

## CRYSTAL AND ELECTRONIC STRUCTURES OF TECHNETIUM CARBONYL HALOGENIDES

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The majority of previously studied Tc carbonyls (except  $[\text{Tc}_2(\text{CO})_{10}]$ ) contained large organic ligands. During several last years a number of Tc(I) carbonylhalogenides without organic ligands have been synthesized in Khlopin Radium Institute. Some of them have been obtained in form of single crystals and studied by X-ray structural analysis. The aim of the present work is to report the results of new structural studies of Tc carbonylhalogenides and to compare their structures with those of similar compounds of some other transition elements.

### $[\text{Tc}(\text{CO})_5\text{I}]$

*Crystal data:* orthorhombic, space group  $Cmcm$ ,  $a = 7.621(3)$ ,  $b = 11.048(3)$ ,  $c = 10.812(4)$  Å (at  $-115^\circ\text{C}$ ),  $R = 0.021$ .

This complex with crystallographic  $C_2$  symmetry has interatomic distances Tc-I 2.807(1) Å, Tc-C 1.938(6) (in *trans*-position to I atom) and 2.015(3) Å (CO-groups in *trans*-position to each other). Two last distances differ significantly showing the *trans*-influence of CO-groups. The C-O distances for two types of CO-groups, 1.147(8) and 1.135(4) Å, are almost equal.  $[\text{Tc}(\text{CO})_5\text{I}]$  is isostructural with  $[\text{Mn}(\text{CO})_5\text{I}]$  [1], but  $[\text{Re}(\text{CO})_5\text{Cl}]$  and  $[\text{Re}(\text{CO})_5\text{Br}]$  have different crystal structure (space group  $Pnma$ ) [2,3].

### $[\text{Tc}(\text{CO})_4\text{I}]_2$

*Crystal data:* monoclinic, space group  $P2/c$ ,  $a = 10.048(2)$ ,  $b = 12.319(5)$ ,  $c = 13.200(3)$  Å,  $\beta = 108.04(2)^\circ$ ,  $R = 0.025$ .

This dimeric complex has average interatomic distance Tc-I 2.811 Å, Tc-C 1.91 (in *trans*-position to I atoms) and 2.00 Å (CO-groups in *trans*-position to each other). As in the previous case, *trans*-influence of CO-groups is significant.  $[\text{Tc}(\text{CO})_4\text{I}]_2$  is isostructural with all similar structurally studied complexes of Mn (with Cl [4], Br [5] and I [6]) or Re (with I [7]). The distortion of nearly square  $\text{M}_2\text{Hal}_2$  core (Hal-M-Hal angle) increases slightly but regularly from Cl to I for Mn compounds and from Re to Mn for iodide compounds.

It is interesting to note, that in spite of nearly equal ionic radii of Tc(I) and Mo(I), the structure of  $[\text{Mo}(\text{CO})_4\text{I}]_2$  [8] differs strongly from those of the above described dimeric complexes. The I-Mo-I angle is  $110.5^\circ$  compared with  $84.3^\circ$  for I-Tc-I in  $[\text{Tc}(\text{CO})_4\text{I}]_2$ . The origin of this difference lies in weak Mo-Mo bond due to odd number of electrons on Mo(I) atoms. The same behavior is typical for Cr(I) and W(I) dimeric carbonyls.