MeO groups in $W_2(\mu\text{-}S)_2(OMe)_4(S_2CNEt_2)_2$, namely, 1.87 ± 0.03 Å.[10]

The W–W distance (2.715 (1) Å) is of special interest. It is very similar to others where a W–W single bond has been assumed to exist. Thus, in the trinuclear species[12] $[W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ the distances are about 2.75 Å. Similarly, the W–W distance in $W_2(\mu\text{-}S)_2(OMe)_4(S_2CNEt_2)_2$ is 2.791 (1) Å. However, while we may say that the W–W distance is consistent with, and even indicative of, the existence of a W–W single bond, the ambiguities about bonding in bridged systems are well-known, and we therefore turn to other structural criteria for additional support of this view.

As noted several years ago with particular reference to face-sharing octahedra,[13] when two octahedra are joined without distortion, on a common element, face or edge, the metal atoms make a contact that is repulsive in the absence of M–M bond formation. Therefore, if no bond is formed, the repulsion should lead to changes in angles that reflect the repulsive force: the $(\mu\text{-}L)\text{–}M\text{–}(\mu\text{-}L)$ angles should decrease while the $M\text{–}(\mu\text{-}L)\text{–}M$ angles increase. Such a result has been clearly seen in the W_2Cl_{10} structure[9] where the two types of angles just mentioned are respectively 81.5 (instead of 90°) and 98.5° (instead of 90°). The W–W distance is 3.814 (2) Å instead of the 3.56 Å it would be if a rectangular W_2Cl_2 bridge system were maintained.

In the present case we find the angle changes indicative of attraction between the metal atoms: the $(\mu\text{-}O)\text{–}W\text{–}(\mu\text{-}O)$ angles are 95.1 (2)° and the $W\text{–}(\mu\text{-}O)\text{–}W$ angles are 84.9 (2)°. W–W distance of 2.715 (0) Å is shorter than that expected for a rectangular bridge system with the observed $W\text{–}(\mu\text{-}O)$ bond lengths, viz., 2.85 Å. We conclude that the totality of the structural evidence clearly favors the presence of a W–W bond in $W_2Cl_4(OEt)_6$.

It is notable that because of the close approach of the tungsten atoms another distortion is introduced into the octahedra. The repulsive nonbonded contact between O(1) and O(2)′ cannot be as close, and, therefore, the W–O(1) and W′–O(2)′ bonds are bent away from each other, giving a more acceptable O(1)···O(2)′ distance of 3.075 (6) Å. The W′–W–O(1) and W–W′–O(2) angles are therefore 95.5 (1) and 95.9 (1)°, respectively.

It is also interesting to note that the stereochemistry at the bridging oxygen atom O(3) is very nearly flat. The sum of the three bond angles is 358.5 (8)°. This may imply, or at least allow, some participation of the O(3) and O(3)′ lone pairs in a π contribution to the bridge bonding, but the importance of this is probably not great.

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Registry No. $W_2Cl_4(OEt)_6$, 12389-29-6; $W_2Cl_4(OEt_4)(EtOH)_2$, 25365-40-6.

Supplementary Material Available: A table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the Octachloroditechnetate(III) Ion in Its Tetra-*n*-butylammonium Salt

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The title compound, $[(n\text{-}C_4H_9)_4N]_2[Tc_2Cl_8]$, has been prepared by the method of Preetz and Peters, and crystals suitable for X-ray study have been obtained. The crystals, isomorphous to those of the rhenium analogue, whose structure was previously determined, have the following parameters: space group $P2_1/c$, a = 10.915 (1) Å, b = 15.382 (3) Å, c = 16.409 (2) Å, β = 122.37 (1)°, V = 2327 (1) Å^3, and Z = 4. The structure has been solved and refined to R_1 = 0.034 and R_2 = 0.040 with the esd of an observation of unit weight equal to 1.021 with the use of 1821 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 209 variables. Hydrogen atoms were included, but not refined, in the final cycles. There is a disorder, with 30.9% of the $[Tc_2Cl_8]^{2-}$ ions oriented perpendicular to the majority (69.1%). The Tc–Tc distances in the major and minor orientations are 2.151 (1) and 2.133 (3) Å, respectively, with a weighted average of 2.147 (4) Å. The mean Tc–Cl distance is 2.320 (4) Å, and the mean Tc′–Tc–Cl angle is 103.8 (4)°. The $[Tc_2Cl_8]^{2-}$ ion resides on a crystallographic inversion center. As in the analogous rhenium compound, the tetra-*n*-butylammonium ions are unusually well-ordered and all atoms in them refined well.

