Table I. Some Bond Distances (Ångstroms) and Angles (Degrees)[a]

Tc–S(1)	2.299 (4)	S(1)–C(1)	1.84 (2)
Tc–S(2)	2.283 (4)	S(2)–C(2)	1.83 (2)
Tc–S(3)	2.305 (4)	S(3)–C(3)	1.82 (2)
Tc–S(4)	2.313 (4)	S(4)–C(4)	1.83 (2)
Tc–S, av	2.300 (13)	S–C, av	1.83 (2)
Tc–O	1.64 (1)	C(1)–C(4)	1.50 (2)
		C(2)–C(3)	1.44 (2)
S(1)–Tc–S(3)	82.4 (2)	S(1)–Tc–O	110.1 (4)
S(1)–Tc–S(4)	84.8 (1)	S(2)–Tc–O	111.3 (4)
S(2)–Tc–S(3)	84.4 (2)	S(3)–Tc–O	109.4 (4)
S(2)–Tc–S(4)	83.5 (1)	S(4)–Tc–O	106.3 (3)
S(1)–Tc–S(2)	138.5 (2)	S(1)–C(1)–C(4)	111 (1)
S(3)–Tc–S(4)	144.4 (4)	S(2)–C(2)–C(3)	113 (1)
		S(3)–C(3)–C(2)	116 (1)
Tc–S(1)–C(1)	107.2 (5)	S(4)–C(4)–C(1)	108 (1)
Tc–S(2)–C(2)	109.5 (5)		
Tc–S(3)–C(3)	104.0 (6)		
Tc–S(4)–C(4)	102.7 (5)		

[a] Figures in parentheses are esd's in the least significant digit.
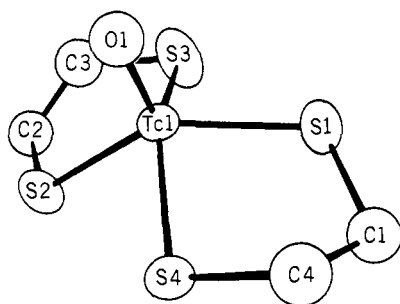
Figure 1. An ORTEP drawing of the [Tc(SCH$_2$CH$_2$S)$_2$O]$^-$ ion. Each atom is represented by its thermal ellipsoid scaled to enclose 50% of its electron density. The atom numbering scheme used in Table I is defined.

The structure of (Ph$_4$As)[TcO(SCH$_2$CH$_2$)S] was solved in the space group *Pbca*, with unit cell dimensions of a = 19.669 (3) Å, b = 18.745 (4), Å, c = 15.122 (3) Å, and Z = 8. Intensity data were collected on a Syntex P1 counter diffractometer using Mo Kα radiation monochromated with a graphite crystal in the incident beam. Using 2555 unique reflections with $I > 1\sigma(I)$ the structure was refined by full-matrix least squares to convergence using anisotropic temperature factors for the technetium, arsenic, and sulfur atoms, isotropic temperature factors for the oxygen and carbon atoms, and omitting hydrogen atoms. The final residuals are R_1 = 0.089 and R_2 = 0.087 with the error in an observation of unit weight equal to 1.34. A final difference Fourier had no peaks of higher intensity than 1.1 e/Å^3.

The structure of the oxotechnetium anion, [(C$_2$H$_4$S$_2$)$_2$-TcO]$^-$, is shown in Figure 1, and bond distances and angles for the oxo anion are listed in Table I. The tetraphenylarsonium ion has no unusual features and a complete list of bond lengths and angles is available as supplementary material, along with a table of all atomic positional and thermal parameters and a table of structure factors.[11]

The coordination geometry around the technetium approximates closely to square pyramidal, although no crystallographic symmetry is imposed. The four sulfur atoms form the square base with the technetium atom 0.761 (2) Å above the mean plane. The average Tc–S bond distance is 2.30 (1) Å. An oxygen atom constitutes the apex of the square pyramid, with a Tc—O bond distance of 1.64 (1) Å.

There appears to be no prior report of a technetium sulfur bond length. The Tc=O bond distance in this compound may be compared with those in the technetium(VII) compound Tc$_2$O$_7$, 1.649 (4) Å,[12] and in TcOF$_4$, 1.66 (3) Å.[13] It is slightly

shorter than that recently found in the closely similar compound[14] [(*n*-C$_4$H$_9$)$_4$N][(SC(O)CH$_2$S)$_2$TcO], 1.672 (8) Å.

