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Nb(III) Trisoxinate & Niobyl Phosphoniobate

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Niobium(III) oxinate and the complex phosphate containing Nb(III) have been isolated in an atmosphere of nitrogen and their analytical, spectral and magnetic data are reported. Both the compounds are susceptible to atmospheric oxidation.

WE have reported earlier the isolation and characterization of potassium disulphatoniobate (III) tetrahydrate in the solid state, the first really stable niobium compound in the trivalent state¹. This has also been employed as a standard analytical reductant². The present note describes the characterization of two other solid Nb(III) compounds viz., the niobium trisoxinate and a niobium phosphate.

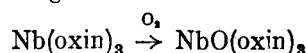
Fluka's 99.8% niobium pentoxide was used in the experiments. All other reagents were of appropriate purity. The infrared spectra were recorded in KBr pellets in a Beckman IR 20 infrared spectrophotometer. Magnetic measurements were done in a Guoy balance. For potentiometric measurements a Cambridge portable pH meter was used.

Niobium(III) trisoxinate [$Nb^{III}(\text{oxin})_3$]—8-Hydroxyquinoline (300 mg) was added to 100 mg of potassium disulphatoniobate(III) tetrahydrate¹ in 10 ml of 3M sulphuric acid. The mixture was neutralized with a saturated aqueous solution of NaHCO_3 till a flocculant precipitate of the oxinate appeared. The mixture was kept well stirred for 1 hr and the precipitate filtered in a sintered bed, washed thoroughly with water and dried by the passage of hot nitrogen. The entire operation was carried out in a specially designed all glass apparatus in an air-free condition and a slow stream of nitrogen was passed through the system throughout. The dry solid was then collected and stored under

nitrogen. All reagents and wash liquid were previously made air-free.

For analysis, a weighed quantity of the compound was digested for a few hours with 6M hydrochloric acid with free access of air. The coagulated hydrated Nb_2O_5 was filtered off and 8-hydroxyquinoline hydrochloride was determined in the filtrate by titration with standard potassium bromate solution in the presence of KBr³. The hydrated Nb_2O_5 was ignited and weighed. For the determination of the oxidation number of niobium, weighed quantity of the compound was taken in an anaerobic condition and a few ml of 4N HCl was added to it. Standard iodine solution was then added to the solution, the mixture shaken for several hours and the excess iodine back titrated with sodium thiosulphate. It was checked beforehand that iodine did not react with free oxine under this condition. The oxidation number of niobium in the compound was found to be +3 [Found: Nb, 17.2; oxine, 81.3; oxidation number, 2.90, 2.88. $\text{Nb}(\text{oxin})_3$ requires Nb, 17.7; oxine, 82.3%].

Niobium(III) oxinate is a deep violet solid insoluble in ethanol, acetone and benzene. It is weakly paramagnetic in nature (after correction for ligands, its μ_{eff} value has been found to be 0.76 BM at 30°). It is quantitatively oxidized to the yellow niobium(V) oxide trisoxinate⁴ in aqueous suspension or even on exposure to atmospheric oxygen. The oxidation reaction is further confirmed by the infrared spectral data. The spectrum of Nb(III) oxinate is completely devoid of any Nb = O band which appears with increasing intensity on gradual exposure of the compound to atmospheric oxygen suggesting the reaction to be



Other characteristic infrared active bands (Table 1) of the oxinate are strikingly similar to other trivalent metal oxinate compounds⁵.

Niobyl phosphoniobate(III) hexahydrate, $\text{NbVO}[\text{Nb}^{III}(\text{PO}_4)_2] \cdot 6\text{H}_2\text{O}$ —Potassium disulphatoniobate(III) tetrahydrate (100 mg) in 3M sulphuric acid (10 ml) was added to a mixture of 0.5 ml of glacial phosphoric acid and Na_2CO_3 (2 g) in water (50 ml). The mixture was neutralized with saturated Na_2CO_3

TABLE 1 — IR BANDS (cm^{-1}) OF NIOBIUM COMPOUNDS IN KBr

$\text{Nb}^{III}(\text{OXIN})_3$	
3200 (m), 3030 (w), 1600 (w), 1570 (s), 1490 (s), 1455 (s), 1420 (w), 1370 (s), 1315 (s), 1270 (s), 1235 (w), 1170 (w), 1100 (s), 1030 (w), 815 (s), 800 (m), 780 (s), 740 (s)	
$\text{NbVO}(\text{OXIN})_3$	
3060 (w), 3020 (w), 1600 (w), 1585 (w), 1565 (s), 1485 (s), 1455 (s), 1415 (m), 1365 (s), 1310 (s), 1260 (s), 1215 (m), 1170 (m), 1100 (s), 1045 (w), 1020 (w), 905 (s), 890 (w), 835 (w), 820 (s), 800 (w), 790 (m), 730 (s), 620 (w), 610 (w), 510 (m), 490 (m)	
$\text{NbVO}[\text{Nb}^{III}(\text{PO}_4)_2] \cdot 6\text{H}_2\text{O}$	
3600-3100 (s), 1630 (s), 1270 (s), 1050-1000 (s), 940 (s), 760 (m), 620 (s), 560 (s)	

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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