Introduction

From the time that the true character of the $[Re_2Cl_8]^{2-}$ ion was recognized,[2] it has seemed reasonable to anticipate the preparation of technetium compounds homologous to this one and to other multiply bonded dirhenium species. To date this expectation has been rather more honored in the breach than the fulfillment. The earliest development was the characterization[3] of the $[Tc_2Cl_8]^{3-}$ ion, the preparation of which had been described earlier[4] without an identification of the product other than its stoichiometry. The structure of the compound in question, $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$, was later described in more detail, including magnetic data that are consistent with the presence of one unpaired electron[5] and a Tc–Tc distance of

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2.13 (2) Å. These magnetic data were later more accurately measured for both $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$ and $Y[Tc_2Cl_8]\cdot 9H_2O$, and the EPR spectrum of the latter was also recorded.[6] The *g* values and hyperfine coupling constants, together with the susceptibility data, left no doubt that the compound contains one unpaired electron per formula unit, delocalized over two equivalent technetium atoms. At about the same time, the crystal structure of $K_3[Tc_2Cl_8]\cdot nH_2O$, which turned out to be isomorphous with the ammonium salt, was determined.[7] Crystallographically it had been impossible to distinguish between N and O atoms in the structure of the ammonium salt, although the presence of three rather than two nitrogen atoms was demonstrated by the nitrogen analysis; in the potassium salt, the crystallographic results showed directly and conclusively that three potassium ions are present, and the Tc–Tc distance was determined more precisely as 2.117 (2) Å. The electronic absorption spectrum of $[Tc_2Cl_8]^{3-}$ has also been studied and assigned.[8] Thus, the existence and characteristic properties of the $[Tc_2Cl_8]^{3-}$ ion became well established.

The $[Tc_2Cl_8]^{2-}$ ion, in the meantime, remained unknown except for the observations[6] that electrochemical conversion of $[Tc_2Cl_8]^{3-}$ to what is probably $[Tc_2Cl_8]^{2-}$ occurs in mixtures of aqueous HCl and ethanol in a quasireversible way at $E_{1/2} = 0.14$ V vs. SCE and that $[Tc_2Cl_8]^{2-}$ (if it is, as supposed, the oxidation product) appears to have a lifetime ($\gg$5 min) sufficient perhaps to allow its isolation. Interestingly, the $[Re_2Cl_8]^{3-}$ ion was found to be extremely short-lived, while $[Re_2Cl_8]^{2-}$ is stable indefinitely.[6]

There the matter rested until, in 1977, it was reported[9] that $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$, isomorphous to $(n\text{-}Bu_4N)_2[Re_2Cl_8]$, had been prepared from TcO_4^- with the use of a H_3PO_2 reduction procedure which had been reported for making $[Re_2Cl_8]^{2-}$ from ReO_4^- many years before.[2a] Attempts to reproduce this work in both of our laboratories consistently failed. Green crystalline products were indeed obtained from HCl solutions by using $n\text{-}Bu_4N^+$ and other large cations, but these proved to be salts of the $[TcOCl_4]^-$ ion.[10] Analytical data cannot reliably distinguish between $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ and $n\text{-}Bu_4N[TcCl_4O]$.

In 1980, Preetz and Peters[11] reported that they had prepared $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ by reduction of $[TcCl_6]^{2-}$ in aqueous HCl with zinc, whereby $(n\text{-}Bu_4N)_3[Tc_2Cl_8]$ was also a product, and the two had to be separated by solvent extraction procedures. The reaction used is, of course, broadly similar to that by which the $[Tc_2Cl_8]^{3-}$ compounds had previously been obtained. However, this paper, unlike that of Schwochau et al., described the preparation and characterization of the product in detail.

We have found that in its essentials the preparative method of Preetz and Peters works as they say, and we have succeeded in isolating crystalline $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ and determining its structure. This affords, at last, incontrovertible proof that stable compounds (or, at least, one stable compound) of the $[Tc_2Cl_8]^{2-}$ ion can be made. However, the chemical and structural relationships of the two ions $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ are still puzzling in many respects. We report here primarily on the structural aspect of the problem.

Experimental Section

Technetium as $NH_4{}^{99}TcO_4$ was obtained as a gift from New England Nuclear, Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity (^{99}Tc is a weak β emitter with a half-life of 2.12×10^5 years and a particle energy of 0.292 MeV). All precautions followed have been explained previously.[10,12] All manipulations were carried out with the use of standard Schlenk-line apparatus and a Vacuum Atmospheres drybox. Optical spectra were recorded with a Cary Model 17 spectrophotometer.

