spectral properties of **9** [^{1}H NMR($CDCl_3$) δ 7.3–7.7 (9 H, m), 1.56 and 1.58 (12 H, two overlapping s); ^{13}C NMR ($CDCl_3$) in aliphatic region: δ 77.2 (s), 45.8 (s), 29.3 (quartet), 25.2 (quartet)] agreed with the assigned structure. Moreover, **9** reacted with lithium in THF at −75 °C to give after carbonation 3-*p*-biphenylyl-2,2,3-trimethylbutanoic acid (**10**), mp 208–209 °C. In contrast, **9** (0.81 g) reacted with Cs–K–Na alloy (6.0 g) in THF at −75 °C to give a red solution, which as soon as it turned green-black was carbonated (50-s reaction time). The usual work-up gave, according to quantitative GLC analysis of the methyl ester, 7% of **10** and 28% of **11** (yields based upon starting **9**) along with considerable nonvolatile acid. The mixture of acids was separated by chromatography on silica gel[13] (0.05–0.20 mm, E. Merck A.-G., Darmstadt) with elution by hexane–ether. Acid **11** has mp 182–183 °C dec and analytical and spectral properties [^{1}H NMR ($CDCl_3$) δ 10.6 (1 H, br s, CO_2H), 7.34 (5 H, br s), 6.01 (4 H, AB quartet, $\Delta\nu$ = 20 Hz, J = 11 Hz), 1.19 and 1.14 (12 H, overlapping s); λ_{max}^{EtOH} 269 (sh, ϵ 377), 218 nm (ϵ 21 900); mass spectrum, M^+ m/e 282] in agreement with the structure of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid. The anion **7**, which is regarded as a precursor of the acid **11**, has a half-life of about 22 min under our usual conditions in THF at −75 °C.

In view of the importance of the structure of anion **7** and the derived carboxylic acid **11** to the understanding of [1,2] aryl migrations and because conceivably yet unknown migrations could be occurring to give a carboxylic acid whose properties are merely like those ascribable to 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, the structure of acid **11** has been determined independently by single-crystal x-ray diffraction analysis.

The acid **11** crystallizes in the triclinic space group $P\bar{1}$ with a = 13.307 (6),[14] b = 8.349 (6), c = 10.217 (2) Å, α = 90.75 (4), β = 126.04 (3), γ = 104.23 (5)°, Z = 2, d_c = d_m = 1.16 g cm^{-3}. The intensity data were measured with a Syntex $P2_1$ four-circle diffractometer, equipped with a graphite monochromator, using the θ–2θ scan technique. The structure, which was solved[15] by direct methods, was refined by least-squares methods (variables included a scale factor, coordinates of all atoms, and anisotropic thermal parameters for all carbon and oxygen atoms; fixed isotropic thermal parameters of 4.0 were used for all hydrogen atoms) to covergence at R = 0.055 and R_w = 0.059 (256 variables, 2160 observations).[19] The structure is illustrated in Figure 1.

It was thought conceivable that x-ray analysis of **11** would reveal that steric compressions had been relieved on going into **7** from the expected precursor of **7**, namely 2-*p*-biphenylyl-1,1,2-trimethylpropylcesium (**12**). In fact the C(9)–C(9′) or C(10)–C(10′) distance in **11** (see Figure 1) is 2.490 (6) Å or about the same as that calculated (2.51 Å) between *gem*-dimethyl groups in a hydrocarbon having the usual tetrahedral angle and 1.54-Å C–C bond distance. Also the distance between vicinal (essentially eclipsed) methyl groups in **11**, C(9)–C(10) or C(9′)–C(10′), is 3.016 (6) Å or again nearly the same value as that calculated (2.93 Å) similarly for vicinal gauche methyl groups in hexamethylethane. Thus the *gem*-dimethyl group effect in the present work does not seem to depend upon important relief of steric compression *if* hydrocarbons can be taken as suitable models for organocesium compounds. Evidently the effect is associated with the destabilizing influence of methyl groups upon the tertiary carbanionic center of **12**, an effect which would be expected to accelerate cyclization,[20] and the stabilizing influence of methyl groups (especially *gem*-dimethyl groups) upon cyclopropane rings.[21,22]

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged. The authors wish to thank Mr. Duncan Cheung for helpful discussions on the solution of structure phases.

