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Synthesis, reactions and structure of Cp′Tc(CO)$_3$ derivatives

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Abstract

A novel procedure for a high yield synthesis of $Tc_2(CO)_{10}$ is reported. Cyclopentadienyl technetium carbonyl complexes of general formula $Cp'Tc(CO)_3$, where $Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$, or $\eta^5\text{-}C_5(Me)_4[(CH_2)_3NMe_2]$, have been prepared by reaction of $Tc(CO)_5I$ with the appropriate lithium cyclopentadienide in THF at room temperature. Quaternization of the amino group in the cyclopentadienyl derivative **3** with methyl iodide is described and the results of an X-ray structure determination are presented. Treatment of $(C_5Me_5)Tc(CO)_3$ with $NOPF_6$ in acetonitrile affords the cationic nitrosyl $[(C_5Me_5)Tc(CO)_2(NO)][PF_6]$ in high yield, while treatment with Br_2/CF_3COOH gives the neutral dicarbonyl $(C_5Me_5)Tc(CO)_2Br_2$ as a mixture of *cis*- and *trans*-isomers.

Introduction

There is a growing interest in the organometallic chemistry of technetium due to the importance of its complexes in nuclear medicine. As part of a project aimed at the development of new radiopharmaceuticals we decided to explore a new area of organotechnetium chemistry based on $Tc_2(CO)_{10}$ as starting material and to focus on the preparation of low-valent pentamethylcyclopentadienyl carbonyl complexes. With ^{99}Tc readily available in the form of ammonium pertechnetate, $NH_4{}^{99}TcO_4$, and with the explosive development of cyclopentadienyl rhenium chemistry [1a–f] in mind, we have synthesized and characterized some new pentamethylcyclopentadienyl complexes of technetium. The results of this research are reported below.

Although reports of carbonyl derivatives of Mn and Re are abundant in the literature [2a–d], only few cyclopentadienyl carbonyls of technetium have been reported so far [3–5]. η^5-Cyclopentadienyl technetium tricarbonyl, $C_5H_5Tc(CO)_3$, has been obtained by neutron bombardment of cyclopentadienyl molybdenum tricarbonyl dimer followed by radioactive decay [3] and by reaction of $TcCl_4$ with sodium cyclopentadienide in ethyleneglycol dimethylether under 325 atm of carbon monoxide [4]. On a small scale, acylation of the ring ligand with benzoyl chloride to

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give $[(C_6H_5COC_5H_4)Tc(CO)_3]$ has also been achieved [5]. A polymeric oxotechnetium complex, $[Tc_2O_3(C_5Me_5)]_n$ has been prepared recently from the reaction of $C_5Me_5Tc(CO)_3$ (**2**) with perhydrol [6]. Complex **2** is briefly mentioned there but no details of its synthesis, characterization or stereochemistry are given.

Results and discussion

Organotechnetium chemistry is much less developed than that of its congeners Mn and Re, but there is a growing interest in this field, and so it is important to have reliable, high yield synthetic procedures to prepare starting compounds.

The decacarbonyl dimer $Tc_2(CO)_{10}$ was first synthesized (7% yield) and characterized by Hileman in 1961 [7] by reaction of Tc_2O_7 with carbon monoxide (350 atm) at 220 °C. We have found that sodium amalgam in THF is able to reduce Tc^{VII}, in the form of TcO_4^-, to Tc^0 and give $Tc_2(CO)_{10}$ when treated with 100 atm of CO at 120 °C for three days. Yields of 70–80% have been obtained by this method. The carbonyl iodide of technetium, $Tc(CO)_5I$, has been prepared by action of iodine on $Tc_2(CO)_{10}$ [8]. We thus decided to use the salt metathesis procedure of Fischer [5] for the preparation of $(C_5H_5)Re(CO)_3$ (eq. 1).

$$Tc(CO)_5I + Cp'Li \xrightarrow{THF} \underset{(\mathbf{1\text{–}3})}{Cp'Tc(CO)_3} + LiI + 2\,CO \qquad (1)$$

[(Cp′: **1**, η^5-C_5H_5 (Cp); **2**, η^5-C_5Me_5 (Cp*); **3**, η^5-$C_5Me_4[(CH_2)_3NMe_2]$ (Cp^a)].

