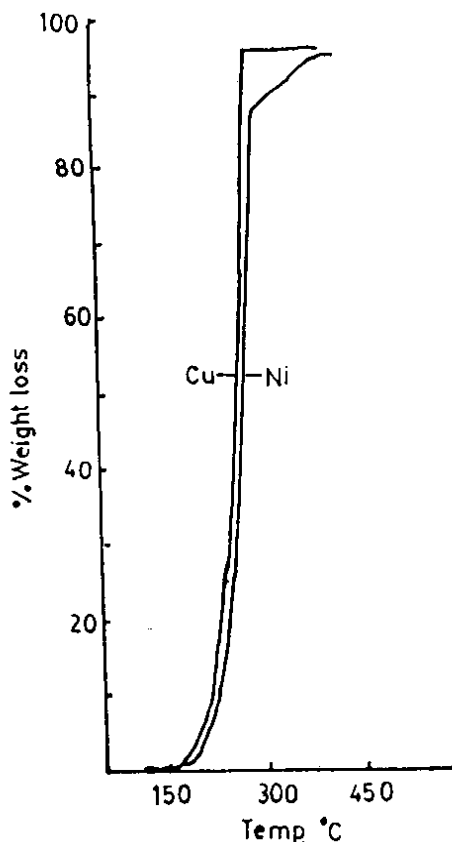


Fig.1: TG of copper(II) and Nickel(II) chelates at a heating rate of $15^{\circ}\text{C}/\text{min}$ and nitrogen flow rate of $20\text{-}25\text{ cm}^3/\text{min}$.

injected on the column ($2\text{m} \times 3\text{ mm}$) packed with OV 101, 3% on Chromosorb 80-100 at a column temperature of 250°C and nitrogen flow rate of $20\text{ cm}^3/\text{min}$. It was found that the variation of temperature of injection port was not critical and the peak area remained constant between $250\text{-}275^{\circ}\text{C}$, but at temperature 240°C a significant band broadening was observed without increase in peak area. However at temperature 280°C an asymmetry in the peak of copper complex was observed, may be due to the decomposition of the complex. Thus the difference in the sensitivities of the metal complexes using FID system can be attributed to column phenomena due to partial decomposition and on column adsorption of metal chelates [13,14].

The optimum conditions of pH, solvent and reagent concentration for the quantitative transfer of metal ion from aqueous to organic phase was investigated. The cyclohexane proved better solvent

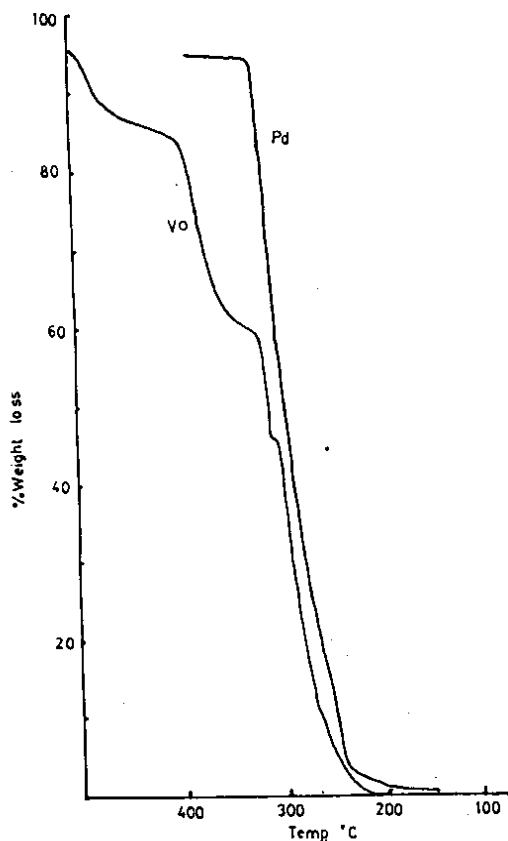


Fig.2: TG of palladium(II) and vanadium(IV) oxide chelates at a heating rate of $15^{\circ}/\text{min}$ and nitrogen flow rate of $50\text{ cm}^3/\text{min}$.

