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Characterization of the Trinegative Octachloroditechnetate Ion[1]

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Received July 28, 1969

The compound $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$, first reported several years ago by Eakins, Humphreys, and Mellish, has been further investigated. Our work, which includes a single-crystal X-ray structural study, confirms the reported composition and demonstrates the presence of the $Tc_2Cl_8^{3-}$ ion having the same nonbridged, eclipsed Cl_4M–MCl_4 structure (idealized D_{4h} symmetry) as the $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ ions. The very short Tc–Tc distance (2.13 ± 0.01 Å) is indicative of a very strong metal to metal bond. The magnetic susceptibility obeys the Curie law with $\mu \approx 2.0$ BM ($\theta = 0 \pm 5°$). Spectrophotometric study of the oxidation to $TcCl_6^{2-}$ showed no evidence for a stable intermediate (such as $Tc_2Cl_8^{2-}$). The $Tc_2Cl_8^{3-}$ ion is evidently analogous to the $Re_2Cl_8^{3-}$ ion, which has been obtained by electrolytic reduction of $Re_2Cl_8^{2-}$ though not yet isolated; it presumably contains four pairs of electrons which constitute a quadruple Tc–Tc bond with one electron in essentially a nonbonding orbital. The ammonium salt crystallized in the trigonal system, space group $P3_221$ (or its enantiomorph) with the following hexagonal unit cell dimensions: $a = 13.04 \pm 0.02$ Å, $c = 8.40 \pm 0.01$ Å. The density calculated for three formula weights per unit cell (2.30 g cm^{-3}) agrees satisfactorily with the reported measured density (2.4 g cm^{-3}). The structure was solved and refined by least squares using 292 independent nonzero reflections recorded by Weissenberg photography. The final conventional residual is 9.8%. The arrangement of NH_4^+ ions and water molecules is complex, involving some fractional site occupancy by water molecules.

Introduction

At the time the compound $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ was reported by Eakins, Humphreys, and Mellish[2] the true nature of the $Re_2Cl_8^{2-}$ ion had just been recognized[3-6] although this species had been prepared and incorrectly formulated earlier.[7] At that time nothing was known of the $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$ species which have since been generated[8] though not yet isolated in solid compounds, but the view that $Re_2X_8^{2-}$ species should have particularly stable, closed-shell structures with Re–Re quadruple bonding had been put forward.[6] Thus in the context of the time the charge of 3− on $Tc_2Cl_8^{3-}$ seemed distinctly surprising and further investigation of the compound $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ was immediately undertaken. These studies, as we have already reported in a preliminary note,[9] confirmed the stoichiometry and revealed the structure of the $Tc_2Cl_8^{3-}$ ion. In this paper, our studies are described in full.

Experimental Section

Preparation.—In its essentials, the method of preparation was the same as that of Eakins, Humphreys, and Mellish. Two grams of ammonium pertechnetate (^{99}Tc) was purchased from the Oak Ridge National Laboratory. The NH_4TcO_4 was converted with about 90% yield to $(NH_4)_2TcCl_6$. This was then reduced with zinc in hot, concentrated hydrochloric acid. Our experience differed in one respect from that reported by Eakins, *et al.* They described the formation of a reddish brown solution (postulated to contain Tc in a lower oxidation state) in hydrochloric acid during the final crystallization step which was immediately oxidized to yield the turquoise solution containing the $Tc_2Cl_8^{3-}$. Several efforts to repeat this part of the procedure were without success. If reduction was carried beyond the stage where the solution is dark blue-green, all the technetium formed an insoluble black precipitate, presumably technetium metal.

The product we obtained, a black crystalline material, always contained traces of $(NH_4)_2TcCl_6$ which were visible under a microscope. Analytical data were satisfactory. *Anal.* Calcd for $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$: NH_4, 9.47. Found: NH_4, 9.25, 9.45.