The complexes were obtained in high yields after relatively short reaction times (2–3 h at room temperature).

The quaternization of the amino group in **3** was achieved by treating the tricarbonyl complex with an excess of MeI and keeping the solution at room temperature for 2 hours (eq. 2)

$$\underset{(\mathbf{3})}{([Me_2N(CH_2)_3]C_5Me_4)Tc(CO)_3} \xrightarrow{MeI} \underset{(\mathbf{4})}{([Me_3N^+(CH_2)_3]C_5Me_4)Tc(CO)_3\,I^-} \qquad (2)$$

The versatility of the nitrosonium ion in organometallic synthesis has been illustrated by its reactions with a variety of transition metal compounds [9]. We have found that, like in the case of the rhenium analogue, $Cp^{\star}Tc(CO)_3$ reacts with $NOPF_6$ in acetonitrile to give the cationic nitrosyl $[Cp^{\star}Tc(CO)_2(NO)][PF_6]$ (**5**) by simple replacement of carbon monoxide (eq. 3).

The reaction of $Cp^{\star}Tc(CO)_3$ with bromine in trifluoroacetic acid at room temperature (eq. 3) was carried out by the procedure for the rhenium analogue [10] and gave $Cp^{\star}Tc(CO)_2Br_2$ (**6**). $CpMA_2B_2$ compounds are known to exist as pairs of *cis*- and *trans*-isomers. A simple and reproducible chromatographic technique for the separation of *cis*-$CpRe(CO)_2Br_2$ and *trans*-$CpRe(CO)_2Br_2$ has been reported by King et al. [11]. The identification of the isomers is based on the intensity ratios of the carbonyl bands in the IR spectra, which permits an estimate of the angle between the carbonyl groups. The isomers, **6a,b**, were separated by column chromatography on Florisil and identified by IR spectroscopy. *trans*-$Cp^{\star}Tc(CO)_2Br_2$

Table 1

Carbonyl stretching bands (cm^{-1}) for the technetium complexes **1**–**6**

$Tc_2(CO)_{10}$ [a]	2064 m	2016 s	1981 m	
$Tc(CO)_5I$ [a]	2146 w	2055 s	2024 w	2000 m
$CpTc(CO)_3$ (**1**) [b]	2035 m	1956 s		
$Cp^\star Tc(CO)_3$ (**2**) [b]	2000 m	1910 s		
$Cp^aTc(CO)_3$ (**3**) [b]	2005 m	1920 s		
$[Cp^aTc(CO)_3]^+$ (**4**) [b]	2010 m	1915 s		
$[Cp^\star Tc(CO)_2(NO)]^+$ (**5**) [b]	2085 m	2035 m		
trans-$Cp^\star Tc(CO)_2Br_2$ (**6a**) [c]	2060 m	1985 m		
cis-$Cp^\star Tc(CO)_2Br_2$ (**6b**) [c]	2040 m	1972 m		

Measured for solutions in [a] CCl_4, [b] CH_3CN and [c] CH_2Cl_2

(**6a**) shows $\nu(CO)$ at 2060 and 1985 cm^{-1}, while for the *cis*-$Cp^\star Tc(CO)_2Br_2$ (**6b**) the carbonyl stretching bands appear at 2040 and 1972 cm^{-1}, both sets of frequencies being very close to those reported for the cyclopentadienyl rhenium analogue [11]. *trans*-$Cp^\star Tc(CO)_2Br_2$ (**6a**) and *cis*-$Cp^\star Tc(CO)_2Br_2$ (**6b**) were isolated in a 3 : 1 ratio after chromatography.

