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trans-Dichlorobis[*o*-phenylenebis(dimethylarsine)]technetium(III), Perchlorate and Chloride Salts

BY R. C. ELDER, ROBERT WHITTLE, KENNETH A. GLAVAN, JUDITH FAYE JOHNSON AND EDWARD DEUTSCH

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, *USA*

(*Received* 22 *January* 1980; *accepted* 12 *March* 1980)

Abstract. *trans*-[TcCl$_2$(diars)$_2$]Cl, diars = *o*-C$_6$H$_4$[As(CH$_3$)$_2$]$_2$, $P2_1/c$, a = 9·354 (5), b = 9·662 (2), c = 15·341 (4) Å, β = 98·75 (6)°, U = 1370·3 Å^3, Z = 2, $d_{\rm meas}$ = 1·86, $d_{\rm calc}$ = 1·88 Mg m^{-3}, R_1 = 0·041, R_2 = 0·049. *trans*-[TcCl$_2$(diars)$_2$]ClO$_4$, $C2$, a = 13·001 (10), b = 10·409 (3), c = 11·796 (8) Å, β = 114·50 (15)°, U = 1452·6 Å^3, Z = 2, $d_{\rm meas}$ = 1·92, $d_{\rm calc}$ = 1·93 Mg m^{-3}, R_1 = 0·027, R_2 = 0·028. The six-coordinate Tc complex has *trans* chloride ligands and four As atoms from two nearly coplanar *o*-phenylenebis(dimethylarsine) ligands, giving ideal D_{2h} symmetry in each case (Cl$^-$ salt, site symmetry $\bar{1}$; ClO$_4^-$ salt, site symmetry 2). The mean Tc—As distance is 2·512 (2) Å (four independent distances, range 0·011 Å), whereas those for Tc—Cl are 2·348 (8), 2·288 (7), and 2·329 (1) Å. The ClO$_4^-$ salt is yellow-orange, whereas the Cl$^-$ salt is dark red.

Introduction. As part of a program studying Tc complexes as radiopharmaceuticals (Deutsch, 1979) we synthesized the title complexes, and, owing to the large difference in color between the two salts, determined the single-crystal structure of each. The syntheses, characterizations and recrystallization procedures will be given elsewhere (Glavan, Whittle, Johnson, Elder & Deutsch, 1980). A dark-red crystal of the Cl$^-$ salt, *trans*-[TcCl$_2$(diars)$_2$]Cl, (0·17 × 0·26 × 0·51 mm) examined *via* precession photographs (*hk*0, *hk*1, *h*0*l*, *h*1*l*) exhibited Laue symmetry and absences consistent with the monoclinic space group $P2_1/c$. Least-squares refinement of 15 pairs of reflections ($\pm 2\theta$) was used to determine cell constants. Intensity data were measured for 4037 reflections (2·5 < 2θ < 55·3°) using Mo $K\alpha$ radiation on a Syntex $P\bar{1}$ diffractometer equipped with a graphite single-crystal monochromator. From these, 3417 unique reflections were obtained by averaging (mean discrepancy for multiply measured reflections, 0·009). Of the unique reflections, 2972 had $I > 2\sigma(I)$. Other conditions of data collection were: scan range 2·0° in 2θ; scan rate 1·0 to 4·0° min^{-1}; four standard reflections measured after every 36 reflections; drift correction (from standards) 1·006 to 0·980. No absorption corrections were applied (μ = 0·562 mm^{-1}) since the crystal had a large cavity of ~30% the volume of the crystal. The estimated maximum error in $|F_o|$ owing to uncorrected absorption is 8%.

All atoms including H were located from Patterson and electron density syntheses. In the final cycles of least-squares refinement, 178 parameters were refined including positional parameters for all atoms and anisotropic thermal parameters for all non-hydrogen atoms. In the last cycle of refinement one parameter [H(23), z coordinate] shifted by 1·1σ and another [H(12), x coordinate] by 0·6σ; the average shift was 0·1σ. The highest peak on a final difference electron density map, 0·70 e Å^{-3}, was within 0·9 Å of Tc. Complex scattering factors corrected for anomalous dispersion were used. Final coordinates for the Cl^- salt are given in Table 1.*