Supplementary Material Available: fractional coordinates (Table I), important bond distances (Table II), important bond angles (Table III), and observed and calculated structure factors (Table IV) (13 pages). Ordering information is given on any current masthead page.

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(13) Only about half of acid **11** survived chromatography on this grade of silica gel; on a closely related grade of silica gel the entire acid was converted to an insoluble material which impeded flow through the chromatography column.

(14) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(15) All computations were carried out on the CDC Cyber 74 System. Standard programs utilized included: Germain, Main, and Woolfson's MULTAN, Zalkin's FORDAP, Iber's NUCLS modification of Busing, Martin and Levy's least-squares program, Busing and Levy's ORFFE, and Johnson's ORTEP. Scattering factors were taken from Cromer and Waber's tabulation[16] for carbon and oxygen; Stewart's hydrogen atom scattering factors[17] were used. Anomalous dispersion factors employed were those given by Cromer.[18]

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(19) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

(20) Cf. the greater rate of addition of *tert*-butyllithium than of *n*-butyllithium to ethylene [P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75,** 1771 (1953)]. Also benzylsodium and -potassium add to propylene and isobutylene to produce primary rather than secondary or tertiary carbanions [H. Pines and V. Mark, *J. Am. Chem. Soc.*, **78,** 4316 (1956); L. Schaap and H. Pines, *Ibid.*, **79,** 4967 (1957)].

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(22) The question of whether or not equilibrium may exist between **12** and 7 is being investigated by a deuterium labeling experiment.

J. A. Bertrand,* Erling Grovenstein, Jr.*
Pang-chia Lu, Don VanDerveer
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

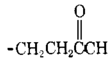
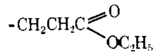
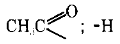
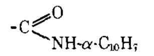
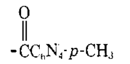
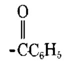
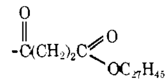
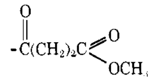
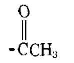
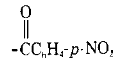
Received August 27, 1976

Progress toward the Development of Totally Synthetic Heme–Protein Models—the Use of Substituents to Control the Oxidation–Reduction Properties of Metal Ions in Complexes with Macrocyclic Ligands

Sir:

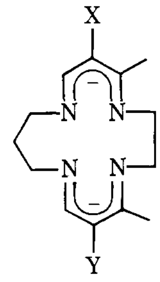
Two general structural assemblages determine the capability of the metal ion to perform its function in a metalloprotein. The first is the coordination sphere of the metal ion which consti-

Table I. Electrochemical Data[a] and d–d Electronic Absorption Bands[b]

Compound[c] no.	γ-Substituents	Oxidation $E_{1/2}$ (V)	Oxidation Δp (mV)	Reduction $E_{1/2}$ (V)	Reduction Δp (mV)	d–d band ν (μm^{-1}) (ϵ)
1	$-CH_2CH_2\text{-}\alpha\text{-}C_5H_5N$	(1) −0.44 (2) +0.15	(75) (irr)	−2.91	(105)	1.724 (287)
2	 $-CH_2CH_2C(=O)CH_3$	(1) −0.40 (2) +0.20	(90) (irr)	−2.87	(50)	1.706 (214)
3	 $-CH_2CH_2C(=O)OC_2H_5$	(1) −0.39 (2) +0.29	(85) (irr)	−2.92	(195)	1.702 (224)
4	−H	(1) −0.36 (2) +0.39	(irr) (irr)	−2.83	(120)	1.715 (169)
5	 $CH_3C(=O)$; -H	(1) −0.14 (2) +0.51	(irr) (irr)	−2.64	(90)	1.832 (197)
6	 $-C(=O)NH\text{-}\alpha\text{-}C_{10}H_7$	(1) +0.03 (2) +0.55	(65) (irr)	−2.59	(100)	1.866 (285)[c]
7	 $-C(=O)C_6N_4\text{-}p\text{-}CH_3$	(1) +0.19 (2) +0.63	(60) (irr)	−2.44	(100)	1.931 (421)
8	 $-C(=O)C_6H_5$	(1) +0.21 (2) +0.64	(55) (irr)	−2.42	(95)	1.927 (433)
9	 $-C(=O)(CH_2)_2C(=O)OC_{27}H_{45}$	(1) +0.21 (2) +0.67	(50) (irr)	−2.48	(120)	1.934 (342)
10	 $-C(=O)(CH_2)_2C(=O)OCH_3$	(1) +0.22 (2) +0.66	(55) (irr)	−2.50	(120)	1.938 (344)
11	 $-C(=O)CH_3$	(1) +0.22 (2) +0.64	(70) (irr)	−2.52	(155)	1.930 (330)
12	$-NNC_6N_4\text{-}p\text{-}NO_2$	(1) +0.305 (2) +0.515	(irr) (irr)	(1) −1.53 (2) −2.22	(80) (irr)	—
13	 $-C(=O)C_6H_4\text{-}p\text{-}NO_2$	(1) +0.31 (2) +0.79	(80) (irr)	(1) −1.47 (2) −2.15	(80) (135)	—
14	$-NO_2$	(1) +0.42 (2) +1.04	(60) (irr)	(1) −2.00 (2) −2.60	(80) (irr)	1.980 (922)