The observed square-pyramidal coordination of Tc(V) is similar to that found in several Re(V) species such as the ReBr$_4$O$^-$ ion,[15] but the Tc—O distance appears significantly shorter than the Re—O bonds which are 1.71 (4) Å[15a] and 1.73 (6) Å.[15c] In the case of the rhenium anion, however, there are weakly coordinated molecules trans to the oxygen atom, which may tend to weaken the Re=O bond slightly.

Supplementary Material Available: A list of bond distances and angles of the tetraphenylarsonium ion, positional and thermal parameters, and a table of structure factors (14 pages). Ordering information is given on any current masthead page.

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 17. Synthesis and Electrical Properties of the First Homologous Series of 1-Dimensional (Pt–Pt) Metals Containing the (FHF)$^-$ and F$^-$ Anions[1]

Sir:

The study of one-dimensional inorganic metals of the partially oxidized tetracyanoplatinate (POTCP) series has been severely restricted by the scarcity of new materials.[2] In an effort to obtain new compounds with improved electrical transport and materials properties over that of the prototype K$_2$[Pt(CN)$_4$]Br$_{0.30}$ · 3H$_2$O (KCP(Br)), we have undertaken a program of new materials synthesis which involves incorporation of complex anions other than Cl$^-$ or Br$^-$ in the TCP crystal lattice. In many cases totally new structure types are produced and recently we reported the syntheses[3] and structures[4,5] of Cs$_2$[Pt(CN)$_4$](FHF)$_{0.39}$ (CsCP(FHF)$_{0.39}$) (Pt–Pt = 2.833 (1) Å)[5] and Rb$_2$[Pt(CN)$_4$](FHF)$_{0.40}$ (RbCP(FHF)$_{0.40}$) (Pt–Pt = 2.798 (1) Å),[4] which are the first anhydrous POTCP salts and which have the shortest Pt–Pt

Table I. Crystal Data and Electrical Conductivity of Partially Oxidized Tetracyanoplatinate Compounds Containing (FHF)⁻ or F⁻ Anions

compd[a]	oxidn[b]	space group	Pt–Pt, Å	$\sigma_{\parallel}$, Ω^{-1} cm^{-1} [c]
$K_2[Pt(CN)_4](FHF)_{0.30}\cdot 3H_2O$	1.5 V or H_2O_2	$P4mm$	2.923 (5)[d]	e
$Rb_2[Pt(CN)_4](FHF)_{0.40}$	1.5 V	$I4/mcm$	2.798 (1)	1600
$Rb_2[Pt(CN)_4](FHF)_{0.26}\cdot 1.7H_2O$	H_2O_2	$C2/c$	2.89	e
$Cs_2[Pt(CN)_4](FHF)_{0.39}$	1.5 V or H_2O_2	$I4/mcm$	2.833 (1)	2000
$Cs_2[Pt(CN)_4](FHF)_{0.23}$	H_2O_2	$I4/mcm$	2.872 (2)	250–350
$[C(NH_2)_3]_2[Pt(CN)_4](FHF)_{0.26}\cdot xH_2O$	1.5 V	e	2.90	e
$Cs_2[Pt(CN)_4]F_{0.19}$	1.5 V[f]	$Immm$	2.886 (1)	e

[a] All materials were analyzed for C, N, and F by Midwest Microlabs, Indianapolis, Ind. In all cases, emission spectrographic analyses for metal content indicated the presence of the expected alkali metal and Pt with <0.01–0.05% of other metal impurities. Water content was measured using a Mettler thermogravimetric balance, or is derived from a complete x-ray diffraction structural study. [b] All compounds were prepared in aqueous systems by oxidation of the Pt(II) salt, $M_2[Pt(CN)_4]$, either with H_2O_2 or electrolytically (see ref 3 for details of electrolytic procedure). [c] These are the maximum values of four probe dc conductivities obtained at room temperature on single crystals. Electrodes were gold wire (0.001 in.) and contacts were made with Aquadag. For comparative purposes we measured the electrical conductivity of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ (Pt–Pt = 2.88 (1) Å) and obtained values of 750–1050 Ω^{-1} cm^{-1}, while for $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$ (Pt–Pt = 2.963 (2) Å) the values were 115–125 Ω^{-1} cm^{-1}. [d] This is the average of the two independent Pt–Pt separations of 2.918 (1) and 2.928 (1) Å.[9] [e] Under study. [f] In this preparation, the pH was maintained at 9.0 ± 0.1 during electrolysis by the addition of CsOH.

spacings yet observed in these complexes.

