

solution (it was used in place of NaHCO_3 to improve the filtrability of the precipitate) till a red-brown precipitate was obtained. It was digested for half an hour on a water-bath, filtered and washed thoroughly with cold water. The precipitate was dried by passing a stream of hot nitrogen gas. The reaction was carried out in the apparatus used for the synthesis of oxinate. The dry solid was stored under nitrogen. It is a brown amorphous solid being slowly oxidized by atmospheric oxygen to a white powder.

For analysis, a weighed quantity of the compound was fused with potassium pyrosulphate. This was extracted with hot dilute sulphuric acid, neutralized with ammonia and digested for 1 hr. The hydrated Nb_2O_5 was filtered, ignited and weighed. Phosphoric acid was determined in the filtrate by precipitation as magnesium ammonium phosphate [Found: Nb, 37.9; P, 12.6. $\text{Nb}_2\text{O}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ requires Nb, 37.2; P, 12.4%].

Oxidation number of niobium was determined in the complex by digesting a weighed quantity of the sample with standard potassium dichromate in 1M sulphuric acid for several hours and then determining excess of Cr(VI) by titration with standard Fe(II) solution. The oxidation number of niobium was found to be +4.05 and +4.06 in two independent determinations.

The complex is weakly paramagnetic (after diamagnetic correction), the μ_{eff} value being 0.68 BM at 30°. The infrared spectrum shows a strong band at 940 cm^{-1} due to $\nu(\text{Nb}=\text{O})$ in addition to the $\nu(\text{OH})$ at 3440 , $\delta(\text{H}-\text{O}-\text{H})$ at 1630 and $\nu(\text{P}-\text{O})$ at $1050-1000\text{ cm}^{-1}$.

The presence of half equivalent of niobium in the complex in the trivalent state has been proved by the potentiometric titration of a known quantity of the compound dissolved in cold 2M hydrochloric acid (the complex is not easily soluble in cold dilute sulphuric acid) with Fe(III) in a manner described earlier⁶. 0.49 mole of the oxidant was consumed per mole of niobium. The E° value for the Nb(V)-Nb(III) couple has been found to be $-0.230 \pm 0.004\text{ V}$ with $n = 1.8$. The value obtained from similar experiment with pure $\text{KNb}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ under identical condition was $E^\circ = -0.232 \pm 0.003\text{ V}$. The complex is thus regarded as a niobyl phosphonobate(III) with the formula $\text{Nb}^{\text{VO}}[\text{Nb}^{\text{III}}(\text{PO}_4)_2] \cdot 6\text{H}_2\text{O}$.

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Complexes of Pt(II) & Pd(II) with 2-(2'-Aminoethyl)pyridine

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Square-planar Pt(II) and Pd(II) complexes of 2-(2'-aminoethyl)pyridine (AEP) of the composition $[\text{M}(\text{AEP})_2\text{X}_2]$ [$\text{M}=\text{Pt}(\text{II})$ or $\text{Pd}(\text{II})$; $\text{X}=\text{Cl}$ or Br] have been isolated and characterized on the basis of analytical, conductance, magnetic moment, electronic and IR spectral data. Electronic spectral studies indicate that the $d-d$ bands are more intense for the mixed bromo complex as compared to those for the chloro complex which can be ascribed to increased ligand participation in the occupied molecular orbital levels derived mainly from the metal d -orbitals. The IR spectral studies show that the metals are coordinated through the nitrogen of the amino group and the pyridine nitrogen atom.

THE present note describes preparation and physico-chemical studies on the square-planar complexes of Pt(II) and Pd(II) with 2-(2'-aminoethyl)pyridine (AEP).

2-(2'-Aminoethyl)pyridine, a known chelating reagent¹⁻³ (M-YTD grade 1614), was procured from Midland Yorkshire Tar Distillers Ltd, England. The organic solvents and other chemicals used were of AR grade.

Preparation of the complexes: Dichloro-2-(2'-aminoethyl)pyridine Pt(II) and dichloro-2-(2'-aminoethyl)pyridine Pd(II)—Potassium tetrachlorometalate (II) (10 mmoles) in 10 ml of water was treated with an aqueous solution of 2-(2'-aminoethyl)pyridine (20 mmoles) and the pH of the reaction mixture adjusted to ~ 2.5 by adding dil. hydrochloric acid. The reaction mixture was heated on a water-bath and the concentrate kept in a desiccator for several days when pale orange crystals of Pt(II) complex and light yellow crystals of Pd(II) complex settled down. These were filtered, washed thoroughly with ethanol-acetone and dried in an oven; yield 50-60%.

