

QUANTUM CHEMICAL STUDY OF CHLOROACETATE BINUCLEAR TECHNETIUM CLUSTER ELECTRON STRUCTURE

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Chloroacetate technetium compound of $Tc_2(CH_3COO)_4Cl$ composition was firstly obtained in [1] by exchange reaction of Cl for acetate in $K_3[Tc_2Cl_8] \cdot 2H_2O$ in CH_3COOH . The structure of this compound was determined in [2]. Studying solvolysis of $[(CH_3)_4N]_3[Tc_6Cl_{14}]$ in the acetate/ethylacetate (1:10) mixture we have obtained the $Tc_2(CH_3COO)_4Cl$ crystals. The molecular and electronic structure of these ones were the same as described in [1,2] (Fig. 1a,b). In this compound, in contrast to halide binuclear cluster (Fig. 1c,d), ligand halogen atoms have been replaced by bidentate bridging acetate ions. The Tc-Tc bonds lengths in these clusters are practically equal (2.116\AA and 2.117\AA correspondingly).

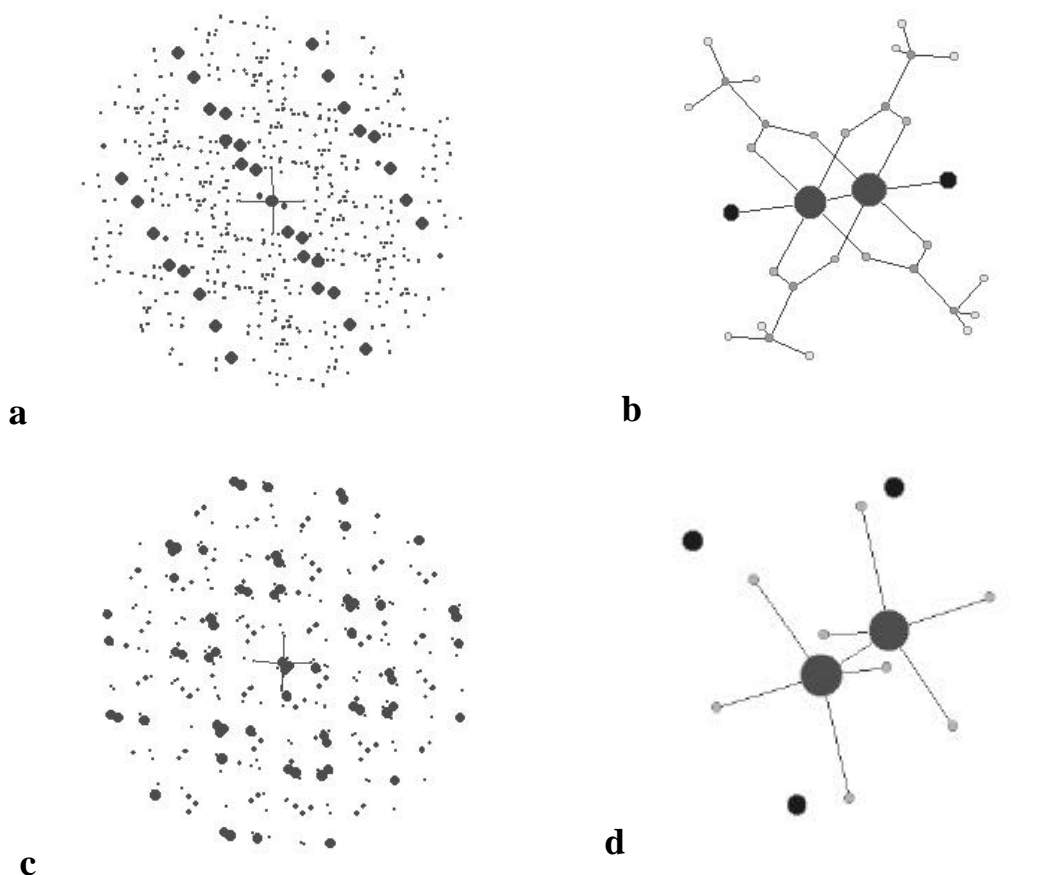


Fig.1 The crystal (a, c - view in the plane which is perpendicular to Tc-Tc bond) and molecular (b-d) structure of $Tc_2(CH_3COO)_4Cl$ and $K_3[Tc_2Cl_8] \cdot 2H_2O$ compounds [2].