Table I. Crystallographic Parameters

space group	$P2_1/c$	μ(Mo Kα), cm^{-1}	21.208
a, Å	10.915 (1)	range 2θ, deg	0–45
b, Å	15.382 (3)	no. of unique data	2125
c, Å	16.409 (2)	no. of data, $F_o^2 > 3\sigma(F_o^2)$	1821
β, deg	122.37 (1)		
V, Å^3	2326.8 (1.2)	no. of variables	209
d_{calcd}, g/cm^3	2.753	R_1	0.034
Z	4	R_2	0.040
fw	964.57	goodness of fit	1.021
crystal size, mm	0.1 × 0.2 × 0.1	largest peak, e/Å^3 (in final difference map)	0.251

Acetone was distilled from $KMnO_4$ under nitrogen, and dichloromethane was distilled from P_2O_5 or CaH_2 under nitrogen. Distilled water was passed through a Barnstead Ultrapure D8902 cartridge, follow by redistillation in a Corning AG-1 water still and purging with Ar. Diethyl ether must be fresh and peroxide free before purging with Ar. All other solvents were thoroughly purged with Ar prior to use. The 30-mesh granular zinc was obtained from Fisher.

Preparation of $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$. This was accomplished by the method of Preetz and Peters[11] with some modifications. A three-neck 100-mL round-bottom flask was charged with $(NH_4)_2TcCl_6$[4] (0.33 g) and 5 mL of concentrated HCl. This was reduced through successive additions of 30-mesh granular zinc, under a counterflow of Ar, until all the yellow solid had dissolved and the solution had changed from yellow through green to brown. This brown solution was stirred for 2 h, and then a small amount of black precipitate which had formed was removed by filtration. The resulting brown solution was evaporated under reduced pressure over 48 h to give a brown oil. This oil was extracted with diethyl ether (5 × 30 mL) to remove the $ZnCl_2$, and the brown powder which formed was separated by filtration. The filtrate was a pale green-brown solution.

The brown solid was dissolved with 2 mL portions of concentrated HCl until dissolution was complete (18 mL) to form a brown solution. After dilution with 50 mL water (containing 1 g of $n\text{-}Bu_4NCl$), this solution had a green-brown tint. It is most important that the concentrated HCl solution be diluted with 2.5–3 volumes of water. To this was added 15 mL of dichloromethane, and the entire mixture was poured (in air) into a separatory funnel. Upon shaking in air, the organic phase became green and the aqueous phase became blue-green and then yellow-brown. Further extractions with CH_2Cl_2 (4 × 15 mL) caused the transport of all colored species into the organic phase to form a green solution and a clear colorless aqueous phase. The dichloromethane solution was evaporated under reduced pressure to yield a green solid. This was washed under Ar with 20 mL of acetone, and a pale green solid remained which was $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ (and not $(n\text{-}Bu_4N)_3[Tc_2Cl_8]$ as reported previously). The yield was 0.162 g, 35% based on Tc.

A small additional amount of $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ as green plates may be recovered upon cooling the acetone filtrate (which was yellow-brown) to −25 °C. The product was easily recrystallized from CH_2Cl_2/Et_2O (1:2 v/v) at −25 °C in high yield, forming green plates or flakes. Examination of the optical spectrum of the yellow-brown acetone filtrate after removal of most of the $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ showed the presence of mostly $TcCl_6^{2-}$ (342 nm), as well as some $Tc_2Cl_8^{3-}$ (weak band at 636 nm). The crystal used in the crystallographic study was grown from CH_2Cl_2 at −25 °C.

Optical spectrum (in Ar-purged CH_2Cl_2): λ_{max} (ϵ in L mol^{-1} cm^{-1}) 678 nm (1400), 455 shoulder, 388 (8200), 301 (9650).

The electrochemistry was studied in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate under argon. An irreversible one-electron reduction was found at $E_{1/2} = -0.13$ V vs. SCE with a rotating-platinum electrode and at $E_{1/2} = -0.07$ V. vs. SCE with a drop-

