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Preliminary Communication

Preparation and Properties of Eight-co-ordinated Diperoxotetrafluoro-niobates(V) and -tantalates(V)

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We have examined the interaction and substitution of electronegative ligands (F^- and OH^-) with peroxide groups in fluoro complexes of niobium and tantalum at various pH values.

From hydrogen peroxide solutions of niobates and tantalates with some excess of hydrofluoric acid (*p*H 1), the known species of monoperoxopentafluoro metalates, $[M(V)(O_2)F_5]^{2-}$, (M = Nb, Ta), can be prepared[1]. After neutralization of these solutions with ammonia or alkali hydroxides (*p*H 4—6), part of the fluorine has been replaced by a peroxide group and a series of new diperoxotetrafluoroniobates(V) and -tantalates(V) were obtained (Table I) in the form of well defined single crystals. The complexes dissolve slowly in water but are insoluble in organic solvents. Further adding of hydroxides leads to the complete substitution of fluorine by the peroxide group and formation of well known tetraperoxo complexes — $[M(V)(O_2)_4]^{3-}$, (M = Nb, Ta).[1,2]

The infrared spectra confirm that the ammonium diperoxotetrafluoroniobates and tantalates are anhydrous, while the sodium and potassium salts are monohydrates. This water molecule cannot be removed by drying *in vacuo* at 80°. In heating the complexes do not melt but decompose and evolve oxygen above temperatures mentioned in Table I.

There are no infrared bands in both groups which can be assigned to M=O or M—O—M—O stretchings. The infrared vibrations observed near 850 cm^{-1} and 500—550 cm^{-1} can be attributed to the bidentate co-ordinated peroxo groups. Such an assignation is confirmed by earlier infrared[2,3] and crystallographic[4] investigations on di- and triperoxo complexes of niobium and tantalum. The M—F stretching vibrations were observed in 420—460 cm^{-1} region.

Values for the molar conductivities in water solutions showed that the complexes are electrolytes of the type 3 : 1. No free fluoride ion can be found in the water solutions of compounds. That means that the complex anion, $[M(V)(O_2)_2F_4]^{3-}$, is mononuclear in solutions.

According to the presented spectra and conductivities niobium and tantalum in these complexes are probably eight-coordinated if we assume that the peroxide groups are bidentate and that the water molecule is not coordinated to the metal. Comparison of crystallographic investigations on hydrated diperoxo complexes of niobium[4] and our data confirm this conclusion.

TABLE I[a]

Complex	Decomposition (^0C)	IR bands (cm^{-1})	Assignment of IR bands (stretching)	Molar conductivity $ohm^{-1} \cdot cm^2$
$(NH_4)_3[Nb(O_2)_2F_4]$	155	885, 868, 535 425	$M(O_2)$ M—F	388
$(NH_4)_3[Ta(O_2)_2F_4]$	160	869, 855, 505 425	$M(O_2)$ M—F	381
$Na_3[Nb(O_2)_2F_4] \cdot H_2O$	240	872, 861, 550 460	$M(O_2)$ M—F	318
$Na_3[Ta(O_2)_2F_4] \cdot H_2O$	250	862, 848, 525 460	$M(O_2)$ M—F	348
$K_3[Nb(O_2)_2F_4] \cdot H_2O$	210	885, 868, 525 430	$M(O_2)$ M—F	367
$K_3[Ta(O_2)_2F_4] \cdot H_2O$	220	865, 850, 510 435	$M(O_2)$ M—F	383

[a] The compounds were analysed for N, F, K, Na, Nb, Ta, and peroxides.
E. g. $(NH_4)_3$ $[Ta(O_2)_2F_4]$, requires: N, 11.2; Ta, 48.3; F, 20.3; (O_2), 17.1; found: N, 11.0; Ta, 48.6; F, 20.7; (O_2), 17.9 %.

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IZVOD

Priprava i svojstva diperoksotetrafluoro-niobata(V) i -tantalata(V) koordinacije osam

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Pripravljeni su novi kompleksni spojevi niobija(V) i tantala(V) sastava A_3 $M(O_2)_2F_4 \times H_2O$, gdje je M = Nb i Ta; A = NH_4, x = 0; A = K, Na, x = 1. Spojevi su pripravljeni iz peroksidnih otopina niobata i tantalata uz prisustvo suviška fluorovodične kiseline pri *p*H 4—6, a karakterizirani su na osnovu elementarne analize, infracrvenih spektara i mjerenja vodljivosti. Pretpostavlja se da niobij i tantal u tim spojevima imaju koordinaciju osam.

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