

Physico-Chemical Properties of Technetium Clusters

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The review report is concerned with spectroscopic (optical spectra in UV, visible and IR regions; ESR; X-ray photoelectron, X-ray K_{α} -emission and ^{57}Fe -Mossbauer spectra) and other physico-chemical (static magnetic susceptibility, measurements of electronic conductivity, electronic and molecular structures) properties of all types of presently known technetium cluster compounds with acido-ligands.

At present the works on a systematic study of optical spectra of cluster technetium compounds are missing. In some cases only experimental characteristics of these spectra for some compounds are reported and they are compared to, for example, rhenium analogous. First of all, this is explained by the difficulties of obtaining of these compounds and interpreting their spectra, because this requires accurate quantum-chemical calculations and precision spectroscopic measurements in polarized light on single crystals. Thus, the most strict spectroscopic studies were performed only on the $\text{K}_3[\text{Tc}_2\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ for which there were quantum-chemical calculations by the SCF- X_{α} -SW method, and on the $[\text{Tc}_2(o\text{-C}_3\text{H}_4\text{ON})_4\text{Cl}]$ for which adequate single crystals with the orientation of all the molecules along the Z axis of a tetragonal unit cell were synthesized [1]. Optical spectra of the most part of binuclear complexes in UV and visible region may be primarily used for the qualitative identification of technetium clusters. In some cases, it is quite possible to refer part of the absorption bands by analogy with $\text{K}_3[\text{Tc}_2\text{Cl}_8]\cdot 2\text{H}_2\text{O}$, $[\text{Tc}_2(o\text{-C}_3\text{H}_4\text{ON})_4\text{Cl}]$ or with rhenium compounds. Most of the identified absorption bands (for example $\pi\text{-}\delta^*$ transition near $\sim 600\text{-}700\text{ nm}$) correlate with the value of the $10D_q$ parameter, characterizing the intensity of the crystalline field created by them [2]. It should be noted that the electronic spectra of polynuclear technetium clusters, as a rule [3], do not have characteristic maxima due to the large number of transitions close in their energy which can not be resolved experimentally.

The IR spectra of technetium clusters have been studied a little better. However, the majority of these spectra are not informative, because the main vibration modes connected with the cluster fragment lie in the long-wave region, and, besides, the most interesting vibrations $\nu(\text{M-M})$ due to the central symmetry in most clusters are forbidden in the IR-spectra, and allowed in Raman spectra but because of the intensive colour of the compounds in most of the cases it is impossible to record Raman spectra. Thus, for most technetium clusters only IR-spectra become accessible, where bands are due to valent characteristic cationic or to Tc-X (where X is a ligand) vibrations. Moreover, the vibrations of the Tc-X type may be singled out from the complex of normal vibrations of a more complex type quite arbitrarily, because due to the large weight of and strong effect of the interrelationship between the ligands, the "characteristic" property becomes rather doubtful. For the compounds of close stoichiometry and structure of the $\nu(\text{Tc-X})$ and $\delta(\text{X-Tc-X})$ bands, normally, shift to the side of low energies by the decrease in the formal degree of oxidation of technetium and substitution of the ligands in the series Cl-Br-I. The given tendencies are also typical for mononuclear halogenocomplexes [4]. It should be noted that in the case of polynuclear technetium clusters a great number of bands appear in the spectra. It is impossible