Magnetic Measurements.—The Gouy method was not used owing to the limited amount of material available and the contamination problems encountered in grinding the solid. An esr measurement indicated the presence of unpaired electrons but was quantitatively inconclusive. The signal was extremely broad. The nmr technique of Evans[10] was not sufficiently sensitive to afford a reliable result although the result obtained was fortuitously close to 2.0 BM. A satisfactory measurement was obtained on the micro-Faraday balance at the Lawrence Radiation Laboratory of the University of California, Berkeley, Calif., through the kindness of Professor B. B. Cunningham and Messrs. B. Bansal and S. Marei. The data they obtained are given in Table I. A plot of χ_g^{-1} *vs.* T gave a straight line which intercepted the T axis at 0 ± 5°. From the slope a value of 2.0 BM was calculated for the magnetic moment. Corrections for diamagnetism were not applied owing to the uncertainty already introduced by the presence of traces of impurities as previously noted. Probably the magnetic moment is reliable only to within ±0.2 BM.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$

Temp, °K	$10^5\chi_g^{-1}$, cgsu	Temp, °K	$10^5\chi_g^{-1}$, cgsu
77	0.92	274	3.04
198	2.24	298	3.40

Electronic Absorption Spectrum.—Both a solution spectrum, using Cary Models 11 and 14, and the reflectance spectrum of the solid, using a Beckman Model DU, were recorded. In order to avoid contamination problems the solid sample was not finely ground and this gave a rather poor-quality spectrum. The solutions were made in concentrated hydrochloric acid purged with nitrogen and maintained in a nitrogen atmosphere. The results are shown in Figure 1.

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[1] Supported by the United States Atomic Energy Commission.

[2] J. D. Eakins, D. G. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 6012 (1963).

[3] *Cf.* F. A. Cotton, *et al.*, *Science*, **145**, 1305 (1964).

[4] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

[5] F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

[6] F. A. Cotton, *ibid.*, **4**, 334 (1965).

[7] *Cf.* B. G. Kuznetsov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963), and references to earlier Russian literature cited therein.

[8] F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 1257 (1965).

[9] W. K. Bratton and F. A. Cotton, *J. Am. Chem. Soc.*, **87**, 921 (1965).

[10] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

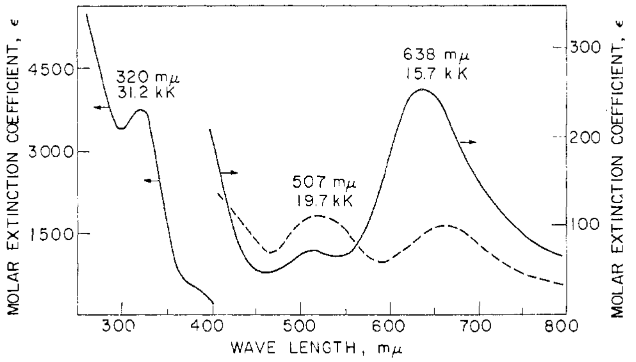

Figure 1.—The electronic absorption spectrum of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$. The solid curve is for a deoxygenated HCl solution. The wavelengths in (mμ) and frequencies (in kilokaisers, kK) of the maxima in this spectrum are noted. The dashed line is the reflectance spectrum on an arbitrary scale of intensity.

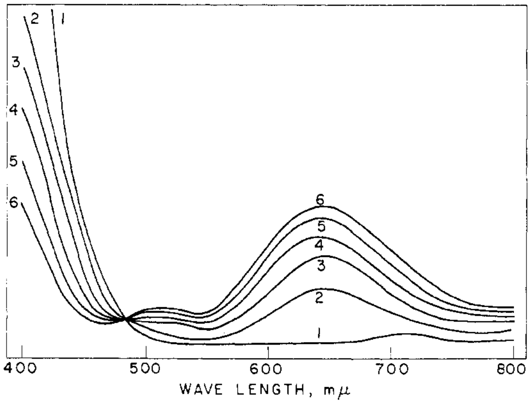

Figure 2.—The spectrum of an HCl solution of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ as a function of time in the presence of oxygen, on an arbitary absorbancy scale.

It was observed that on exposure to oxygen the hydrochloric acid solutions of $Tc_2Cl_8^{3-}$ became green and finally yellow, the yellow solution being stable and having the spectrum of $TcCl_6^{2-}$. In order to see if any intermediate species, as, for example, $Tc_2Cl_8^{2-}$, might be detectable in the green solution, the oxidation was followed spectrophotometrically for 2 days. The six curves shown in Figure 2 were recorded at roughly equal intervals, *i.e.*, about every 8 hr. There is only one isosbestic point and no evidence for an intermediate.

Eakins, *et al.*,[2] reported a maximum at 615 mμ, with ε 185. This is in disagreement with our spectrum.

