

Syntheses and Characterization of Three Tris Complexes of the Ligand 5,6-Dihydro-1,4-dithiin-2,3-dithiolate. Crystal Structure of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$

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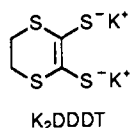
Received March 15, 1989

The reaction between $TiCl_3$ and the potassium salt of the dithiolene ligand 5,6-dihydro-1,4-dithiin-2,3-dithiolate ($DDDT^{2-}$) under an argon atmosphere resulted in the isolation of $Ti(DDDT)_3^{2-}$ as the tetraphenylarsonium salt. A single-crystal structural analysis has been performed and is the first reported crystal structure of a titanium dithiolene. The salt crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 20.643$ (4) Å, $b = 20.743$ (5) Å, $c = 27.822$ (9) Å, and $Z = 8$. The large unit cell contains four cations and two anions in the asymmetric unit, and the structure refined to a value of $R = 0.095$ and $R_w = 0.097$. In each of the unique anions, the six ligated sulfur atoms form a distorted octahedron around the titanium with an average Ti-S bond length of 2.42 (2) Å. One parameter relevant to distorted octahedral coordination is the S-Ti-S (trans) angle of 159 (1)°, which is intermediate between the values for trigonal-prismatic (~136°) and corrected octahedral coordination (172.5°). The tris complexes of Mn and Nb with $DDDT^{2-}$ have been isolated as tetraalkylammonium salts. The Mn product, $[(C_2H_5)_4N]_2[Mn(DDDT)_3]$, is extremely air sensitive, while that of Nb, $[(C_4H_9)_4N][Nb(DDDT)_3]$, is stable in air as a solid. Details of the syntheses, cyclic voltammograms, and UV/vis/near-IR spectra are discussed for all three complexes.

Introduction

The study of transition-metal dithiolenes has been an area of great interest for a number of years. The study of these complexes has been due in part to the recognition of trigonal-prismatic coordination in some of the tris complexes. The first structures reported were those of $Mo(S_2C_2H_2)_3$, $Re(S_2C_2Ph)_3$, and $V(S_2C_2Ph)_3$,¹⁻³ all exhibiting trigonal-prismatic geometry. Shortly thereafter, the coordination of the dianion $V(S_2C_2(CN)_2)_3^{2-}$ was described as a distorted octahedron.⁴ It has also been shown that tris complexes like their bis counterparts undergo reversible one-electron-transfer reactions resulting in stable species differing in oxidation state. These oxidation states can only be stated formally, since the dithiolate ligands can themselves be oxidized to dithiodiketones. These observations stimulated research on transition-metal dithiolenes and have resulted in a number of detailed reviews.⁵⁻⁹

Bis complexes of the relatively new dithiolene 5,6-dihydro-1,4-dithiin-2,3-dithiolate isolated as the potassium salt (K_2DDDT) have been studied extensively and include the complexes of Ni, Pd, Pt, Cu, Au, and Co.¹⁰⁻¹⁴ However, the only tris complexes



reported are two vanadium species that differ by one electron.¹⁵ In a continuation of the effort to characterize the coordination chemistry of this dithiolene, the Mn, Nb, and Ti complexes of $DDDT^{2-}$ have been isolated and the structure of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$ has been determined by X-ray crystallography.

Syntheses of $DDDT^{2-}$ complexes vary from metal to metal. The reaction with Cu and the Ni group metals yields oxidized products in the presence of air and nonoxidized species if the reaction is carried out under Ar.¹⁰⁻¹² Both reaction conditions yield oxidized products of V with the extent of oxidation greater for the synthesis in air.¹⁵ A Co species can only be isolated under Ar, and its formula indicates oxidation.¹⁴ The synthesis of the Mn complex requires air and yields an oxidized product, $Mn(DDDT)_3^{2-}$, while the Ti dianion is an oxidized species but synthesized under Ar. The Nb complex, $Nb(DDDT)_3^-$, is also synthesized under Ar but shows no evidence of oxidation. The formal oxidation states of the metals in these complexes are Mn(IV), Ti(IV), and Nb(V).

