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Oxotechnetium(V)bis(dithiolato) Complexes

HARTMUT SPIES and BERND JOHANNSEN

Central Institute of Nuclear Research, Rossendorf, 8051 Dresden, PSF 19, G.D.R.

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A series of ten bis(dithiolato)oxotechnetate(V) complexes has been prepared using ligand exchange reaction. Starting from Tc(V)gluconate in aqueous or aqueous/ethanolic solution, complexes with saturated, olefinic and aromatic dithioles have been obtained. Mass, infrared, n.m.r., and UV–visible data of the resulting compounds are reported.

Introduction

Because of increasing interest in obtaining definite technetium compounds of known structure for fundamental pharmacological studies, we are engaged in the synthesis, characterization and structure-pharmacokinetics studies of technetium thiolato complexes.

Despite the fact that Tc thiole compounds are used for analytical purposes, synthetic methods for the preparation of Tc thiolato complexes have scarcely been published so far. Preparations using stannous chloride as a reducing agent yield compounds at different oxidation states of technetium. More successful are methods using sodium borohydride [1] and thioglycolic acid [2] as reducing agents. An alternative route is based on the ligand exchange reaction of Tc(V) gluconate with thiols [3, 4]. Until now, some complexes of the type bis(dithiolato)oxotechnetate(V) with saturated dithiols [1, 5, 6], mercaptoacetic acid [2], and the unsaturated 1,2-dithiole maleonitrile dithiole [7] could be prepared.

In this paper we describe a series of bis(dithiolato)oxotechnetate(V) complexes with aliphatic, olefinic, and aromatic dithiols synthesized by the method of exchange reaction of Tc(V) gluconate with dithiole ligands. The compounds were characterized by chemical analysis, infrared and mass spectra.

Experimental

Preparations

All compounds were prepared by ligand exchange reaction starting from Tc(V) gluconate as described in [7].

Tetraethylammonium bis(toluene-3.4-dithiolato)oxotechnetate(V) (*9*) was also prepared by the reaction of pertechnetate with toluene-3.4-dithiole in the following manner:
250 μmol of toluene-3.4-dithiole in 2 ml 0.1 N ethanolic hydrochloric acid were added to a solution of 50 μmol of NH_4TcO_4 in 0.5 ml of the same solvent. After one hour 15 mg of tetraethylammonium bromide in 0.5 ml ethanol were added to form a brown precipitate, which was collected, dissolved in acetone and reprecipitated with ether. The brown solid was crystallized from acetone/methanol to give 12.4 mg (22.5 μmol, 45% yield) redbrown crystals, M.Pt.225–227 °C.

Tetraphenylarsonium bis(ethane-1.2-dithiolato)oxotechnetate(V) was prepared in the same way as the tetraethylammonium salt (*1*), except that tetraphenylarsonium chloride was used instead of tetraethylammonium bromide. After crystallization from methanol red crystals of M.Pt. 233–235 °C were obtained (yield 20%, M.Pt. found in [5]: 230–235 °C).

Physical Measurements

Measurements of mass spectra were carried out by the electron attachment method [8]. Infrared spectra were recorded on a UR 20 spectrometer, uv–visible spectra on a Beckmann-DK-2A spectrometer. ^1H n.m.r. spectra were measured on a spectrometer WH 90 DS (Brucker Spectrospin). Molar conductivities were estimated in acetonitrile/water (4:1).

Results and Discussion

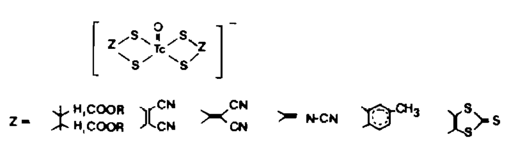
In aqueous gluconic acid solution pertechnetate can be reduced by stannous chloride to the oxidation state +V. Although the composition of the resulting Tc(V) gluconate has remained unknown until now, it has been found to be a useful starting material for the synthesis of Tc(V) dithiolato complexes. According to the reaction scheme

$$TcO_4^- \xrightarrow{Sn^{2+}/\text{gluconic acid}} \text{Tc(V) gluconate}$$

$$\text{Tc(V) gluconate} + 2\,H_2L \longrightarrow [TcOL_2^-] + \text{gluconic acid}$$

(H_2L = dithiole ligand),

Tc(V) gluconate is completely converted into a dithiolato complex by addition of two mol of dithioles. The colour of the reaction mixture becomes red-yellow, due to the rapid formation of Tc dithiolato complexes (*1–10*) which were isolated in the form of its tetraethylammonium salts. Experimental and analytical data are summarized in Table I.



