

Reactions of Niobium and Tantalum Hexanuclear Halide Clusters with Nitrogen Bases. Clusters of the Type $[M_6X_{12}L_6]X_2$, $L = NH_3, CH_3CN, C_5H_5N$

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Microcrystalline substances of the composition $[M_6X_{12}L_6]X_2$, $M = Nb, Ta$, $X = Cl, Br$, $L = NH_3, CH_3CN, C_5H_5N$, were prepared by the reaction of ethanolic solutions of $[M_6X_{12}(C_2H_5OH)_6]X_2$ with ammonia gas or simply by dissolving these clusters in acetonitrile or pyridine. The spectral data point to the occupancy of all octahedral coordination sites by nitrogen donor ligands.

The preparation and properties of $[M_6X_{12}]^{n+}$, $M = Nb, Ta$, $X = Cl, Br$, $n = 2, 3, 4$, clusters with weakly coordinated, especially neutral, ligands are of considerable interest in creating new chemical reactions. Loosely coordinated $[M_6X_{12}]^{n+}$ species may serve as versatile starting materials in the synthesis of more complex species. An example of a family of suitable hexanuclear clusters of niobium and tantalum that might serve for this purpose are those with coordinated aliphatic alcohols: $[M_6X_{12}(ROH)_6]X_2$; $R = CH_3, C_2H_5, i-C_3H_7, i-C_4H_9$.¹ The cluster $[Ta_6Cl_{12}(CH_3OH)_6]Cl_2$ was subsequently used as starting material for the preparation of $[Na_2(CH_3OH)_9] [Ta_6Cl_{12}(OCH_3)_6] \cdot 3CH_3OH$.²

In these investigations the precursors were the substances with coordinated ethanol $[M_6X_{12}(C_2H_5OH)_6]X_2$. These clusters are readily soluble in dry acetonitrile and pyridine and if these clear solutions were left at room temperature for several days, microcrystalline solids of the composition $[M_6X_{12}L_6]X_2$,

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L = CH₃CN, C₅H₅N, crystallized out. Clusters with coordinated ammonia were prepared by introducing the ammonia gas into an ethanolic solution of [M₆X₁₂(C₂H₅OH)₆]X₂. Solid substances [M₆X₁₂(NH₃)₆]X₂ started to form immediately. All these substances are moisture sensitive and all operations were carried out in vacuum and under a dry nitrogen atmosphere. Crystalline substances are not soluble in common organic solvents except strong oxygen donors like dimethylsulphoxide and N,N-dimethylformamide.

Coordination of nitrogen donor ligands is indicated by analytical and infrared spectral data (Table I). In all compounds, only six ligand molecules per mol of cluster were found, as required for occupation of all octahedral coordination sites. The coordination of NH₃ molecules was confirmed from infrared spectral data.³ The NH₃ stretching mode is present in the region of 3100–3400 cm⁻¹ as a triplet band. The NH₃ degenerate deformation mode is observed as the sharp, medium intensity band in the region of 1607–1611 cm⁻¹ as given in Table I. The same intensity band present in the region of 1282–1299 cm⁻¹ originates from the NH₃ symmetric deformation mode. The metal-nitrogen stretching vibration for niobium and tantalum chloro derivatives is observed at 344 and 346 cm⁻¹ respectively, while for bromo clusters it appears above 400 cm⁻¹. The absorption band (doublet) present in the spectrum of free CH₃CN at 2283 and 2242 cm⁻¹ originating from the C≡N stretching vibration⁴ is shifted to higher frequencies upon coordination and is observed at 2300 and 2270 cm⁻¹ for all [M₆X₁₂(CH₃CN)₆]X₂ derivatives. A similar position of this absorption band is observed in the spectrum of ZnCl₂(CH₃CN)₂⁵ (2314 and 2287 cm⁻¹) or [Rh₂(CH₃CN)₁₀](BF₄)₄⁶ (2342, 2317