The structure of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$ represents the first single-crystal analysis of a titanium dithiolene. The complex $Ti(mnt)_3^{2-}$ ($mnt = S_2C_2(CN)_2^{2-}$) was reported to be severely distorted from trigonal-prismatic geometry on the basis of X-ray powder diffraction data.¹⁶ The structure of $Ti(bdt)_3^{2-}$ ($bdt =$

$S_2C_6H_4^{2-}$) is stated to be octahedral although we are unaware of a formal report.¹⁷ The isoelectronic complex $V(DDDT)_3^-$ is trigonal prismatic, and thus several coordination types could be expected for the TiS_6 core of the $DDDT^{2-}$ complex.

Experimental Section

Reagents. Potassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K_2DDDT) was prepared by literature methods¹⁰ and characterized by IR and NMR spectroscopy. Anhydrous titanium trichloride, anhydrous niobium pentachloride, manganese chloride tetrahydrate, tetraethylammonium bromide, tetrabutylammonium bromide, tetraphenylarsonium chloride hydrate and the solvents acetonitrile and dimethylformamide were purchased from Aldrich Chemical Co. Tetraethylammonium perchlorate was purchased from Southwestern Analytical Chemicals. Acetone and tetrahydrofuran were purchased from Fisher Scientific Co., and the latter was dried over Na/benzophenone and distilled prior to use. Ethyl ether was purchased from EM Science, and ethyl alcohol was purchased from Aaper Alcohol and Chemical Co. Argon was purchased from Air Products Inc. Unless otherwise stated, all chemicals were used without further purification.

Procedures. Elemental analyses were performed by Atlantic Micro-labs, Atlanta, GA. Ethanol was degassed with Ar for 45 min prior to addition of reactants in the Ti complex synthesis.

Syntheses. $[(C_2H_5)_4N]_2[Mn(S_4C_4H_4)_3]$. In the presence of air, 0.05 g of $MnCl_2 \cdot 4H_2O$ (2.5×10^{-4} mol) in 6 mL of H_2O was added dropwise to 24 mL of a 1:1 EtOH/ H_2O mixture containing 0.6 g of K_2DDDT (2.3×10^{-3} mol) and 0.2 g of $(C_2H_5)_4NBr$ (9.5×10^{-4} mol). The solution was stirred for a few minutes after complete addition of the $MnCl_2$ solution, and then it was filtered by suction. The total time from start of addition to filtration was 15 min. The dark green solid was rinsed several times with acetone to remove a yellow residue. A final rinse with

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Table I. Single-Crystal X-ray Crystallographic Data

formula	TiC ₆₀ H ₅₂ S ₁₂ As ₂	Z	8
M _r	1355.59	dens calcd, g/cm ³	1.51
cell dimens	a = 20.643 (4) Å	radiation	Mo Kα
	b = 20.743 (5) Å	temp, K	298
	c = 27.822 (9) Å	linear abs coeff, cm ⁻¹	16.9
V	11913 (4) Å ³	final R index	R = 0.095
space group	P2 ₁ 2 ₁ 2 ₁		R _w = 0.097

^aThe data fit criteria (based on reflections having $I > 3\sigma(I)$) were $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(\Delta F)^2 / \sum F_o^2]^{0.5}$, and $GOF = \sum (w - ||F_o| - |F_c||)^2 / [N_o - N_v]^{0.5}$.

ether dried the product sufficiently before transferring the hairlike mass to a Schlenk tube where it was stored under an Ar atmosphere. The yield was 0.12 g (55%) of very fine dark green needles: mp 160 °C; IR (KBr) 2960 (m), 2920 (w), 2890 (m), 1475 (s), 1445 (m), 1385 (s), 1360 (m), 1280 (s), 1165 (s), 1110 (w), 995 (s), 945 (w), 910 (m), 870 (w), 830 (s), 770 (s), 355 (s), 325 (m) cm⁻¹. Anal. Calcd for MnC₂₈H₅₂N₂S₁₂: C, 39.27; H, 6.12; N, 3.27; S, 44.93. Found: C, 39.11; H, 6.16; N, 3.21; S, 44.77.

