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The Synthesis and Characterisation of the Trichloronitrosyl(acetylacetonato)-technetium(II) Anion, a Novel Technetium(II) Complex

D. S. BROWN, J. L. NEWMAN, J. R. THORNBACK*

Department of Chemistry, Loughborough University of Technology, Ashby Road, Loughborough, Leics. LE11 3TU, U.K.

R. M. PEARLSTEIN, A. DAVISON

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

and A. LAWSON

M. R. C. Clinical Research Centre, Norwick Park Hospital, Harrow, Middlesex, U.K.

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Abstract

The reaction of $[TcNOCl_4]^-$ with acetylacetone was found to give the complex $[TcNO(acac)Cl_3]^-$. This complex has been fully characterised by X-ray crystallography and FAB$^-$ Mass spectrometry. The former shows that one of the oxygens of the acac is *trans* to the nitrosyl which is essentially linear, although disorder in the crystal prohibits accurate measurements of the bond angle. The latter shows facile loss of a single chlorine which suggests that ligand exchange of this may be facile. The ESR spectrum at room temperature shows the expected 10 lines due to splitting by the technetium. At −196 °C the spectrum may be modelled as having three g values, $g_x = 2.0107$, $g_y = 2.02225$ and $g_z = 1.9460$.

Introduction

The chemistry of technetium is of continued interest since the radionuclide $^{99m}Tc(t_{1/2} = 6.02\ h)$ is the major isotope used in diagnostic nuclear medicine. To isolate identifiable amounts of new complexes it is necessary to use the long lived isotope $^{99}Tc(t_{1/2} = 2.1 \times 10^5\ y)$. Although the initial radiopharmaceuticals prepared were principally technetium(V) and technetium(IV) complexes [1], with the development of the $^{99m}Tc(RNC)_6^+$ (R = alkyl) compounds [2], which have found use in the diagnosis of myocardial ischaemia, synthetic routes to new technetium(I) and technetium(II) complexes are of importance.

Recently we reported the preparation [3] and X-ray structure [4] of the complex $[Tc(NO)Cl_4(MeOH)]^-$. This technetium(II) complex is an ideal starting material for the synthesis of a range of technetium(I) and technetium(II) novel complexes, which may have application as radiopharmaceuticals. In this study we report the preparation and characterisation of the first of these, $[Tc(NO)(acac)Cl_3]^-$ (acac = acetylacetonato) which was isolated as its tetraphenylarsonium salt.

Experimental

$NH_4{}^{99}TcO_4$, as an aqueous solution, was obtained as a gift from Amersham International plc. Vibrational spectra were obtained using a Perkin-Elmer 257 spectrometer with the material dispersed in a KBr disc. FAB$^-$ mass spectra were observed using a Varian Mat731 spectrometer operating at 10 kV. The matrix employed was thioglycerol/erythreitol/dithioerythreitol. Electrophoresis experiments were carried out using a Shandon Southern 602 chamber with a Volkam 400/100 power pack. Whatman 3MM paper strips 25 cm long and pH 7 phosphate buffer were used and the experiment was run for 2 h at 300 V. The single crystal X-ray structure determination was carried out using a Stoë Weissenberg diffractometer and is described fully elsewhere [5].

The ESR spectra were observed using a Varian E-line X band spectrometer with an E-9 magnet, E-234 cavity and E-101 microwave bridge. The samples were dissolved in ethanol and placed in a 5 mm OD quartz tube. All measurements were relative to a DPPH standard. The simulation of the low temperature spectrum was carried out using the POWDER programme [6].

Reactions which required heating were performed in sealed 20 ml glass vials in a Gallenkamp AUX200G portable autoclave.

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*Author to whom correspondence should be addressed. Present address: Harvard Medical School, 50 Binney Street, Boston, Mass. 02115, U.S.A.

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Preparation of the Trichloronitrosyl(acetylacetonato)-technetium(II) Anion

To an aqueous solution of NH_4TcO_4 (1 ml, 0.15 mM) was added conc. HCl (1 ml) and the mixture was heated for 30 min. The resulting solution was cooled, diluted with water (1 ml), mixed with a solution of hydroxylamine hydrochloride in water (1 ml, 2.3 M), and heated for a further 30 min. The resulting green solution contains the species $[TcNOCl_4X]^{n-}$ ($X = Cl^-$, H_2O). To this solution was added acetylacetone (0.5 ml, 5 mmol), and the solution was heated for another 30 min. From the red solution produced the desired product was extracted into CH_2Cl_2 (10 ml) leaving the unreacted $[TcNOCl_4X]^{n-}$ in the aqueous phase. Evaporation of the CH_2Cl_2 layer gave a red oily residue which was redissolved in 5 ml of methanol/water (80:20). Addition of tetraphenylarsonium chloride (0.02 g in 1 ml of methanol) followed by evaporation of the solution to low volume gave a red precipitate. Recrystallisation of this red solid from methanol/water gave kite shaped plates suitable for X-ray analysis.