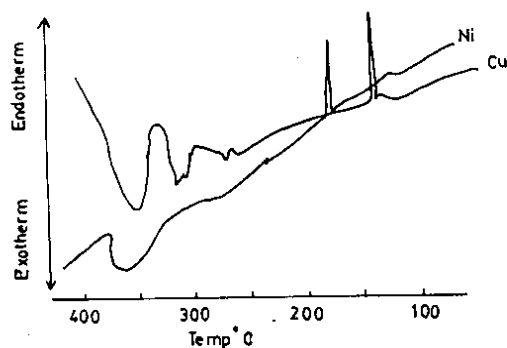


Fig.3: DSC curves of copper(II) and nickel(II) chelates at a heating rate of $16^{\circ}\text{C}/\text{min}$ and nitrogen flow rate of $50\text{ cm}^3/\text{min}$.

with respect to solubility of reagent and metal complexes. Benzene on the other hand eluted with a high degree of tailing producing disturbance in the base line. The reagent concentration 1-1.5% W/V proved adequate for practical purposes. The effect of pH (Fig. 6A & B) on the extraction of copper

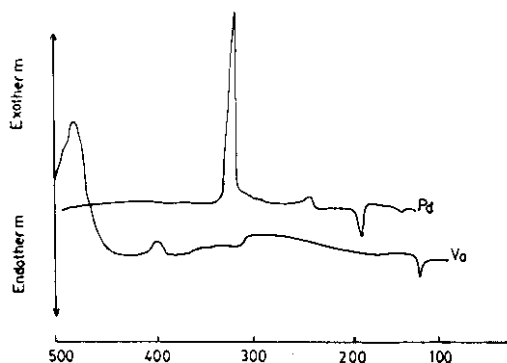


Fig. 4: DTA curves of palladium(II) and vanadium(IV) oxide chelates at a heating rate of 15°C/min and nitrogen flow rate of 50 cm³/min.

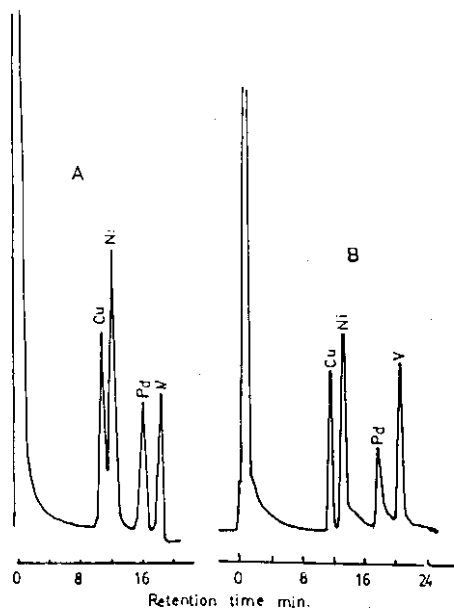


Fig. 5: Gas chromatographic separation of copper(II), nickel(II), palladium(II) and vanadium(IV) oxide complexes on stainless steel column (A) 2m x 3mm (B) 3m x 3mm packed with 3% OV101 on Chromosorb WHP 80-100.

(A) Column temp. 240°C with programmed rise in temp. 1°C/min upto 265°C, injection port 265°C and nitrogen flow rate 20 cm³/min. (B) Column temp. 250°C with programmed rise in temp. 0.25°C/min upto 270, injection port 275°C and nitrogen flow rate 30 cm³/min.

and nickel in cyclohexane indicates that there is good agreement between the results of % extraction on GLC and atomic absorption. It can be seen that the effect of pH on the extraction of copper (II) is not critical and 90-98% of metal is extracted in the pH range 6-10 with maximum at pH 9. This quantitative transfer is achieved within shaking time of 10 min.