The data collection, structure solution and refinement for the ClO_4^- salt were carried out in an analogous fashion with the following differences: crystal size 0·06 × 0·12 × 0·14 mm; cell constants refined on 11 pairs of reflections; intensity data, maximum $2\theta = 54^\circ$, 1974 (measured), 1665 (unique), 1370 [$I > 2\sigma(I)$]; mean discrepancy for multiply measured reflections 0·01; scan range 1·6° in 2θ; scan rate 1·0 to 8·0° min^{-1}; calculated transmission coefficients ranged from 0·786 to 0·572 (checked against Ψ scans); ClO_4^- disorder treated with two sets of half-population O atoms; H atoms placed at fixed positions (ideal geometry); refinement of model in space group $C2/m$ led to significantly poorer agreement (Hamilton, 1965); choice of enantiomer tested by refinement of alternate model; highest peak on final electron density difference map 0·3 e Å^{-3}; final model, $R_1 = 0{\cdot}027$, $R_2 = 0{\cdot}028$. Final coordinates for the ClO_4^- salt are in Table 2.

Bond lengths for both complexes are presented in Table 3 and selected bond angles are given in Table 4.

Discussion. The structure of [$TcCl_2$(diars)$_2$]$^+$ as the Cl^- salt is shown in Fig. 1. The idealized symmetry of the six-coordinate complex cation is D_{2h}. In the Cl^- salt the site symmetry is $\bar{1}$, requiring a *trans* complex. In the ClO_4^- salt, the site symmetry is 2, which could allow a *cis* or *trans* structure, although the *trans* structure is in fact found. The similarity between the structures of the complex cation in the Cl^- salt and in the ClO_4^- salt is

Table 1. *trans*-[$TcCl_2$(diars)$_2$]Cl: *atom coordinates* (×10^4)

	x	*y*	*z*
Tc	0 (0)	0 (0)	0 (0)
As(1)	2088 (1)	−1580 (1)	−117 (1)
As(2)	841 (1)	1139 (1)	−1303 (1)
Cl(1)	1469 (1)	1426 (1)	981 (1)
C(11)	2293 (4)	−34 (3)	−1726 (2)
C(12)	2829 (5)	278 (4)	−2489 (3)
C(13)	3965 (5)	−513 (5)	−2738 (3)
C(14)	4505 (5)	−1614 (4)	−2226 (3)
C(15)	3942 (5)	−1951 (4)	−1463 (3)
C(16)	2831 (4)	−1181 (4)	−1200 (2)
C(20)	−585 (6)	1469 (6)	−2338 (3)
C(21)	1810 (7)	2917 (6)	−1156 (4)
C(30)	3837 (5)	−1453 (5)	750 (3)
C(31)	1639 (5)	−3532 (4)	−163 (3)
Cl(3)	5000 (0)	0 (0)	5000 (0)

Table 2. *trans*-[$TcCl_2$(diars)$_2$]ClO_4: *atom coordinates* (×10^4)

	x	*y*	*z*
Tc	0 (0)	0 (0)	0 (0)
As(1)	−178 (1)	−13 (4)	−2209 (1)
As(2)	2081 (1)	−27 (4)	535 (1)
Cl(1)	0 (0)	−2256 (7)	0 (0)
Cl(2)	0 (0)	2198 (7)	0 (0)
C(11)	2287 (4)	−15 (21)	−1017 (5)
C(12)	3362 (5)	−46 (28)	−995 (5)
C(13)	3495 (5)	−50 (23)	−2088 (6)
C(14)	2573 (6)	−183 (28)	−3220 (6)
C(15)	1509 (5)	23 (25)	−3238 (5)
C(16)	1345 (5)	99 (29)	−2172 (5)
C(20)	3001 (11)	−1458 (10)	1445 (12)
C(21)	2931 (13)	1441 (17)	1430 (15)
C(30)	−995 (12)	−1456 (19)	−3226 (11)
C(31)	−782 (14)	1461 (19)	−3317 (16)
Cl(3)	0 (0)	4811 (16)	5000 (0)
O(1)	−74 (39)	3550 (36)	4802 (71)
O(2)	−142 (24)	5231 (37)	6028 (28)
O(3)	1256 (14)	4666 (54)	5582 (19)
O(4)	−163 (39)	5618 (66)	4065 (38)

Table 3. *Bond lengths* (Å)

