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Soluble μ-F^i bridged niobium clusters: synthesis and crystal structures of $(Et_4N)_6[Nb_6F^i{}_6Br^i{}_6(NCS)^a{}_6]Br_2$ and $Cs_{1.6}K_{2.4}[Nb_6F^i{}_6I^i{}_6(NCS)^a{}_6]$†

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Two new anions $[Nb_6F^i{}_6X^i{}_6(NCS)^a{}_6]^{4-}$ (X = Br, I) based on octahedral niobium clusters with edge-bridging F ligands have been prepared by reaction of $Cs_3Nb_6F_6Br_{12}$ and $Cs_4Nb_6F_{8.5}I_{9.5}$ with aqueous solution of KSCN. The anions were isolated as $(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ (1) and $Cs_{1.6}K_{2.4}[Nb_6F_6I_6(NCS)_6]$ (2) salts.

The chemistry of octahedral niobium cluster compounds based on Nb_6L_{12} cluster core (L = Cl, Br, O) has been extensively studied.[1–3] On the other hand, Nb_6F_{15}[4] was for a long time the single example of cluster fluoride reported in the literature. Recently, new niobium octahedral clusters coordinated with fluorine have been isolated, *via* high temperature solid state reactions, by the combined use of fluorine with another halogen: Na_2NbF_6-$Nb_6(F^i{}_{12-x}X^i{}_x)F^{a-a}{}_{6/2}$ (X = Cl, Br) series, $Cs_2[Nb_6Br^i{}_5F^i{}_7F^a{}_4F^{a-a}{}_{2/2}]$ or $Nb_6Br^i{}_5F^i{}_7Br^{a-a}{}_{6/2}$[5] and more recently $Cs_4[Nb_6F^i{}_{8.5}I^i{}_{3.5}F^a{}_6]$[6] ($L^i$ = edge-bridging inner ligand and L^a = apical ligand according to the Schäfer's notation[7]). In this communication, we report the preparation, *via* solution chemistry route, and the crystal structures of two novel soluble salts, namely $(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ (**1**) and $Cs_{1.6}K_{2.4}[Nb_6F_6I_6(NCS)_6]$ (**2**), based on the new $[Nb_6F^i{}_6X^i{}_6]^{2+}$ (X = Br, I) octahedral niobium cluster core with ordered μ-F^i and μ-X^i inner ligands.

$(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ (**1**) was prepared with moderate yield starting from $Cs_3Nb_6F_6Br_{12}$.[8]‡ During reaction the excess of NCS^- ligand acts as reducing agent as it was observed earlier in.[9] The structure of (**1**) is built up from $[Nb_6F^i{}_6Br^i{}_6(NCS^a)_6]^{4-}$ discrete anionic units in which the octahedral cluster is edge-bridged by twelve inner ligands and additionally coordinated by six apical NCS groups (Fig. 1). The six bromine ligands as well as the six fluorine ones are ordered on the inner positions. The six μ-F^i ligands are located in a plane forming a ring arrangement between the two Nb_3 triangles edge-bridged by the six μ-Br^i ligands. A similar O/Cl inner ligand ordering within $[M_6Cl^i{}_6O^i{}_6Cl^a{}_6]$ units was previously found in $PbLu_3Nb_6Cl_{15}O_6$,[10] and $(Et_4N)_2[\alpha\text{-}W_6O_6Cl_{12}]$.[11] Owing to the discrepancy between the ionic radii of fluorine and bromine ligands, the Nb_6 cluster is strongly distorted. The Nb–Nb bond lengths deviate from 2.8214(8) Å for the μ-F bridged bonds to 2.919(1) Å for the μ-Br bridged ones, resulting in a contraction of the Nb_6 cluster along the 3-fold axis. The mean Nb–Nb bond length, equal to 2.8702 Å, lies between those found in Nb_6F_{15} (2.80 Å) and in bromides based on $[Nb_6Br_{18}]^{4-}$ cluster unit as for instance $CsErNb_6Br_{18}$ (2.954(1) Å).[12] The Nb–Br^i distances (mean 2.6174 Å) are similar to those found in other $[Nb_6Br^i{}_{12}]^{2+}$ cluster cores.[12,13] The Nb–F^i bond lengths (mean 2.080 Å) are slightly longer than those reported for Nb_6F_{15} (2.049 Å). This feature may be attributed to their different VEC values (Valence Electron Count: 16 in $(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ and 15 in Nb_6F_{15}) since the HOMO level of the $[Nb_6L^i{}_{12}L^a{}_6]$ molecular orbital diagram is characterised by a Nb–L^i antibonding contribution.[14]