$$\begin{tikzcd} & Cp^\star Tc(CO)_2(NO)^+ \ (\mathbf{5}) \\ Cp^\star Tc(CO)_3 \ (\mathbf{2}) \arrow[ur, "NOPF_6"] \arrow[dr, "Br_2/CF_3CO_2H"'] & \\ & Cp^\star Tc(CO)_2(Br)_2 \ (\mathbf{6a,b}) \end{tikzcd} \qquad (3)$$

Due to safety regulations governing work with radioactive materials it was not possible to obtain elemental analysis for the compounds, and so NMR and IR spectroscopy were used to establish the identity of these complexes. Infrared data (Table 1) for cyclopentadienyltechnetium tricarbonyl complexes **1**–**4** are consistent with C_{3v} local symmetry ($A_1 + E$). As expected, substitution of hydrogen atoms (Cp) by methyl groups ($Cp^\star$) increases the electron density on the metal facilitating the transfer of electrons to the carbonyl ligands via π-backbonding. As a result of this, the C–O bond order decreases and hence, $\nu(CO)$. All data point to the expected piano stool geometry of these complexes as demonstrated by an X-ray structure determined on the tetraalkyl ammonium derivative **4**.

Molecular structure of 4

The molecular structure of the technetium cation **4** is shown in Fig. 1. Relevant bond lengths and bond angles are summarized in Table 2. Details of the determination are given in Table 3.

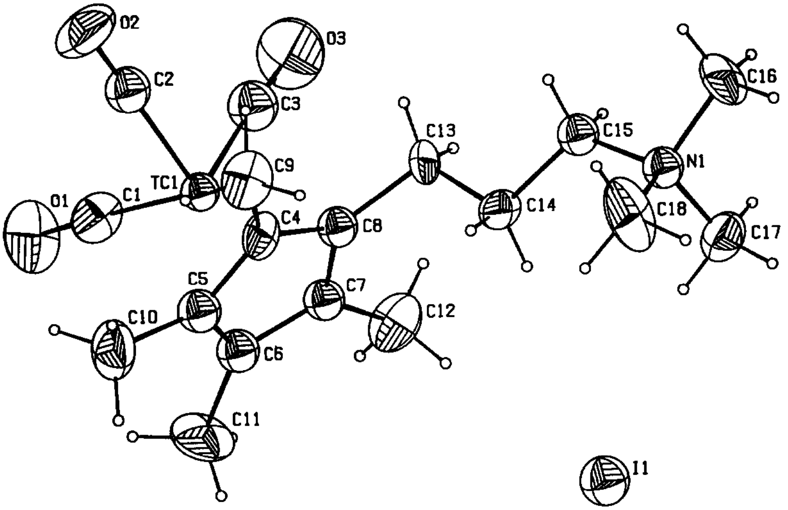

Fig. 1. X-Ray structure of $[([Me_3N(CH_2)_3]C_5Me_4)Tc(CO)_3]^+ I^-$ with the adopted numbering scheme.

The molecule is monomeric, with a technetium atom coordinated to one η^5-$C_5Me_4[(CH_2)_3N^+Me_3]$ and three terminal CO ligands, giving the metal a formal coordination number 4.

The geometry around the technetium atom is best described as a piano stool with a symmetrically bonded cyclopentadienyl ligand and a side chain bearing the ammonium group pointing away in open space. The cyclopentadienyl group is η^5-coordinated, with Tc–C(ring) bond distances between 2.275(9) and 2.30(1) Å. The C–C distances within the ring are comparable with those in other transition metal complexes containing the η^5-C_5Me_5 ligand with an average value of 1.4228(6) Å. The distance between the projection of the technetium atom on the ring is 1.94(4) Å. The distance from the metal to the ring is the same within the esd.