X-Ray Data.—The crystals were in the form of brittle, black, prismatic needles of hexagonal cross section. Several small crystals were sealed in glass capillaries, and one, which had a mean diameter of about 0.15 mm and a length of 0.40 mm, was selected for study.

The unit cell parameters were determined from an oscillation photograph and a precession photograph for *c* and from the *hk*0 Weissenberg photograph for *a* and *b*. Uncertainty intervals represent average deviations from the mean. The hexagonal cell has the following dimensions: $a = 13.04 \pm 0.02$ Å, $c = 8.40 \pm 0.01$ Å. The symmetry observed on the Weissenberg films and the single systematic extinction condition $l \neq 3n$ for 00*l*, observed on a precession photograph, indicated the space group to be either $P3_121$ or $P3_221$. The two enantiomorphs are indistinguishable within the limits of our film data; the latter was used in refinement of the structure. Assuming three formula weights in the unit cell, a density of 2.3 g cm^{-3} is calculated, in satsfactory agreement with the reported density[2] of 2.4 g cm^{-3}.

Intensities were measured using equiinclination Weissenberg multiple-film records of the six levels *hk*0–*hk*5, made with copper Kα radiation. The intensities of 412 reflections within a twelfth sphere bounded by $\theta < 49°$ were estimated visually by comparison with a series of timed exposures of a strong zero-level reflection. Reflections too weak to be read (120) were assigned an uncorrected intensity equal to half the intensity of the weakest observable reflection.

The film data were corrected for Lorentz and polarization factors using a computer program DFSET-4 made available by Professor M. J. Buerger and for absorption (μ = 270 cm^{-1}) using a cylindrical approximation and data tabulated in ref 11. The radioactivity of the substance did not affect the data in any detectable way.

Solution and Refinement of the Structure

From a three-dimensional map of the Patterson function the technetium atoms were assigned coordinates of a sixfold general position. These parameters, as well as six independent scale factors for the six Weissenberg levels, were subjected to two cycles of full least-squares refinement and used to calculate phases for an electron density map. This map revealed the locations of all four independent chlorine atoms, which lie on general positions. Two further cycles of refinement of all the positional parameters, independent isotropic atom temperature factors, and six film-scale factors using unit weights for all reflections led to a conventional R value of 17.7% ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) for all 412 reflections. A difference Fourier map calculated from these parameters showed peaks of 2.0–4.0 e$^-$/Å^3 which were reasonable locations for NH_4^+ ions and water molecules, as well as peaks of similar intensity near the heavy-atom positions. One set of general-position peaks and one special-position set were assigned to ammonium ions. A second general position, as well as another special position, appeared to be occupied by water molecules. If the two independent water positions were fully occupied, there would be three water molecules in the cell per dimeric anion. However, the general-position peaks were somewhat lower in intensity than those due to the special-position water molecule, suggesting a possible fractional occupancy of the general-position site. The positional and isotropic thermal parameters of the light atoms as well as occupancy factors for the two water molecules were introduced and refined together with the previously determined parameters for three cycles of least-squares refinement, resulting in convergence and an unweighted R of 13.6%. The occupancy factors of the water molecules had refined to values of 0.5 ± 0.2 for the general position (O_1) and 0.8 ± 0.2 for the special position (O_2). This indicates ~1.8 water molecules per dimer, in agreement with the published analytical results.

At this point a detailed comparison of the observed and calculated structure factors was made, and the error for the data observed as zero was found to be very large (R = 55%) compared to that for the other observations. The variation in error with $|F_o|$ also indicated that the use of equal unit weights for all observations was invalid, as had been anticipated. Four further cycles of refinement were carried out using only the

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(11) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, Table 5.3.5B.

292 nonzero observed reflections and a Cruickshank-type of weighting scheme [$w = 1/(2 + 0.01F_o^2)$]. The occupancy and thermal parameters of the two water atoms refined to unrealistic values, presumably because the rejected zero data generally occurred at high angles and were important in determining the thermal parameters. The occupancy factors were therefore fixed at 0.5 for O(1) and 1.0 for O(2) and four final cycles of refinement were carried out on all the other variables. The final values for R_1 and R_2 were 9.8 and 13.0%, respectively ($R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$). The variation of error with $|F_o|$ and $(\sin \theta)/\lambda$ was satisfactorily small and random, and the esd of an observation of unit weight was 1.13, indicating that the weighting scheme chosen was satisfactory. A final difference Fourier map showed peaks as high as 1.6 $e^-/Å^3$ near the heavy atoms, but no other peaks suggesting the presence of other atoms in the unit cell were observed.