$Cs_{1.6}K_{2.4}[Nb_6F_6I_6(NCS)_6]$ (**1**) was prepared with low yield from starting compound $Cs_4Nb_6F_{8.5}I_{9.5}$[6] ¶. The $[Nb_6F^i{}_6I^i{}_6(NCS)^a{}_6]^{4-}$ anion (Fig. 2) exhibits the same F/X ordered repartition of ligands around the cluster as in (**1**). The six Nb–Nb bonds (mean 2.831 Å) bridged by F^i ligands are close to those found in (**1**) but, as expected, the six (mean 2.940 Å) bridged by I^i ligands are larger than the μ-Br^i bridged ones in (**1**) owing to a more important steric effect. Let us note that μ-I^i bridging ligand is unusual for octahedral niobium clusters. Indeed, with the exception of $Nb_6Cl_{10.8}I_{3.2}$,[15] Nb_6 iodides are based on $[Nb_6I^i{}_8I^a{}_6]$ units in which μ_3-inner iodine

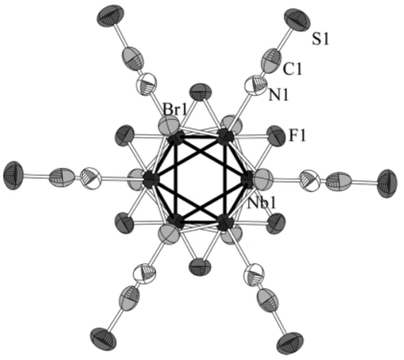

Fig. 1 Structure of $[Nb_6F^i{}_6Br^i{}_6(NCS)^a{}_6]^{4-}$ anion in **1** with ellipsoids at the 50% probability level. Selected bond distances (Å): Nb1–Nb1 2.8214(8); Nb1–Nb1 2.919(1); Nb1–F1 2.081(2); Nb1–F1 2.082(2); Nb1–Br1 2.6134(7); Nb1–Br1 2.6212(7); Nb1–N1 2.282(5).§