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Nonhydrogen Atoms

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Tc(1)	−0.02111 (6)	0.06137 (4)	0.02155 (4)	3.70 (2)	2.96 (2)	3.34 (2)	−0.24 (2)	2.21 (1)	−0.32 (2)
Tc(2)	−0.09925 (13)	0.00440 (9)	−0.06851 (8)	3.57 (4)	3.10 (6)	3.20 (4)	−0.38 (5)	2.07 (3)	−0.24 (5)
Cl(1)	−0.2623 (1)	0.0499 (1)	−0.02578 (9)	4.42 (4)	5.00 (7)	6.29 (5)	0.26 (5)	3.59 (3)	−0.08 (5)
Cl(2)	0.1983 (1)	0.1359 (1)	0.09220 (9)	5.00 (5)	4.31 (7)	5.14 (5)	−1.32 (5)	3.10 (3)	−1.32 (5)
Cl(3)	0.0361 (1)	0.0365 (1)	0.17746 (8)	6.95 (5)	5.64 (8)	3.90 (4)	−1.15 (6)	3.52 (3)	−0.95 (5)
Cl(4)	−0.1012 (1)	0.1490 (1)	−0.11273 (9)	5.63 (5)	4.50 (7)	5.61 (5)	0.51 (5)	3.29 (3)	1.47 (5)
N	0.2832 (4)	0.3058 (3)	0.3415 (2)	4.5 (1)	3.0 (2)	4.1 (1)	−0.5 (1)	2.86 (9)	−0.9 (1)
C(1)	0.3713 (5)	0.3094 (4)	0.2946 (3)	4.7 (2)	4.3 (3)	4.0 (2)	−0.1 (2)	2.7 (1)	−0.7 (2)
C(2)	0.3902 (5)	0.3967 (4)	0.2617 (3)	4.9 (2)	5.3 (3)	4.4 (2)	−1.3 (2)	2.7 (1)	−1.0 (2)
C(3)	0.4820 (6)	0.3888 (5)	0.2184 (3)	5.5 (2)	9.4 (4)	4.5 (2)	−1.7 (3)	3.1 (1)	−1.0 (3)
C(4)	0.5120 (7)	0.4755 (6)	0.1887 (4)	8.7 (3)	12.8 (5)	6.7 (2)	−5.1 (3)	4.8 (2)	−0.7 (3)
C(5)	0.3574 (5)	0.3556 (3)	0.4359 (3)	5.8 (2)	3.1 (2)	5.0 (2)	−0.4 (2)	3.7 (1)	−0.6 (2)
C(6)	0.4966 (5)	0.3176 (4)	0.5182 (3)	5.8 (2)	3.9 (3)	5.3 (2)	−0.1 (2)	3.4 (1)	−0.4 (2)
C(7)	0.5627 (5)	0.3772 (4)	0.6054 (3)	5.1 (2)	6.1 (3)	4.3 (2)	−0.5 (2)	2.5 (1)	−1.0 (2)
C(8)	0.6991 (8)	0.3447 (5)	0.6907 (5)	7.9 (4)	9.1 (5)	6.9 (3)	−1.5 (4)	2.9 (2)	−2.1 (3)
C(9)	0.1366 (5)	0.3474 (3)	0.2781 (3)	5.0 (2)	2.8 (2)	5.2 (2)	0.3 (2)	3.0 (1)	0.1 (2)
C(10)	0.0397 (5)	0.3075 (4)	0.1784 (4)	5.3 (2)	3.8 (3)	5.9 (2)	−0.1 (2)	3.2 (1)	−0.1 (2)
C(11)	−0.1040 (6)	0.3525 (4)	0.1260 (4)	6.0 (3)	5.4 (3)	6.1 (3)	1.0 (3)	2.5 (2)	0.3 (3)
C(12)	−0.2018 (7)	0.3223 (5)	0.0245 (5)	5.4 (3)	7.6 (4)	7.7 (3)	−0.2 (3)	2.3 (2)	0.9 (3)
C(13)	0.2686 (5)	0.2102 (3)	0.3579 (3)	4.5 (2)	3.0 (2)	4.8 (2)	−0.1 (2)	2.4 (1)	−0.6 (2)
C(14)	0.1773 (5)	0.1916 (4)	0.4002 (3)	5.8 (2)	4.1 (3)	6.1 (2)	−0.1 (2)	4.0 (1)	−0.1 (2)
C(15)	0.1942 (6)	0.0998 (4)	0.4333 (3)	8.5 (3)	4.2 (3)	4.9 (2)	−0.6 (2)	4.1 (2)	−0.0 (2)
C(16)	0.1012 (7)	0.0787 (5)	0.4718 (4)	11.7 (3)	5.7 (4)	7.8 (2)	−0.9 (3)	6.6 (2)	0.3 (3)