1–4 5 6,7 8 9 10

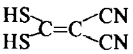
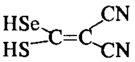
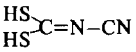
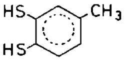
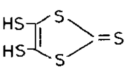
The toluene-3.4-dithiolato complex (*9*) could also be prepared by reduction of pertechnetate with the ligand itself in acidic ethanolic solution. The products obtained with both methods were found to be identical. The tetraphenylarsonium bis(ethane-1.2-dithiolato)oxotechnetate(V) described above [1, 5] was also prepared by our method. All crystalline complexes are soluble in methylene chloride and acetone, weakly soluble in alcohols and insoluble in nonpolar solvents. They are indefinitely stable in air. The compounds are diamagnetic in solution (no e.s.r. signals) as expected for Tc(V) in low spin d^2 configuration. Analytical data as well as infrared, ^{1}H n.m.r. and mass spectra, which will be discussed below, confirm that the complexes are tetraethylammonium salts of bis(dithiolato)oxotechnetate(V) complexes in accordance with results published previously [1, 2, 5–7].

As can be seen from Table I, complexes of this type are formed with saturated, olefinic, and aromatic 1.2-dithioles as well as olefinic 1.1-dithioles, the latter forming four membered chelate rings with the metal. A first example of a complex in which the Tc is coordinated to sulphur and selenium occurs in compound *7*.

Mass Spectra

Mass spectra of compound *5* with an olefinic ligand, and of compound *9* with an aromatic ligand were recorded. The electron attachment spectra of both compounds have an intensive peak corresponding to the complex anion (m/z 395 in the spectrum

TABLE I. Yields, Melting Points and Analytical Data of Complexes $[TcOL_2]^-$ (tetraethylammonium salts).

Compound	Ligand H_2L	Yield [%]	M.Pt. [°C] (solvent[a])	Formula	Analytical data (%) (found/calc.) C	H	N	S
1	$HS{-}CH_2$ $HS\ CH_2$	20	180–183 (methanol)	$C_{12}H_{28}NOS_4Tc$	34.09 33.55	6.87 6.57	3.07 3.26	– 29.85
2	$HS{-}CH{-}COOH$ $HS{-}CH{-}COOH$ (racemic)	28	200–204 (nitromcthanc)	$C_{16}H_{28}NO_9S_4Tc$	31.50 31.73	4.42 4.66	1.66 2.31	21.10 21.18
3	$HS{-}CH{-}COOCH_3$ $HS{-}CH{-}COOCH_3$ (meso)	60	170–171 (methanol)	$C_{20}H_{36}NO_9S_4Tc$	36.91 36.30	5.75 5.48	2.35 2.12	19.23 19.38
4	$HS{-}CH{-}COOCH_3$ $HS{-}CH{-}COOCH_3$ (racemic)	54	154–155 (methanol)	$C_{20}H_{36}NO_9S_4Tc$	36.45 36.30	5.53 5.48	1.45 2.12	19.48 19.38
5	$HS{-}C{-}CN$ $HS{-}C{-}CN$	84	180–182 (ethanol/water)	$C_{16}H_{20}N_5OS_4Tc$	36.81 36.56	3.94 3.84	13.33 13.32	24.50 24.40
6	 $(HS)_2C{=}C(CN)_2$	84	158–160 (ethanol)	$C_{16}H_{20}N_5OS_4Tc$	36.12 36.56	4.22 3.84	12.47 13.32	24.60 24.40
7	 $(HSe)(HS)C{=}C(CN)_2$	52	152–154 (ethanol)	$C_{16}H_{20}N_5OS_2Se_2Tc$	30.73 31.02	3.33 3.25	10.95 11.31	
8	 $(HS)_2C{=}N{-}CN$	39	96–98 (ethanol)	$C_{12}H_{20}N_5OS_4Tc$				
9		64	225–227 (ethanol)	$C_{22}H_{32}NOS_4Tc$	48.00 47.72	5.47 5.82	1.72 2.53	23.07 23.16
10		35	196–203 (methylene chloride/ iso-propanol)	$C_{14}H_{20}NOS_{10}Tc$	25.94 26.36	3.00 3.16	1.78 2.20	49.10 50.26

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[a] Solvent used for crystallization.

of *5*, m/z 423 in the spectrum of *9*). The fragmentation spectra show peaks at m/z 211, 179, 147, which belong to $TcOS_n^-$ (n = 3, 2, 1), and peaks assigned to ligand fragmentation (m/z 140 ($S_2C{=}C(CN)_2^-$) and 108 ($SC{=}C(CN)_2^-$) in the spectrum of *5*, m/z 154 ($S_2C_6H_3CH_3^-$) and 123 ($SC_6H_4CH_3^-$) in the spectrum of *9*, due to the cleavage of Tc–S and C–S bonds. The spectra are in agreement with the formulae and will be discussed in detail elsewhere.