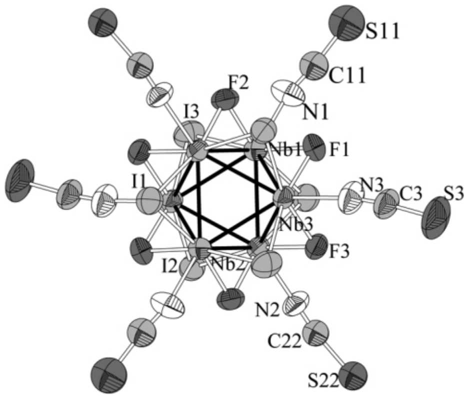

Fig. 2 Structure of $[Nb^i{}_6F^i{}_6I^a{}_6(NCS)^a{}_6]^{4-}$ anion in **2** with ellipsoids at the 50% probability level. Only one orientation of disordered NCS groups is shown. Selected bond distances (Å): Nb1–Nb3 2.8243(14); Nb1–Nb2#1 2.8368(16); Nb1–Nb3#1 2.9420(17); Nb1–Nb2 2.9430(16); Nb2–Nb3 2.8313(15); Nb2–Nb1#1 2.8368(16); Nb2–Nb3#1 2.9339(15); Nb3–Nb2#1 2.9339(15); Nb3–Nb1#1 2.9420(17); Nb1–F2 2.081(6); Nb1–F1 2.096(6); Nb2–F3 2.094(6); Nb2–F2#1 2.100(7); Nb3–F1 2.089(7); Nb3–F3 2.091(6); Nb1–I1 2.8105(15); Nb1–I3 2.8191(14); Nb2–I2 2.8001(13); Nb2–I1 2.8111(15); Nb3–I2#1 2.8010(14); Nb3–I3#1 2.8286(15); Nb1–N1 2.153(11); Nb2–N2 2.198(9); Nb3–N3 2.215(11) (symmetry transformation: −x, −y, −z −1 ‖)

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† Electronic supplementary information (ESI) available: figures of anions in two projections, $Nb_6L^i{}_{12}$ cluster core in parent $Cs_4Nb_6F_{8.5}I_{9.5}$, in isolated **2** and possible isomers of $Nb^i{}_6F^i{}_{12-x}I^a{}_x$, x = 3 to 6. See http://www.rsc.org/suppdata/cc/b4/b400668b/

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atoms are face-capping the Nb_6 cluster.[16] The Nb–F^i interatomic distances (mean 2.092 Å) are very close to those found in (**1**) and in parent $Cs_4[Nb_6F^i_{8.5}I^i_{3.5}I^a_6]$. The Nb–$I^i$ bond lengths (mean 2.812 Å) are also close to those found in the latter fluoro-iodide (mean 2.783 Å) but larger than those found in the edge-bridged $Nb_6Cl_{10.8}I_{3.2}$ chloro-iodide (mean 2.695 Å). Let us recall that the starting $Cs_4[Nb_6F^i_{8.5}I^i_{3.5}I^a_6]$ is based on a unit in which three iodine and six fluorine ligands are ordered on nine inner positions, whilst the three last are randomly occupied by fluorine and iodine with an I/F ratio close to 0.5/2.5 (see ESI†). This disorder is related to the co-existence of cluster units with different I/F stoichiometries in the parent solid and disordered on the same position (see ESI†). During dissolution all isomers came to solution but evaporation in air resulted in oxidation of the less symmetrical isomers to hydrated $Nb_2O_5{\cdot}xH_2O$ and only $[Nb_6F^i_6I^i_6(NCS)^a_6]^{4-}$ was isolated, and only in low yield.

IR spectra of compounds recorded in the 4000–400 cm^{-1} region revealed vibrations of coordinated NCS^- ligand and Nb–F^i stretch vibrations (compound **1** also has bands belonging to Et_4N^+ cations). In contrast to parent Nb_6F_{15} having two bands at 454 and 543 cm^{-1} attributed to bridging fluoride,[17] both complexes each demonstrate only one Nb–F^i stretch vibration, at 495 and 483 cm^{-1} respectively. The shift of this band in **2** to lower energies compared to **1** by 12 cm^{-1} can be explained by weakened bonding in the iodine derivative and correlates with the slight elongation in the mean of the Nb–F^i bonds.

In conclusion, the number of soluble entities containing metal–metal bonds bridged by fluorine is strictly limited.[18] The obtained $[Nb_6F^i_6X^i_6(NCS)^a_6]^{4-}$ anions (X = Br, I) have opened a field of new and promising chemistry based on soluble niobium cluster compounds with μ-F edge bridging ligands. The higher electronegativity of fluorine ligands compared to that of other halogens should greatly affect the properties of Nb_6 cluster. The study of such entities should increase knowledge about the formation of metal–metal bonding in fluorine chemistry. The preparation and isolation of ordered $[Nb_6F^i_6X^i_6L^a_6]^{4-}$ units with various L^a ligands will offer some new insights into the halide coordination in terms of the electronic and physical mismatch between fluoride and iodide (or bromide). The presence of a mixture of different units with different F/I ratio in the solid state opens the way for preparation of other members of $Nb_6F^i_{12-x}X^i_x$ family. The identification and isolation of new $[Nb_6F^i_{12-x}X^i_x(NCS)^a_6]^{4-}$ units and in particular $[Nb_6F^i_9I^i_3(NCS)^a_6]^{4-}$ is under progress.

