NMR (benzene-d_6): s, δ 3.53 (6 H); s, δ 2.15 (6 H); s, δ 1.77 (6 H). Melting point 127–128 °C; reported 127 °C, R. Criegee and F. Zanker, *Angew. Chem.*, **76**, 716 (1964); (b) **4a** reacts with dma at a rate comparable to that for **4c**; however, NMR observation indicates a more complex product mixture, due apparently to the higher lability of phosphine in **4a** and/or the triphenylphosphine congener of **10**. Compound **9** is observed along with a variety of products formed by direct reaction of dma with free PPh_3 (see footnote 12).

(11) ^1H NMR (benzene-d_6): (η^5-C_5H_5) s, δ 4.60 (5 H); $-[C_2(CO_2CH_3)_2]$ s, δ 3.53 (6 H); $-P(CH_3)_3$d($^2J_{^{31}P-^1H}$ = 10 Hz), δ 0.71 (9 H). **10** exhibits an intense visible absorption at 510 nm, the appearance of which was followed in the kinetic measurements.

(12) Dimethylacetylene dicarboxylate reacts rapidly with phosphines, even at −50 °C, thus precluding experiments in the presence of free phosphine. See, for example, N. E. Waite, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc. C*, 110 (1969).

(13) An alternate mechanism we cannot rule out would involve an 18-electron transition state with coordinated dma, PMe_3, and η^3-cyclopentadienyl.

(14) Alfred P. Sloan Fellow, 1976–1978.

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Received November 12, 1976

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 9. The New One-Dimensional Tetracyanoplatinates, $M_2[Pt(CN)_4](FHF)_{0.39}\cdot xH_2O$ (M = Rb, Cs), and a New Lower Limit for the Platinum–Platinum Separation (2.80 Å)[1]

Sir:

Although the prototype one-dimensional tetracyanoplatinate (TCP) conductors $K_2[Pt(CN)_4]X_{0.3}\cdot 3H_2O$, termed "KCP(X)" where X = Cl or Br, have been extensively studied,[2] all attempts to prepare a fluoride derivative have as yet been unsuccessful.[3] From neutron diffraction structure studies of KCP(Br)[4] and KCP(Cl)[5] we pointed out the importance of water molecule hydrogen bonding [$H—O—H\cdots{}^-N{\equiv}C$ and X^-] in stabilizing the KCP(X) structures. Presumably if interchain coupling is increased,[6,7] e.g., by inclusion of a strong hydrogen bond forming ion such as F^-, the one-dimensional properties might be so modified as to suppress the Peierls distortion in the Pt chain. In an attempt to increase interchain coupling in this manner we have prepared the new anion-deficient fluorine containing salts $K_2[Pt(CN)_4](FHF)_{0.30}\cdot xH_2O$ and $M_2[Pt(CN)_4](FHF)_{0.39}\cdot xH_2O$ where M = Rb or Cs, referred to here as MCP(FHF). Details regarding the preparation and characterization of CsCP(FHF) are presented here. The Cs and Rb complexes contain the shortest intrachain Pt-Pt separations (2.832 (1) and 2.798 (1) Å, respectively) yet observed in partially oxidized tetracyanoplatinate (POTCP) salts.