[a] In DMF solvent vs. Ag/AgNO$_3$ (0.1 M) reference electrode with 0.1 M (n-Bu)$_4$NBF$_4$. [b] In CHCl$_3$ solvent unless otherwise noted. [c] In DMF solution.

tutes the ligand field and determines the electronic properties of the metal ion. The second involves the noncoordinated structural array in the vicinity of the active metal site—the *associated proximate structure*. The latter may serve one or more of several functions, such as providing propitiously oriented functional groups or determining the polarity in that region. We are concerned with the development of relatively simple ligands incorporating proper design of both kinds of structural assemblages, in an effort to reproduce certain essential functions that occur in natural metal-containing substances, specifically the heme proteins. Much interest exists today in studies of this kind and considerable success has been achieved with systems based on modified porphyrin structures.[1-3] We are concerned with totally synthetic systems. Because the functions of the various heme-proteins are redox related, the demonstration of control of redox potentials in suitable structures fulfills the first requirement; i.e., generation of the appropriate ligand fields in suitable coordination environments. We report here the synthesis and use of ligands of general structure I to control closely the value of $E_{1/2}$ for a metal ion couple (Ni^{II}/Ni^{III}) and to produce a remarkable range of potentials (>0.8 V) for that couple while retaining the metal ion in a constant macrocyclic ligand framework. Closely similar correlations with $E_{1/2}$ and electronic absorption bands demonstrate the dependence of the electrode potential behavior on changes in the ligand field.



I

The Ni^{II} complex of I with X = Y = CH$_3$C=O, I, was first synthesized by Jäger.[4] It has previously been shown in these laboratories[5,6] that the acetyl groups can be removed by acid catalysis in nucleophilic solvents yielding the parent compound

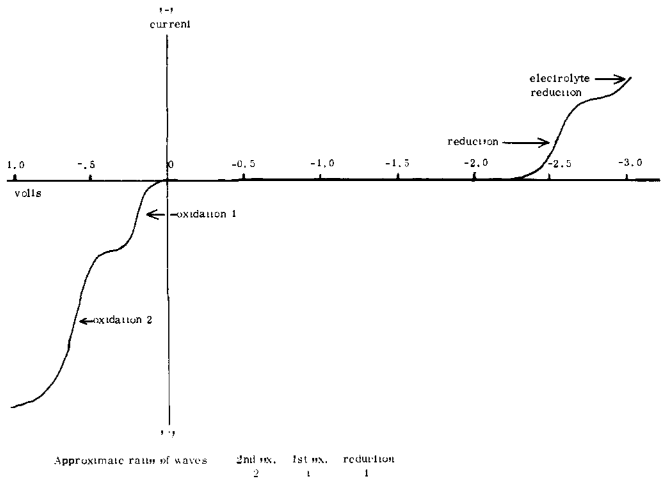


Figure 1. Voltammogram for the diacetyl derivative, compound 11, Table I, DMF Solvent, Ag|$AgNO_3$ (0.1 M) reference electrode, 0.1 M (n-$Bu)_4NBF_4$ supporting electrolyte, 25 °C.