Atomic scattering factors used throughout were taken from Cromer and Waber[12] for Tc and Cl and from Ibers[13] for N and O. Anomalous dispersion corrections[14] for Tc and Cl were included in the calculations in the manner prescribed by Ibers and Hamilton.[15] The structure was actually refined in both of the space groups $P3_121$ and $P3_221$ using real and imaginary parts of the anomalous dispersion correction. The results of *both* refinements were the same in terms of both R values and molecular dimensions. Computer programs used were SFLS5 and FORDAP in their local forms.

Results

The structure of the $Tc_2Cl_8^{3-}$ ion and the location of the ammonium ions with respect to it are shown in Figure 3. A crystallographic twofold axis bisects the metal–metal bond and passes through the special position ammonium ion, N(2). Figure 4 shows the crystal packing viewed down the unique axis. Table II contains the final calculated and observed structure amplitudes for the observed reflections. The reflections observed as zero are not reported. The calculated amplitudes for these unobserved reflections are in most cases smaller than that of the minimum observed value, and in no case do they exceed twice the minimum observable. Table III lists the final positional and thermal parameters of the atoms. The occupancy factors of O(1) and O(2) were fixed at 0.5 and 1.0, respectively. Intramolecular distances and angles are reported in Table IV, and Table V lists other crystal contacts up to 4 Å.

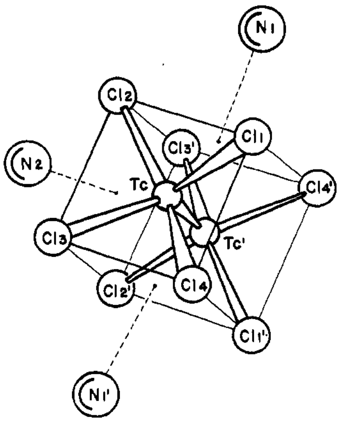

Figure 3.—A perspective view of the $Tc_2Cl_8^{3-}$ ion and its nearest nitrogen atom neighbors. A crystallographic twofold axis bisects the metal–metal bond and passes through N(2).

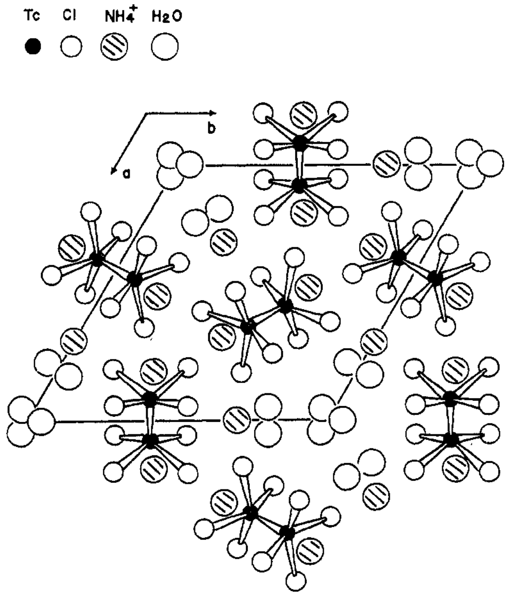

Figure 4.—A diagram showing the crystal packing in projection down the trigonal axis.