	Cl^- salt	ClO_4^- salt
Tc–As(1)	2·507 (1)	2·518 (2)
Tc–As(2)	2·510 (1)	2·511 (2)
Tc–Cl(1)	2·329 (1)	2·348 (8)
Tc–Cl(2)		2·288 (7)
As(1)–C(16)	1·935 (4)	1·966 (7)
As(1)–C(30)	1·949 (4)	1·941 (17)
As(1)–C(31)	1·931 (4)	1·957 (19)
As(2)–C(11)	1·954 (4)	1·957 (6)
As(2)–C(20)	1·939 (5)	1·933 (11)
As(2)–C(21)	1·939 (6)	1·924 (16)
C(11)–C(12)	1·375 (6)	1·388 (9)
C(12)–C(13)	1·408 (7)	1·369 (10)
C(13)–C(14)	1·372 (6)	1·383 (9)
C(14)–C(15)	1·392 (7)	1·391 (12)
C(15)–C(16)	1·388 (6)	1·361 (10)
C(16)–C(11)	1·418 (5)	1·409 (7)

Table 4. *Selected bond angles* (°)

	Cl^- salt	ClO_4^- salt
As(1)–Tc–As(2)	82·4 (1)	83·5 (1)
As(1)–Tc–Cl(1)	89·0 (1)	89·7 (1)
As(2)–Tc–Cl(1)	91·7 (1)	89·4 (1)
C(16)–As(1)–C(30)	101·5 (2)	110·4 (9)
C(16)–As(1)–C(31)	105·5 (2)	95·1 (9)
C(16)–As(1)–Tc	109·0 (1)	108·5 (2)
C(30)–As(1)–C(31)	104·0 (2)	103·2 (7)
C(30)–As(1)–Tc	119·7 (2)	115·8 (5)
C(31)–As(1)–Tc	115·5 (2)	121·7 (6)
C(11)–As(2)–C(20)	104·4 (2)	103·4 (7)
C(11)–As(2)–C(21)	102·5 (2)	103·8 (8)
C(11)–As(2)–Tc	109·2 (1)	108·4 (1)
C(20)–As(2)–C(21)	101·6 (3)	103·0 (5)
C(20)–As(2)–Tc	117·7 (2)	120·2 (5)
C(21)–As(2)–Tc	119·6 (2)	116·3 (6)

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* Lists of structure factors, thermal parameters, r.m.s. displacements, bond angles, hydrogen atom coordinates, bond lengths involving hydrogen atoms and least-squares ligand planes for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35208 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

apparent on inspection of Tables 3 and 4. Tc—As, As—C and C—C distances as well as the diars ligand angles are quite similar for both structures. However, the Tc—Cl distances show large differences, caused apparently by the different distortions from ideal symmetry in each structure. In the Cl^- salt, with $\bar{1}$ site symmetry, the two Tc—Cl distances are equal by symmetry at 2·329 (1) Å. This value agrees reasonably with the average value, 2·318 (6) Å, found for the ClO_4^- salt. However, in the latter structure the two crystallographically independent Tc—Cl distances differ by 0·060 (11) Å. Two factors seem responsible for this rather large difference. First, the two diars ligands are both tipped by ~4·0° toward Cl(1), resulting in significantly greater repulsion between the diars methyl H atoms and Cl(1) [Cl(1)···H, closest neighbors: 2·89 and 3·00 Å] and relieving the Cl(2) to diars ligand repulsion [Cl(2)···H, closest neighbors: 3·08 and 3·10 Å]. Second, the repulsion between Cl(1) and neighboring ions is less [Cl(1), closest neighbor ion contacts: 3·27 and 3·14 Å] than that for Cl(2) [Cl(2), closest neighbor ion contacts: 3·11 and 2·93 Å]. Thus intramolecular forces tend to elongate Tc—Cl(1), 2·348 Å, and intermolecular forces tend to compress Tc—Cl(2), 2·288 Å. It should be noted that any discussion of the ClO_4^- salt structure must be regarded with some caution. Although refinement converged to relatively low R factors, the ClO_4^- is rotationally disordered, the phenylene rings are not as planar as would be expected (r.m.s. deviation from least-squares plane; ClO_4^- salt, 0·056 Å; Cl^- salt, 0·007 Å) and only 1474 observations were used to refine 155 parameters.