Table II. Linear Free Energy Parameters for Electrochemical Data

σ	$\rho_{E_{1/2}}$	$(E_{1/2})_{\sigma=0}$	r
σ_p^-	0.645	−0.362	0.994
σ_p	1.013	−0.345	0.993
σ_m	1.016	−0.331	0.978

Table III. Linear Free Energy Parameters for Spectral Data

σ	ρ_{d-d}	$(E_{d-d})_{\sigma=0}$	r
σ_p^-	2.205	17.243	0.991
σ_p	3.508	17.308	0.987
σ_m	3.947	17.371	0.958

having X = Y = H. Earlier studies also showed that the complexes of the parent ligand are highly reactive nucleophiles.[7,8] We now report the synthesis of a broad range of substituted derivatives, all produced by electrophilic reaction at the γ-carbons of the parent compound. The reactions include mono- and diacylation with acetic anhydride, diacylation with para-substituted benzoyl chlorides, Michael addition of methyl vinyl ketone, ethylacrylate, and 2-vinylpyridine, condensation with α-naphthylisocyanate, coupling with p-nitrobenzenediazonium hexafluorophosphate, and nitration with concentrated nitric acid in acetic acid. The latter reaction has previously been reported from these laboratories.[9] The structures of the products have been established by elemental analyses, infrared spectroscopy, and, in well-behaved cases, by NMR and mass spectroscopy. Analytically pure samples were obtained for the measurements described below. All complexes contain low-spin, presumably planar Ni^{II}.

The voltammogram (Figure 1) for the diacetylated complex illustrates the electrochemical behavior of these compounds. All measurements were made at 25 °C, in DMF solvent, using an Ag|$AgNO_3$ (0.1 M) reference electrode and 0.1 M (n-$Bu)_4NBF_4$ as supporting electrolyte. The compounds show two oxidations and a single reduction wave, the latter occurring at very cathodic potentials. The first oxidation wave has been assigned elsewhere[10] as involving principally the Ni^{II}/Ni^{III} couple. Table I lists the $E_{1/2}$ values and indicates the character of the electrode processes as determined by cyclic voltammetry under the conditions given above. The first oxidation wave is generally well-behaved and is either reversible or quasi-reversible except for those compounds having hydrogen atoms on the γ-carbons. The second oxidation process has been associated with ligand oxidation,[10] a transformation that has been well demonstrated using chemical oxidizing agents.[11,12]

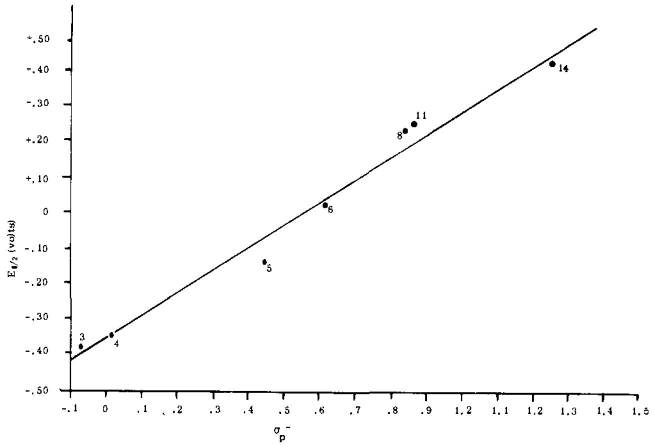


Figure 2. Correlation of $E_{1/2}$ with σ_p^- for nickel complexes listed in Table I.

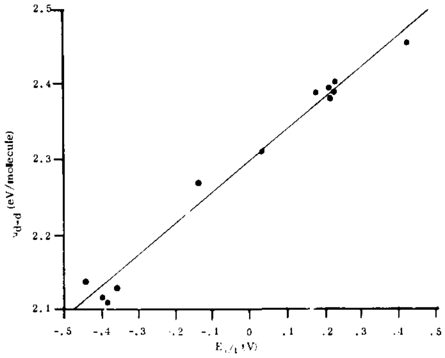


Figure 3. Correlation of d–d transition energies with $E_{1/2}$ for nickel complexes listed in Table I.