TABLE I
Analytical and infrared spectral data

Compound	Found (Calc.)/%			δ(HNH), ν(CN), ν(ring vib.)/cm ⁻¹
	Nb, Ta	Cl, Br	N	
[Nb ₆ Cl ₁₂ (NH ₃) ₆]Cl ₂	46.95 (48.20)	42.50 (42.95)	6.80 (7.30)	1611m
[Nb ₆ Br ₁₂ (NH ₃) ₆]Br ₂	31.02 (31.35)	62.73 (62.90)	4.48 (4.75)	1607mv
[Ta ₆ Cl ₁₂ (NH ₃) ₆]Cl ₂	64.55 (64.45)	28.95 (29.50)	5.00 (5.00)	1611v
[Ta ₆ Br ₁₂ (NH ₃) ₆]Br ₂	46.10 (47.05)	47.85 (48.50)	4.15 (3.65)	1609m
[Nb ₆ Cl ₁₂ (CH ₃ CN) ₆]Cl ₂	44.31 (42.88)	38.14 (38.18)	5.89 (6.46)	2300m, 2270m
[Nb ₆ Br ₁₂ (CH ₃ CN) ₆]Br ₂	29.51 (29.00)	59.33 (59.19)	4.20 (4.37)	2299s, 2270s
[Ta ₆ Cl ₁₂ (CH ₃ CN) ₆]Cl ₂	61.05 (59.38)	27.41 (27.15)	4.35 (4.60)	2300m, 2270m
[Ta ₆ Br ₁₂ (CH ₃ CN) ₆]Br ₂	45.05 (44.30)	44.99 (45.65)	3.03 (3.43)	2300m, 2270m
[Nb ₆ Cl ₁₂ (C ₅ H ₅ N) ₆]Cl ₂	36.95 (36.47)	32.39 (32.48)	5.65 (5.50)	1603m
[Nb ₆ Br ₁₂ (C ₅ H ₅ N) ₆]Br ₂	26.35 (25.92)	51.46 (52.02)	4.11 (3.91)	1602m
[Ta ₆ Cl ₁₂ (C ₅ H ₅ N) ₆]Cl ₂	53.55 (52.79)	24.11 (24.13)	3.81 (4.09)	1604m
[Ta ₆ Br ₁₂ (C ₅ H ₅ N) ₆]Br ₂	41.20 (40.53)	40.48 (41.76)	3.37 (3.14)	1606m

and 2300 cm^{-1}). The degenerate CH_3 rocking vibration mode present in the spectrum of the free ligand at 1037 cm^{-1} is moved to lower frequencies and observed at 1026 cm^{-1} for all complexes. Similar considerations are applicable to the pyridine derivatives. Here the most significant changes in the IR spectra are related to the aromatic ring vibrations.^{7,8} With coordination of pyridine all of these vibrations are moved to higher frequencies.⁹ The absorption bands observed in the spectrum of the free ligand at 1578 , 601 and 403 cm^{-1} are moved to the region of $1602\text{--}1606\text{ cm}^{-1}$, 625 and $422\text{--}425\text{ cm}^{-1}$ respectively. The observed changes in the spectra of these complexes are in agreement with the position of these bands in known complexes with coordinated pyridine.⁹ In the IR spectra of these complexes, no absorption bands at 1640 , 1530 , 1327 and 1250 cm^{-1} that might indicate the presence of pyridine in the cationic form, pyH^+ , are observed.

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SAŽETAK

Reakcije heksanuklearnih halogenidnih klustera niobija i tantala s dušikovim bazama. Klusteri oblika $[M_6X_{12}L_6]X_2$, $L = \text{NH}_3$, CH_3CN , $\text{C}_5\text{H}_5\text{N}$

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Reakcijom etanolnih otopina spojeva $[M_6X_{12}(\text{C}_2\text{H}_5\text{OH})_6]X_2$ s plinovitim amonijakom ili njihovim otapanjem u acetonitrilu ili piridinu priređene su mikrokristalne supstancije sastava $[M_6X_{12}L_6]X_2$, $L = \text{NH}_3$, CH_3CN , $\text{C}_5\text{H}_5\text{N}$. Spektralni podaci ukazuju na zaposjednutost svih oktaedarskih koordinacijskih položaja dušikovim bazama.