Analyses—Required for $[\text{Pt}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{Cl}_2)]$: C, 21.65; H, 2.59; N, 7.22; Cl, 18.27; Pt, 50.26% (Found: C, 21.49; H, 2.61; N, 7.15; Cl, 18.01; Pt, 50.07%). Required for $[\text{Pd}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{Cl}_2)]$: C, 28.07; H, 3.36; N, 9.35; Cl, 23.68; Pd, 35.53% (Found: C, 28.11; H, 3.29; N, 9.36; Cl, 23.18; Pd, 35.58%).

Dibromo-2-(2'-aminoethyl)pyridine Pt(II) and dibromo-2-(2'-aminoethyl)pyridine Pd(II)—A procedure similar to that used for the preparation of chloro compounds was employed using sodium bromide (1 g) prior to the treatment of ligand. Orange-yellow crystals of Pt(II) complex and dull-yellow crystals of Pd(II) complex were obtained in 40-45% yield.

Analyses—Required for $[\text{Pt}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{Br}_2)]$: C, 17.62; H, 2.11; N, 5.83; Br, 33.50; Pt, 40.89% (Found: C, 17.59; H, 2.02; N, 5.81; Br, 33.10; Pt, 40.94%). Required for $[\text{Pd}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{Br}_2)]$: C, 21.64;

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H, 2.59; N, 7.21; Br, 41.15; Pd, 27.39% (Found: C, 21.62; H, 2.54; N, 6.99; Br, 40.92; Pd, 27.47%).

Analytical results show that the complexes have 1:1 (metal-ligand) stoichiometry. Conductance measurements in *N,N'*-dimethylformamide (8.14 ohm⁻¹ cm² mole⁻¹) and nitromethane (4.8 ohm⁻¹ cm² mole⁻¹) showed that the complexes are non-electrolytes. As expected the present Pt(II) and Pd(II) complexes of AEP are diamagnetic.

Electronic spectra of [Pt(C₇H₁₀N₂)Cl₂] and [Pt(C₇H₁₀N₂)Br₂]—The observed electronic spectral bands along with their assignments are given in Table 1.

The first spin-allowed *d-d* transition (¹A_{1g}→¹A_{2g}) in the spectra of PtCl₄²⁻ is observed at 25000 cm⁻¹. This transition is reported to undergo a shift of 18000 cm⁻¹ towards higher frequency side in the spectra of Pt(II) complexes with amine ligands because of spectrochemical differences in the amine and halide ligands^{4,5}. This transition is observed at 34900 and 32400 cm⁻¹ in the present chloro and bromo complexes respectively. The second spin-allowed band due to the transition ¹A_{1g}→¹E_g is observed at 29700 cm⁻¹ in PtCl₄²⁻. This assignment is supported by magnetic moment and circular dichroism studies. The band is observed as a weak shoulder in the present chloro and bromo complexes at 36000 and 34150 cm⁻¹ respectively. The band at 38200 cm⁻¹ in the chloro complex and at 36800 cm⁻¹ in the bromo complex may be due to spin-allowed transition. The first band appearing at 20500 cm⁻¹ in the chloro complex and at 19000 cm⁻¹ in the bromo complex may be due to a spin-forbidden (¹A_{1g}→³E_g, ³A_{2g}) transition⁶. The last band at 44500 cm⁻¹ in the chloro complex and 38100 cm⁻¹ in the bromo complex is a charge-transfer band (ligand→metal).

In general the bands in the bromo complex occur at lower frequencies but are more intense compared to those for the chloro complex. This may be due to increased ligand participation in the mole-

cular orbitals derived mainly from the metal *d*-orbitals.

Electronic spectra of [Pd(C₇H₁₀N₂)Cl₂] and [Pd(C₇H₁₀N₂)Br₂]—In contrast to the spectra of Pt(II) complexes, the spectra of Pd(II) complexes do not show the presence of any spin-forbidden transition. Only spin-allowed bands are observed at 28000, 30600 cm⁻¹ for [Pd(C₇H₁₀N₂)Cl₂] and at 25200, 27050 cm⁻¹ for [Pd(C₇H₁₀N₂)Br₂] along with the two charge-transfer bands at 37800, 48500 cm⁻¹ and 34200, 46000 cm⁻¹ respectively. The detailed assignments of the bands are given in Table 1.