Table 2

Selected geometrical data (standard deviations in the last decimal place are given in parentheses)

Bond distances (Å)			
Tc(1)–C(1)	1.89(1)	C(4)–C(5)	1.42(1)
Tc(1)–C(2)	1.91(1)	C(4)–C(8)	1.42(1)
Tc(1)–C(3)	1.90(1)	C(5)–C(6)	1.42(1)
Tc(1)–C(4)	2.291(9)	C(6)–C(7)	1.43(1)
Tc(1)–C(5)	2.30(1)	C(7)–C(8)	1.44(1)
Tc(1)–C(6)	2.30(1)		
Tc(1)–C(7)	2.293(9)		
Tc(1)–C(8)	2.275(9)		
Bond angles (deg.)			
C(1)–Tc(1)–C(2)	89.0(4)		
C(1)–Tc(1)–C(3)	89.9(5)		
C(2)–Tc(1)–C(3)	90.6(5)		

Conclusions

We have found a high yield synthetic route to the starting material $Tc_2(CO)_{10}$ and have shown that cyclopentadienyl ligands can be readily introduced to form a variety of tricarbonyl complexes by simple substitution of carbon monoxide ligands.

Experimental

Tc-99 was supplied by Mallinckrodt Diagnostica (Holland) laboratories in the form of dry NH_4TcO_4. All reactions were carried out under nitrogen in Schlenk glassware. Solvents were dried by conventional methods and distilled under nitrogen. Infrared spectra were measured on a Pye Unicam model SP3-300 spectrophotometer in NaCl cells using solutions (CCl_4, CH_3CN, CH_2Cl_2) or Nujol mulls. ^{1}H-NMR spectra were recorded on a Bruker WH-90 spectrometer. Chemical shifts are reported in ppm; they were determined by reference to the residual protons in deuterated solvents [THF-d_8 (3.57; 1.52), CH_3CN-d_3 (1.93)]. The autoclave used was a General Purpose Bomb (PARR) type 4763 (450 ml). 1-[3(*N*,*N*-dimethyl)aminopropyl]-2,3,4,5-tetramethylcyclopentadiene and its lithium salt were prepared following a procedure developed in our laboratory [12].

$Tc_2(CO)_{10}$

NH_4TcO_4 (0.50 g, 2.76 mmol) was placed in a 450 ml autoclave together with 26.7 g of 2% sodium amalgam and 15 ml THF. The bomb was pressurized with carbon monoxide to 70 atm/25 ° C and heated for 72 h at 120 ° C, while the pressure increased to 100 atm. After cooling the autoclave was outgassed slowly through a trap at -78 ° C. The pale yellow solution was transferred to another flask and the solvent removed by evaporation. Sublimation of the residue (50 ° C/10^{-2} mmHg) yielded 0.46 g (0.96 mmol, 70% yield) of $Tc_2(CO)_{10}$. IR (CCl_4): ν(CO) 2064 (m), 2016 (s), 1981 (m) cm^{-1} (identical to the data reported in the literature [7]).

$Tc(CO)_5I$ [8]

Direct action of I_2 (0.212 g, 0.84 mmol) on $Tc_2(CO)_{10}$ (0.20 g, 0.42 mmol) in 5 ml THF under 70 atm CO at 100 ° C for 40 h afforded $Tc(CO)_5I$ in 90% yield (0.24 g). The product was purified by sublimation (60 ° C/10^{-2} mmHg). IR (CCl_4): ν(CO) 2146 (w), 2055 (s), 2024 (w), 2000 (m) cm^{-1}.