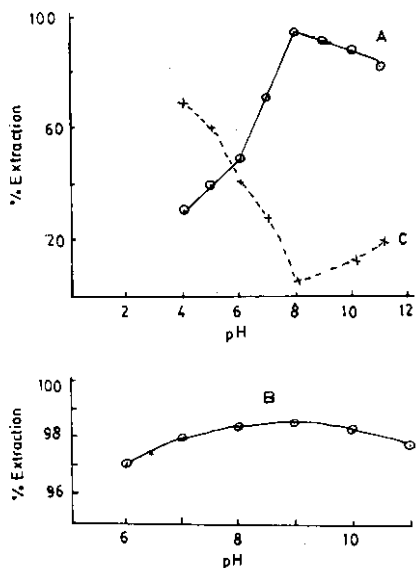


Fig. 6: Effect of pH on the extraction of (A) Nickel (B) Copper in Cyclohexane as evaluated using GLC. (C) % of Nickel remaining in the aqueous solution after extraction, determined by atomic absorption spectrometer.

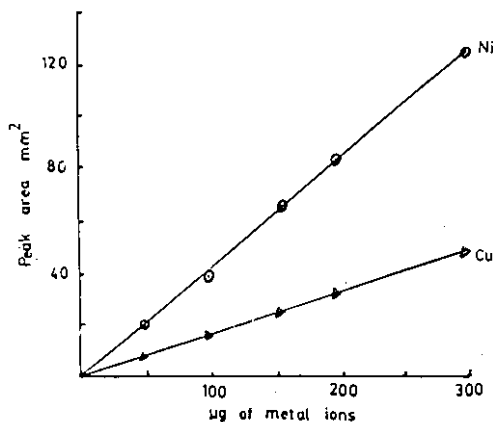


Fig. 7: Calibration plots of copper(II) and nickel(II) metal ions extracted as chelates of H₂IVA₂en in cyclohexane.

The extraction of nickel on the other hand is pH dependent at pH 4, 40% of the metal ion extracted which rose to 96% at pH 8, and decreasing at higher values (Fig. 6A). The equilibrium of nickel between aqueous and organic phase is slow as compared to copper(II) and required warming the contents at 45°C for five to ten min. and increasing the shaking time to 50 min, for quantitative extraction. The variation on replicate extractions of copper and nickel (100 µg) were in the range of 98-99% and 92-94% respectively at pH 8, reagent 1% W/V, heating time 10 min. and shaking time of

1 hr. The palladium(II) when extracted under these conditions was found to transfer from aqueous to organic phase upto 50%. However when reagent concentration was increased to 1.5% W/V and NaBr was added, the extraction of palladium considerably improved in the range of 82-90%. The extraction of vanadium(IV) oxide was also checked and was found that only fraction of vanadium (IV) oxide could be extracted on these conditions, which was far from being quantitative.

Linear calibration curves were obtained from the aliquot of the solution containing 50-300 μg of copper and nickel and 0.24-1.5 μg of palladium (Fig. 7). The analysis of test solutions of copper and nickel separately showed % relative error within $\pm 0-6\%$ with relative average deviation of 2% (six replicates) for the extraction of 100 μg of copper and nickel and 500 μg of palladium.

Fe(II), Mn(II), Cr(III) react with the reagent to form colour solution in neutral to slight acidic medium, but the complexes are not extractable in cyclohexane. Fe(II), Fe(III), Al(III), Mn(II) and Cr(III) could form metal oxides at pH 8 and interfere the quantitative extraction of copper and nickel [9]. However, Fe(II), Fe(III), Al(III), Ag(I), Mn(II), Cd(II), Mo(IV), U(VI), Ca(II), Mg(II), PO_4^{3-} , ClO_4^- , F^- , when added at ten times the concentration of copper did not interfere the extraction of copper. Cobalt is simultaneously extracted, but its complex lacks sufficient thermal stability and elutes as decomposed products, disturbing the elution of copper and nickel complexes, Cr(III), decreased the extraction of copper and nickel. Fe(II), Fe(III), Al(III) and Mn(II) also decreased the extraction yield of nickel, but interfering effects of Fe(II) and Fe(III) and Mn(II) were successfully removed with the addition of 1 ml of 2% ammonium tartrate to each of the solution prior to the complexation. Al(III) could be masked with 1% ammonium fluoride. Citrate and borate slightly suppressed the extraction of copper and nickel, but

the effect disappeared by increasing the concentration of the reagent to 1.5% W/V.

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