

TABLE 1 — SYNTHESIS AND CHARACTERISTICS OF Sb(III)-SCHIFF BASE COMPLEXES

| Molar ratio | Reflux period hr | Mol. formula | Found (%) (calc.) | |
|---|------------------|---|-------------------|----------------|
| | | | Sb | N |
| SCHIFF BASE FROM <i>n</i> -PROPYL AMINE | | | | |
| 1:1 | 4½ | Sb(OPri) ₂ (C ₁₀ H ₁₂ NO)* | 30.62 (30.35) | 3.64 (3.49) |
| 1:2 | 7 | Sb(OPri)(C ₁₀ H ₁₂ NO) ₂ † | 23.96 (24.12) | 5.45 (5.54) |
| 1:3 | 9½ | Sb(C ₁₀ H ₁₂ NO) ₃ ‡ | 19.74 (20.03) | 6.64 (6.91) |
| SCHIFF BASE FROM <i>n</i> -BUTYL AMINE | | | | |
| 1:1 | 3 | Sb(OPri) ₂ (C ₁₁ H ₁₄ NO)* | 25.36 (26.05) | 3.28 (3.36) |
| 1:2 | 7 | Sb(OPri)(C ₁₁ H ₁₄ NO) ₂ † | 21.98 (22.85) | 5.14 (5.25) |
| 1:3 | 8½ | Sb(C ₁₁ H ₁₄ NO) ₃ ‡ | 18.53 (18.74) | 6.49 (6.46) |
| SCHIFF BASE FROM ANILINE | | | | |
| 1:1 | 3 | Sb(OPri) ₂ (C ₁₃ H ₁₀ NO)† | 27.54 (27.93) | 3.16 (3.21) |
| 1:2 | 4 | Sb(OPri)(C ₁₃ H ₁₀ NO) ₂ ‡ | 20.64 (21.23) | 4.62 (4.88) |
| 1:3 | 8 | Sb(C ₁₃ H ₁₀ NO) ₃ ‡ | 16.62 (17.14) | 5.76 (5.91) |

*Compounds obtained as yellow liquids.

†Compounds obtained as yellow semisolids.

‡Compounds obtained as yellow solids.

O as well as N atoms. A strong band in the region 1640-1620 cm⁻¹ in the Schiff bases due to >C=N— group remains almost unaltered in the resulting derivatives^{6,9-11}. In the IR spectra of the complexes, the appearance of a new strong band at 600 ± 10 cm⁻¹ may be attributed to νSb—O.

The antimony isopropoxide was prepared by the sodium chloride method⁵ and was distilled (105°/14 mm) before use. Schiff bases⁶ and their derivatives⁴ were synthesized as usual. The experimental details of all the reactions are summarized in Table 1. Antimony was estimated as antimonous pyrogallate⁷, while nitrogen by Kjeldahl's method. Isopropanol was estimated by oxidimetric method⁸ using 1N K₂Cr₂O₇ in 12.5% H₂SO₄.

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Pd(II) Chelate of 2,4-Dihydroxyvalerophenone Oxime

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2,4-Dihydroxyvalerophenone oxime forms water insoluble complex with Pd(II) which is extractable into chloroform to give a yellow solution having λ_{max} at 400 nm. It has been found to be a good and selective reagent for gravimetric estimation of palladium and for its separation from other ions. The structure of the 1:2 (metal:ligand) chelate has been confirmed by elemental analysis, pH-metric titration, spectrophotometric, IR and UV spectral studies. The stability constant of the chelate is 6.4 × 10⁷. Beer's law is obeyed in the concentration range 35-75 ppm of Pd(II). Limits of interference due to the presence of foreign ions in the spectrophotometric and gravimetric determinations have been determined.

IN continuation of our studies¹⁻⁴ on the chelates of 2,4-dihydroxyvalerophenone oxime (DHVOX), this note deals with the gravimetric and spectrophotometric determination of Pd(II) with DHVOX. The composition and structure of the Pd(II) chelate have also been determined on the basis of analytical, pH-metric titration, IR and UV spectral data.

All the measurements were carried out after equilibrating the solutions at 30° ± 0.2° for 30 min. DHVOX was prepared as reported earlier¹. Solution of Pd(II) was prepared by dissolving palladium chloride (BDH, AR) in 0.05N HCl. All the other chemicals used were of BDH, AR grade and were used as such.