In the crystal structure, the $[\text{Tc}_2(\text{CH}_3\text{COO})_4]^+$ fragments are bounding one another by axial Cl^- anions. Tc-Cl 2.66Å distance is much longer than typical Tc-Cl lengths 2.32-2.36Å and even longer Tc-Br 2.47-2.51Å. At the same time the formal electron configuration d^4-d^5 , the presence of one unpaired electron and the local symmetry similar D_{4h} with eclipsed ligands conformation are like $[\text{Tc}_2\text{Cl}_8]^{3-}$ -which is the basic structural element of $\text{M}_3[\text{Tc}_2\text{Cl}_8] \cdot n\text{H}_2\text{O}$. The Tc formal oxidation state +2.5 and the Tc-Tc bond formal multiplicity 3.5 in these complexes are the same, and their magnetic properties are similar as well [3].

The electronic structure of these clusters was calculated earlier by the semi-empirical EHT method [3-4] and the non-empirical X_a -SW results for idealized D_{4h} $[\text{Tc}_2\text{Cl}_8]^{3-}$ complex were given in [5-6]. According to EHT the effective Tc charges in chloroacetate and octachloride clusters are almost equal: +1.13 and +1.06. However, the energy mixing of the Tc-Tc and Tc-L bonds π -parts is more vast in former cluster and the $\Delta\varepsilon$ ($\pi-\delta$) interval of Tc-Tc bond is less.

In this work we present the results of the more accurate $[\text{Tc}_2(\text{CH}_3\text{COO})_4\text{Cl}_2]^-$ and $[\text{Tc}_2\text{Cl}_8]^{3-}$ non-empirical X_a -DV calculation including crystal lattice electrostatic field by DVSCAT code [7] (see table below).

Some of the electron structure items	$\text{Tc}_2(\text{CH}_3\text{COO})_4\text{Cl}_2^-$	$\text{Tc}_2\text{Cl}_8^{3-}$
Atom charge for Tc; Cl; O	+1.13; -0.66; -0.61	+0.41; -0.48
Bond order for Tc-Tc; Tc-Cl; Tc-O	0.740; 0.307; 0.236	0.732; 0.481
Electron configuration of $\tilde{O}\tilde{n}$	$4d^{5.11} 5s^{0.32} 5p^{0.44}$	$4d^{5.37} 5s^{0.48} 5p^{0.73}$
{Tc4d Cl3p} band width, eV	5.06 (with O2p 9.38)	5.66
Occupied MO (energies from HOMO δ^* , eV)	$\sigma(1.74) \delta(1.82)$ Cl3p(2.07-3.20)	$\delta(0.77) \pi(1.78) \pi(1.91)$ Cl3p(2.1-3.0)
HOMO composition, % (Tc;Cl;O;C;H)/(Tc;Cl)	62; 0; 15; 11; 12	74; 26

The calculated ratio of Tc effective charges corresponds to the XPS data for core electrons [8]. The E (Tc2p_{5/2}) binding energy for chloroacetate complex 255.8eV is the same as for $[\text{Tc}_2\text{Cl}_8]^{2-}$, whereas for $[\text{Tc}_2\text{Cl}_8]^{3-}$ it is less by 0.3eV. The M-L bonds in former complex have more ionic character, however M-M bond strengths are equal, which correspond to M-M bond lengths. The calculated molecular structure of former cluster is actually M_2X_{10} , but not M_2X_8 , as it was in the halide complex. There is only one electron that occupies δ^* -type HOMO. HOMO composition confirms the earlier made conclusion [3-4] that magnetism of these compounds insignificantly depends on ligand nature. For chloroacetate complex the insensibility of EPR spectrum to the axial ligand replacement (Br instead Cl) is explained by