Table III. Positional Parameters for Hydrogen Atoms[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H(1,1)	0.3252	0.2724	0.2398	H(9,1)	0.1517	0.4067	0.2696
H(1,2)	0.4653	0.2876	0.3401	H(9,2)	0.0866	0.3440	0.3108
H(2,1)	0.4364	0.4350	0.3154	H(10,1)	0.0255	0.2475	0.1850
H(2,2)	0.2977	0.4192	0.2145	H(10,2)	0.0848	0.3134	0.1428
H(3,1)	0.4328	0.3526	0.1631	H(11,1)	−0.0877	0.4131	0.1251
H(3,2)	0.5720	0.3630	0.2648	H(11,2)	−0.1509	0.3424	0.1600
H(4,1)	0.5699	0.4667	0.1621	H(12,1)	−0.2908	0.3534	−0.0046
H(4,2)	0.4229	0.5020	0.1418	H(12,2)	−0.1569	0.3326	−0.0107
H(4,3)	0.5621	0.5123	0.2436	H(12,3)	−0.2201	0.2619	0.0242
H(5,1)	0.2909	0.3597	0.4563	H(13,1)	0.3631	0.1876	0.4008
H(5,2)	0.3785	0.4123	0.4235	H(13,2)	0.2258	0.1811	0.2976
H(6,1)	0.5634	0.3105	0.4984	H(14,1)	0.0782	0.2020	0.3523
H(6,2)	0.4768	0.2627	0.5351	H(14,2)	0.2068	0.2292	0.4535
H(7,1)	0.4938	0.3849	0.6233	H(15,1)	0.2927	0.0902	0.4828
H(7,2)	0.5823	0.4317	0.5874	H(15,2)	0.1684	0.0624	0.3803
H(8,1)	0.7334	0.3856	0.7419	H(16,1)	0.1155	0.0197	0.4920
H(8,2)	0.6815	0.2905	0.7104	H(16,2)	0.1266	0.1153	0.5252
H(8,3)	0.7700	0.3373	0.6744	H(16,3)	0.0022	0.0876	0.4227

[a] All isotropic thermal parameters were held constant at 5.000 Å².

ping-mercury electrode. There was no evidence for another reductive process out to −2.3 V.

Collection of Data. Data were collected on an Enraf-Nonius CAD-4 automated diffractometer at 21 °C using Mo Kα radiation monochromated by a graphite crystal. An automatic searching routine located and centered 25 reflections having $20° < 2\theta < 35°$. An indexing routine gave a unit cell in space group $P2_1/n$ with $a = 10.915$ Å, $b = 15.382$ Å, $c = 14.022$ Å, and $\beta = 98.74°$. However, since the isomorphous structure of $(n\text{-}Bu_4N)_2Re_2Cl_8$ was reported[13,14] in space group $P2_1/c$, the structure was refined in $P2_1/c$ for comparison purposes. No absorption correction was applied because of the small absorption coefficient. Data collection and refinement parameters are summarized in Table I.

Solution of Structure.[15] The coordinates of all the atoms in the $n\text{-}Bu_4N^+$ and $Tc_2Cl_8^{2-}$ units were taken from the structure of the isomorphous rhenium homologue mentioned above. The metal units were expected to be disordered as before; therefore, the occupancy of the two Tc_2 units was set at 0.75 and 0.25. These values were then refined by least squares until the two isotropic temperature factors were approximately equal, giving occupancies of 0.691 and 0.309.

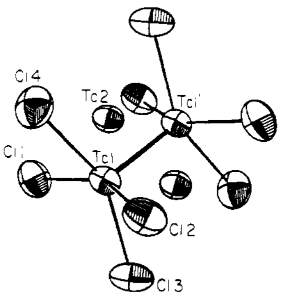

Figure 1. ORTEP drawing of the $[Tc_2Cl_8]^{2-}$ ion.

Anisotropic temperature factors were assigned to all 23 atoms, and three cycles of least-squares refinement gave $R_1 = 0.054$ and $R_2 = 0.063$.

The positions of the 36 hydrogen atoms of the Bu_4N^+ ion were calculated by using bond lengths of 0.95 Å and isotropic temperature factors of 5.0. These values were not refined, but use of the positions to calculate structure factors in the final three cycles of least-squares refinement gave the final discrepancy factors listed in Table I.

