tinate compounds form nonlinear Pt–Pt chains in which equal metal-repeat separations are maintained even though they are not required crystallographically. At this time there is no evidence to indicate that the Pt chain deformation is caused by a charge density wave or Peierls distortion[14] as in $K_2Pt(CN)_4Br_{0.3}·3H_2O$. The full structural study will be reported at a later date.

Table I.[a] Published Structural Data on $K_{1.75}[Pt(CN)_4]·1.5H_2O$

Compound formulation	Crystal system	Cell data a, Å (α, deg)	 b, Å (β, deg)	 c, Å (γ, deg)	ρ_{obsd}, g/cm^3 (ρ_{calcd})	V_{cell} (Å^3)	Pt–Pt separation (Å)	Ref
$K_7Pt_4(CN)_{16}·6H_2O$[b] or $K_{1.75}[Pt(CN)_4]·1.5H_2O$	—	— —	— —	— —	— —	—	—	Levy,[8] (1912)
$K_{1.74}[Pt(CN)_4]·1.8H_2O$	Triclinic[c]	15.59 (92.5)	10.01 (92.5)	2.96 (92.1)	2.79 (2.87)	460.6	2.96 (c length)	Krogmann and Hausen,[4] (1968)
$K_{1.78}[Pt(CN)_4]Br_{0.034}·2H_2O$	Triclinic[d]	10.32 (1) (102.6 (1))	11.80 (1) (106.2 (1))	9.29 (1) (114.8 (1))	—	910.4	2.95 (b/4 length)	Minot et al.[6] (1973)
$K_{1.75}[Pt(CN)_4]·1.5H_2O$	Triclinic[e] $[C_i^1\text{-}P\bar{1}]$ $[Z = 4]$	10.36 (2) (102.4 (1))	11.83 (2) (106.4 (1))	9.30 (2) (114.7 (1))	2.82 (1) (2.85)	918.3	2.96 (b/4 length)	This work

[a] The estimated standard deviations are given in parentheses and refer to the least-significant figures. [b] Original formulation by Levy.[8] [c] Powder x-ray diffraction data; faint lines referred to as "superlattice" lines indicate c axis length should be doubled (5.92 Å). [d] Single-crystal x-ray data. Triclinic cell data are those for the primitive Delauney-reduced cell. [e] Single-crystal neutron data. Data for the primitive Delauney-reduced cell are given.[10] X-Ray powder patterns of this material are identical with those reported by Krogmann and Hausen;[4] hence all materials reported in this table appear to have the same molecular structure.

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References and Notes

(1) Research 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 (1975).
(3) J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Peterson, *Phys. Rev. Lett.*, **33**, 1079 (1974); J. M. Williams, M. Iwata, S. W. Peterson, K. A. Leslie, and H. J. Guggenheim, *Phys. Rev. Lett.*, **34**, 1653 (1975); 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); C. Peters and C. F. Eagen, *Phys. Rev. Lett.*, **34**, 1132 (1975); G. Heger, B. Renker, H. Deiseroth, H. Schulz, and G. Scheiber, *Mater. Res. Bull.*, **10**, 217 (1975).
(4) K. Krogmann and H. D. Hausen, *Z. Naturforsch. B*, **23**, 1111 (1968).
(5) Private communication with Dr. J. S. Miller, Xerox Corporation, Webster, N.Y.
(6) M. J. Minot, J. H. Perlstein, and T. J. Kistenmacher, *Solid State Commun.*, **13**, 1319 (1973).
(7) Chemical analysis of our compound for C, H, N, and halogen agrees very well with the formula obtained from the diffraction study, except for a trace of halogen (<1.0%) which apparently originated in our $K_2Pt(CN)_4·3H_2O$ starting material. A final Fourier difference density map is virtually featureless and, at this stage, gives no indication of any possible halide position. However, this is a matter of continuing study.
(8) L. A. Levy, *J. Chem. Soc.*, 1081 (1912).
(9) J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Am. Chem. Soc.*, **96**, 6610 (1974).
(10) All coordinates given, and Figure 1, refer to the triclinic cell used in data collection (a = 10.360 (17) Å, b = 9.303 (15) Å, c = 11.832 (19) Å, α = 77.57 (9)°, β = 114.74 (5)°, and γ = 73.64 (7)°). Cell parameters were derived from a least-squares refinement of 28 intense neutron reflections (40° < 2θ < 60°). Calibration of the neutron wavelength of 1.142 (1) Å was made with two standard cubic crystals: NaCl (a = 5.6397 Å) and Si (a = 5.4308 Å) at 22 ± 2°. The Delauney-reduced cell parameters presented in Table I were derived using the computer program "TRACER II, A Fortran Lattice Transformation-Cell Reduction Program" written by Dr. S. L. Lawton.
(11) Although the Pt–Pt separations in K(def)TCP are equal the *environments* about individual Pt atoms are not identical. Using photoelectron spectroscopy we are investigating these effects in an attempt to discern if the Pt atoms all have equivalent (fractional) valence states.
(12) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).
(13) T. W. Thomas, C.-H. Hsu, M. M. Labes, P. S. Gomm, A. E. Underhill, and D. M. Watkins, *J. Chem. Soc., Dalton Trans.*, 2050 (1972). The conductivity of K(def)TCP does not appear to be well characterized and merits further investigation.
(14) R. Comès, M. Lambert, H. Launois and H. R. Zeller, *Phys. Rev. B*, **8**, 571 (1973); C. F. Eagen, S. A. Werner, and R. B. Saillant, *Phys. Rev.*, submitted for publication.
(15) Research participants sponsored by the Argonne Center for Educational Affairs from (a) Oklahoma University, Norman, Oklahoma, and (b) Middlebury College, Middlebury, Vermont.