We now wish to report the preparation, crystal lattice type, and electrical conductivity of a number of unique new POTCP complexes containing (FHF)⁻ (see Table I). These results demonstrate, for the first time, the existence of nonidentical POTCP complexes which contain identical cations and anions; i.e., they constitute a homologous series of POTCP complexes. In addition, we have synthesized the first known POTCP complex containing the monofluoride (F⁻) anion.

As indicated in Table I, synthesis of the POTCP complexes may be accomplished electrolytically or chemically (H_2O_2) from a solution containing $M_2[Pt(CN)_4]$, MF, and HF (M = K, Rb, or Cs).[3-5] In the case of $KCP(FHF)_{0.30}\cdot 3H_2O$[9] and $CsCP(FHF)_{0.39}$, either synthetic method yields identical products given the same initial starting material concentrations. However, with the Rb⁺ analogues, the two oxidation procedures yield POTCP complexes that differ in their degree of partial oxidation (DPO), Pt–Pt repeat distance, space group, and degree of hydration.

An even more intriguing finding involves the anhydrous and isostructural homologues $CsCP(FHF)_{0.39}$ and $CsCP(FHF)_{0.23}$. The only difference between the two complexes is the anion content, which alters the degree of partial oxidation (i.e., the Pt oxidation state) and the Pt–Pt *intra*chain separation. This is accomplished by varying the initial concentrations of the reactants, such that $CsCP(FHF)_{0.39}$ and $CsCP(FHF)_{0.23}$ are prepared from solutions with initial HF molarities of 8.7 and 0.076, respectively. The (FHF)⁻ crystal sites, common to both $CsCP(FHF)_{0.39}$ and $CsCP(FHF)_{0.23}$, are only partially occupied (and disordered), such that the highest possible degree of "loading" of (FHF)⁻ into the lattice would yield $CsCP(FHF)_{0.50}$. This suggests a type of solid solution formation and that numerous other homologues may exist. The ability to obtain a variety of complexes containing (FHF)⁻ is probably, in part, based on the fact[6] that HF is a weak acid ($K_a = 7.2 \times 10^{-4}$), while H(FHF) is a strong acid ($K_a = 5.5$) and the concentrations of F⁻ and (FHF)⁻ are dependent on the initial HF concentration.

In the case of the $KCP(X)_{0.30}$ (X = Cl⁻, Br⁻) salts, only a single stoichiometry is obtained which is totally independent of the concentrations or relative concentrations of the starting materials.[2] It is interesting to note that, if no acid is present and $Cs_2[Pt(CN)_4]$ is electrolyzed in a basic solution (pH maintained at 9.0 ± 0.1) containing CsF, a monofluoride complex is obtained with the formula $Cs_2[Pt(CN)_4]F_{0.19}$.[7]

Single-crystal electrical conductivities (4 probe) have been measured and for internal comparison we have also measured the conductivity of KCP(Br) and $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$

(K(def)TCP) (see Table I). As one would predict, those complexes with the shorter Pt–Pt separations and correspondingly higher DPO also tend to have higher conductivities. In fact, the room temperature conductivities of Rb- or $CsCP(FHF)_{0.4}$ are approximately double that of KCP(Br). Low temperature electrical conductivity studies are underway elsewhere.[8]

An added advantage with some of the new compounds is that, being anhydrous, they should be more stable with respect to variation of temperature, pressure, and humidity compared with the hydrated prototype KCP(Br). In our studies of conductivities measured above ambient temperature, we have found that, for $CsCP(FHF)_{0.39}$, there is a 10–20% rise in conductivity between room temperature and 75 °C. These measurements are reproducible as long as the temperature is not raised above ~80 °C, at which an irreversible transition to an insulating state occurs.

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