$CpTc(CO)_3$ (1)

Lithiumcyclopentadienide (0.068 g, 0.94 mmol) was added to 0.344 g (0.94 mmol) of $Tc(CO)_5I$ in 10 ml THF. The mixture was stirred at room temperature for one hour (the IR spectra of the solution at this point indicated complete conversion to **1**) and the solvent was then removed in vacuum. The residue was extracted with 30 ml of dry diethyl ether in three portions and the combined extracts were evaporated to dryness to afford 0.202 g (87%) of the product which was purified by vacuum sublimation (75 ° C/10^{-2} mmHg). IR (Nujol): ν(CO) 2035 (m), 1956 (s) cm^{-1}. ^{1}H-NMR (THF-d_8): δ 4.62 (s, C_5H_5).

$Cp^*Tc(CO)_3$ (2)

Lithiumpentamethylcyclopentadienide (0.134 g, 0.94 mmol) was added to 0.344 g of $Tc(CO)_5I$ (0.94 mmol) in 10 ml THF. The mixture was stirred for two hours at room temperature and the solvent then removed in vacuum and the residue extracted with 30 ml of dry diethyl ether in three portions. The combined ether extracts were evaporated to dryness and the product was purified by vacuum sublimation (80 °C/10^{-2} mmHg) to give 270 mg (0.85 mmol, 90% yield) of $Cp^{\star}Tc(CO)_3$. IR (CH_3CN): ν(CO) 2000 (m), 1910 (s) cm^{-1}. ^{1}H-NMR (CH_3CN-d_3): δ 2.03 (s, C_5Me_5).

$[Cp^{\star}Tc(NO)(CO)_2][PF_6]$ (5)

$Cp^{\star}$ $Tc(CO)_3$ (0.1 g, 0.31 mmol) in 5 ml acetonitrile was treated with 0.08 g $NO[PF_6]$ (0.39 mmol). Reaction was instantaneous and after 3–4 minutes the product was precipitated by addition of 40 ml of diethyl ether. The white, microcrystalline solid was collected and washed with small portions of ethanol and diethyl ether to give 0.12 g of product (82% yield). IR (CH_3CN): ν(CO) 2085 (m), 2035 (m), ν(NO) 1745 (s) (br) cm^{-1}. ^{1}H-NMR (CH_3CN-d_3): δ 2.12 (s, C_5Me_5).

$Cp^{\star}Tc(CO)_2Br_2$ (6a, b)

0.100 g (0.63 mmol) of bromine in 1 ml of trifluoroacetic acid was added dropwise to a solution of $Cp^{\star}Tc(CO)_3$ (0.200 g, 0.63 mmol) in 5 ml trifluoroacetic acid at room temperature. The mixture was stirred for 15 min, the reaction then quenched by addition of 50 ml of water at 25 °C, and the resulting brown precipitate was extracted with CH_2Cl_2 (3 × 10 ml). The dichloromethane solution was concentrated and chromatographed on a Florisil column in dichloromethane to separate the unreacted $Cp^{\star}Tc(CO)_3$ and the two isomers of $Cp^{\star}Tc(CO)_2Br_2$. Elution with CH_2Cl_2 gave first the unreacted tricarbonyl, then the *trans*- and finally the *cis*-isomer, which was recrystallized from dichloromethane–carbon tetrachloride. Maroon plates of *trans*-$Cp^{\star}Tc(CO)_2Br_2$ were recovered in 55% yield (0.155 g). IR(CH_2Cl_2): ν(CO) 2060 (m), 1985 (s) cm^{-1}. ^{1}H-NMR (CH_3CN-d_3): δ 1.93 (s, C_5Me_5), while dark brown *cis*-$Cp^{\star}Tc(CO)_2Br_2$ was recovered in 18% yield (0.05 g). IR (CH_2Cl_2): ν(CO) 2040 (m), 1972 (s) cm^{-1}. ^{1}H-NMR (CH_3CN-d_3): δ 2.13 (s, C_5Me_5).