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A Partially Oxidized One-Dimensional Complex Containing a Distorted Platinum Chain. The Molecular and Crystal Structure of $K_{1.75}$ $Pt(CN)_4·1.5H_2O$

Sir:

With the observation of anisotropic metallic properties in $K_2Pt(CN)_4Br_{0.3}·3H_2O$ and in various organic charge trans-

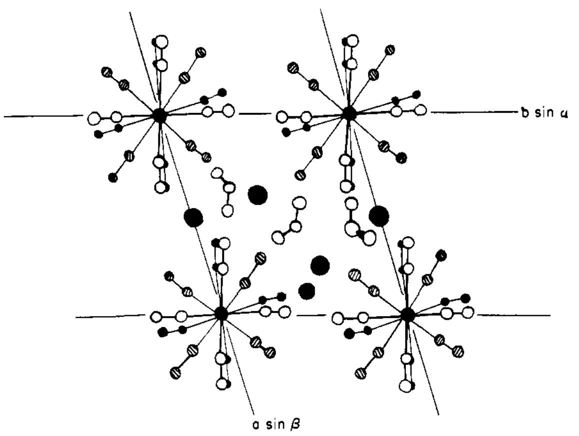

Figure 1. An asymmetric unit of $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$ projected onto (001). The black circles represent Pt, CN groups at $Z \simeq 0$, and K^+ ions; the lined circles CN groups at $Z \simeq 0.25$; and the open circles CN groups at $Z \simeq 0.5$ and water molecules. Additional CN groups related by centers of symmetry at $Z = 0$ and $Z = 0.5$ are added for clarity.

fer salts, there has been an increased interest in the characterization of additional highly conducting complexes to further the understanding of the chemistry and physics of one-dimensional (1-D) systems. Because of the ease of obtaining suitable single crystals, immense interest has been shown in the properties of the one-dimensional metal $K_2Pt(CN)_4{\cdot}Br_{0.3}{\cdot}3H_2O$.[1-5] X-ray[6,7] and neutron[8,9] diffuse scattering studies have combined to demonstrate the existence of an incommensurate superlattice which is attributed to either a charge density wave instability or a Peierls distortion involving the free electron band formed from the d_{z^2} like atomic orbitals.[10] The superlattice or satellite reflection intensities have been interpreted as due to longitudinal sinusoidal displacements of small magnitude of the tetracyanoplatinate (TCP) groups.[7-9]

We wish to report, as a result of a three-dimensional single-crystal x-ray crystallographic study of another partially oxidized platinum complex—the cation deficient complex, $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$—the existence of a transversely distorted nonlinear Pt atom chain with a commensurate repeat of 11.865 Å involving four Pt atoms. The amplitude of the transverse distortion wave is 0.198(1) Å.

