

## X-ray K absorption edges of some niobium complexes

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X-ray K absorption edges in some niobium complexes containing fluorine have been measured and the observations are discussed in terms of the oxidation states and ionicity character of the complex ions involved.

### 1 INTRODUCTION

The shifts in the positions of X-ray K absorption edges of the second transition series are of recent interest (Barmiskii 1954, Blide *et al* 1968, Blide *et al* 1970, Bariniskii *et al* 1972, Nemnov *et al* 1969). Studies have been confined to simple compounds of Y and Nb (Blide *et al* 1968, Blide *et al* 1970) in absorption while the L emission spectra of simple carbides and nitrides of Nb were recorded by Nemnov *et al* (1968). A few complexes of Nb have been studied by Barmiskii (1954) earlier. The present note reports the measurements made on certain oxyfluorides of Nb.

### 2 EXPERIMENTAL

The complexes were prepared by the standard methods already described in the literature (Picin 1892, Maignac 1866, Balke *et al* 1908) except  $(\text{NH}_4)_3\text{NbOF}_6$  which was made by adding a solution of 3%  $\text{H}_2\text{O}_2$  (by volume) in an aqueous solution of  $(\text{NH}_4)_3(\text{NbO F}_6)$ . On concentrating the solution on a water bath white crystals were obtained, which were filtered and recrystallized from the aqueous solution.

A Matchlett sealed X-ray tube with Mo-target was used as a source of X-rays operating at 30 KV and 10 mA. The spectra were registered photo-

graphically by a bent crystal spectrography employing a mica crystal curved to a radius of 40 cm and oriented to reflect from (201) planes. The absorbing screens were prepared by compressing the powdered compounds between the two cellophane paper strips and were kept immediately in front of the X-ray tube window, because of the small quantity of compounds. The reference lines were  $\text{MoK}\alpha_{1,2}$  and  $\text{K}\beta_{1,3}$ . The exposure times ranged from 4–10 hours. The dispersion on the film was 12 x.U./mm. The spectrograms were scanned on a moll microphotometer at a magnification of 50

Table 1 Niobium  $K$  edge Wavelengths and shifts in different complexes

No.	Complex	$\lambda$ X.U	$\Delta\lambda$ $\pm 0.1\lambda u$	$\nu/R$	$\Delta\nu/R$	$\Delta eV$
	Nb Metal	651.63	—	1398.45	—	—
1.	$\text{K}_2\text{NbO}_2\text{F}_6\text{H}_2\text{O}$	651.25	0.38	1399.26	0.81	10.9
2.	$\text{K}_2\text{NbO}(\text{F}_6\text{H}_2\text{O})$	651.36	0.27	1399.03	0.58	7.9
3.	$\text{K}_3\text{NbOF}_6$	651.44	0.19	1398.86	0.41	5.6
4.	$(\text{NH}_4)_2\text{NbOF}_6$	651.29	0.34	1399.18	0.73	9.9
5.	$(\text{NH}_4)_3\text{NbOF}_6$	651.45	0.18	1398.84	0.39	5.3
6.	$(\text{NH}_4)_2\text{NbO}_2\text{F}_6$	651.53	0.10	1398.67	0.21	2.8
7.	$\text{CsNbF}_6$	651.34	0.29	1399.06	0.01	8.6

Table 2. Positions of the extended structures measured from the main edge in eV and the edge widths

No.	Complex	$K_2$	$K_1$	$A$	$\alpha$	$B$	$\beta$	$K_1 - A$ (widths)
1.	$\text{K}_2\text{NbO}_2\text{F}_6\text{H}_2\text{O}$	—	0.0	31	62	85	109	31
2.	$\text{K}_2\text{NbOF}_6\text{H}_2\text{O}$	—	0.0	28	46	—	—	28
3.	$\text{K}_3\text{NbOF}_6$	-18	0.0	23	46	—	—	23
4.	$(\text{NH}_4)_2\text{NbOF}_6$	—	0.0	28	—	—	—	28
5.	$(\text{NH}_4)_3\text{NbOF}_6$	(?)	0.0	15	23	31	—	15
6.	$(\text{NH}_4)_2\text{NbO}_2\text{F}_6$	—	0.0	30	—	—	—	30
7.	$\text{CsNbF}_6$	-16	0.0	23	—	—	—	23

### 3 RESULTS AND DISCUSSION

The wave-length corresponding to the  $K$  edge of Nb in different complexes are given in table 1. The edge shifts were calculated with respect to the edge in the element metal. In table 2 the position of the fine structures and the kink

on the slope of the absorption edge shown by the complexes are given. The main edge has been designated as  $K_1$  while the kink as  $K_2$  (figure 1). Since the structures of these complexes are not known, the concept of the ligand field theory cannot be applied to obtain the quantitative results. Further more the different features of  $L$ -band that are compared with the ligand field calculation lie well within 3 eV (Barimiski *et al* 1972). Also owing to the far too low resolution in the  $K$ -edge region the detail as predicted by the theory could not be obtained. Therefore, these results can only be discussed qualitatively in terms of the charges and size of the complex ions.

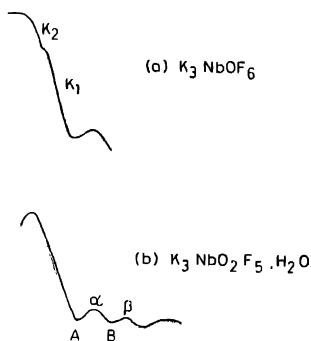


Fig. 1.

In the complexes  $K_2NbO_2F_5 \cdot H_2O$  and  $K_3NbOF_6$ ,  $(NbOF_6)^{-3}$  should be larger anion as compared to  $(NbOF_5)^{-2}$  and thus the electrostatic interaction in  $(NbOF_6)^{-3}$  will be weaker relative to that in  $(NbOF_5)^{-2}$  in spite of the same oxidation state of Nb (+5) in both the complexes. This should result in the lower shift in the case of  $(NbOF_6)^{-3}$ . This corresponds to our observations. Besides, the symmetry of  $(NbOF_6)^{-3}$  will be different from that of  $(NbOF_5)^{-2}$ . This will give the difference in the energy levels, which may also lower the  $K$ -shift value in  $(NbOF_6)^{-3}$ . Similar interpretation may be valid to explain the relative shift in  $(NH_4)_2NbOF_5$  &  $(NH_4)_3NbOF_6$  &  $(NH_4)_3NbO_2F_6$  and  $C_6NbF_6$ .

In complexes  $K_2NbO_2F_5 \cdot H_2O$  and  $K_2NbOF_5 \cdot H_2O$  the charges on anion are the same but the oxidation state of Nb are different. This may be the reason to explain the difference in the shifts in Nb  $K$ -edge.

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