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Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]technetium(I) Chloride–Tetrabutylammonium Chloride (1/1)

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(*Received* 22 *December* 1992; *accepted* 28 *June* 1993)

Abstract

The complex $[TcCl(NO)(C_{10}H_{16}As_2)_2]^+$ lies on a crystallographic inversion centre with disordering of the *trans* chloro and nitrosyl ligands. The coordination about Tc is close to octahedral with Tc—As distances of 2.479 (1) and 2.502 (2) Å. The As—C mean distance is 1.924 (15) Å and the angles at As are within 10° of tetrahedral.

Comment

The title compound, in which Tc is in the monovalent state, was prepared (Hildreth, 1992) in the context of a search for low-oxidation-state Tc complexes as potential radiopharmaceuticals (Cheah, Newman, Nowotnik & Thornback, 1987).

Although the presence of the nitrosyl ligand is indicated by IR spectroscopy and fast-atom bombardment mass spectrometry (Hildreth, 1992), the X-ray results do not show separate Cl and nitrosyl groups as a result of packing disorder. The Tc atom lies on a centre of symmetry with the chloro and nitrosyl substituents equivalent and indistinguishable on Fourier difference maps. A large peak at *ca* 2.3 Å from Tc was taken to represent $\frac{1}{2}$(Cl + NO). The postions of the N and O atoms were calculated using the known covalent radii of the elements involved, such that the Tc—N—O angle was close to 180°. Atomic coordinates are given in Table 1 and Fig. 1 shows the atomic numbering scheme.

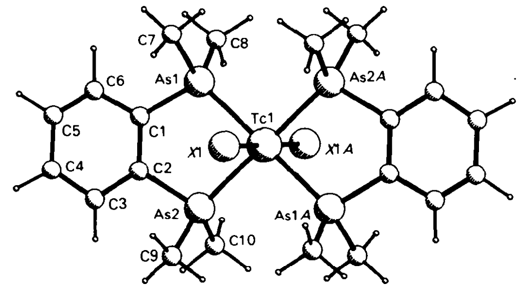

Fig. 1. The complex cation showing the atomic numbering scheme. *X*1 and *X*1*A* represent $\frac{1}{2}$(Cl + NO).

The overall coordination about Tc is close to octahedral; as a result of symmetry requirements the four As atoms and the central Tc are precisely coplanar. Selected bond lengths and angles are shown in Table 2. The Tc—As distances reported here represent the first determination of such a bond involving Tc^{I}. They are a little shorter than those found in the perchlorate and chloride salts of dichlorobis[*o*-phenylenebis(dimethylarsine)]Tc^{III} (Elder, Whittle, Glavan, Johnson & Deutsch, 1980), where the mean Tc—As length is 2.512 Å, compared to 2.491 Å in the present structure. The Tc—Cl distance [2.391 (15) Å] is some 0.02–0.07 Å greater than those found in a Tc^{II} complex [mean 2.357(5) Å (Brown, Newman, Thornback & Davison, 1987)], a Tc^{III} complex [mean 2.322 (17) Å (Elder *et al.*, 1980)] and a Tc^{IV} complex [mean 2.373 (11) Å (Bush, Hamor, Hussain, Jones, McCleverty & Rothin, 1987)]. There is no obvious correlation between the Tc oxidation state and the Tc—Cl length. However, because of the disorder involving Cl and NO, the Tc—Cl distance in the present structure is probably more uncertain than indicated by the calculated e.s.d.

The valence angles at arsenic are in the range 99.8–118.7°. The pattern of variation from the ideal tetrahedral value [large Tc—As—C_{methyl} angles of mean 117.8 (4)° and small C_{phenyl}—As—C_{methyl} angles of mean 101.8 (7)°] is also observed in the dichlorobis[*o*-phenylenebis(dimethylarsine)]technetium(III) cation [the corresponding mean values are 118.3 (8) and 103.3 (15)°, respectively].