The method of Vosburg and Cooper⁵ showed that Pd(II) forms only one complex which has λ_{max} at 400 nm. The complex can be extracted in chloroform, carbon tetrachloride or ethyl acetate. However, chloroform is found to be a better solvent for extraction. The subsequent studies were carried out in this medium. In all the experiments 8 ml of chloroform was used for extraction. Preliminary studies showed that the absorption is maximum between pH 2.0 and 5.0. Subsequent studies were carried at pH 3.0. Four-fold excess of the ligand was necessary for maximum colour intensity. Beer's law is followed over the concentration range 35-75 ppm of Pd(II). From the slope ratio curve the molar extinction coefficient was found to be 7.68 × 10³ and sensitivity = 0.139 μg Pd/cm².

Composition of the complex—The composition of the complex was found to be 1:2 by mole-ratio method⁶, slope-ratio method⁷ and Job's method of continuous variation, extended to a two phase system by Irving and Pierce⁸.

The stability constant of the complex was calculated by the molar ratio method, using the relation:

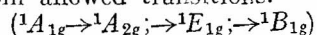
$$K = (1-\alpha)/4C^2\alpha^3 \text{ and } \alpha = (E_m - E_s)/E_m$$

where E_m , E_s , α and C have their usual meanings. The stability constant was found to be 6.4 × 10⁷ at 400 nm and standard energy of formation ($-\Delta F = RT \ln K$) was found to 10.38 kcal/mole at 30°C.

The composition of the complex was further confirmed by potentiometric, conductometric and analytical studies. Metal-ligand ratio was also determined by the method of Fenger *et al.*⁹ and found to be 1:2.

The IR spectrum of DHVOX showed strong bands at 3500 cm^{-1} (νOH), 3380 cm^{-1} (νOH chelated), 3280 cm^{-1} (νOH of $=\text{N}-\text{OH}$), 2980 cm^{-1} and 2800 cm^{-1} (νCH of methylene groups), 1650 cm^{-1} ($\nu\text{C}=\text{N}$), 830 cm^{-1} (1,2,4-trisubstituted benzene) and 990 cm^{-1} ($\nu\text{N}-\text{O}$). Examination of the IR spectrum of the chelate shows that the phenolic hydrogen is replaced by the metal because the band at 3280 cm^{-1} due to hydroxyl group of the oximino moiety appears more or less at the same position in both, the ligand and the complex, and 3380 cm^{-1} peak of the chelated OH disappears in the complex. In the chelate the band at 1650 cm^{-1} disappears and a stronger band appears at 1590 cm^{-1} , which can very likely be assigned to $\nu\text{C}=\text{N}$ shifting downfield, due to complexation. The $\nu\text{N}-\text{O}$ band appearing at 990 cm^{-1} in the ligand shifts downfield to 960 cm^{-1} in the chelate. The position of $\nu\text{N}-\text{O}$ band has been confirmed by various workers^{10,11}. The band at 3500 cm^{-1} in the spectrum of chelate is assigned to the hydroxyl group at position-4 which does not take part in coordination. New bands appearing at 580 and 515 cm^{-1} may be attributed to metal-nitrogen and metal-oxygen stretching modes respectively^{12,13}. On the basis of above data structure (I) may be assigned to the complex.

Three spin allowed $d-d$ transitions are expected for square-planar Pd(II) complex. Only two bands at 28570 and 42850 cm^{-1} have been observed in the electronic spectra of $\text{Pd}(\text{C}_{11}\text{H}_{14}\text{NO}_3)_2$. Following the assignment of Mason and Gray¹⁴ the band at 28570 cm^{-1} can be treated as a combination of all the three spin allowed transitions.



The other band at 42850 cm^{-1} is due to the transition¹⁵ ${}^1A_g \rightarrow {}^3E_u$. The values of ligand field parameters Δ_1 , Δ_2 and Δ_3 have been found to be 32070, 1500 and 500 cm^{-1} respectively.

Procedure for the spectrophotometric determination of Pd(II)—A suitable aliquot of palladium solution containing 35-50 μg of Pd(II) was taken and sufficient excess of DHVOX was added. The pH was kept at 3.0 by adding 2 ml of suitable buffer and ethanol concentration was 25% in the final dilution. The precipitate was extracted into 8 ml of chloroform. The organic layer was separated, water droplets removed by centrifugation and the absorbance measured at 400 nm against reagent blank prepared under similar conditions. From the absorbance value, concentration of metal can be evaluated with help of the previously prepared calibration curve.