Infrared Spectra

Tc=O stretching frequencies and ligand bands are summarized in Table II. The solid state spectra of all complexes have single bands in the 930–980 cm^{-1} region. This band is assigned to $\nu_{(Tc=O)}$, because Mo=O vibrations in isoelectronic bis(dithiolato)-oxomolybdenum(IV) complexes [9] are in the 900–920 cm^{-1} region, and Tc=O vibrations in bis-(ethane-1.2-dithiolato)oxotechnetate(V) [5] and in bis(thiomercaptoacetato)oxotechnetate(V) [2] are found at 940 cm^{-1} and 950 cm^{-1}, respectively. In accordance with these data, complexes with saturated ligands (*1–4*) absorb in the 940–955 cm^{-1} region. In complexes with olefinic ligands (*5–8*), the Tc=O vibration is shifted to the 960–980 cm^{-1} region, a fact obviously caused by an increase of the bond order of the Tc=O group by electron-withdrawing substituents. Consistent with this result is the high value of the Tc=O vibration of 1020 cm^{-1} found in tetra-n-butylammonium oxochlorotechnetium(V) [10]. The Tc=O absorptions in complexes with more electron-releasing aromatic dithiole ligands (*9, 10*) are found to occur at 930 and 935 cm^{-1}. Additional bands are assigned to ligand groups (C=O, C≡N). The absence of SH absorptions confirms the complete binding of dithiole.

^{1}H N.m.r. Spectra

Further support of the structure is given by ^{1}H n.m.r. spectral data (Table III) of compounds *3* and *9*. Both substances show a triplet and a quartet in a ratio of 3:2, which belong to the ethyl group of the tetraethylammonium cation. The two singlets (1:3) in compound *3* are assigned to ligand S–CH protons and O–CH_3 protons. In compound *9*, two additional signals (1:1) are observed. The multiplet in the region of 6.8 to 7.3 ppm is assigned to the aromatic protons in 2-, 5- and 6-position of tolyl ring, and the singlet corresponds to the methyl group.

TABLE III. ^{1}H N.m.r. Spectral Data for Complexes $[TcOL_2]^-$ (tetraethylammonium salts) with H_2L = Meso-2.3-dimercaptosuccinic Acid Dimethylester *3* and H_2L = Toluendithiol *9*^{a}.

Compound	Protons	δ [ppm]
3	S–CH	4.4 (s)
	O–CH_3	3.6 (s)
	N–CH_2–CH_3	3.2 (q)
	N–CH_2–CH_3	1.2 (t)
9	CH (arom.)	6.8–7.3 (m)
	CH_3	2.2 (s)
	N–CH_2–CH_3	2.6 (q)
	N–CH_2–CH_3	0.8 (t)

^{a}The spectra were measured in CD_2Cl_2. s = singlet, t = triplet, q = quartet, m = multiplet.

UV–Visible Spectra

The spectra of all complexes are characterized by an intensive band in the 360–420 nm region (peak positions and molar absorptivities are given in Table II) and by one or more absorptions at shorter wavelengths. The first intensive band is found to absorb at shorter wavelengths in complexes with unsaturated ligands than in complexes with saturated dithioles. In all dithiolene complexes a second intensive band is observed at 260–270 nm despite the different nature of the chromophoric system of the ligand. The data

TABLE II. Infrared Data and First Intensive Band in UV–Visible Spectra of Complexes $[TcOL_2]^-$ (tetraethylammonium salts).

Compound	Infrared^a		First intensive band in UV–visible spectra^b
	ν(Tc=O)	Ligand bands	
1	940		400 (3.65)
2	955	1690 C=O, strong	398 (3.63)
3	940	1730 C=O, strong	403 (3.48) 425 sh
4	950	1730 C=O, strong	406 (3.50)
5	960	2210–20 C≡N, strong	338 (4.36)
6	980	2225 C≡N, strong	350 (4.78)
7	970	2220 C≡N, strong	350 (4.79)
8	980	2195 C≡N, strong	365 (4.42)
9	935		360 (4.09)
10	930	1070 C=S, strong	365 (4.05)

^{a}KBr pellets with values in cm^{-1}. ^{b}Peak positions in nm with lg molar absorptivities in parenthesis, compound dissolved in ethanol.

are provided only as an aid to future characterization, and no attempt has been made to assign the various transitions.

Molar Conductivities

The molar conductivities of two samples are 132 cm^2 ohm^{-1} mol^{-1} (compound *3*) and 118 cm^2 ohm^{-1} mol^{-1} (compound *9*). Tetraethylammonium bromide was found to have a value of 122 cm^2 ohm^{-1} mol^{-1} under the same conditions. As expected for 1:1 electrolytes, the slope of conductivity *versus* the square root of concentration is small.

Conclusions

The reported reaction of dithioles with Tc(V) gluconate is a convenient method of preparing five-coordinated bis(dithiolato)oxotechnetium(V) complexes. The synthesis of this type of complexes with different dithiole ligands also demonstrates the ability of technetium to form thiole complexes, the preferable oxidation state is +V. One of our compounds (*1*) proved to have been described by Byrne and Smith [5] in the form of its tetraphenylarsonium salt. This compound has a square-pyramidale structure [1]. We assume that the complexes have the same structure, at least the analogous compounds with saturated ligands.

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