$K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$ was originally prepared in 1912[11] by the oxidation of $K_2Pt(CN)_4{\cdot}3H_2O$ with H_2O_2 in acidic solution.[12,13] The bronze needles which form are triclinic, space group $P\bar{1}(C_i{}^1)$. The primitive cell that was chosen for data collection had unit cell dimensions $a = 10.323$ (14) Å, $b = 9.285$ (13) Å, $c = 11.865$ (17) Å, $\alpha = 77.31$ (3), $\beta = 114.85$ (5)°, $\gamma = 73.84$ (2)°, and $Z = 4$; the needle axis was assigned as c. There are two previous reports of trinclinic cells[12,13] for the potassium deficient complex, but both are related to our cell by simple transformations, thus we conclude that $K_{1.78}Pt(CN)_4{\cdot}1.8H_2O$[12] and $K_{1.74}Pt(CN)_4{\cdot}Br_{0.038}{\cdot}2H_2O$[13] are identical with the material reported herein.

X-ray photographs gave strong intensities for all reflections for which $l = 4n$ and much weaker intensities for those with $l \neq 4n$. X-ray intensity data were collected on an automated G.E. diffractometer using Mo Kα radiation in the θ-2θ scan mode to a 50° 2θ limit. The data were corrected for absorption and were assigned weights based on counting statistics plus the term $(0.03I)^2$. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. At the present stage of refinement in which $\Sigma w(\Delta F^2)^2$ was minimized the R factor (R_F) is 0.054 for the 1840 observed reflections for which $F_o > 3\sigma(F_o)$.

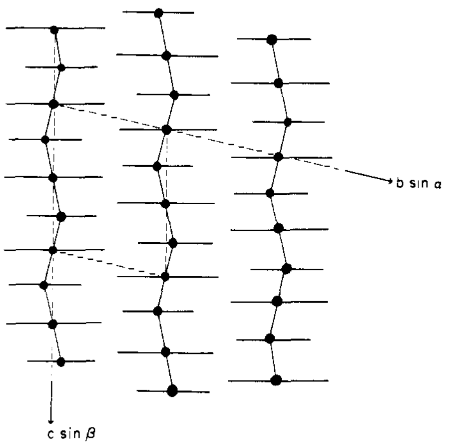

Figure 2. Schematic illustration of the TCP chains projected onto (100). CN groups are displayed as horizontal lines of varying length depending on the staggering of each group. A single unit cell is inscribed by dotted lines.

The main findings of the structure analysis which relate to the one-dimensional character of $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$ are the following. (1) The nearly planar TCP groups stack in a slightly distorted chain directed parallel to c. (2) There are three nonequivalent Pt atoms in the cell, Pt1 at (0,0,0), Pt2 at ±(0.0092, −0.0218, 0.2566), and Pt3 at (0,0,½) giving rise to two Pt-Pt distances 2.966 (1) and 2.978 (1) Å. (3) The Pt chain sequence is . . . Pt2-Pt1-Pt2-Pt3-Pt2 . . . with inversion centers at Pt1 and Pt3; thus unlike $K_2Pt(CN)_4{\cdot}X_{0.3}{\cdot}3H_2O$[14,15] the repeating unit contains four TCP ions. (4) The Pt chain distortion is defined by the Pt1-Pt2-Pt3 bond angle equal to 173.08 (2)°; also Pt2 is displaced by 0.198(1) Å from the straight line defined by the Pt atoms at (0,0,0) and (0,0,½). (5) Although $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$ is nonstoichiometric, the unit cell contains $K_7[Pt(CN)_4]_4{\cdot}6H_2O$ which is stoichiometric and possesses an odd number of electrons suggesting the possibility of a metallic state.[16] (6) All atoms are assigned to fully occupied crystallographic sites.

