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Synthesis and Characterization of a New Technetium Complex Tris(monothiodibenzoylmethanato)technetium(III)

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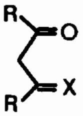
The widespread use of ^{99m}Tc radiopharmaceuticals has stimulated investigations in the field of the coordination chemistry of the long-lived radionuclide technetium-99 [1]. Despite the fact that in recent years an increasing number of technetium compounds has been prepared and characterized in order to obtain more knowledge of the basic chemistry of this element, little is known about complexes of technetium with 1,3-dicarbonyl ligands and their corresponding sulfur analogues.



X = O,S

Diketonato chelates of technetium have been described by Mazzi and co-workers [2], who synthesized pentane-2,4-dionato technetium complexes with one, two, or three molecules of ligand per atom of the metal.

Although monothio-β-diketones (X = S) are known to be good chelating agents for transition metals [3], the reaction of technetium with this class of ligands has not yet been taken into consideration. In the present paper we deal with our preliminary results on the preparation of a technetium chelate with the O,S donor ligand thiodibenzoylmethane (X = S, R = phenyl).

Experimental

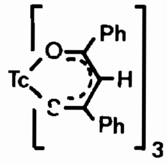
The technetium content was determined by neutron activation analysis as is described in [4].

Preparation of Tris(monothiodibenzoylmethanato)-technetium(III)

A mixture of 50 μmol hexakis(thioureato)technetium(III) trichloride [5] and 150 μmol of monothiodibenzoylmethane in 3 ml of methanol was heated under reflux. The dark red solution began to deposit a microcrystalline dark solid within one hour. After 3 h, the precipitate was collected, washed twice with methanol and air-dried. Yield: 33.9 mg (83%). Recrystallization from acetone/methanol give dark blue plates. M. Pt. 215–217 °C. *Anal.* Calculated for $C_{45}H_{33}O_3S_3Tc$: C: 66.16%; H: 4.07%; S: 11.77%; Tc: 12.12%. Found: C: 66.01%; H: 3.92%; S:12.37%; Tc: 12.31%. Optical spectrum (acetone) (in nm (lgε)): 670sh (3.85), 558(4.18), 500 broad (4.18). Infrared spectrum (KBr): 1535(s), 1470(s), 1430(s), 1340(m), 1270(s), 1190(m), 955(m), 770(s), 695(s) cm^{-1}.

Results and Discussion

Hexakis(thioureato)technetium(III) trichloride has proved to be a good starting material from which the Tc complex of monothiodibenzoylmethane could be obtained in a ligand exchange reaction in high yield. Due to its insolubility in methanol, the compound precipitates in pure form. The complex is stable in air, it is soluble in acetone, chloroform and ether and insoluble in alcohol and water. Reaction route and analytical data show that the resulting compound is a neutral Tc(III) tris-ligand complex. In the solid state the infrared spectrum of the complex is a bathochromic shift of the C=O vibration compared to the disulfide of monothiodibenzoylmethane, which as standard for the non-coordinated carbonyl group has a vibration of 1638 cm^{-1} [6]. This indicates that the ligand is coordinated via both the sulfur and oxygen ligator atoms.



Further support of the structure is given by ^1H NMR spectral data. The paramagnetic Tc(III) gives rise to a high splitting of the ligand protons. The phenyl protons of the free ligand show a multiplet with the centre at 7.8 ppm whereas in both phenyl rings of the complex the *ortho*- and *para*-protons are low-field shifted and the *meta* protons are high-field shifted. All peaks belonging to ring A are at lower fields than the corresponding peaks of ring B. Attempts to assign the positions of the rings to be adjacent to the sulfur or to the oxygen atom, *e.g.* by comparing the NMR spectrum with that of the Tc complex of the isomeric ligand α-phenyl-β-mercaptocinnamyl aldehyde, could not be made with certainty. The intensity of the chelate ring proton signal confirms the statement that the ligand is coordinated in its deprotonated form. The very large high-field

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TABLE I. ^{1}H NMR Spectral Data.[a]

δ (ppm)	Rel. intensity	Assignments
15.58 (d)	2	*o*-position ring A
11.83 (t)	1	*p*-position ring A
6.02 (t)	2	*m*-position ring A
9.50 (broad)	2	*o*-position ring B
8.47 (t)	1	*p*-position ring B
5.74 (d)	2	*m*-position ring B
−12.85(s)	1	α-H

[a] The spectrum was measured in acetone-d_6. s = singlet, d = doublet, t = triplet.

shift is quite different from that of Tc(acac)$_3$, whose α-H signal has been found at 7.43 ppm [7]. From the well resolved spectrum and the sharpness of the lines it is likely that the structure of the complex has high symmetry and should be rather rigid.

Acknowledgements

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