Focusing attention on the first oxidation process (Table I), it is most obvious that electron withdrawing substituents (X and Y) are highly effective at producing more positive potentials while alkyl substituents produce potentials at least as negative as that of the unsubstituted compound. Substitution of NO_2 for H drives the potential from −0.36 to +0.42 V, while the substituent-$CH_2CH_2C_5H_4N$ produces a potential of −0.44 V for a total range of 0.86 V.

The responsiveness of $E_{1/2}$ to substitution is shown most clearly by linear free energy relationships as exemplified by Figure 2. The correlations of $E_{1/2}$ values with σ_p, σ_p^-, σ_m have been evaluated for those cases where σ values could be found or estimated. Most of the values were taken from Gordon and Ford;[13] that for -CH_2CH_2COOH was used for -$CH_2CH_2COOC_2H_5$;[13] that for X = H and Y = $CH_3C{=}O$ is taken to be half the value used for X = Y = $CH_3C{=}O$;[14,15] that for -$CONH_2$ was used for $CONHC_{10}H_7$.[13] Table II displays the quality of the correlations (r = correlation coefficient) assuming the equation below:

$$E_{1/2} = \rho_{E_{1/2}}\sigma + (E_{1/2})_{\sigma=0}$$

The correlation based on σ_p values is essentially as good as that based on σ_p^- and that based on σ_m is rather good. This suggests that resonance interactions may be of limited importance.

It is concluded that the effects of substituents on ligand electron density are transmitted strongly to the metal ion in these structures and that such substituents can be used to exercise precise control over the redox properties of the metal ion. This is further emphasized by a parallel correlation between the substituent constants and the frequencies (μm^{-1}) of the low-energy electronic transitions for these complexes (Tables I and III). These transitions exhibit extinction coefficients and fall in a range generally observed for the d–d transitions of square planar, low-spin Ni^{II} complexes.[16] Thus, the electron density changes produced by the substituents are reflected in the ligand field strength of the substituted macrocycles. The spectral and electrochemical correlations are both strikingly good, and it is significant that both the functional property ($E_{1/2}$) and the diagnostic property (ν) are sensitive to substituent effects. Correlation between the spectral and electrochemical parameters is evident in Figure 3 (correlation coefficient, 0.98).

The compounds reported here are well suited to continuing studies in which substituents having appropriate electronic effects are used to append additional components to the structure as required by the other major structural consideration stated in the introductory paragraph above, the associated proximate structure. This and the incorporation of biologically important metal ions will be the subjects of subsequent reports.

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Dale G. Pillsbury, Daryle H. Busch*
Chemistry Department, The Ohio State University
Columbus, Ohio 43210

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A Novel Partially Oxidized Distorted One-Dimensional Platinum Chain in $K_{1.6}Pt(C_2O_4)_2\cdot 1.2H_2O$[1]

Sir:

Partially oxidized one-dimensional anion-deficient complexes, $K_2Pt(CN)_4\cdot Cl_{0.32}\cdot 3H_2O$[2] and $K_2Pt(CN)_4\cdot Br_{0.30}\cdot 3H_2O$,[3] and cation-deficient complexes, $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$[4] and $Mg_{0.82}Pt(C_2O_4)_2\cdot 5.3H_2O$,[5] have been recently structurally characterized by x-ray and neutron diffraction techniques. These materials show metallic properties including high conductivity along the crystalline needle axis.[6] $K_{1.6}Pt(C_2O_4)_2\cdot xH_2O$ was first synthesized by Söderbaum[7] in 1888 and has been shown only recently to have one-dimensional properties.[8] However, the structure of this material has been rather elusive. The first Pt–Pt distance reported for a material with stoichiometry $K_{1.6}Pt(C_2O_4)_2\cdot 2.5H_2O$ was 2.75 Å,[9] somewhat shorter than that in Pt metal.[10] Later it was claimed,[11] based on x-ray powder evidence, that at least five different crystalline phases exist and a stoichiometry $K_{1.64}Pt(C_2O_4)_2\cdot 4H_2O$ was reported for one of them. This latter phase (called phase A) was found to exist in three different forms, which gave different single-crystal diffraction patterns but identical powder patterns. Pt–Pt spacings of 2.84 Å, deduced from the substructure periods, were reported[11] for the three forms of phase A material. Except for these approximate metal spacings, no other structural results have been reported for the partially oxidized potassium bisoxalate complexes. We wish, therefore, to report the synthesis and the molecular and crystal structure of $K_{1.6}Pt(C_2O_4)_2\cdot 1.2H_2O$ (KDOX), as deduced from single-crystal x-ray diffraction data.