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES IN UNITS OF 0.1 ELECTRON

H	K	FOBS	FCAL
L = 0**			
2	0	1171	927
3	0	170	135
4	0	356	357
5	0	310	359
6	0	426	397
7	0	816	938
8	0	590	622
1	1	1888	1731
2	1	645	609
3	1	268	272
4	1	327	341
5	1	297	331
6	1	835	764
7	1	484	472
8	1	381	406
9	1	202	204
0	2	863	927
1	2	638	609
2	2	167	128
4	2	611	590
5	2	748	753
7	2	478	447
8	2	223	234
9	2	262	316
0	3	156	155
1	3	244	272
3	3	1237	1313
4	3	1025	1082
5	3	1238	1097
6	3	197	194
7	3	266	304
8	3	381	420
9	3	478	488
0	4	356	357
1	4	298	341
2	4	581	590
3	4	1112	1082
4	4	594	573
5	4	729	717
6	4	504	540
7	4	504	455
8	4	308	313
0	5	340	359
1	5	325	331
2	5	719	753
3	5	1031	1097
4	5	698	717
5	5	265	291
7	5	215	210
0	6	442	397
1	6	916	764
4	6	485	540
0	7	941	938
1	7	530	472
2	7	544	447
3	7	293	304
4	7	486	455
5	7	215	210
0	8	626	622
1	8	418	406
2	8	244	234
3	8	418	420
4	8	337	313
2	9	314	316
3	9	606	488
0	10	200	215
L = 1**			
2	0	1054	1057
3	0	409	335
4	0	2960	2327
7	0	739	780
8	0	428	510
9	0	480	600
10	0	431	487
1	1	395	420
2	1	728	598
3	1	876	637
6	1	277	313
7	1	1251	1126
0	2	1611	1780
1	2	155	176
2	2	546	501
3	2	335	281
4	2	754	654
6	2	575	581
7	2	473	473
8	2	400	463
1	3	1577	1686
2	3	956	941
3	3	210	295
4	3	1053	1055
5	3	570	606
7	3	479	512
8	3	251	322
0	4	1645	1551
1	4	342	371
2	4	365	399
3	4	1324	1341
4	4	923	868
5	4	673	667
0	5	882	920
1	5	886	783
2	5	1275	1095
3	5	647	729
5	5	524	536
7	5	218	204
1	6	179	211
3	6	514	519
4	6	766	390
5	6	277	271
0	7	1114	1027
1	7	320	352
3	7	479	452
4	7	436	433
1	8	225	233
4	8	382	384
2	9	391	342
0	10	360	331
1	10	727	633
L = 2**			
2	0	315	322
4	0	227	281
6	0	684	653
7	0	520	521
8	0	891	790
9	0	229	239
10	0	222	214
1	1	615	670
2	1	572	559
3	1	314	285
4	1	240	238
6	1	772	685
7	1	837	394
8	1	299	357
9	1	272	272
1	2	360	426
2	2	929	966
3	2	215	192
4	2	255	282
5	2	866	654
6	2	692	641
7	2	675	572
0	3	3117	3421
1	3	946	1127
2	3	895	934
4	3	781	810
5	3	449	482
6	3	465	488
7	3	433	498
8	3	294	277
0	4	1886	2016
1	4	1000	1035
2	4	974	1012
3	4	745	826
4	4	682	641
5	4	386	389
6	4	300	329
7	4	427	472
0	5	1086	1107
1	5	689	565
3	5	539	567
4	5	500	479
5	5	252	280
6	5	357	328
7	5	409	386
1	6	232	244
4	6	274	302
5	6	565	510
0	7	216	234
3	7	360	375
5	7	519	459
0	8	246	240
3	8	709	628
0	9	549	497
1	9	544	409
0	10	606	468
L = 3**			
1	0	922	938
3	0	190	203
4	0	1336	1276
5	0	1110	971
7	0	995	1056
8	0	247	327
9	0	427	122
0	1	195	191
1	1	424	494
2	1	849	851
3	1	674	666
4	1	715	701
6	1	891	911
7	1	268	242
8	1	470	481
0	2	348	331
1	2	1020	1067
3	2	877	715
4	2	548	556
5	2	441	415
8	2	466	513
1	3	745	823
2	3	809	879
3	3	377	418
4	3	1090	1048
5	3	579	610
7	3	246	289
0	4	1759	1606
1	4	1029	990
2	4	548	579
3	4	555	538
5	4	295	302
7	4	456	478
0	5	1110	1141
2	5	335	359
3	5	264	237
6	5	381	287
0	6	362	446
1	6	404	452
4	6	358	346
5	6	381	308
0	7	659	601
1	7	294	294
3	7	428	459
4	7	788	656
1	8	272	237
2	8	883	666
L = 4**			
1	0	426	470
2	0	283	255
3	0	2758	2143
4	0	547	504
5	0	952	787
7	0	537	590
8	0	376	451
9	0	688	676
0	1	555	532
1	1	454	429
2	1	463	433
3	1	1193	1042
4	1	792	710
5	1	424	457
6	1	280	337
7	1	711	665
0	2	644	523
2	2	1071	892
3	2	564	577
4	2	290	367
7	2	259	263
8	2	250	322
1	3	953	990
2	3	226	272
0	4	870	776
1	4	276	283
0	5	409	456
1	5	424	474
5	5	256	310
0	6	394	482
1	6	307	358
2	6	491	433
4	6	369	386
0	7	1018	857
2	7	539	493
3	7	551	608
0	8	849	788
1	8	308	338
0	9	252	212
L = 5**			
1	0	914	834
2	0	982	801
4	0	927	825
5	0	550	623
6	0	237	277
7	0	938	803
8	0	560	596
0	1	287	230
3	1	1290	1061
4	1	323	354
5	1	384	485
0	2	451	419
1	2	462	415
2	2	613	544
3	2	378	477
5	2	344	315
6	2	236	260
7	2	253	322
0	3	1103	1093
1	3	746	724
2	3	242	298
4	3	285	385
0	4	258	281
1	4	367	376
2	4	262	362
0	5	361	340
1	6	413	377
2	6	343	325
0	7	713	614
1	7	848	757
2	7	277	285
0	8	367	437