The tetrabutylammonium cation lies on the twofold axis at $x = 0$, $y = \frac{1}{4}$, with two of the atoms C(13) and C(16) disordered, each partially occupying two sites. These 'half atoms' were refined with isotropic temperature factors. A number of other atoms have very large thermal parameters, possibly indicative of some degree of disorder also at these sites. Considering the unprimed sites for the disordered atoms (Table 1), the butylammonium chains are in the extended antiperiplanar–antiperiplanar conformation.

ISSN 0108-2701

The chloride counter ions Cl(1) and Cl(2) are also disordered, occupying general positions with site occupancies of $\frac{1}{2}$.

Experimental

Crystal data

$[TcCl(NO)(C_{10}H_{16}As_2)_2]Cl.$-$[N(C_4H_9)_4]Cl$
$M_r = 1049.9$
Monoclinic
$C2/c$
$a = 20.069$ (5) Å
$b = 13.249$ (3) Å
$c = 20.431$ (4) Å
$\beta = 116.03$ (5)°
$V = 4881.4$ Å^3
$Z = 4$
$D_x = 1.429$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–$15°$
$\mu = 3.31$ mm^{-1}
$T = 295$ K
Rod
0.8 × 0.2 × 0.2 mm
Yellow
Crystal source: crystallized from dichloromethane

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.65$, $T_{max} = 0.83$
5141 measured reflections
4301 independent reflections
2463 observed reflections [$F > 5\sigma(F)$]

$R_{int} = 0.079$
$\theta_{max} = 25°$
$h = -23 \rightarrow 21$
$k = 0 \rightarrow 15$
$l = -3 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity variation: <5%

Refinement

Refinement on F
$R = 0.076$
$wR = 0.108$
$S = 2.625$
2460 reflections
212 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F)]$

$(\Delta/\sigma)_{max} = 0.19$
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}
Extinction correction: three reflections discarded
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Tc	$\frac{1}{4}$	$\frac{1}{4}$	0.0	0.044
As(1)	0.3240 (1)	0.3506 (1)	0.1107 (1)	0.055
As(2)	0.1833 (1)	0.1946 (1)	0.0724 (1)	0.055
Cl(1)†	0.3348 (8)	0.1129 (12)	0.0499 (6)	0.074
Cl(2)†	0.5553 (4)	0.5921 (6)	0.2124 (4)	0.057
Cl(3)†	0.4971 (6)	0.4791 (9)	0.0728 (5)	0.107
N(1)†	0.3198	0.1366	0.0436	0.055 (14)‡
O(1)†	0.3606	0.0702	0.0691	0.166 (22)‡
C(1)	0.2933 (10)	0.3195 (12)	0.1840 (8)	0.070
C(2)	0.2317 (9)	0.2548 (13)	0.1687 (8)	0.063
C(3)	0.2068 (14)	0.2277 (17)	0.2226 (9)	0.101
C(4)	0.2470 (16)	0.2665 (20)	0.2911 (12)	0.117
C(5)	0.3088 (22)	0.3326 (17)	0.3060 (14)	0.157
C(6)	0.3295 (13)	0.3580 (13)	0.2557 (9)	0.084
C(7)	0.4314 (8)	0.3236 (17)	0.1598 (10)	0.097
C(8)	0.3123 (12)	0.4969 (12)	0.1034 (10)	0.111
C(9)	0.1821 (11)	0.0547 (13)	0.0933 (11)	0.087
C(10)	0.0862 (9)	0.2409 (13)	0.0437 (11)	0.079
N(2)	0.0	0.4195 (14)	$\frac{1}{4}$	0.067
C(11)	0.0361 (26)	0.3462 (34)	0.3042 (18)	0.283
C(12)	0.0670 (18)	0.3320 (23)	0.3727 (13)	0.164
C(13)†	0.0965 (30)	0.2478 (40)	0.4205 (31)	0.121 (16)‡
C(14)	0.1425 (32)	0.2354 (28)	0.4864 (14)	0.291
C(15)	0.0373 (17)	0.4851 (22)	0.2230 (16)	0.167
C(16)†	0.0810 (30)	0.4738 (44)	0.1829 (30)	0.129 (18)‡
C(17)	0.1050 (30)	0.5862 (33)	0.1611 (31)	0.229
C(18)	0.1283 (27)	0.5349 (30)	0.1291 (32)	0.241
C(13′)†	0.1380 (23)	0.2782 (30)	0.4309 (23)	0.086 (12)‡
C(16′)†	0.0342 (31)	0.5508 (45)	0.1805 (30)	0.130 (18)‡