Comparison with two published structures, *trans*-[CoCl(diars)$_2$]ClO_4 (Pauling, Porter & Robertson, 1970) and *trans*-[$NiCl_2$(diars)$_2$]Cl (Kreisman, Marsh, Preer & Gray, 1968), would seem especially appropriate. The diars ligand structure in each of these is very similar to those found here and the comments by Pauling *et al.* concerning the angles about As clearly apply here as well. The Co complex is isostructural* with *trans*-[$TcCl_2$(diars)$_2$]ClO_4. However, the refinement in space group $C2$ was artificially constrained to have C_{2h} symmetry in the Co complex and was based on only 549 observations, so no additional insights into the cation distortion may be gained. Unfortunately, the Ni complex, which is isostructural with *trans*-[$TcCl_2$(diars)$_2$]Cl [Ni complex cell constants: a = 9·33 (1), b = 9·67 (7), c = 14·87 (2) Å, β = 98·6 (1)°, space group $P2_1/c$] was published without details and only refined to R = 0·14. The Ni—Cl length, given as 2·43 Å by Kreisman *et al.*, is suspiciously long. This value is 0·21 Å longer than the Co—Cl length found in [$CoCl_2$(diars)$_2$]ClO_4. The difficulty with the reported Ni—Cl bond length of 2·43 Å becomes more obvious on comparing cell constants for *trans*-[$CoCl_2$(diars)$_2$]ClO_4 and *trans*-[$NiCl_2$(diars)$_2$]ClO_4 (Pauling, Porter & Robertson, 1970). Specifically, the value of b is 10·27 (2) Å for the Co complex and 10·37 (3) Å for the Ni complex. Since the Cl—M—Cl vector is required to be coincident with the b axis, it would seem more likely that Co—Cl and Ni—Cl would differ at most by one-half the difference in cell constants, or 0·05 Å.

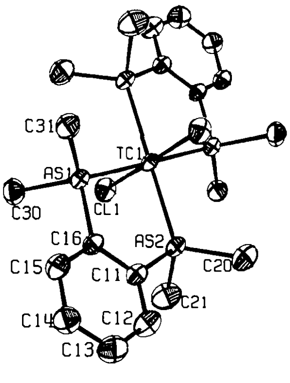

Fig. 1. The complex cation in *trans*-[$TcCl_2$(diars)$_2$]Cl with H atoms omitted.

The average Tc—Cl lengths found here [Cl^- salt, 2·329 (1) Å; ClO_4^- salt, 2·318 (6) Å] may be compared with recently determined values for $(NH_4)_2[TcCl_6]$, 2·353 (1) Å (Elder, Estes & Deutsch, 1979), for $[TcCl_4O]^-$, 2·31 (1) Å (Cotton, Davison, Day, Gage & Trop, 1979) and for [$TcCl_2(Hbpz_3)O$], 2·328 (6) Å (Thomas, Estes, Elder & Deutsch, 1979). Thus the Tc^{III}—Cl bond length determined here falls within the range of those found for Tc^{IV}—Cl and Tc^{V}—Cl and indicates that the Tc—Cl distance does not vary systematically with oxidation state.

Finally, the striking difference in color between the Cl^- salt (dark red) and the ClO_4^- salt (yellow-orange) deserves comment. Obviously, this does not arise from the originally suspected geometrical isomerism, since both salts contain the *trans* isomer. The Tc complex is centrosymmetric in the Cl^- salt and not in the ClO_4^- salt. The relaxation in selection rules expected with the loss of an inversion center might possibly explain the difference in color, although the complex lacking the inversion center would be expected to be the darker of the two. It appears more likely that the color difference is due to a charge-transfer transition, specifically involving the Cl^- anion which is absent from the ClO_4^- salt.

This study was supported by the National Institutes of Health (Grant No. HL-21276).

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* The cell constants for *trans*-[$CoCl_2$(diars)$_2$]ClO_4, a = 12·67 (2), b = 10·27 (2), c = 13·43 (2) Å, β = 127·5 (3)°, are for a non-conventional monoclinic cell, space group $C2$. They may be transformed to a conventional cell, space group $C2$, with a = 12·67 (2), b = 10·27 (2), c = 11·57 (2), β = 112·9 (3)°.

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