A view of the structure projected onto (001) is shown in Figure 1. Only one asymmetric unit is shown with additional CN groups added across the centers of symmetry at (0,0,0) and (0,0,½). The TCP groups which are separated by ~½c are nearly eclipsed (≃5°) while those separated by ¼c are staggered (≃44°). The six H_2O molecules in the cell hydrogen bond to N atoms of adjacent TCP stacks. The seven K^+ ions, one in a special position and six in general positions, are located close to CN groups and H_2O molecules and also serve to knit the structure together.

Figure 2 displays the Pt chain distortion (not to scale) which is transverse to the chain direction. The distortion would appear to be related to the crystalline environment rather than to an electronic effect although no detailed analysis has been made. Adjacent Pt chains are displaced along c when referred to an orthogonal coordinate system. The phase relation between chains is fixed by the triclinic coordinate system. The shortest interchain Pt-Pt spacing is 9.058 (12) Å.

The exact stoichiometry and thus the degree of partial oxidation (and degree of band filling) is of theoretical importance in the understanding of the physical properties of this system. The stoichiometry indicated by the formulation $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$ has been obtained by the refinement of atom multipliers in the least-squares process. It is also in essential agreement with the earlier formulations.[11-13] However, there is some evidence for the presence of small amounts of halide ion in the potassium deficient product.[13] Elemental analysis has verified the possibility of a trace of halogen in the species,[17] and a formulation $K_{1.75}Pt(CN)_4 \cdot X_{0.038} \cdot 1.5H_2O$ where X is Br^- or Cl^- is a possibility. We have searched for evidence of extra electron density in our Fourier maps and have attempted to refine very weak peaks (probably noise) with no success. The present stage of our crystallographic analysis suggests a halogen free complex with all platinum atoms being in the equivalent oxidation state of 2.25. The crystallographic properties of this system suggest the observation of high conductivity and possibly a metallic state at room temperature. The optical, electrical, and magnetic properties of this system are currently being investigated.

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References and Notes

(1) K. Krogmann, *Angew. Chem., Int. Ed. Eng.*, **8**, 35 (1969).
(2) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972).
(3) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).
(4) H. R. Zeller, *Adv. Solid State Phys.*, **13**, 31 (1973).
(5) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1975).
(6) R. Comès, *Lect. Notes Phys.*, **34**, 32 (1975).
(7) R. Comès, M. Lambert, H. Launois, and H. R. Zeller, *Phys. Rev. B* **8**, 571 (1973).
(8) C. F. Eagen, S. A. Werner, and R. B. Saillant, *Phys. Rev.*, in press.
(9) B. Renker, H. Rietschel, L. Pintschovius, W. Gläser, P. Bruesch, D. Kuse, and M. J. Rice, *Phys. Rev. Lett.*, **30**, 1144 (1973); B. Renker, L. Pintschovius, W. Gläser, H. Rietschel, R. Comès, and W. Drexel, *ibid.*, **32**, 836 (1974); B. Renker, L. Pintschovius, W. Gläser, H. Rietschel, and R. Comès, *Lect. Notes Phys.*, **34**, 53 (1975).
(10) H. R. Zeller and P. Bruesch, *Phys. Status Solidi B*, **65**, 537 (1974).
(11) L. A. Levy, *J. Chem. Soc.*, 108 (1912).
(12) K. Krogmann and H. D. Hausen, *Z. Naturforsch. B*, **23**, 1111 (1968).
(13) M. J. Minot, J. H. Perlstein, and T. J. Kistenmacher, *Solid State Commun.*, **13**, 1319 (1973).
(14) J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Peterson, *Phys. Rev. Lett.*, **33**, 1079 (1974).
(15) J. M. Williams, M. Iwata, S. W. Peterson, K. Leslie, and H. J. Guggenheim, *Phys. Rev. Lett.*, **34**, 1653 (1975).
(16) J. S. Miller, *Adv. Chem. Ser.*, in press.
(17) J. M. Williams, private communication.
(18) Participant in the undergraduate research participation program sponsored by the Argonne Center for Educational Affairs.