the non-sharing of a halogen orbital in HOMO. The EHT conclusions on the occupied boundary $\tilde{\Pi}$'s list have not been confirmed. There is no occupied MO of π type in the boundary area of the electronic structure of $\text{Tc}_2(\text{CH}_3\text{COO})_4\text{Cl}_2^-$. However there is σ -type level close to $\delta\text{-}\tilde{\Pi}$. Our results are strongly supported by the comparison of the computed electron density with XPS valence data (Fig. 2) (for the $[\text{Tc}_2(\text{CH}_3\text{COO})_4\text{Cl}_2]^-$ case we used the spectrum reported for the similar bromoacetate compound in [8]).

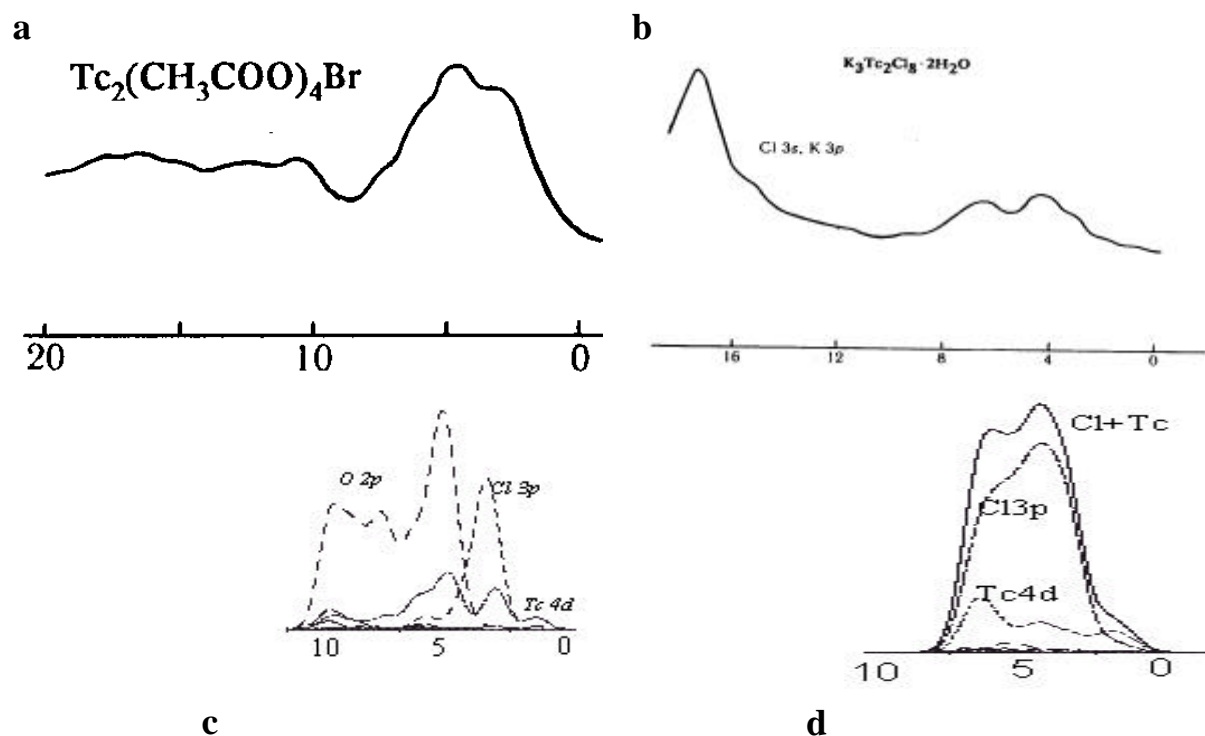


Fig.2. Experimental XPS [8] (a-b) and density of states (c-d)

This work was partially supported by the Russian Fund of Fundamental Researches (code 199-03-32642).

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