$Cp^aTc(CO)_3$ (3)

0.300 g $Tc(CO)_5I$ (0.82 mmol) in 10 ml THF were treated with 0.18 g (0.85 mmol) of Cp^aLi. The colour of the solution immediately changed from light to dark yellow. The mixture was stirred under nitrogen at room temperature until the IR spectrum showed total conversion to $Cp^aTc(CO)_3$ (3 h). The solvent was removed in vacuum and the residue was extracted three times with small portions of diethyl ether. The combined ether extracts were evaporated to leave an oil which crystallized upon standing; yield 0.234 g (64%) of $Cp^aTc(CO)_3$. IR (CH_3CN): ν(CO) 2005 (m), 1920 (s) cm^{-1}. ^{1}H-NMR (CH_3CN-d_3): δ 2.04 (s, 6H, ring CH_3), 2.06 (s, 6H, ring CH_3), 2.76 (s, 6H, amine CH_3).

Preparation of the quaternary ammonium salt 4

$Cp^aTc(CO)_3$ (0.100 g, 0.26 mmol) was treated with excess methyl iodide in the absence of solvent and allowed to stand 15 h at room temperature. The crystals formed were isolated on a frit, washed with diethyl ether and dried in vacuum to afford 0.131 g of $[([Me_3N^+(CH_2)_3]C_5Me_4)Tc(CO)_3]I^-$ (4) (96% yield). IR (CH_3CN): ν(CO) 2010 (m), 1915 (s) cm^{-1}. ^{1}H-NMR (CH_3CN-d_3): δ 2.05 (s, 6H, ring CH_3), 2.07 (s, 6H, ring CH_3), 2.36–2.58 (m, 2H, $-CH_2-N$), 3.06 (s 9H, amine CH_3) 3.26–3.48 (m, 2H, $-CH_2-$ from side chain).

X-Ray data collection, structure determination and refinement for 4

The crystal used for characterization was an irregular fragment cleaved from a larger colourless crystal. This fragment was glued on the tip of a glass fiber and mounted on an Enraf–Nonius CAD-4F diffractometer. Unit cell dimensions and their standard deviations were determined from the setting angles of 22 reflections in the range $14.66° < \theta < 21.48°$. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86) [13]. After completion of the

Table 3

Crystal data, summary of intensity data collection and structure refinement for 4

Chemical formula	$C_{18}H_{27}ITcO_3N$
Formula weight, g mol^{-1}	403.42
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants	
a, Å	14.081(2)
b, Å	9.089(1)
c, Å	17.207(3)
β, deg	91.13(1)
V, Å^3	2201.8(6)
Z	4
D_{calc}, g cm^{-3}	1.600
$F(000)$, electrons	1048
μ(Mo-K_α), cm^{-1}	20.3
Approx. crystal dimension, mm	$0.17 \times 0.20 \times 0.25$
Diffractometer	Enraf–Nonius CAD-4F
Radiation, Å	Mo-K_α, 0.71073
Monochromator	Graphite
Temperature, K	295
θ range; min. max., deg	1.19, 25.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.85 + 0.35 \text{ tg } \theta$
Data set	h: $-16 \rightarrow 16$; k: $-1 \rightarrow 10$; l: $0 \rightarrow 20$
Total data	4836
Unique data	3867
Observed data ($F \geq 4.0\sigma(F)$)	2937
Refinement	
Number of reflections	2920
Number of refined parameters	218
Final agreement factors:	
$R_F = \Sigma(\lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert)/\Sigma\lvert F_o \rvert$	0.053
$wR = [\Sigma(w(\lvert F_o \rvert - \lvert F_c \rvert)^2)/\Sigma w \lvert F_o \rvert^2]^{1/2}$	0.059
Weighting scheme	1
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(m-n)]^{1/2}$ (m = number of observations, n = number of variables)	3.342
Residual electron density in final difference Fourier map, e/Å^3	-1.35, 1.11
Max. (shift/σ) final cycle	0.29×10^{-3}
Average (shift/σ) final cycle	0.60×10^{-4}