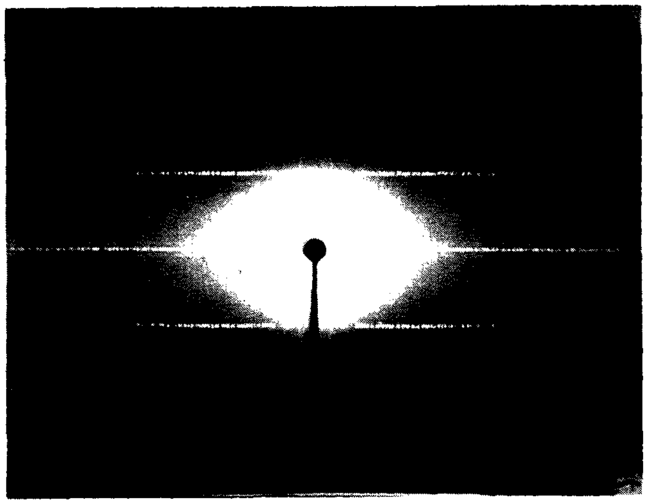

Figure 1. A rotation photograph of a crystal of $K_{1.6}Pt(C_2O_4)_2\cdot 1.2H_2O$ mounted along the c axis showing the metal lattice (c_m), the intermediate cell (4 × c_m), and the incommensurate metal superlattice (10.25 × c_m).

KDOX was prepared first by the method of Krogmann and Dodel,[11] yielding small copper-colored triclinic needles. Later, somewhat larger coppery needle and lath shaped crystals were obtained by air oxidation of $K_2Pt(C_2O_4)_2\cdot 2H_2O$ in aqueous oxalic acid solution (pH ~ 2) at 40 °C. Both methods yielded crystals which gave identical diffraction patterns and were triclinic, space group $P\bar{1}$ (C_i^1, no. 2) with cell dimensions a = 9.744 (12), b = 10.700 (13), c = 11.377 (14) Å, α = 80.23 (6), β = 77.97 (7), γ = 115.87 (3)°, and Z = 4. The molecular weight (455.18 g/equiv) and unit cell volume (997.02 Å^3) give a calculated density of 3.031 g/cm^3, which is in good agreement with an observed density of 3.00 (1) g/cm^3.

Figure 1 shows an x-ray rotation photograph of a crystal of KDOX mounted along the c axis. The KDOX lattice may be described in terms of three cells which differ in their c axis length. The smallest cell (most intense reflection spacing on the photograph) represents a metal–metal spacing along the c axis of 2.844 Å (c_m), the intermediate cell (weak commensurate levels on the photograph) a spacing of exactly 4 × c_m, which is indicative of the ligand repeat and transverse chain distortion; and the largest cell (weak *incommensurate* levels bracketing the most intense lattice reflections) a spacing of 10.25 × c_m, which may be indicative of longitudinal displacements of the metal–ligand groups along the chain axis. Three-dimensional x-ray data were collected on automated Picker-FACS-1 (small cell data) and G.E. XRD-490 (small and intermediate cell data) diffractometers using Mo$K\alpha$ radiation in the θ–2θ scan mode to a 55° 2θ limit. The data were corrected for absorption and the structure solved by a combination of Patterson, Fourier, and least-squares refinement techniques. At the present stage of refinement, with all Pt and K^+ atoms refined anisotropically and all C and O atoms refined isotropically, the R factor is 0.057 for the 1772 observed reflections.

The structural properties which relate to the one-dimensional character are quite similar to those observed in $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$.[4] They include: (1) The formation of parallel zigzag Pt atom chains aligned along the c axis. (2) A transverse Pt atom displacement of 0.056 (5) Å (somewhat smaller than in $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$),[4] and a Pt(1)–Pt(2)–Pt(3) bond angle of 177.8 (2)°. (3) There are three non-