Derivatives of KCP(X) have generally been prepared by cocrystallization of the unoxidized Pt^{2+}, and the halogenated Pt^{4+} salt, in a 5:1 ratio to form the partially oxidized $Pt^{2.3+}$ salt. The synthesis of an analogous KCP(F) complex by this route has not been possible since the fluorinated Pt^{4+} salt apparently cannot be successfully prepared.[2] Utilizing an electrolytic process first reported by Terrey[8] for the preparation of $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, K(def)TCP, and extended recently by Miller,[9] we have now prepared lustrous metallic gold-colored crystals of $M_2[Pt(CN)_4](FHF)_y\cdot xH_2O$ (M = K, y = 0.30; M = Cs or Rb, y = 0.39). For the cesium analogue, a saturated solution of $Cs_2[Pt(CN)_4]$[10] is adjusted to pH ~2 using 18 M HF, CsF (99.9%) is added until the solution is saturated, and the solution is then electrolyzed (polyethylene beaker, Pt electrodes with ~5 mm separation) at ~1.5 V.[11] Lustrous metallic gold-colored crystals of $Cs_2[Pt(CN)_4](FHF)_{0.39}\cdot H_2O$ begin forming immediately at the cathode and grow to a length of ~5 mm within 24 h. These crystals are strikingly different in appearance from KCP(Br) or KCP(Cl) which have a metallic reddish bronze color. The crystals were washed with cold H_2O and two independent elemental analyses[12,13] yielded the results given in Table I.

Table I. Observed and Calculated Analyses for $Cs_2[Pt(CN)_4](FHF)_{0.39}\cdot H_2O$[a]

	Cs	Pt	C	N	H	F
Obsd[12]	43.69	33.96	8.19	7.28[b]	0.23	2.41
	43.67	34.04				2.39
Obsd[13]			8.18[c]	9.32[c]	0.17[c]	2.80[c]
			8.36[d]	9.39[d]		2.11[c]
						2.69[d]
						2.54[d]
Av	43.68	34.00	8.24	9.36[b]	0.20	2.49 ± 0.24
Calcd	44.46	32.63	8.04	9.37	0.40	2.49

[a] Emission spectrographic analyses[14] for metal content indicated only Cs and Pt were present with very faint traces (<0.001%) of Na and Rb. Elemental analyses for halogen other than F was 0.0%. [b] Nitrogen analyses from Galbraith Laboratories were consistently low and are not included in any subsequent calculations. [c] Prepared electrolytically at 0.6 V. [d] Prepared electrolytically at 1.5 V (battery).

The platinum oxidation state of +2.35 was determined by iodine-thiosulfate[14] titrations. However, the elemental analyses indicate the existence of twice the number of fluorine atoms per platinum as expected for a partially oxidized $Pt^{2.35+}$ complex containing F^- ions. Since the complex was prepared in a very acidic HF medium, we believe that fluorine exists as the bifluoride ion, $(FHF)^-$. The infrared spectrum[15] is complicated but it indicates that H_2O (not H_3O^+) may be present, although further structural study is required to confirm the presence of $(FHF)^-$. Preliminary single-crystal x-ray diffraction analysis on a Syntex $P2_1$ diffractometer revealed that CsCP(FHF) is body-centered tetragonal with $a = b$ = 13.057 (2) Å, and c = 5.665 (1) Å. The Rb complex is also body-centered tetragonal, with $a = b$ = 12.689 (2) Å and c = 5.595 (1) Å, while photographs of KCP(FHF) indicate a primitive tetragonal cell with $a = b$ = 9.80 (2) Å and c = 5.82 (1) Å. In addition, x-ray powder photographs indicate that CsCP(FHF) is not isostructural with KCP(Br) which has a primitive tetragonal space group with $a = b$ = 9.907 (3) Å, and c = 5.780 (2) Å. By contrast $Cs_{1.75}[Pt(CN)_4]\cdot xH_2O$ is monoclinic.[16]

