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PRELIMINARY NOTE

On the Syntheses of Xenon (VI) Fluoroniobates (V)

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So far, only the reactions of xenon hexafluoride with vanadium and tantalum Va group pentafluorides were reported [1,2]. Analogous reaction with niobium pentafluoride was, however, not studied although niobium pentafluoride appears to be more reactive than the tantalum pentafluoride [3]. Taking into consideration the estimated Lewis acid strength of this series of pentafluorides ($TaF_5 > NbF_5 > VF_5$) the existence of xenon (VI) fluoroniobates seems to be quite possible. Indeed, we have found that the reaction of excessive xenon hexafluoride with niobium pentafluoride yields two new compounds, $2XeF_6 . NbF_5$ and $XeF_6 . NbF_5$.

The reactions were carried out in a 100 ml nickel pressure reaction vessel equipped with a nickel valve. Xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride as a catalyst at 120°C [4]. Niobium pentafluoride was prepared by the action of excessive fluorine on niobium powder (Koch and Light Lab., Ltd.) in a bomb at 200°C [5]. In a typical run first about 5-6 mmoles of niobium pentafluoride were prepared in situ and than 20-30 mmoles of xenon hexafluoride were sublimed onto it. The reactor was than held at 90°C for several hours. Weight-loss of the reaction products versus time of pumping curves were recorded. At 0°C the curve levelled off at the composition $2XeF_6.NbF_5$ while at 60°C $XeF_6.NbF_5$ was obtained.

$2XeF_6.NbF_5$ is a white solid with negligible vapor pressure at 0°C. In a dynamic vacuum, however, it slowly decomposes, already at room temperature yielding $XeF_6.NbF_5$ and XeF_6. The rate of the decomposition at room temperature is less than 0.5wt% per hour. At 60°C white solid of the composition $XeF_6.NbF_5$ was isolated. It sublimes without decomposition and it is stable up to 200°C. The observed thermal stability of both xenon(VI) fluoroniobates(V) is consistent with the properties of both vanadium and tantalum analogues. Both newly isolated compounds were chemically analysed. Calcd. for $2XeF_6.NbF_5$: Nb, 13.69%; F, 47.60%. Found: Nb, 13.7%; F, 47.3%. Calcd. for $XeF_6.NbF_5$: Nb, 21.44%; F, 48.24%. Found: Nb, 21.4%; F, 48.0%.

X-ray powder diffraction patterns of powdered materials held in quartz capillaries were obtained by Debye-Scherrer method using $CuK_{-\alpha}$ radiation with Ni filter [6]. X-ray powder photography has shown that $XeF_6.NbF_5$ and $XeF_6.TaF_5$ are isostructural like the analogous compounds with xenon difluoride [7].

Although i.r. spectra (Table 1) show absorption bands which may be attributed to $Xe_2F_{11}^+$ and XeF_5^+ stretches this are the only structural data we have at present.

TABLE 1

Infrared spectra of solid $2XeF_6.NbF_5$ and $XeF_6.NbF_5$ (frequencies in cm^{-1})

$2XeF_6.NbF_5$	437m, 475(br)w, 504m, 522m, 570sh, 595vs, 615s, 642s, 664sh, 674sh, 710m
$XeF_6.NbF_5$	415m, 485m, 570sh, 595vs, 655s, 666sh, 712m

Intensity: s - strong, m - medium, w - weak, v - very,

Shape: br - broad, sh - shoulder

The stoichiometry of $2XeF_6.NbF_5$ alone suggests relationship to $2XeF_6.MF_5$ (M = Ru, Ir, Pt) [8] which are isomorphous with $2XeF_6.AuF_5$ [9] the crystal structure of which has established the formulation $Xe_2F_{11}^+ AuF_6^-$. Similarly $XeF_6.NbF_5$ may well be like $XeF_6.RuF_5$ which was interpreted on the basis of crystal structure as $XeF_5^+ RuF_6^-$ [10].

The most probable formulations for the isolated compounds are ionic $Xe_2F_{11}^+ NbF_6^-$ and $XeF_5^+ NbF_6^-$ though some covalent contributions to the bonding is also possible. Further spectroscopic study on these compounds is in progress.

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