Results

The structure of $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ is strictly isomorphous with that of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$.[14] There is a slight difference in the extent of disordering, with the minor orientation of the

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Table IV. Bond Distances (Å) and Angles (Deg) in the $[Tc_2Cl_8]^{2-}$ Ion

Tc(1)–Tc(1)′	2.151 (1)	average	2.147 (4)
Tc(2)–Tc(2)′	2.133 (3)		
Tc(1)–Cl(1)	2.318 (2)	Tc(1)–Cl(4)	2.318 (2)
Tc(1)–Cl(2)	2.328 (2)	average	2.320 (4)
Tc(1)–Cl(3)	2.317 (2)		
Tc(2)–Cl(1)	2.342 (2)	Tc(2)–Cl(4)	2.337 (2)
Tc(2)–Cl(2)′	2.350 (2)	average	2.338 (9)
Tc(2)–Cl(3)′	2.321 (2)		
Tc(1)′–Tc(1)–Cl(1)	103.16 (6)	Tc(1)′–Tc(1)–Cl(4)	103.66 (6)
Tc(1)′–Tc(1)–Cl(2)	104.56 (6)	average	103.8 (4)
Tc(1)′–Tc(1)–Cl(3)	103.87 (6)		
Tc(2)–Tc(2)′–Cl(1)	102.1 (1)	Tc(2)–Tc(2)′–Cl(4)	102.9 (1)
Tc(2)–Tc(2)′–Cl(2)	103.5 (1)	average	103.1 (6)
Tc(2)–Tc(2)′–Cl(3)	104.0 (1)		
Cl(1)–Tc(1)–Cl(2)	152.28 (6)	Cl(1)–Tc(2)–Cl(3)′	153.9 (1)
Cl(3)–Tc(1)–Cl(4)	152.47 (6)	Cl(2)′–Tc(2)–Cl(4)	153.6 (1)
Cl(1)–Tc(1)–Cl(3)	86.78 (6)	Cl(2)–Tc(1)–Cl(4)	87.18 (6)
Cl(1)–Tc(1)–Cl(4)	86.75 (6)	average	86.7 (3)
Cl(2)–Tc(1)–Cl(3)	86.22 (6)		
Cl(1)–Tc(2)–Cl(2)′	88.16 (7)	Cl(3)′–Tc(2)–Cl(2)′	85.62 (7)
Cl(1)–Tc(2)–Cl(4)	85.79 (7)	Cl(3)′–Tc(2)–Cl(4)	88.63 (7)

Table V. Bond Distances (Å) and Angles (Deg) in the $N(C_4H_9)_4$ Ion

N–C(1)	1.520 (6)	C(6)–C(7)	1.517 (8)
N–C(5)	1.516 (7)	C(7)–C(8)	1.481 (9)
N–C(9)	1.506 (7)	C(9)–C(10)	1.523 (8)
N–C(13)	1.520 (6)	C(10)–C(11)	1.495 (8)
C(1)–C(2)	1.501 (8)	C(11)–C(12)	1.492 (9)
C(2)–C(3)	1.511 (8)	C(13)–C(14)	1.516 (8)
C(3)–C(4)	1.515 (10)	C(14)–C(15)	1.489 (8)
C(5)–C(6)	1.509 (8)	C(15)–C(16)	1.490 (9)
C(1)–N–C(5)	111.2 (4)	N–C(5)–C(6)	116.7 (5)
C(1)–N–C(9)	111.1 (4)	C(5)–C(6)–C(7)	110.6 (5)
C(1)–N–C(13)	106.2 (4)	C(6)–C(7)–C(8)	114.6 (6)
C(5)–N–C(9)	106.3 (4)	N–C(9)–C(10)	116.2 (5)
C(5)–N–C(13)	111.0 (4)	C(9)–C(10)–C(11)	110.0 (5)
C(9)–N–C(13)	111.1 (4)	C(10)–C(11)–C(12)	113.7 (6)
N–C(1)–C(2)	117.4 (5)	N–C(13)–C(14)	114.8 (5)
C(1)–C(2)–C(3)	110.6 (6)	C(13)–C(14)–C(15)	111.3 (5)
C(2)–C(3)–C(4)	113.2 (7)	C(14)–C(15)–C(16)	112.5 (6)

$[Tc_2Cl_8]^{2-}$ ions being 30.9% in this case as compared to 26.1% in the rhenium compound. The atomic parameters are listed in Tables II and III. The numbering scheme used here was chosen to correspond exactly to that used in the rhenium structure. For convenience it is defined for the $[Tc_2Cl_8]^{2-}$ ion in Figure 1. Table IV gives the bond distances and angles in the anion, and Table V gives the same information for the tetra-*n*-butylammonium cations. The $[Tc_2Cl_8]^{2-}$ anion resides on a center of inversion, and thus only half of it is crystallographically independent, whereas an entire cation is part of the asymmetric unit. In Table IV the average value for the Tc–Tc distance is obtained by weighting Tc(1)–Tc(1)′ three times as heavily as Tc(2)–Tc(2)′. All other average values were calculated for each of the Tc(1)- and Tc(2)-containing units individually. In no case, with the exception of the *trans*-Cl–Tc–Cl angles, are the differences statistically significant. For all practical purposes, the dimensions of the Tc(1)-containing unit may be taken as definitive.