Notes and references

‡ $(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ (**1**) was prepared by the following procedure: first, $Nb_6F^i_6Br^i_6Br^{a-a}{}_{6/2}{}^{a5a}$ was synthesised in a niobium container from a stoichiometric mixture of Nb_6F_{15} and $NbBr_5$ at temperature ranging from 500 °C to 600 °C. The resulting product was mixed with 3 equivalents of CsBr and treated at 500–600 °C for 48 h, that gave $Cs_3Nb_6F_6Br_{12}$.[8] 200 mg of $Cs_3Nb_6F_6Br_{12}$ were treated with a deoxygenated KSCN aqueous solution (200 mg; 50 ml) and 200 mg of Et_4NBr was added. Precipitated $(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ was filtered off, washed with deoxygenated water and dried in Ar. Yield: 156 mg (65% based on starting Nb_6F_{15} cluster). The compound is readily soluble and stable in deoxygenated CH_3CN, DMF and other polar solvents. EDAX for heavy atoms: Nb:F:Br:S = 6:5.9:8.2:5.9 (normalised for Nb_6). IR (KBr) (cm^{-1}): 2060 (s. br. ν(CN)), 495 (m, ν(Nb–F^i)), 476 (m. δ(NCS)) (bands of Et_4N^+ are omitted). UV-Vis (nm): 223, s, 245, s., 300 sh m., 420 m., 914 m. br.

§ Crystal data for **1**: $C_{54}H_{120}Br_8F_6N_{12}Nb_6S_6$: $Mr = 2440.68$, trigonal, $R\bar{3}$, $a = 18.149(5)$, $c = 25.435(5)$ Å, $V = 7255.5(3)$ Å^3, $Z = 3$, $T = 293$ K, 30088 reflections, $R1 = 0.084$, $wR2 = 0.114$, $\Delta\rho_{\min/\max} = -0.56/0.60$ e.Å^{-3}, CCDC 225283. See http://www.rsc.org/suppdata/cc/b4/b400668b/ for crystallographic data in .cif or other electronic format.

¶ 50 mg of $Cs_4Nb_6F_{8.5}I_{9.5}$[6] were treated with a solution of 100 mg of KSCN in 10 ml deoxygenated water during 24 h. The resulting solution was filtered and evaporated in air. In the resulting white-colored mixture, few (20–30) black crystals corresponding to $Cs_{1.6}K_{2.4}[Nb_6F_6I_6(NCS)_6]$ (**2**) were found. The compound is soluble and stable in deoxygenated H_2O and DMF but insoluble in CH_3CN and CH_2Cl_2. EDAX for heavy atoms: K:Cs:Nb:F:I:S = 2.5:1.5:6:5.9:6.2:5.8 (normalised for Nb_6). IR (KBr) (cm^{-1}): 2055 (s., br. ν(CN)), 483 (m. ν(Nb–F^i)), 474 (m. δ(NCS)). UV-Vis (nm): 222, 362, 403sh, 580sh, 940 m.br.

‖ Crystal data for **2**: $C_6Cs_{1.6}K_{2.4}N_6Nb_6F_6I_6S_6$: $Mr = 2087.84$, monoclinic, $C2/c$, $a = 17.406(5)$, $b = 12.237(5)$, $c = 23.155(5)$ Å, $\beta = 103.307(5)°$, $V = 4800(3)$ Å^3, $Z = 4$, $T = 293$ K, 23177 reflections, $R1 = 0.0648$, $wR2 = 0.1772$, $\Delta\rho_{\min/\max} = -1.273/1.835$ e.Å^{-3}, CCDC 225284. See http://www.rsc.org/suppdata/cc/b4/b400668b/ for crystallographic data in .cif or other electronic format.

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