† Site occupancy $\frac{1}{2}$.
‡ Isotropic U refined.

Table 2. *Geometric parameters* (Å, °)

Tc—As(1)	2.479 (1)	As(1)—C(8)	1.951 (17)
Tc—As(2)	2.502 (2)	As(2)—C(2)	1.943 (15)
Tc—Cl(1)	2.391 (15)	As(2)—C(9)	1.905 (18)
As(1)—C(1)	1.896 (21)	As(2)—C(10)	1.875 (17)
As(1)—C(7)	1.972 (15)		
As(1)—Tc—As(2)	83.1 (1)	C(7)—As(1)—C(8)	106.7 (9)
Cl(1)—Tc—As(1)	89.4 (3)	Tc—As(2)—C(2)	108.6 (6)
Cl(1)—Tc—As(2)	89.4 (4)	Tc—As(2)—C(9)	118.7 (8)
Tc—As(1)—C(1)	109.4 (5)	Tc—As(2)—C(10)	118.2 (7)
Tc—As(1)—C(7)	116.8 (6)	C(2)—As(2)—C(9)	102.8 (8)
Tc—As(1)—C(8)	117.4 (5)	C(2)—As(2)—C(10)	99.8 (8)
C(1)—As(1)—C(7)	102.7 (8)	C(9)—As(2)—C(10)	106.0 (9)
C(1)—As(1)—C(8)	101.9 (9)		

The structure was solved in space group *Cc* but was found to exhibit the higher symmetry of space group *C2/c*. Refinement was carried out in *C2/c*. The high *R* value is probably due to the disorder affecting parts of the structure. Computer programs used were *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986) and *PLUTO* (Motherwell & Clegg, 1978). The H atoms of the complex cation were placed in calculated positions and allowed to ride on their respective bonded atoms. Those of the tetrabutylammonium cation were not included.

We thank the SERC and Amersham International PLC for the award of a CASE studentship to HJB, and Drs J. L. Hildreth and J. R. Thornback for suggesting this problem and for a crystal of the title compound.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete bond distances and angles involving non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71440 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1044]

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[Bis(5-oxoprolinato)]platinate(II) d'Ammonium Hydrate (3/8), 3{[NH_4][Pt($C_5H_5NO_3$)($C_5H_6NO_3$)]}.8H_2O

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(*Reçu le* 15 *février* 1993, *accepté le* 14 *juin* 1993)

Abstract

In tris{ammonium [5-oxoprolinato(1 −)-*N*,*O*][5-oxoprolinato(2 −)-*N*,*O*]platinate} octahydrate, the [Pt($C_{10}H_{11}N_2O_6$)]$^-$ anion is almost planar and its geometry very similar to those previously described. The Pt atom displays a square planar *cis* coordination. Each amino acid molecule is coordinated through the N amidic atom and one O atom of the carboxylic group. In each ligand, the amide function takes the tautomeric iminoalcohol form. The NH_4^+ cation is surrounded by six O atoms for which the N···O distances are in the range 2.78 (2)–3.16 (2) Å. The cation seems to be involved in four hydrogen bonds, two of them being bifurcated.