Discussion

It is convenient to consider first the structure of the $Tc_2Cl_8^{3-}$ ion, since the structure forms a basis for discussion of the other properties of the compound. As

(12) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(13) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(14) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(15) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

TABLE III

POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	y	z	B, Å^2
Tc	0.6336 (5)	0.5520 (4)	0.0639 (7)	3.7 (2)
Cl(1)	0.7402 (16)	0.6837 (14)	0.2682 (22)	5.0 (4)
Cl(2)	0.4940 (13)	0.4384 (14)	0.2642 (23)	4.6 (4)
Cl(3)	0.5695 (13)	0.3645 (13)	−0.0595 (18)	3.9 (3)
Cl(4)	0.8132 (15)	0.6174 (14)	−0.0683 (25)	4.5 (4)
N(1)	0.483 (5)	0.673 (4)	0.416 (7)	5 (1)
N(2)	0.299 (7)	0.299[b]	0.0000	7 (2)
O(1)	0.180 (8)	0.231 (7)	−0.275 (11)	4 (2)
O(2)	0.0000	0.053 (7)	−0.167 (10)	13 (3)

[a] Numbers in parentheses following each parameter, here and in the following tables, are estimated standard deviations in the last significant figure, as obtained from the final cycle of least-squares refinement. [b] This coordinate is fixed equal to x by symmetry and was not refined.

TABLE IV

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG)[a]

Bond Distances

Atoms	Distance	Atoms	Distance
Tc–Tc′	2.13 (1)	Tc–Cl(1)	2.33 (2)
Tc–Cl(2)	2.38 (2)	Tc–Cl(3)	2.39 (2)
Tc–Cl(4)	2.33 (2)		

Nonbonded Distances

Cl(1)–Cl(2)	3.20 (2)	Cl(1)–Cl(4)	3.24 (3)
Cl(1)–Cl(4)′	3.31 (3)	Cl(2)–Cl(3)	3.20 (3)
Cl(2)–Cl(3)′	3.41 (3)	Cl(3)–Cl(4)	3.24 (2)

Interbond Angles

Atoms	Angle	Atoms	Angle
Tc′–Tc–Cl(1)	105.4 (6)	Tc′–Tc–Cl(2)	104.5 (6)
Tc′–Tc–Cl(3)	106.6 (5)	Tc′–Tc–Cl(4)	103.8 (6)
Cl(1)–Tc–Cl(2)	85.8 (6)	Cl(2)–Tc–Cl(3)	84.4 (6)
Cl(3)–Tc–Cl(4)	86.6 (6)	Cl(1)–Tc–Cl(4)	87.8 (7)

[a] Bonds and angles in Tables IV and V were calculated with BONDLA, a part of the X-Ray 67 package written by F. A. Kundell, J. M. Stewart, and R. V. Chastain.

