

**NOVEL WATER-SOLUBLE TECHNETIUM(I)
TRICARBONYLHYDROXYFLUORIDE**

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On heating a mixture of HCOOH, 45 % HF, and KTcO_4 in an autoclave at 200°C and 120-150 atm of CO new $[\text{Tc}_4(\text{CO})_{12}\text{F}_3\text{OH}]$ and known $[\text{Tc}_4(\text{CO})_4\text{OH}]_4$ [1] were formed. The ratio of these complexes depends on the HCOOH:HF ratio. The fluoride complex occurs in the mother liquor and technetiumtricarbonylhydroxide in the precipitate contaminated with TcO_2 by-product. No other carbonylfluoride complexes were obtained. The mother liquor was evaporated under reduced pressure. $[\text{Tc}_4(\text{CO})_{12}\text{F}_3\text{OH}]$ was isolated from the solid residue by vacuum sublimation.

$[\text{Tc}_4(\text{CO})_{12}\text{F}_3\text{OH}]$ is yellow air-stable crystals soluble in water and polar organic solvents. This compound sublimes in vacuum at 210-230°C with partial decomposition. The IR spectrum of $[\text{Tc}_4(\text{CO})_{12}\text{F}_3\text{OH}]$ in the carbonyl region contains two bands at 2048 cm^{-1} and 1930 cm^{-1} that is typical for $\text{Tc}(\text{CO})_3$ fac-configuration. There are two sharp bands at 3650 and 3620 cm^{-1} in the region of OH vibration. The composition of this compound was confirmed by elemental analysis for Tc and F.

As shown by powder X-ray diffraction, the crystal structure of $[\text{Tc}_4(\text{CO})_{12}\text{F}_3\text{OH}]$ considerably differs from that of $[\text{Tc}(\text{CO})_3\text{OH}]_4$ [1]. The single crystal X-ray study revealed that $[\text{Tc}_4(\text{CO})_{12}\text{F}_3\text{OH}]$ crystallized in the orthorhombic cell, space group Pnma, $a = 14.315(9)$, $b = 14.030(10)$, $c = 9.874(5)$ Å (at -125°C). The positions of F⁻ and OH⁻ ions in the cubane-like complex seem to be disordered. The main (average) interatomic distances are: Tc-(O, F) 2.20 Å, Tc-C 1.86 Å, C-O 1.17 Å, Tc...Tc 3.44 Å. The packing of the molecules in the crystal structure differs from that of $[\text{Tc}(\text{CO})_3\text{Cl}]_4$ and $[\text{Tc}(\text{CO})_3\text{Br}]_4$ [2] or $[\text{Tc}(\text{CO})_3\text{I}]_4$ [3], thus representing a new structural type for tetrameric cubane-like carbonyl complexes.

References

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