An additional charge-transfer band observed at 48500 and 46000 cm⁻¹ in the spectra of the present chloro and bromo complexes may be due to the transition Lσ→dσ* (¹A_{1g}→b¹E_u).

IR spectra of Pt(II) and Pd(II) complexes—The ν_{as}NH₂ and ν_sNH₂ modes absorb in the region 3333-3175 cm⁻¹ in the free ligand. On coordination, both the bands are considerably lowered along with changes in δNH₂, δwNH₂ and δrNH₂ modes. This indicates that the nitrogen of the NH₂ group serves as a coordination centre⁷.

Of the IR bands associated with the pyridine ring, the ν_sC=C, ν_{as}C=C and νC=N vibrations have been observed as strong bands⁸ at 1597, 1663, 1471 and 1429 cm⁻¹ in the free ligand. On complexation, new bands appear as follows: band-I, 1615-1595 cm⁻¹; band-II, 1585-1564 cm⁻¹; band-III, 1480-1472 cm⁻¹ and band-IV, 1435-1430 cm⁻¹. The positions of these bands in the spectra of complexes are similar to those observed for pyridinium ion⁹. In addition, the shifting of these bands to higher positions compared to those for free ligand is an indication of coordination of the pyridinium nitrogen to the metal atom.

Four bands have been observed in the far IR spectra of the free ligand at 592, 516, 415 and 395 cm⁻¹ which may involve skeletal vibrations of the framework^{10,11}. The presence of weak bands in the spectra of present complexes in the region

TABLE 1 — ELECTRONIC SPECTRAL DATA OF SQUARE-PLANAR Pt(II) AND Pd(II) COMPLEXES*

| Compound | Band position | Assignment | Δ ₁ | Δ ₂ | Δ ₃ |
|---|---------------|---|----------------|----------------|----------------|
| Pt(C ₇ H ₁₀ N ₂)Cl ₂ | 20500 | ¹ A _{1g} → ³ E _g , ³ A _{2g} | | | |
| | 34900 | → ¹ A _{2g} | | | |
| | 36000 (wsh) | → ¹ E _g | | | |
| | 38200 | → ¹ B _{1g} | | | |
| | 44500 | → ¹ A _{2u} , a ¹ E _u | 38400 | 2600 | 2700 |
| Pt(C ₇ H ₁₀ N ₂)Br ₂ | 19000 | ¹ A _{1g} → ³ E _g , ³ A _{2g} | | | |
| | 32400 | → ¹ A _{2g} | | | |
| | 34150 (wsh) | → ¹ E _g | | | |
| | 36800 | → ¹ B _{1g} | | | |
| | 38100 | → ¹ A _{2u} , a ¹ E _u | 35900 | 3250 | 2850 |
| Pd(C ₇ H ₁₀ N ₂)Cl ₂ | 28000 | ¹ A _{1g} → ¹ A _{2g} , ¹ E _g | | | |
| | 30600 | → ¹ B _{1g} | | | |
| | 37800 | → ¹ A _{2u} , a ¹ E _u | 31500 | 1500 | 3100 |
| | 48500 | → b ¹ E _u | | | |
| Pd(C ₇ H ₁₀ N ₂)Br ₂ | 25200 | ¹ A _{1g} → ¹ A _{2g} , ¹ E _g | | | |
| | 27050 | → ¹ B _{1g} | | | |
| | 34200 | → ¹ A _{2u} , a ¹ E _u | 28700 | 1500 | 2350 |
| | 46000 | b ¹ E _u | | | |

*Energies in cm⁻¹; interelectronic repulsion parameters are calculated taking B = 500 cm⁻¹ and C = 3500 cm⁻¹ (ref. 4).

332-322 cm^{-1} may be due to $\nu\text{M-X}$ ($\text{X}=\text{Cl}, \text{Br}$) vibrations while those in the region 318-290 cm^{-1} may be due to $\nu\text{M-N}$ (pyridine) vibrations.

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Complexes of Cr(III) with Glycine, Alanine, Valine & Leucine

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Cr(III) forms 1:3 (metal-ligand), green as well as purple complexes with glycine, alanine, valine and leucine. The coordination through carboxylate and amino group is revealed by the IR spectra of the complexes. The IR data also reveal the presence of coordinated water molecules.