TABLE V

IMPORTANT INTERMOLECULAR CONTACTS

Atoms	Contact distance, Å	Position of contact atom[a]
Tc–Cl(3)	3.66 (2)	$y - x, -x, {}^1/_3 + z$
N(1)–Cl(1)	3.52 (7)	x, y, z
N(1)–Cl(2)	3.38 (7)	x, y, z
N(1)–Cl(3)	3.33 (6)	$y, x, -z$
N(1)–Cl(4)	3.42 (6)	$y, x, -z$
N(1)–Cl(1)	3.52 (6)	$y, x, 1 - z$
N(1)–Cl(2)	3.42 (6)	$y, x, 1 - z$
N(1)–Cl(2)	3.40 (6)	$1 - x, 1 + y - x, {}^2/_3 - z$
N(1)–Cl(3)	3.30 (7)	$1 - x, 1 + y - x, {}^2/_3 - z$
N(1)–Cl(3)	3.41 (6)	$x - y, 1 - y, {}^1/_3 - z$
N(2)–Cl(2)	3.17 (5)	x, y, z[b]
N(2)–Cl(3)	3.23 (9)	x, y, z
N(2)–O(1)	2.7 (1)	x, y, z
N(2)–Cl(1)	3.33 (9)	$1 - y, x - y, -{}^1/_3 + z$
O(1)–O(2)	2.5 (1)	x, y, z
O(1)–Cl(2)	3.40 (7)	$y, x, -z$
O(1)–Cl(4)	3.1 (1)	$1 - y, x - y, -{}^1/_3 + z$
O(1)–Cl(1)	3.4 (1)	$y - x, 1 - x, -{}^2/_3 + z$
O(1)–Cl(1)	3.7 (1)	$x - y, 1 - y, {}^1/_3 - z$
O(1)–Cl(4)	3.3 (1)	$x - y, 1 - y, -{}^2/_3 - z$
O(2)–O(2)	3.04 (4)	$y, x, -z$[b]

[a] The first atom is taken to be at the x, y, z coordinates given in Table III, while the second atom is at a position defined in terms of its coordinates of Table III, transformed as indicated in column 3 of this table. [b] Each contact listed for a special-position atom (N(2), O(2)) represents two equal contacts arising from a crystallographic twofold axis passing through these atoms.

indicated by Figure 3 and the distances and angles in Table III, the structure is very similar to those found for the $Re_2Cl_8^{2-}$ ion[5,7] and, more recently, for the $Mo_2Cl_8^{4-}$ ion.[16,17] It consists of two $TcCl_4$ groups joined by a very short Tc–Tc bond (2.13 (1) Å) to give an eclipsed rotational configuration.

The $Tc_2Cl_8^{3-}$ structure is most directly comparable to that of $Mo_2Cl_8^{4-}$. The metal–metal distances, 2.13 (1) and 2.134 (1) Å, respectively, are virtually identical in the two structures, and the M–M–Cl and acute Cl–M–Cl angles have very similar average values. The most notable difference between the two structures occurs in the M–Cl bond lengths, which have a mean value of 2.45 Å in $Mo_2Cl_8^{4-}$ and 2.36 Å in $Tc_2Cl_8^{3-}$. As a result of this the Cl···Cl nonbonded contacts are shorter, particularly those between Cl atoms bound to the same metal atom, the mean values being 3.22 Å in $Tc_2Cl_8^{3-}$ and 3.35 Å in $Mo_2Cl_8^{4-}$.

There is little with which to compare the mean Tc–Cl distance, 2.36 Å, found in this structure. The only previously reported structure containing Tc–Cl bonds is that of $TcCl_4$ in which the distances range from 2.24 Å for the bonds to nonbridging Cl atoms to 2.38 and 2.49 Å for bonds to bridging Cl atoms.[18]

The electronic absorption spectrum of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ is shown in Figure 1. The main absorption in the visible region, which accounts for the turquoise blue color of the solutions, has a maximum at 638 mμ. Eakins, Humphreys, and Mellish[2] stated that a solution of the compound in concentrated hydrochloric acid showed a maximum at 615 mμ. Our measurements have been repeated several times on two different instruments; assuming that we are dealing with the same compound, it appears that there is an inaccuracy in the previous report. Figure 1 also shows the reflectance spectrum of the solid compound. The difficulties involved in finely powdering a radioactive solid without special handling equipment forced us to use a rather coarsely ground sample, thus impairing the quality of the spectrum. However, it seems that the results are consistent with the idea that the same species is present in the solid and in concentrated hydrochloric acid solution.