It was observed that for a 50 ppm concentration of palladium, 2000 ppm concentration of CH_3COO^-

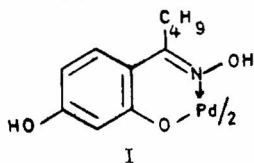


TABLE 1 — DETERMINATION OF PALLADIUM

| Palladium taken (mg) | (pH of the solution 3.0) | | Error (%) |
|----------------------|---------------------------------|----------------------|------------|
| | Palladium complex obtained (mg) | Palladium found (mg) | |
| 5.00 | 24.60 | 5.02 | +0.40 |
| 5.38 | 26.20 | 5.38 | ± 0.00 |
| 7.50 | 36.80 | 7.51 | +0.13 |
| 16.00 | 78.60 | 16.00 | ± 0.00 |
| 21.34 | 104.40 | 21.32 | -0.09 |
| 26.72 | 131.00 | 26.74 | +0.08 |
| 32.00 | 156.00 | 31.86 | -0.40 |
| 37.38 | 182.20 | 37.20 | -0.50 |
| 42.68 | 209.00 | 42.66 | -0.005 |

and SO_4^{2-} ; 1000 ppm concentrations of Ba(II), Sr(II), Ca(II), Be(II), Cd(II), Fe(II), Mg(II), K(I), $\text{NH}_4(\text{I})$, Na(I), Cl⁻, Br⁻, NO_3^- and ClO_4^- ; 500 ppm concentration of Cr(III), Pb(II), Ag(I), citrate and tartrate; 100 ppm concentrations of Co(II), Ni(II) and Mn(II) could be tolerated. But Fe(III), Cu(II) and V(V) interfere seriously.

Gravimetric estimation of Pd(II)—An aliquot containing ~ 10 mg of Pd was diluted to 100-125 ml and pH adjusted between 2.0 and 8.0 with hydrochloric acid and ammonia buffer. The contents were heated to 70-80° and treated with 0.5% ethanolic solution of DHVOX added dropwise with constant stirring (about twice the theoretical amount). The yellow precipitate obtained was digested on a water-bath for 30 min and filtered through a G-4 sintered glass crucible. It was washed with hot water several times and finally with 20% ethanol and dried at 110-20° to a constant weight. It has been found that the precipitation of palladium is quantitative in the pH range 2.0-8.0 although precipitation starts at pH 1.0. The conversion factor (metal/metal complex) is 0.20413. Some representative results are given in Table 1.

Determination of palladium in the presence of other ions—The procedure was the same as in the absence of foreign ions. The interference in some cases was removed by working at low pH to prevent the precipitation of corresponding hydroxides. Interference due to Sb(III), Bi(III), Fe(III) and As(III) was removed by adding tartaric acid (2 g). By suitable adjustment of pH, about 5 to 10 times excess of a large number of cations could be tolerated, e.g. Fe(II), Fe(III), Bi(III), Sb(III) and As(III) at pH 2.5; and Ni(II), Co(II), Zn(II), Cd(II), Mo(VI), Mn(II), Mg(II), W(VI) and U(VI) at pH 3.5 could be tolerated. About 10-100-fold excess of several anions, e.g. PO_4^{3-} , Cl⁻, Br⁻, I⁻, F⁻, $\text{B}_4\text{O}_7^{2-}$, SO_3^{2-} and tartrate could be tolerated at pH 3.0.

From the solution containing both palladium and nickel, palladium was first precipitated as indicated above at pH 3.0 and from the filtrate nickel was precipitated by addition of more reagent and adjustment of pH in the range 7.0-8.0 as reported² earlier. The results are reproducible with an error $\pm 0.5\%$ for amounts of Pd(II) ranging from 5.0 to 43.0 mg. The reagent is readily prepared and is less expensive than the various other reagents reported in the literature.

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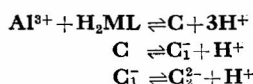
Malate Complex of Al(III)

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Malate complex of aluminium has been studied pH-metrically in the pH range 2.8-8.0. Al³⁺ reacts with malic acid in the pH range 2.8-3.4 to form a neutral complex (C) with simultaneous liberation of 3 protons. At higher pH, the neutral complex (C) undergoes step-wise dissociation to form anionic complexes (C₁⁻) and (C₂²⁻). The equilibrium constants of the three reactions,



are found to be 4.12×10^{-6} , 1.91×10^{-5} and 2.58×10^{-5} respectively.

PAVLINOVA and Vysotskaya¹ have studied the complex formation between Al³⁺ and malic acid by potentiometric and conductometric titrations. This note reports the pH-metric determination of stability constants of malate complexes of Al(III) in the pH range 2.8-8.0.