[(C₆H₅)₄N]Nb(S₄C₄H₄)₃. Under an Ar Atmosphere and with use of standard Schlenk techniques, 0.6 g of NbCl₅ (2.2 × 10⁻³ mol) was added to 1.4 g of K₂DDDT (5.4 × 10⁻³ mol) in 50 mL of THF. The mixture was stirred for 1 h, during which time the solution changed color from green to black. After filtration to remove any residue, 1.2 g of (C₆H₅)₄NBr (3.7 × 10⁻³ mol) in 35 mL of 100% EtOH was added to the filtrate causing immediate precipitation. The solution was stirred for 15 min before filtering. The product was dried in vacuum prior to recrystallization in acetonitrile. Heated green solutions were cooled quickly to 0 °C and allowed to sit overnight. The recrystallization solution was filtered and yielded 0.5 g (32%) of dark green crystals: mp 200 °C; ¹H NMR (Me₂SO-*d*₆) 3.23 (s, SCH₂CH₂S), 3.10 (m, CH₂N), 1.34 (m, CH₂CH₂), 0.93 ppm (t, CH₃); IR (KBr) 2950 (s), 2865 (m), 1460 (m), 1400 (s), 1320 (m), 1280 (s), 1170 (m), 1120 (w), 985 (m), 920 (m), 880 (m), 770 (w), 750 (w), 735 (w), 430 (w), 370 (s) cm⁻¹. Anal. Calcd for NbC₂₈H₄₈NS₁₂: C, 38.37; H, 5.52; N, 1.60; S, 43.90. Found: C, 38.22; H, 5.34; N, 1.57; S, 43.94.

[(C₆H₅)₄As]₂Ti(S₄C₄H₄)₃. Under an Ar atmosphere and with use of standard Schlenk techniques, 0.4 g of TiCl₃ (2.6 × 10⁻³ mol) was added to a solution of 1.0 g of K₂DDDT (3.9 × 10⁻³ mol) and 1.6 g of (C₆H₅)₄AsCl (3.8 × 10⁻³ mol) in 100 mL of 100% EtOH. The mixture was stirred for 1 h, during which time the solution changed color from purple to gray-black. Filtration yielded a blackish solid, which was dried in vacuum. Recrystallization of the solid in acetonitrile yielded a purple solution. After being heated and filtered, the solution was chilled quickly to 0 °C and allowed to sit overnight. Filtration of the recrystallization solution yielded 0.6 g (34%) of dark green crystals: mp 188 °C; ¹H NMR (MeCN-*d*₃) 7.73 (m, C₆H₅), 3.10 ppm (s, SCH₂CH₂S); IR (KBr) 1570 (w), 1475 (m), 1435 (s), 1330 (w), 1305 (w), 1275 (m), 1180 (m), 1155 (m), 1115 (w), 1075 (s), 1020 (w), 990 (s), 910 (m), 870 (w), 840 (m), 735 (s), 680 (s), 465 (s), 455 (s), 420 (m), 345 (s) cm⁻¹. Anal. Calcd for TiC₆₀H₅₂S₁₂As₂: C, 53.16; H, 3.87; S, 28.38. Found: C, 52.94; H, 3.83; S, 28.02.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range of 4000–300 cm⁻¹. UV/vis/near-IR spectra were recorded on a Cary 2300 spectrophotometer in DMF. All electrochemical measurements were performed by using a BAS CV-27 instrument. A platinum wire was employed for both the working and auxiliary electrodes, and a Ag/AgCl electrode, as the reference electrode. The solutions used for all techniques consisted of 0.1 M tetraethylammonium perchlorate as supporting electrolyte in DMF with metal complex concentrations of 10⁻³ M. Solutions were degassed with Ar for 15 min prior to making measurements.

