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Lipophilic Technetium Complexes. Part I. Dithiocarbamato Complexes of Technetium(III) and -(V)

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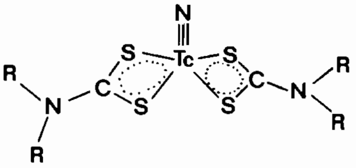
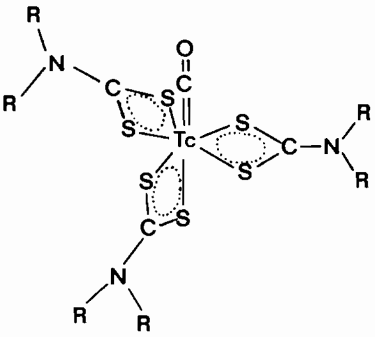
In recent years great interest has been shown in neutral, lipid-soluble technetium complexes for use in nuclear medicine. Therefore we prepared a series of dithiocarbamato complexes of the long living isotope ^{99}Tc (half life time: 2.12 X 10^5 years) using different alkylsubstituted ligands. In order to isolate the Nitridobis(dialkyldithiocarbamato)technetium(V) complexes (I) and Carbonyltris(dialkyldithiocarbammato)technetium(III) (II) the reduction was carried out by hydrazine and formamidine sulphinic acid ($NH_2(NH))CSO_2H$), respectively [1–3].



I



II

We report both chemical behaviour and infrared-, nmr- and UV/visible data of the prepared compounds. This is the first report dealing with a consistent row of technetium complexes with dialkyl-varied dithiocarbamates.

Experimental

The syntheses of the used ligands were carried out by literature methods [4, 5]. The technetium complexes were synthesized as described for bis(diethyldithiocarbamato)nitridotechnetium(V) [1, 2] and carbonyltris(diethyldithiocarbamatotechnetium-(III) [3]. Typical preparations were carried out in a 50 µmol scale.

Infrared spectra were recorded in KBr pellets with an UR 20-instrument and the UV/visible spectra with a Specord M 40 of Carl-Zeiss-Jena. ^{1}H nmr measurements were carried out using a WX 90 DS (Bruker Spectrospin).

Results and Discussion

The yields and analytical data of the investigated complexes are summarized in Table I. The nitrido complexes of the more stable ligands (R = ethyl, i-propyl) can be prepared in high yields directly from hydrazine-reduced pertechnetate according to the method of Baldas and co-workers [1]. For the more sensitive ligands (R = n-butyl, i-butyl, $-(CH_2)_5-$, $-(CH_2)_2-O-(CH_2)_2-$) the ligand exchange reaction starting from $TcNCl_2(Ph_3P)_2$ [2] yields better results. The reduction using formamidine sulphinic acid gives in all cases the appropriate carbonyl complexes in good yields [3].

The melting points were determined by fast heating of the complexes. For all compounds after careful heating considerable decomposition commenced at temperatures below their melting points.

Compounds 4 and 9 only could be isolated as oils, but their elemental analyses, nmr spectra, electronic spectra and chemical behaviour confirm their nature as the declared complexes.

All compounds are soluble in chloroform and acetone, weakly soluble in alcohols and insoluble in ether and hydrocarbons. They are indefinitely stable in air.

Infrared and UV/Visible Spectra

Typical infrared bands and the first intensive band in the electronic spectra of the complexes are given in Table II. In addition to the ligand frequencies the nitrido complexes 2, 3, 5 and 6 show a new intensive band in the 1050–1100 cm^{-1} region. This can be assigned to Tc≡N- bonding because the same type of rhenium compounds show Re≡N stretching frequencies from 1000 to 1100 cm^{-1} [6]. The IR spectrum of 1 does not show such a new intensive band in the considered frequency range, but we can observe a higher intensity of the ligand band at 1076 cm^{-1}. Providing that this increase in the intensity is caused by superimposition of nitrido

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TABLE I.

Yields and Analytical Data of the Prepared Complexes $TcN(S_2CNR^1R^2)_2$ and $TcCO(S_2CNR^1R^2)_3$.

Compound	R^1	R^2	Yield % (prep. method)	M.Pt. °C	Analytical data % (found/calc.)			
					C	H	N	S
$TcN(S_2CNR^1R^2)_2$								
1	ethyl	ethyl	80 a	256–8	29.41	4.85	10.15	24.23
			85 b		29.34	4.89	10.27	24.20
2	i-propyl	i-propyl	75 a	324–6	36.47	6.04	9.04	26.97
			70 b		36.13	6.13	9.03	27.54
3	n-butyl	n-butyl	10 a	95–7	43.17	7.29	7.38	24.73
			55 b		41.45	6.91	8.06	24.57
4	i-butyl	i-butyl	15 a		42.80	7.31	7.52	25.03
			60 b	c	41.45	6.91	8.06	24.57
5	$-(CH_2)_5-$		35 a	314–6	31.98	4.07	9.15	29.03
			80 b		33.25	4.62	9.69	29.55
6	$-(CH_2)_2-O-(CH_2)_2-$		30 a	306–9	28.02	3.79	9.03	29.32
			70 b		27.46	3.66	9.61	29.29
$TcCO(S_2CNR^1R^2)_3$								
7	ethyl	ethyl	40	187	33.74	4.73	7.13	33.41
					33.74	5.27	7.55	33.74
8	i-propyl	i-propyl	45	208–10	41.14	6.65	5.83	28.55
					40.36	6.41	6.41	29.31
9	n-butyl	n-butyl	35	c	47.13	7.92	5.01	26.37
					45.47	7.44	5.68	25.98
10	i-butyl	i-butyl	40	139–43	46.30	7.78	5.27	25.73
					45.47	7.44	5.68	25.98
11	$-(CH_2)_5-$		55	271–3	38.33	4.57	6.32	31.69
					37.56	4.96	6.92	31.63
12	$-(CH_2)_2-O-(CH_2)_2-$		45	149–52	31.14	3.97	6.56	30.12
					31.32	3.92	6.85	31.32

[a]Preparation according to [1]. [b]Preparation according to [2]. [c]Isolated as oil only.

and ligand bands the band at 1076 cm^{-1} can be assigned to the $Tc{\equiv}N$-frequency too.