In Figure 2 are shown stereoviews, looking along each crystallographic axis of the arrangement in the unit cell. These views, none of which was previously published for the rhenium compound, will be useful to anyone trying to visualize the orientations of the $[M_2Cl_8]^{2-}$ units in either compound in connection with the interpretation of polarized spectra of crystals.

Discussion

Chemical Properties. There appear to be some minor differences between the description of Preetz and Peters[11] and our experience with the preparation. Contrary to their suggestion, no more than trace amounts of $(n\text{-}Bu_4N)_3[Tc_2Cl_8]$ were found in this preparation. Also, we find that $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ is not very soluble in acetone and may even crystallize from the filtrate as it is being dissolved from the frit.

The major side product of the reduction and workup in our hands is $(n\text{-}Bu_4N)_2TcCl_6$, which is easily separated from $(n\text{-}Bu_4N)_3[Tc_2Cl_8]$ due to its much greater solubility in acetone. We have also found that the title compound can be prepared from the literature preparation[4,6] of $[Tc_2Cl_8]^{3-}$ by simply shaking the blue HCl solution with old ether or by extracting this solution with $n\text{-}Bu_4NCl$ and CH_2Cl_2 in air. The brown intermediate which is isolated in both preparations has thus far evaded our attempts at characterization.

The $[Tc_2Cl_8]^{2-}$ ion is redox active in solution (both aqueous and nonaqueous), but its behavior is quite sensitive to concentration, acidity, and other factors. Attempts now being made to sort this out will be the subject of a future report. Let us turn now to the structure of the $[Tc_2Cl_8]^{2-}$ ion.

Structural Relationships. The X-ray crystallographic study of $(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ gives a Tc–Tc bond distance of 2.147 (4) Å. This distance is considerably longer than would have been anticipated from use of three different methods of extrapolation from previous data.

(1) The most obvious extrapolation would be from the distance of 2.117 (2) Å in $[Tc_2Cl_8]^{3-}$. The removal of the δ^* electron might be expected to shorten the bond; there is no obvious basis to expect a lengthening. The anticipated shortening might be anywhere from 0.000 to 0.060 Å, on the basis of data[16,17] for pairs like $[Mo_2(SO_4)_4]^{4-}$–$[Mo_2(SO_4)_4]^{3-}$ and $Re_2Cl_6(PEt_3)_2$–$Re_2Cl_4(PEt_3)_4$ where the changes are 0.054 (3) and ~0.00. Thus in the $[Tc_2Cl_8]^{2-}$ ion a distance of 2.09 ± 0.03 Å might have been anticipated.

(2) We note that in group 6 the decreases from W–W to Mo–Mo are 0.116 (3) and 0.132 (2) Å for $[M_2(CH_3)_8]^{4-}$[18] and $M_2Cl_4(PMe_3)_4$,[19] respectively. Since the Re–Re distance in $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ is 2.222 (2) Å,[13] we would predict a Tc–Tc distance of 2.10 ± 0.01 Å.

(3) From the $[W_2(CH_3)_8]^{4-}$ ion to the $[Re_2(CH_3)_8]^{2-}$ ion, the M–M distance[20] decreases by 0.086 (3) Å. Since the Mo–Mo distances in the various compounds containing the $[Mo_2Cl_8]^{4-}$ ion are in the range 2.134 (1)–2.150 (5) Å, we might expect for $[Tc_2Cl_8]^{2-}$ a distance of 2.06 ± 0.01 Å.

Thus, the anticipated range of Tc–Tc distances in $[Tc_2Cl_8]^{2-}$ would be 2.06–2.10 Å, whereas the distance we have found is 2.147 (2) Å. We do not know how to account for this, and we shall abstain, at least for the present, from speculation.

It should be noted that, in the two other reported Tc–Tc distances, there is also a lack of obvious, simple regularity, although nothing as seemingly contrary as the comparisons just discussed. It has already been noted that in the two isomorphous compounds,[21] $M_2(O_2CCMe_3)_4Cl_2$, with M = Tc or Re, the Tc–Tc and Re–Re distances (2.192 (2) and 2.236 (1) Å) differ by only 0.044 (2) Å, but this may be explained by the fact that in the Tc compound the axial chloride ligands