isotropic refinement empirical absorption corrections based on $(F_o - F_c)$ difference were applied (correction in the range 0.83 to 1.33) with the program DIFABS [14]. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (XTAL) minimizing the function $Q = \Sigma_h[w(|F_o| - |F_c|)^2]$. Some of the hydrogen atom positions could be located on a difference Fourier map but did not refine well. The hydrogen atoms were ultimately included with their positions calculated by using sp^2 or sp^3 hybridization at the C-atom as appropriate and a fixed C–H distance of 0.98 Å; the H atom positions thus found served to determine the conformation of the methyl groups. The hydrogen atoms were refined in the riding mode with a fixed C–H bond length of 0.98 Å. Refinement on F by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one common isotropic thermal parameter for the hydrogen atoms converged at $R_F = 0.053$ ($wR = 0.059$). The minimum and maximum residual densities in the final difference Fourier map of -1.35 and 1.11 e/Å^3 were observed in the neighbourhood of the I atom. Seventeen reflections with $(w(||F_o| - |F_c||) > 20)$ were excluded from the final refinement cycle. All the excluded reflections had a far too high F_o, probably due to some problems with the discriminator of the diffractometer. The details of the final refinements are included in Table 3. The final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are

Table 4

Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms with esd's in parentheses.

	x	y	z	U_{eq} (Å^2) [a]
I(1)	0.02560(6)	0.20758(9)	0.11515(4)	0.0610(3)
Tc(1)	0.39308(5)	0.27089(9)	0.39455(5)	0.0361(2)
O(1)	0.6069(5)	0.277(1)	0.3650(6)	0.089(4)
O(2)	0.4277(7)	0.383(1)	0.5594(5)	0.092(4)
O(3)	0.3982(9)	−0.051(1)	0.4462(7)	0.117(5)
N(1)	−0.1147(5)	0.1625(9)	0.3727(5)	0.041(3)
C(1)	0.5252(7)	0.271(1)	0.3776(6)	0.057(4)
C(2)	0.4178(7)	0.335(1)	0.4984(6)	0.051(4)
C(3)	0.4002(8)	0.071(1)	0.4269(8)	0.063(4)
C(4)	0.2614(6)	0.418(1)	0.3835(6)	0.043(3)
C(5)	0.3311(7)	0.475(1)	0.3327(6)	0.046(3)
C(6)	0.3493(6)	0.367(1)	0.2753(6)	0.045(3)
C(7)	0.2905(6)	0.242(1)	0.2905(5)	0.042(3)
C(8)	0.2367(6)	0.274(1)	0.3588(5)	0.039(3)
C(9)	0.2197(8)	0.504(1)	0.4484(7)	0.063(4)
C(10)	0.3720(9)	0.626(1)	0.3336(8)	0.075(5)
C(11)	0.4109(8)	0.383(2)	0.2053(7)	0.084(5)
C(12)	0.2779(9)	0.107(1)	0.2404(7)	0.069(5)
C(13)	0.1576(6)	0.183(1)	0.3921(6)	0.050(3)
C(14)	0.0617(6)	0.225(1)	0.3567(5)	0.047(3)
C(15)	−0.0135(6)	0.142(1)	0.4005(5)	0.041(3)
C(16)	−0.1787(7)	0.091(1)	0.4312(7)	0.069(5)
C(17)	−0.1317(8)	0.089(1)	0.2964(6)	0.068(5)
C(18)	−0.1382(7)	0.324(1)	0.3663(9)	0.086(6)

[a] U_{eq} = one-third of the trace of the orthogonalized U_{ij} tensor.

given in Table 4. Tables of hydrogen atoms positions, thermal parameters, comprehensive lists of bond distances and angles and tables of F_o, F_c and $\sigma(F)$ (23 pages) are available from the authors as supplementary material. Scattering factors were taken from Cromer and Mann [15]. Anomalous dispersion factors taken from Cromer and Liberman [16] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL [17] and EUCLID [18] (calculation of geometric data).

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