Single-Crystal X-ray Analysis. A representative crystal was surveyed, and cell dimensions were obtained by a least-squares fit of setting angles of 25 high-angle reflections (2θ > 20°). A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochromator and molybdenum radiation (λ = 0.71069 Å). Systematic absences indicated that the crystal belonged to the orthorhombic space group P2₁2₁2₁ (h00, h = 2n + 1; 0k0, k = 2n + 1; 00l, l = 2n + 1). Two check reflections collected every 48 reflections revealed no unexpected variation in intensity. Data were corrected by Lorentz and polarization effects but not for absorption owing to the low absorption coefficient (16.9 cm⁻¹). Atomic scattering factors for all atoms were taken from ref 18. Pertinent crystallographic data are summarized in Table I, while a full tabular

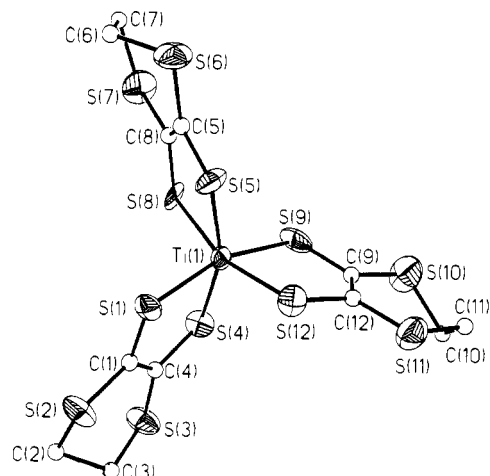


Figure 1. Structure of Ti(DDDT)₃²⁻ with labeling of atoms (anion 1). Thermal ellipsoids (50% probability) are shown for the titanium and sulfur atoms only. All other atoms are shown as spheres. Hydrogen atoms are not shown.

Table II. Bond Lengths (Å)

Ti(1)–S(1)	2.42 (2)	Ti(1)–S(4)	2.43 (2)
Ti(1)–S(5)	2.44 (2)	Ti(1)–S(8)	2.41 (2)
Ti(1)–S(9)	2.42 (2)	Ti(1)–S(12)	2.41 (2)
S(1)–C(1)	1.74 (5)	C(1)–S(2)	1.80 (4)
C(1)–C(4)	1.36 (8)	S(2)–C(2)	1.79 (5)
C(2)–C(3)	1.53 (8)	C(3)–S(3)	1.82 (4)
S(3)–C(4)	1.77 (5)	C(4)–S(4)	1.74 (3)
S(5)–C(5)	1.76 (4)	C(5)–S(6)	1.78 (5)
C(5)–C(8)	1.36 (5)	S(6)–C(6)	1.80 (5)
C(6)–C(7)	1.58 (5)	C(7)–S(7)	1.87 (5)
S(7)–C(8)	1.81 (4)	C(8)–S(8)	1.73 (5)
S(9)–C(9)	1.75 (4)	C(9)–S(10)	1.78 (4)
C(9)–C(12)	1.37 (5)	S(10)–C(10)	1.81 (5)
C(10)–C(11)	1.53 (5)	C(11)–S(11)	1.85 (5)
S(11)–C(12)	1.78 (4)	C(12)–S(12)	1.73 (5)
Ti(2)–S(13)	2.42 (2)	Ti(2)–S(16)	2.41 (2)
Ti(2)–S(17)	2.45 (2)	Ti(2)–S(20)	2.42 (2)
Ti(2)–S(21)	2.40 (2)	Ti(2)–S(24)	2.41 (2)
S(13)–C(13)	1.73 (3)	C(13)–S(14)	1.78 (5)
C(13)–C(16)	1.35 (8)	S(14)–C(14)	1.81 (4)
C(14)–C(15)	1.55 (8)	C(15)–S(15)	1.81 (5)
S(15)–C(16)	1.81 (4)	C(16)–S(16)	1.73 (4)
S(17)–C(17)	1.71 (4)	C(17)–S(18)	1.82 (4)
C(17)–C(20)	1.37 (5)	S(18)–C(18)	1.83 (4)
C(18)–C(19)	1.52 (6)	C(19)–S(19)	1.79 (4)
S(19)–C(20)	1.81 (4)	C(20)–S(20)	1.75 (4)
S(21)–C(21)	1.73 (4)	C(21)–S(22)	1.80 (4)
C(21)–C(24)	1.38 (5)	S(22)–C(22)	1.82 (4)
C(22)–C(23)	1.54 (6)	C(23)–S(23)	1.81 (5)
S(23)–C(24)	1.80 (4)	C(24)–S(24)	1.76 (4)
As(1)–C(30)	1.95 (3)	As(1)–C(36)	1.90 (3)
As(1)–C(42)	1.88 (3)	As(1)–C(48)	1.91 (3)
As(2)–C(54)	1.88 (3)	As(2)–C(60)	1.91 (3)
As(2)–C(66)	1.89 (3)	As(2)–C(72)	1.92 (2)
As(3)–C(78)	1.84 (3)	As(3)–C(84)	1.94 (3)
As(3)–C(90)	1.90 (3)	As(3)–C(96)	1.89 (3)
As(4)–C(102)	1.95 (3)	As(4)–C(108)	1.93 (3)
As(4)–C(114)	1.91 (3)	As(4)–C(120)	1.90 (3)

