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# Preparation and Characterization of Tetraethylammonium Bis(1,2-dicyanoethylenedithiolato)oxotechnetate(V)

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Transition metals are known to form a series of bis, tris and tetrakis complexes with unsaturated 1,2-dithiolate ligands (1,2-dithiolenes) [1], but as far as we know no studies have been performed with technetium until now. Extending our investigations on the reaction of pertechnetate with thiols, we wish to report here our preliminary results of the preparation of a technetium complex with the unsaturated 1,2-dithiolate ligand 1,2-dicyanoethylenedithiolate (mnt$^{--}$).

## Experimental

Technetium(V) gluconate was prepared according to [2] by stepwise addition of a solution of 30 $\mu$mol stannous chloride in 1 ml of 0.1 *N* hydrochloric acid to a solution of 30 $\mu$mol $NH_4TcO_4$ and 80 mg Na gluconate in 2 ml of water. 100 mg tetraethylammonium bromide were added and a solution of 11.2 mg (60 $\mu$mol) $Na_2$mnt in 0.5 ml of water was dropped into the Tc gluconate solution under vigorous shaking. After 2 hours, the precipitate was collected, washed twice with water and recrystallized from ethanol/water to give brown cyrstals. M.Pt. 180–182 °C. Yield 13.2 mg (84%). *Anal.* Calculated for $C_{16}H_{20}N_5OS_4Tc$: C: 36.56%, H: 3.84%, N: 13.32%, S: 24.40%. Found: C: 36.81%, H: 3.94%, N: 13.33%, S: 24.50%.

## Results and Discussion

The complex was prepared by ligand exchange reaction starting from Tc(V) gluconate in high yield. This method is a convenient synthetic route to technetium complexes with mercapto compounds [3]. Because of the instability of the ligand, the alternative preparation by direct reduction of pertechnetate with an excess of the ligand in acidic solution is not applicable.

The analytical data show that the resulting compound (I) can be formulated as a tetraethylamonium salt of bis(1,2-dicyanoethylenedithiolato)oxotechnetate. The identification of the complex as an oxotechnetium species is confirmed by the presence in the infrared spectrum of an intense band assignable to Tc–O at 960 $\text{cm}^{-1}$ (further bands are assigned to C≡N (2210–20 $\text{cm}^{-1}$) and perturbed C=C (1520 $\text{cm}^{-1}$)). Its electronic spectrum has an intense band at 340 nm in $CH_2Cl_2$ solution. The formal oxidation number +V of Tc follows from the preparation route and the formula.

I obviously resembles the oxotechnetium complexes of saturated 1,2-dithiolate ligands recently described by DePamphilis *et al.* [4] and Smith *et al.* [5], and no traces of a tris complex could be obtained. This preferable formation of an oxo-complex with mnt$^{--}$ might be caused by the use of Tc gluconate as starting material and/or water as solvent. However, it is interesting to note that a corresponding oxo complex of the isoelectronic Mo(IV) is obtained as a by-product from the reaction of $MoCl_5$ with mnt$^{--}$ in ethanol [6].

Further studies on Tc dithiolene complexes are in progress.

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