The intensive bands at about 1900 cm^{-1} in the IR spectra of the carbonyltris(dialkyldithiocarbamato)-technetium(III) complexes can be assigned to the CO stretching frequencies. Their low values as well as those of the analogous rhenium complexes [7] represent a relatively weak CO bond order (ν_{CO} in the free carbon monoxide: 2143 cm^{-1}) and hence indicate strong metal–carbonyl bondings. The influence of steric effects on the carbonyl stretching frequencies is not significant. The failure of ligand exchange reactions with other π-acceptor ligands confirms the inertness of the Tc–carbonyl bondings.

The $C\overset{\cdot\cdot\cdot}{-}N$ frequencies in the spectra of the carbonyl complexes show a bathochromic shift to those in the spectra of the corresponding nitrido complexes. This is also in accordance with the stronger acceptor behaviour of the carbonyl ligand compared with those of the nitrido nitrogen.

The UV/visible spectra of the nitrido as well as the carbonyl compounds are characterized by an intensive band at about 370 nm and about 400 nm, respectively. As expected, a change of the substituent R in the chelate molecules does not effect a change in the chromophoric system of the compounds. The data are provided as an aid to further characterization only, and no attempts have been made to assign the transitions.

^1H Nmr Spectra

Further support of the structure of the prepared chelates is given by ^1H nmr data (Table III).

Number and multiplicity of the measured signals are in accordance with the stated formulae. Their line widths (about 3 Hz) suggest the compounds to be

TABLE II.

Typical Infrared Frequencies (in cm^{-1}) and UV/visible Data (in nm (lgε)).

Compound	Tc≡N	Carbonyl	C=N	First intensive band in the electronic spectrum
1	1076^a		1534	368 (2.89)
2	1083		1512	369 (2.88)
3	1065		1519	368 (2.80)
4	b		b	368 (2.79)
5	1072		1515	367 (2.78)
6	1079		1520	369 (2.81)
7		1900	1521	393 (3.66)
8		1898	1494	396 (3.77)
9		b	b	395 (3.53)
10		1895	1505	394 (3.71)
11		1891	1505	395 (3.71)
12		1907	1508	400 (3.65)

^{a}Superimposition with ligand frequency. ^{b}Not measured.

diamagnetic, as expected for seven coordinated Tc(III)- and square-pyramidal Tc(V) complexes, respectively [8]. The downfield shift of the ^{1}H nmr signals of the nitrido–Tc(V) species in comparison with the corresponding carbonyl–Tc(III) complexes (up to 0.14 ppm) indicates a weaker shielding of the alkyl protons in the square-pyramidal complexes.

Chemical Behaviour

All described complex compounds are indefinitely stable in air. Even solutions can be stored under aerobic conditions for some weeks.

Attempts to substitute the carbonyl ligand in the Tc(III) complexes by other acceptor ligands failed. After refluxing for 24 hours with triphenylphosphine and triphenylarsine, respectively, only the starting materials could be recovered.

The technetium(V)–nitrido complexes are oxidizable by bromine to yield Tc(VI) species. After addition of adequate amounts of bromine in chloroform solution the yellow colour of the bis(dialkyldithiocarbamato)nitridotechnetium(V) chelates changes to deep green and after standing for some hours a brownish colour is detectable. This reaction can be monitored by the EPR technique, because the resulting Tc(VI) species give room temperature EPR signals according to the d^1 configuration of this rare oxidation rate of technetium.

The course of the oxidation and the nature of the resulting paramagnetic products will be discussed in detail and described elsewhere [9].

TABLE III.

^{1}H Nmr Spectral Data Measured in $CDCl_3$ (chemical shift in ppm relatively to TMS)^a.

Compound	CH_3	C-CH_2	N-CH_2	Others	Compound	CH_3	C-CH_2	N-CH_2	Others
1	1.34 t (3 H)		3.87 qu (2 H)		7	1.29 t (3 H)		3.76 qu (2 H)	
2	1.51 d (6 H)			4.77 m (CH) (1 H)	8	1.47 d (6 H)			4.67 m (CH) (1 H)
3	1.01 t (3 H)	1.42 m (4 H)	3.72 t (2 H)		9	0.95 t (3 H)	1.33 m (4 H)	3.68 t (2 H)	
4	0.93 d (6 H)		3.68 d (2 H)	2.32 m (CH) (1 H)	10	0.91 d (6 H)		3.64 d (2 H)	2.27 m (CH) (1 H)
5		1.75 m (6 H)	3.99 m (4 H)		11		1.70 m (6 H)	3.85 m (4 H)	
6				3.83 m (CH_2)	12				3.81 m (CH_2)

^{a}d = doublet, t = triplet, qu = quartet, m = multiplet.

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