Anal.: Found (calc. for $C_{29}H_{27}NO_3Cl_3TcAs$): C, 48.81(48.50); H, 3.79(3.76); N, 1.89(1.95)%. IR (KBr disc): 1770(s), 1570(m), 1520(m), 1480(m), 1435(m), 1365(m), 1275(m), 1180(m), 1160(m), 1080(m), 1020(w), 995(m), 930(w), 895(m), 845(w), 785(w), 740(s), 685(s), 475(sh), 450(m), 320(m) cm^{-1}. FAB-MS$^-$; m/z 333 (calc. for $C_5H_7NO_3Cl_3Tc$ m/z 333). Crystal structure: $[(C_6H_5)_4As][Tc(NO)Cl_3(C_5H_7O_2)]$ $M_r = 717.5$, triclinic, $P\bar{1}$, $a = 10.261(4)$, $b = 11.261(10)$, $c = 13.686(10)$ Å, $\alpha = 101.7(5)$, $\beta = 91.9(5)$, $\gamma = 97.3(5)°$, $V = 1532.93$ Å^3, $Z = 2$, $D = 1.554$ g cm^{-3}, (Mo K) = 0.71069 Å, $\mu = 18.17$ cm^{-1}, $F(000) = 717.87$, $T = 293$ K, $R = 0.073$ for 2008 observed reflections with $I > 3\sigma(I)$.

Results and Discussion

The reduction of TcO_4^- by conc. HCl gives $TcCl_6^{2-}$ or $TcOCl_4^-$ depending upon the conditions [7]. Under those employed here $TcCl_6^{2-}$ is produced. The reaction of $TcCl_6^{2-}$ with NH_2OH gives a quantitative yield of $[TcNOCl_4X]^{n-}$ where X is either Cl^- or H_2O [3]. This former complex was synthesised as an intermediate by Taube and Armstrong in the synthesis of $[TcNO(NH_3)_4(H_2O)]^{2+}$ [8]. Attempts by both us and the previous workers have failed to yield identifiable products when the latter complex is reacted with a wide range of ligands. However, the green intermediate product is highly reactive and even in solutions with high chloride ion concentration it is possible to replace some if not all of the coordinated chlorine atoms by other ligands. With π acid ligands such as bipyridyl and 1,10-phenanthroline the complexes formed are technetium(I) species, while with acetylacetone the technetium(II) oxidation state is maintained. The product isolated by Taube and Armstrong can in this context be seen as anomalous. The technetium(I) complexes referred to will be reported in subsequent papers. In this preliminary report the synthesis and identification of the parent of a series of possible acetylacetonato derivatives, $[TcNO(acac)Cl_3]^-$ is discussed.

The preparation of acetylacetonato containing technetium complexes has been noted previously. Mazzi *et al.* reacted TcX_6^{2-} and $TcX_4(PPh_3)_2$ ($X = Cl^-$, Br^-) with acacH and isolated a series of species including $[TcCl_4(acac)]^-$ and other technetium(IV) containing species with mixtures of chloride, PPh_3 and acetylacetonato ligands [9]. Interestingly the technetium(III) complex $TcX(acac)_2(PPh_3)$ and $TcX_2(acac)(PPh_3)_2$ were also isolated depending upon the conditions employed [10]. Davison *et al.* isolated $Tc(acac)_3$ directly from pertechnetate reduction by sodium dithionite [11]. The complex $[TcNO(acac)Cl_3]^-$ is the first example of a technetium(II) acetylacetonato complex, the lower oxidation state being stabilised by the presence of the nitrosyl group. The IR spectrum of the complex has a strong absorption at 1770 cm^{-1} typical of the ν(NO) stretching vibration for linear nitrosyls, which may be considered as NO^+. The similar absorption in $[TcNOCl_4X]^{n-}$ varies between 1805 and 1795 cm^{-1} depending upon the nature of the *trans* ligand, X [3].

The X-ray data of the triclinic crystal show that the trichloro(acetylacetonato)nitrosyltechnetium(II) anion has a distorted octahedral geometry with two chlorides mutually *trans* and the other chloride and the nitrosyl occupying disordered positions *trans* to the chemically equivalent oxygens of the pentane-2,4-dionate ligand (Fig. 1).