CHROMIUM(III) is the recent addition to the list of elements which are biologically important in trace amounts. Cr(III) is involved in glucose tolerance and in the metabolic processes of fats and proteins¹. The characteristic property of chromium at the physiological pH is the ololation, i.e. forming polymeric structures through OH^- bridging and its consequent deactivation^{2,3}. The extent to which ololation will be inhibited, thus rendering chromium biologically available, depends on the complexing ability of the ligands for chromium against OH^- . Such ligands include the naturally occurring keto acids and the amino acids. Partly for this reason and partly for the reason that chromium aids in the transportation of amino acids through the cell membrane⁴, prompted us to study the amino acid complexes of Cr(III).

The complexes were isolated by a direct reaction between the hydrated metal salt and the amino acid in the ratio 1:3 (metal-ligand) in 50% aq. ethanol. The product thus obtained was washed with ethanol and dried *in vacuo*. With each amino acid green as well as purple complexes were obtained. The green complex, however, changed to purple on standing. A permanent purple complex could

TABLE 1 — Cr(III) COMPLEXES OF GLYCINE, ALANINE, VALINE AND LEUCINE

| Complex* | Colour | $10Dq$ (cm^{-1}) | B (cm^{-1}) | β |
|--|--------|--------------------------------|-----------------------------|---------|
| Cr.Gly ₃ .3H ₂ O | Violet | 18-293 | 466-68 | 0-50 |
| Cr.Ala ₃ .3H ₂ O | do | 17-957 | 448-93 | 0-49 |
| Cr.Val ₃ .3H ₂ O | do | 18-229 | 473-03 | 0-51 |
| Cr.Leu ₃ .3H ₂ O | do | 19-097 | 496-03 | 0-54 |
| [Cr.Gly ₂ .2H ₂ O]Cl | Green | 19-194 | 487-24 | 0-53 |
| [Cr.Ala ₂ .2H ₂ O]Cl | do | 17-927 | 589-71 | 0-64 |
| [Cr.Val ₂ .2H ₂ O]Cl | do | 17-609 | 566-22 | 0-61 |
| [Cr.Leu ₂ .2H ₂ O]Cl | do | 16-764 | 634-55 | 0-69 |

*All the complexes gave satisfactory elemental analyses.

be obtained by heating the reaction mixture. For leucine the reaction mixture had to be kept for about 70 hr with repeated heatings.

All the complexes isolated in the present investigation are shown in Table 1. In all the cases the solid state reflectance spectra showed two absorption bands around 17,000 and 23,000 cm^{-1} which were assigned to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ respectively. Using the method described by Figgis⁵ the values of $10Dq$, B and β have been calculated assuming octahedral symmetry for the complexes, and the values are listed in Table 1. The results in Table 1 indicate that the amino acid complexes are weak complexes, yet are stronger than the aquo complexes. Furthermore, the values of β are indicative of more ionic character in the purple complexes than for the green complexes. The results of conductivity experiments, however, indicate that the green complexes are 1:1 electrolytes. This implies that the Cl^- is present in the outer sphere of coordination.

The infrared spectra of the complexes in nujol showed a strong band ~ 1600 cm^{-1} indicating coordination through carboxylate as well as amino groups⁶. The broad absorption around 3100-3400 cm^{-1} is due to the overlapping of both $-\text{NH}_2$ as well as HOH frequencies. However, the shift in the frequency of the carbon-nitrogen bond at 890 cm^{-1} (symmetric stretching)⁷ is indicative of coordination through amino group. The peak due to coordinated water at 880 cm^{-1} (ref. 8) is masked by the aforesaid $\nu\text{C-N}$. However higher intensity of the peak in the complexes have been attributed to the presence of coordinated water.

Amino acid complexes are strong enough to compete with OH^- ions. Possibly in the biological systems too, amino acids can act as stronger ligands for Cr(III) and may weaken the ololation effect of the cation. In addition, because of the low stability of the complexes, Cr(III) can be made biologically available in the active form by complex formation with other ligands in the presence of amino acids⁹. Furthermore, the covalent character of these complexes suggest that the charge on the metal ion is sufficiently delocalized through coordination as a result of which the complexes can be lipid solubilized thereby aiding the transport of amino acids through cell membrane.

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