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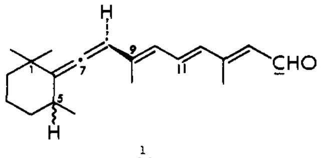
Allenic Retinals and Visual Pigment Analogues

Sir:

As part of our studies directed towards clarifying the steric factors involved in rhodopsin formation,[1,2] we have studied the spectral properties of artificial rhodopsin analogues prepared by the binding of bovine opsin to the various double bond isomers of 6,7-didehydro-5,6-dihydroretinals ("6-allenic retinals"), e.g., all-trans allenic retinal **1**.[3] These unique chromophores are of particular interest in studying the steric (including chiroptical) limitations imposed on the retinal moiety by the apoprotein opsin since: (i) the allenic bond fixes the cyclohexane ring at right angles with the pendant polyene thus providing models for comparing the role of twist about the 6-s-bond in normal retinals, and (ii) they contain two chiral centers, C-5 and C-6,[3] and therefore enable one to gain information on the opsin chiroptical requirements.



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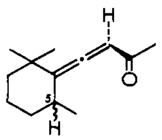

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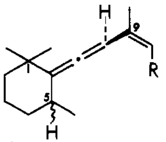
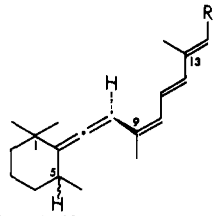
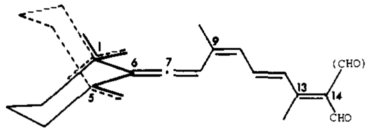


3 9-cis: R = COOEt
(4 9-trans: R = COOEt)
5 9-cis: R = CHO



7 9-cis,13-trans: R = COOEt
(8 9-cis,13-cis : R = COOEt)
9 9-cis,13-trans: R = CHO

6 $(C_2H_5O)_2POCH_2(CH_3)C{=}CHCOOEt$



(the 14-CHO in parentheses is for 9,13-dicis isomers)

10a 5R,6S: ring moiety indicated by solid line
10b 5S,6S: ring moiety indicated by dotted line

The various double bond isomers were prepared separately by routes analogous to that exemplified in the following,[4] or by photoirradiation of the all-trans isomer (analogous synthesis) and separation by high-pressure liquid chromatography (HPLC).

Condensation of the known diastereomeric allenic ketone **2**[3,5] (with 2 mol of triethyl phosphonoacetate, *n*-butyllithium, ether, 25°, 3 days), and chromatography (silica gel, 30–50% CH_2Cl_2-hexane) of the product afforded diastereomeric 9-cis ester **3** (31%), 8-H at 7.52 ppm ($CDCl_3$), and the 9-trans ester **4** (53%), 8-H at 5.96 ppm. Reduction of the 9-cis ester **3** with diisobutylaluminum hydride (dibal) (hexane, −78°) followed by MnO_2 oxidation (hexane, 0°, 2 h) yielded the crude aldehyde **5**. Reaction of aldehyde **5** with phosphonosenecioate **6**[6] (NaH, THF, 0–25°) gave a mixture of the 13-trans/cis esters **7**[3] and **8**[3] (54% from **3**), which were separated by silica gel chromatography (30% CH_2Cl_2-hexane). Reduction of the 9-cis-13-trans ester **7** with dibal (hexane, −78°) and subsequent MnO_2 oxidation (CH_2Cl_2, 25°, 2 h) gave the crude diastereomeric 9-cis-13-trans aldehydes **9**,[3] 80% yield from ester **7**. HPLC,[1] μ-porasil, 1 ft × 0.25 in. (two), 1.5% ether in hexane, 2 ml/min flow rate, monitored at 350 nm, was employed to purify the respective retinals thus synthesized or to separate the double bond mixture resulting from photoisomerization of the all-trans isomer.

Both diastereomers of all-trans, 9-cis, 13-cis, and 9,13-dicis isomers could, respectively, be separated by running a second HPLC in 1% ether-hexane and at a flow rate of 1:1 ml/min (a few other peaks were present, presumably due to other isomers, but due to their minute quantity they were not pursued further). The double bond configurations of various allenic retinals thus obtained were determined by 270-MHz FT-NMR (Table I) by reference to the data for normal retinals.[7] All allenic retinals had uv spectra, in 3-methylpentane, consisting of a fine-structured triplet centered around 350 nm.[8]

Except for the 9-cis isomer, the three other isomers were