The analysis of the data proved a nonroutine problem because of the disorder. The two positions *trans* to the oxygens of the pentane-2,4-dionato ligand have random occupancy of chlorine and nitrosyl. As chlorine and nitrosyl have a similar number of electrons differentiation was not possible from the initial Fourier map. However, the positions of the individual atoms were eventually determined through careful analysis of difference maps and the atoms refined isotropically with occupancy factors of 0.5.

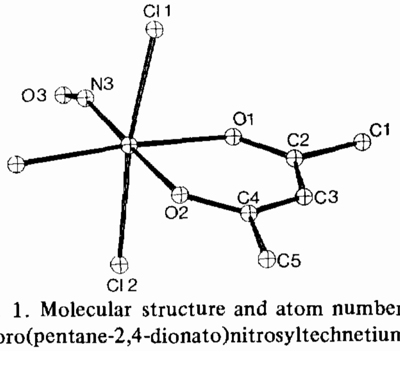

Fig. 1. Molecular structure and atom numbering for the trichloro(pentane-2,4-dionato)nitrosyltechnetium(II) anion.

The bond angles (Table I) for Tc–N(3)–O(3) and Tc–N(4)–O(4) are 154.0(30)° and 155(30)° respectively which is considerably different from that of $[TcNOCl_4(CH_3OH)]^-$ which has a bond angle of 175.5(10)°. The disorder and slight axial displacement of the two ligands result in some loss of accuracy in the bond lengths and angles and detailed discussion of these is not appropriate. The pentane-2,4-dionato ligand bond distances and angles are comparable to other known distances.

TABLE I. Bond Distances (Å) and Bond Angles (°) for the Anion $[TcNO(acac)Cl_3]^-$

Tc–Cl(1)	2.385(7)
Tc–Cl(2)	2.372(8)
Tc–Cl(3)	2.36(2)
Tc–Cl(4)	2.29(1)
Tc–N(3)	1.74(3)
Tc–N(4)	1.71(3)
N(3)–O(3)	1.20(3)
N(4)–O(4)	1.16(5)
Tc–O(1)	2.06(1)
Tc–O(2)	2.08(1)
O(1)–C(2)	1.27(2)
O(2)–C(4)	1.27(2)
C(1)–C(2)	1.53(3)
C(2)–C(3)	1.38(3)
C(3)–C(4)	1.42(3)
C(4)–C(5)	1.47(3)
Tc–N(3)–O(3)	158.6(33)
Tc–N(4)–O(4)	152.1(47)
Cl(1)–Tc–Cl(2)	172.6(2)
Cl(1)–Tc–Cl(3)	97.5(5)
Cl(1)–Tc–Cl(4)	93.0(5)
Cl(1)–Tc–O(1)	86.8(5)
Cl(1)–Tc–O(2)	86.9(4)
Cl(1)–Tc–N(3)	92.0(10)
Cl(1)–Tc–N(4)	90.6(20)
Cl(2)–Tc–Cl(3)	87.8(5)
Cl(2)–Tc–Cl(4)	92.0(5)
Cl(2)–Tc–O(1)	88.1(5)
Cl(2)–Tc–O(2)	87.7(4)
Cl(2)–Tc–N(3)	93.3(11)
Cl(2)–Tc–N(4)	94.2(20)
Cl(3)–Tc–O(1)	89.8(6)
Cl(3)–Tc–O(2)	175.3(6)
Cl(3)–Tc–N(4)	93.8(17)
Cl(4)–Tc–O(1)	178.7(6)
Cl(4)–Tc–O(2)	89.7(6)
Cl(4)–Tc–N(3)	91.2(13)
O(1)–Tc–O(2)	89.0(5)
O(1)–Tc–N(3)	90.1(13)
O(1)–Tc–N(4)	175.8(19)
O(2)–Tc–N(3)	178.6(14)
O(2)–Tc–N(4)	87.6(17)
Tc–O(1)–C(2)	126.3(14)
Tc–O(2)–C(4)	126.8(14)
C(1)–C(2)–C(3)	120.3(17)
C(2)–C(3)–C(4)	128.4(19)
C(3)–C(4)–C(5)	121.1(19)

The FAB^- mass spectrum of the complex has a major ion at $m/z = 333$ due to $[TcNO(acac)Cl_3]^-$ with the expected isotope pattern due to the three chlorine atoms. Fragmentation occurs via the loss of one chlorine to $m/z = 298$. The ions at $m/z = 269$ and 262 correspond to $[M - Cl - NO + H]^-$ and $[M - 2Cl + H]^-$ respectively. The other lower mass ions at 233 and 204 are due to $[TcCl(acac)]^-$ and $[TcCl_3]^-$. The facile loss of a single chlorine indicates that the parent complex may readily undergo ligand exchange of this ligand while loss of the acac group may be difficult.