Using Pauling's theory[17] of the metallic bond we have shown[18] that it is possible to *predict* metal-metal separations in TCP complexes if the degree of partial oxidation is known, and vice versa. The metal spacing in CsCP(FHF) may be calculated from the lattice constants ($c/2$) and we obtain Pt-Pt = 2.83 Å. From it we may calculate[18] the degree of partial oxidation n from $D(1) - D(n) = 0.600 \log n$, where $D(1)$ = 2.59 Å for Pt and $D(n)$ = 2.83 Å, and therefore n_{calcd} = 0.39. The calculated metal valence is therefore $Pt^{2.39+}$, which is in good agreement with that obtained from the elemental chemical analysis (0.39). The finding of a 2.83 Å Pt repeat separation, as opposed to 2.88 Å in KCP(Br) and 2.96 Å in K(def)TCP, is highly significant and shows that within the anion-deficient POTCP family it is possible to vary the metal-metal separation by appropriately changing the cation and anion which in turn affects the degree of partial oxidation. Most important, Pauling's equation qualitatively predicts a trend of higher partial oxidation resulting in a shorter Pt-Pt separation. This is the case for the series of POTCP complexes composed of CsCP(FHF) ($D(n)$ = 2.83 Å, n = 0.39), KCP(Br) ($D(n)$ = 2.88 Å, n = 0.30) and K(def)TCP ($D(n)$ 2.96 Å, n = 0.25). The RbCP(FHF) is anomalous to some extent, since its degree of partial oxidation based on analytical data appears at this time to be the same as that of CsCP(FHF), but it has a significantly shorter Pt-Pt separation. In fact, the Pt-Pt distance of 2.798 (1) Å found in RbCP(FHF) is the shortest spacing yet observed in a POTCP salt. However, these findings do demonstrate that the anion content is not fixed at 0.30-0.33 as has been observed for KCP(Br,Cl).

Finally, room temperature resistance measurements of polycrystalline pellets of the family of compounds KCP(X), where X = $(FHF)^-$, Cl^-, and Br^-, has revealed that they all have high conductivity. Only four-probe single-crystal measurements (in progress) will determine the true conductivity ratios. It is very likely that, based on the shortened Pt-Pt separation, the Rb and Cs bifluoride complexes are better room temperature conductors than the prototype KCP(Br).

References and Notes

(1) Work performed under the auspices of the U.S. Energy Research and Development Administration.
(2) For a review see J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976).
(3) K. Krogmann and H. D. Hansen, *Z. Anorg. Allg. Chem.*, **358**, 67 (1968).
(4) J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Peterson, *Phys. Rev. Lett.*, **33**, 1079 (1974); J. M. Williams, F. K. Ross, M. Iwata, J. L. Petersen, S. W. Peterson, S. C. Lin, and K. D. Keefer, *Solid State Commun.*, **17**, 45 (1975); J. M. Williams, M. Iwata, F. K. Ross, J. L. Petersen, and S. W. Peterson, *Mater. Res. Bull.*, **10**, 411 (1975); J. M. Williams, *Ferroelectrics*, in press.
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(9) J. S. Miller, *Science* **194**, 189 (1976).
(10) R. L. Maffly, J. A. Abys, and J. M. Williams, *Inorg. Synth.*, **19**, in press.
(11) The electrolysis may be accomplished using a 1.5-V dry cell battery.
(12) Galbraith Laboratories, Knoxville, Tenn.
(13) Midwest Microlabs, Indianapolis, Ind. This laboratory does not perform Cs and Pt analyses.
(14) Emission spectrographic analyses were performed by J. P. Faris, and iodine-thiosulfate analyses by E. Streets and K. Jensen, all of Argonne National Laboratory.
(15) We wish to thank Drs. J. R. Ferraro and L. J. Basile for the infrared results.
(16) P. L. Johnson and J. M. Williams, work in progress.
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(18) J. M. Williams, *Inorg. Nucl. Chem. Lett.*, **12**, 651 (1976).
(19) Associated Colleges of the Midwest Research Participant sponsored by the Argonne Center for Educational Affairs from Cornell College, Mt. Vernon, Iowa.

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An Isotope Effect Study of Triple Bond Participation during a Homopropargyl Rearrangement[1,2]

Sir:

The degree of rate acceleration owing to neighboring group participation[3] during the cyclization rearrangements[4] of homopropargyl esters has never been established, although all evidence points to involvement of the triple bond in the rate-determining formation of vinyl cation intermediates.