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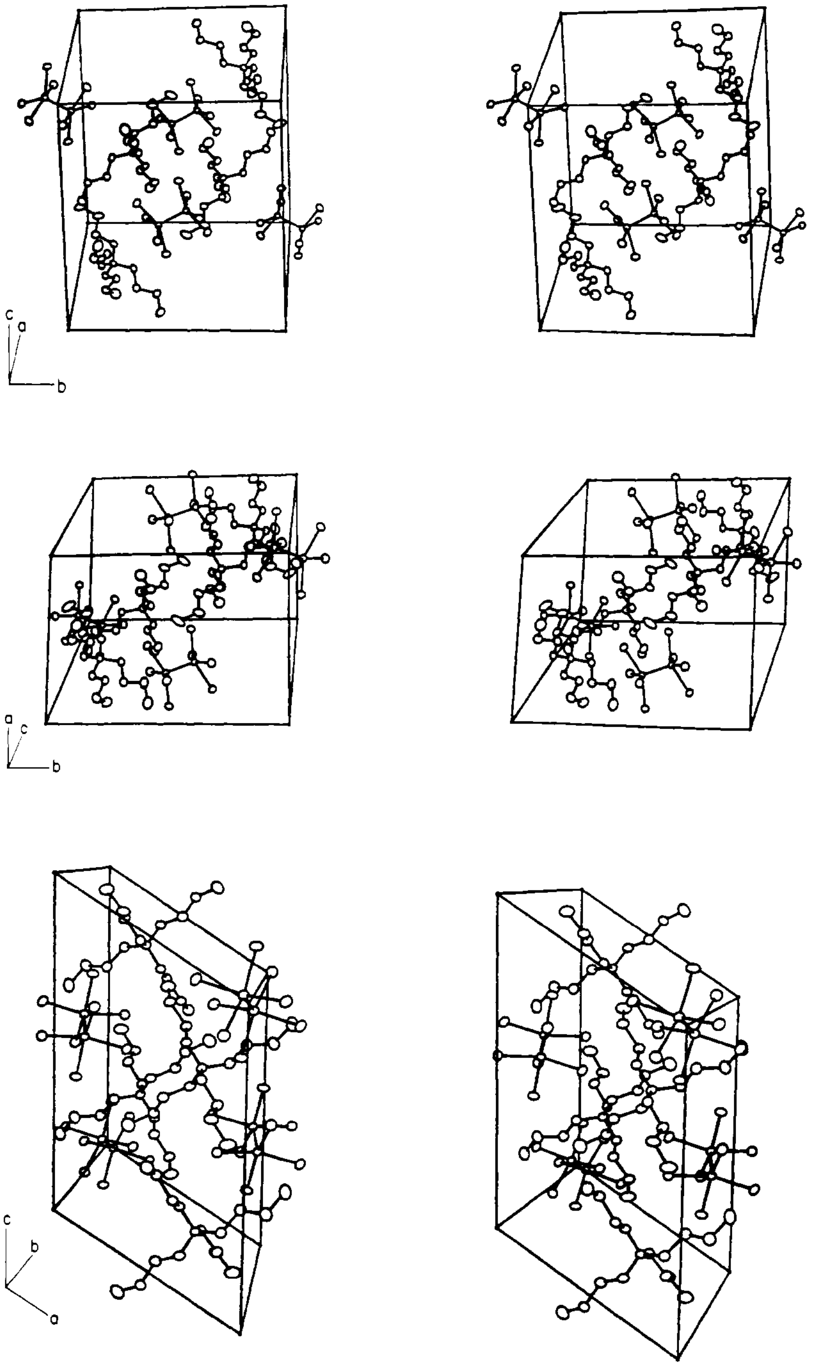

Figure 2. Stereoviews of the unit cell viewed in each of the three crystal directions.

are more strongly bound (Tc–Cl = 2.41 Å) than in the Re compound (Re–Cl = 2.48 Å), which should weaken the Tc–Tc bond. In $Tc_2(hp)_4Cl$,[22] the Tc–Tc distance is much shorter (2.095 (1) Å) despite the fact that here again we have a δ^* electron. This may be due to the fact that hp and mhp type ligands characteristically favor shorter bonds, by ca. 0.04 Å, and the Tc···Cl distances here are quite long (2.68 Å).

On the narrow data base of four structures, the only tentative generalization that emerges is that species with quadruple ($\sigma^2\pi^4\delta^2$) bonds, i.e., $[Tc_2Cl_8]$ and $Tc_2(O_2CCMe_3)_4Cl_2$, have Tc–Tc bonds that appear to be "too long" in comparison with those in similar species with bond orders of 3.5 ($\sigma^2\pi^4\delta^2\delta^*$), i.e., $[Tc_2Cl_8]^{3-}$ and $Tc_2(hp)_4Cl$. Clearly, more work will have to be done to determine (1) whether this generalization is more broadly valid and (2) to identify the cause of this "anomaly".

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Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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