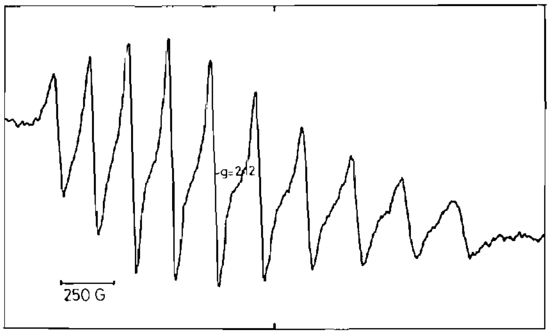

Fig. 2. The ESR spectrum of an ethanolic solution of $[TcNO(acac)Cl_3]^-$ at ambient temperature.

The electron spin resonance spectra of the complex in ethanol were recorded at ambient temperature and –196 °C. The spectrum at ambient temperature is that expected with the signal split into 10 by the $I = 9/2$ technetium nuclear spin (Fig. 2). The $g_{av} = 2.12$ and $a_{av} = 135 \times 10^{-4}$ cm^{-1} were measured directly. Since the complex has low symmetry the frozen solution gave a complex spectrum which could only be resolved into its component parameters using the POWDER simulation programme (Fig. 3). These are reported in Table II. Several other technetium(II) nitrosyl complexes have been prepared and the ESR spectra measured. Kirmse and coworkers [12, 13] reported the spectrum of $TcNOCl_3(PMe_2Ph)_2$ which appears to have the two phosphines mutually *trans*. However, it was assumed that their spectrum could be modelled as axially symmetric. The complexes, $[TcNOX_5]^{2-}$ (R = halide, NCS^-) were modelled in a similar fashion. Our complex, $[TcNO(acac)Cl_3]^-$, is unusual since one of the oxygens of the acetylacetonate ligand is *trans* to nitrosyl and thus the spectrum cannot be satisfactorily modelled as axial.

Thus, in conclusion we have isolated and characterised the first of a possible series of novel technetium(II) complexes which may find use as radiopharmaceuticals.

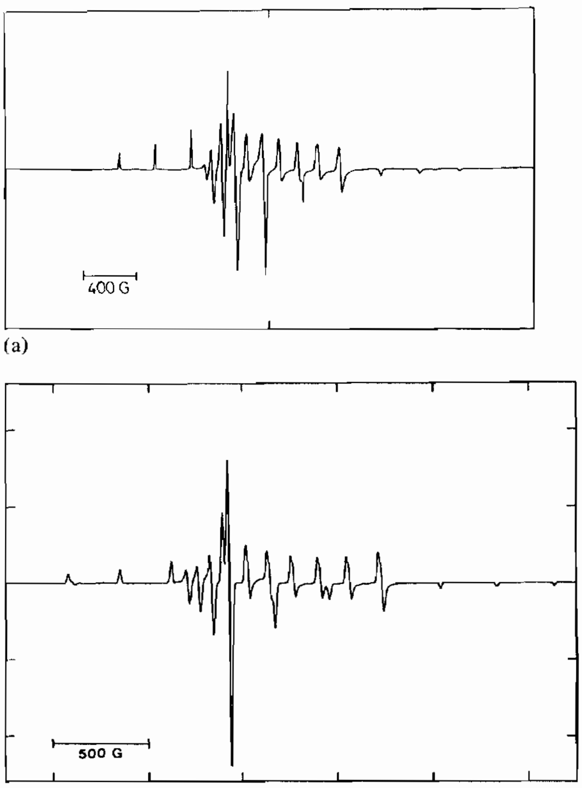

Fig. 3. The ESR spectrum of an ethanolic solution of $[TcNO(acac)Cl_3]^-$ at −196 °C (a) and the simulated spectrum from the POWDER program (b).

TABLE II. ESR Parameters for $[TcNO(acac)Cl_3]^-$

$\langle g \rangle$	2.12	$\langle a \rangle$	94.0
g_x	2.0107[a]	a_x	105.4[a]
g_y	2.02225[a]	a_y	105.4[a]
g_z	1.9460[a]	a_z	258.4[a]

Hyperfine constants are given in 10^{-4} cm^{-1}. [a]Values from the POWDER simulation program.

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