Commentaires

Le bis(5-oxoprolinato)platinate(II) d'ammonium hydrate (3/8) a été obtenu en ajoutant $PtCl_2$ finement pulvérisé à une solution aqueuse contenant un excès d'acide pyroglutamique (5-oxoproline) préalablement neutralisé par l'ammoniaque. A la température ambiante, des cristaux ayant la forme de prismes hexagonaux se forment au bout de quelques jours. Ils sont séparés et lavés avec une solution aqueuse d'éthanol. Leur étude structurale a été entreprise dans le but de préciser l'environnement de l'atome de platine. Elle fait suite à celle d'une série de composés de coordination formés par le platine(II) avec la 5-oxoproline (Viossat, Rodier, Nguyen-Huy & Guillard, 1986; Viossat, Khodadad & Rodier, 1990, 1991*a*,*b*, 1993; Viossat, Khodadad, Rodier & Guillard, 1990).

Les coordonnées atomiques relatives et les facteurs de température isotropes équivalents sont rapportés dans le Tableau 1, les principales distances interatomiques et les angles des liaisons dans le Tableau 2. La Fig. 1 représente l'anion [Pt($C_{10}H_{11}N_2O_6$)]$^-$ et indique les noms des atomes qu'il contient.

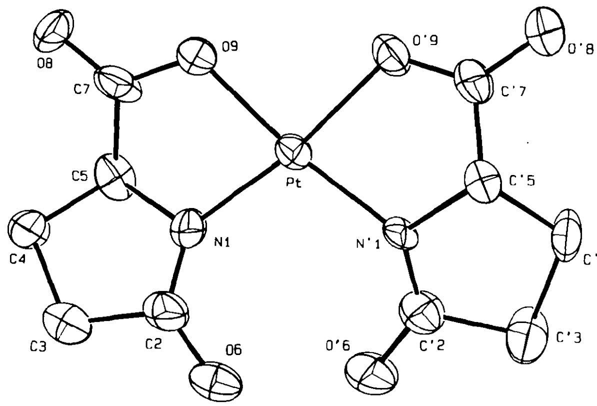

Fig. 1. Dessin de l'anion [Pt($C_{10}H_{11}N_2O_6$)]$^-$ et noms des atomes qu'il contient.

L'atome de platine est lié à deux molécules d'acide pyroglutamique. Chacune de celle-ci est coordinée par l'atome N amidique et par l'un des atomes O du groupement carboxylique. Les deux distances Pt—N sont égales à 1,98 (1) Å et les deux distances Pt—O à 2,01 (1) et à 2,022 (8) Å. Les angles formés par les droites joignant Pt à deux sommets contigus du quadrilatère N(1)N′(1)O′(9)O(9) ont les valeurs suivantes: N(1)—Pt—N′(1) 107,2 (5)°, O(9)—Pt—O′(9) 90,6 (4)°, N(1)—Pt—O(9) 80,8 (4)° et N′(1)—Pt—O′(9) 81,6 (4)°. Dans le tétra[bis(5-oxoprolinato)platinate(II) de potassium] pentahydrate (Viossat et *al.*, 1986), les distances Pt—N sont comprises entre 1,97 (2) et 2,05 (1) Å et les distances Pt—O entre 1,99 (1) et 2,05 (1) Å. Quant aux angles formés par les liaisons issues de Pt, leurs valeurs sont très voisines de celles rapportées ci-dessus pour leurs homologues respectifs.

Les distances N(1)—C(2) et N′(1)—C′(2) [1,28 (2) Å] indiquent que les groupements amide sont sous la forme tautomère iminoalcool. Les longueurs des différentes liaisons C—C présentent une dispersion inhabituelle puisqu'elles vont de 1,47 (2) à 1,58 (2) Å. Toutefois, en raison des incertitudes dont elles sont entachées, ces longueurs ne sont pas incompatibles avec les valeurs généralement admises

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