Aluminium perchlorate was prepared by dissolving a known amount of aluminium hydroxide (prepared from a known amount of aluminium sulphate) in a known weight of standardized 70% perchloric acid. The solution was diluted to one litre and then aluminium estimated as Al₂O₃ (ref. 2) and as Al(C₉H₆ON)₃ (ref. 3). The excess perchloric acid present in the solution was neutralized by standard sodium hydroxide solution after the addition of known amount of malic acid.

The following solutions (total volume 200 ml) were titrated against 0.1M NaOH:

- (i) $6.063 \times 10^{-4}M$ malic acid + $0.01M$ NaClO₄

- (ii) $4.997 \times 10^{-4}M$ Al(ClO₄)₃ + $6.063 \times 10^{-4}M$ malic acid + $0.01M$ NaClO₄
- (iii) $2.425 \times 10^{-3}M$ malic acid + $0.01M$ NaClO₄
- (iv) $4.997 \times 10^{-4}M$ Al(ClO₄)₃ + $2.425 \times 10^{-3}M$ malic acid + $0.01M$ NaClO₄
- (v) $6.25 \times 10^{-4}M$ sodium malate + $0.01M$ NaClO₄
- (vi) $4.997 \times 10^{-4}M$ Al(ClO₄)₃ + $6.25 \times 10^{-4}M$ sodium malate + $0.01M$ NaClO₄
- (vii) $2.5 \times 10^{-3}M$ sodium malate + $0.01M$ NaClO₄
- (viii) $4.997 \times 10^{-4}M$ Al(ClO₄)₃ + $2.5 \times 10^{-3}M$ sodium malate + $0.01M$ NaClO₄.

As observed in the case of cadmium citrate⁴, manganese tartrate⁵ and other systems^{6,7}, the amount of acid liberated during the complex formation between Al³⁺ and malic acid remains the same even though the metal-ligand ratio is increased from 1:1.25 to 1:5 indicating the formation of a 1:1 complex. The reaction between malic acid and aluminium perchlorate [titrations (i)-(iv)] may be represented by Eq. 1.



$$K = \frac{[\text{C}] \times [\text{H}^+]^n}{[\text{Al}^{3+}][\text{H}_2\text{ML}]} \quad \dots(2)$$

By proceeding in the same manner as described in the case of cadmium citrate⁴ system, it can be shown that,

$$\frac{\Delta[\text{NaOH}] - a/b\Delta[\text{ML}]}{[\text{C}]} = n - a/b \quad \dots(3)$$

where $\Delta[\text{NaOH}] = [\text{NaOH}]_B - [\text{NaOH}]_A$
 $\Delta[\text{ML}] = [\text{ML}]_B - [\text{ML}]_A$

$$a = \frac{k_1}{[\text{H}^+]} + \frac{2k_1k_2}{[\text{H}^+]^2}, \quad b = 1 + \frac{k_1}{[\text{H}^+]} + \frac{k_1k_2}{[\text{H}^+]^2}$$

k_1 and k_2 , the dissociation constants of malic acid⁸ are 5.5×10^{-4} and 2.1×10^{-5} respectively.

When the formation of the complex is complete, it can be shown that,

$$\frac{\Delta[\text{NaOH}] - a/b\Delta[\text{ML}]}{[\text{Al}(\text{ClO}_4)_3]} = n - a/b \quad \dots(4)$$

Using Eq. 4, the n values at different pH can be calculated from the titration curves (i) and (ii) and the values are found to be higher than 3 and 4 at pH ≥ 3.6 and 6.2 respectively. Below pH 3.6, a neutral complex C is formed and assuming the n value to be 3, below pH 3.6, K values were calculated and found to be 4.68×10^{-6} , 4.22×10^{-6} , 4.24×10^{-6} , 3.94×10^{-6} and 3.52×10^{-6} at pH 2.8, 2.9, 3.0, 3.1 and 3.3 respectively. The mean value of K is 4.12×10^{-6} .

In the pH range 3.6-6.2, the n values are greater than 3, but less than 4. This indicates the dissociation of neutral complex (C) according to Eq. 5.



and

$$K_1 = \frac{[\text{C}_1^-][\text{H}^+]}{[\text{C}]} \quad \dots(6)$$

It can be shown as in the case of cadmium citrate complex⁴ that,

$$K_1 = \frac{(n-3)[\text{H}^+]}{(4-n)} \quad \dots(7)$$

The values of K_1 were calculated using Eq. 7 and found to be 1.56×10^{-5} , 2.62×10^{-5} , 2.33×10^{-5} ,