It might be expected that a stable species $Tc_2Cl_8^{2-}$, analogous to $Re_2Cl_8^{2-}$, could be formed by oxidation of $Tc_2Cl_8^{3-}$. When it was observed that a hydrochloric acid solution of $Tc_2Cl_8^{3-}$ is slowly oxidized to a yellow solution of the $TcCl_6^{2-}$ ion, passing through an intermediate green stage, an attempt was made to observe an intermediate species. The course of this oxidation, over a period of 2 days, was followed spectrophotometrically, with the results shown in Figure 2. There is only one isosbestic point in the range examined and no

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(16) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

(17) J. V. Brencic and F. A. Cotton, *ibid.*, **8**, 2698 (1969).

(18) M. E. Elder and B. R. Penfold, *ibid.*, **5**, 1197 (1966).

evidence for a species intermediate between $Tc_2Cl_8^{3-}$ and $TcCl_6^{2-}$.

The magnetic properties of the solid compound are consistent with the presence of one unpaired electron per $Tc_2Cl_8^{3-}$ ion. This fact, together with the structure of the anion, leads us to the following description of the electronic structure of $Tc_2Cl_8^{3-}$. There are nine electrons beyond those in Tc–Cl bonds and nonbonding electrons on Cl atoms. Eight of these occupy the σ, 2π, and δ orbitals constituting a Tc–Tc quadruple bond.[6,19] The remaining electron then resides in one of the more or less nonbonding σ orbitals directed away from the center of the molecule. The possibility of the odd electron occupying the δ^* orbital appears to us remote though perhaps not wholly out of the question since some doubt must exist as to the precise ordering of the nonbonding and weakly antibonding orbitals.[19,20]

The X-ray crystallographic part of this investigation was carried out with a single, well-defined, and restricted objective: to determine the nature of the technetium-containing anion present. The data *are* adequate to do this satisfactorily. It appears that the crystal also contains a hydrogen-bonded array of NH_4^+ ions and H_2O molecules of unusual complexity and, possibly, special interest. The data *are not* adequate to provide an entirely unambiguous picture of this peripheral (as far as we are concerned) aspect of the structure. We present below, very briefly, our interpretation of the NH_4^+–H_2O part of the structure; we freely concede that this is not definitive.

The general-position ammonium ion (N(1)) lies above one of the faces of the distorted cube of chlorine atoms formed by the eight chlorine atoms of the dimer. Contacts with this face range from 3.33 to 3.52 Å, indicating possible N–H···Cl bonding. A total of five other chlorine atoms have contacts with this ammonium ion at van der Waals distances or below, suggesting that the NH_4^+ ion might best be considered to be totally disordered within this cage of negative atoms.

The special-position ammonium ion (N(2)) lies on the twofold crystallographic axis which bisects the $Tc_2Cl_8^{3-}$ ion and is thus centered on another rectangular face of the chlorine "cube" formed by the dimer. The contacts to the face are shorter in this case than for the general-position ammonium ion, being 3.17 and 3.23 Å. In addition to the four short contacts to the chlorine face, four other short contact distances are shown in Table V, one pair to the general-position water molecule and another pair to chlorine atoms on two different dimers. Both of these pairs of contacts are within H-bonding range, with the latter pair being slightly longer than the N–Cl contacts to the dimer face. The eight atoms which form short contacts to N(2) form a distorted cubic array around it and offer a possible explanation for the partial occupancy of general water position 1. If four hydrogen bonds are presumed to be formed by the ammonium ion in more or less tetrahedral directions, then two sets of H-bonded neighbors exist: O(1) and Cl(3) or Cl(1) and Cl(2). If in fact the ammonium ion is distributed equally over these two sets by a fourfold rotational disorder, then only half of the O(1) water molecules will be involved in strong N–H···O bonding in accord with our value of 0.5 for its occupancy.

The proposed partial occupancy of the general-position water site is supported by consideration of the environment of O(1). In addition to the short contact with N(2), this atom has a very short contact with O(2) and a total of five fairly short chlorine contacts. The high-temperature factor of O(2) may be explained by the half-absence of O(1). When no H bond exists with O(1), then O(2) will be fairly loosely held, since no other very near neighbors exist, except for those in its own symmetry-related spiral. Presumably the O(2) molecules will move in closer to the 3_2 axis to enhance H bonding with themselves.

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[19] F. A. Cotton and C. B. Harris, *Inorg. Chem*, **6**, 924 (1967).

[20] M. J. Bennett, K. G. Caulton, and F. A. Cotton, *ibid.*, **8**, 1 (1969).