For example, in the trifluoroethanolysis of 1-pent-3-ynyl triflate[5] (**1**) (triflate = trifluoromethanesulfonate), homoallylic rearrangement has been ruled out: (1) by the demonstration[5] that trifluoroethanol does not add to the triple bond under the conditions of the reaction, and (2) by trapping[4] of the vinyl cation B as the ether **3**.[6]

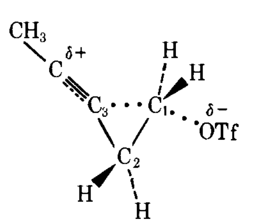


Figure 1. Presumed transition state for trifluoroethanolysis of 1-pent-3-ynyl triflate (**1**).

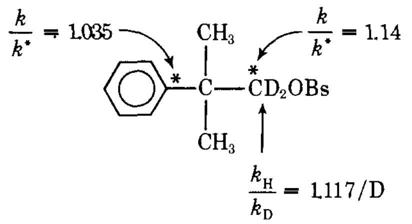
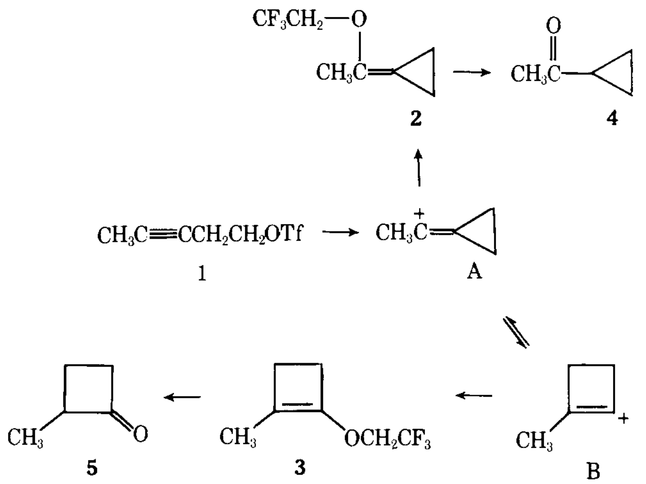


Figure 2. Isotope effects[9] in the trifluroacetolysis of neophyl brosylate.



We have now applied the isotope effect criterion[7] to the trifluoroethanolysis of **1**. Although an S_N1 reaction, the transition state (Figure 1) is surely S_N2-like, but not nearly so linear with respect to entering and leaving groups as for a typical S_N2 reaction. Consequently, a study of the ^{14}C-isotope effects (k/k^*) at C_1 and C_3, and the α-deuterium isotope effect at C_1 should provide us with estimates of the timing involved with respect to the incoming and departing groups about C_1.

Using standard procedures[4,8] we prepared the isotope position isomers **1**-*1*-^{14}C, **1**-*3*-^{14}C, and **1**-*1,1*-d_2-*3*-^{14}C and determined their isotope effects[8c]

$$CH_3C{\equiv}CCH_2\overset{*}{C}H_2OTf$$
1-*1*-^{14}C
$k/k^* = 1.048 \pm 0.003$

$$CH_3C{\equiv}\overset{*}{C}CH_2CH_2OTf$$
1-*3*-^{14}C
$k/k^* = 0.990 \pm 0.005$

$$CH_3C{\equiv}\overset{*}{C}CH_2CD_2OTf$$
1-*1,1*-d_2-*3*-^{14}C
$k_H/k_D = 1.098 \pm 0.004$
(per deuterium)

for trifluoroethanolysis at 30.0 °C. Under the conditions used, the reactions proceeded quantitatively to ketone **5** with only a trace of **4**. The values for each isomer are shown under the appropriate structures. After solvolysis of **1**-*1,1*-d_2-*3*-^{14}C, the deuterium in the 2-methylcyclobutanone (**5**) produced was shown by NMR analysis to be distributed equally between positions 3 and 4.

Our isotope effect data can be compared with the results of Ando and co-workers[9] (Figure 2) in the trifluoroacetolysis of