presentation is available as supplementary material.

The four arsenic atoms were located by the direct-methods subroutine RANT of the crystallographic program package SHELXTL.¹⁹ The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by the full-matrix least-squares technique using SHELXTL PLUS²⁰ on the MicroVAX II computer. The quantity minimized was $\sum w(\Delta F)^2$, where $w = 1/(\sigma_F^2 + 0.0003F^2)$. The Ti, S, and As atoms were refined with anisotropic temperature factors. Carbon atoms in the ligands were re-

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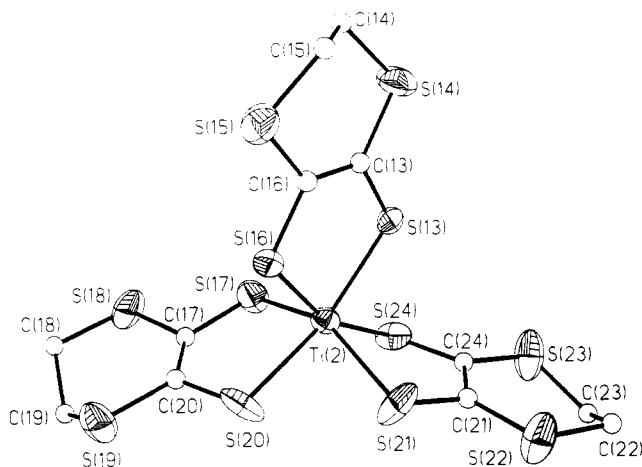


Figure 2. Structure of $\text{Ti}(\text{DDDT})_3^{2-}$ with labeling of atoms (anion 2). Thermal ellipsoids (50% probability) are shown for the titanium and sulfur atoms only. All other atoms are shown as spheres. Hydrogen atoms are not shown.

Table III. Bond Angles (deg)

S(1)-Ti(1)-S(4)	83.5 (6)	S(1)-Ti(1)-S(5)	85.4 (7)
S(4)-Ti(1)-S(5)	161.6 (9)	S(1)-Ti(1)-S(8)	105.6 (8)
S(4)-Ti(1)-S(8)	86.7 (6)	S(5)-Ti(1)-S(8)	82.2 (7)
S(1)-Ti(1)-S(9)	162 (1)	S(4)-Ti(1)-S(9)	84.3 (7)
S(5)-Ti(1)-S(9)	109.5 (6)	S(8)-Ti(1)-S(9)	86.2 (7)
S(1)-Ti(1)-S(12)	88.9 (7)	S(4)-Ti(1)-S(12)	106.4 (9)
S(5)-Ti(1)-S(12)	88.0 (7)	S(8)-Ti(1)-S(12)	161.7 (6)
S(9)-Ti(1)-S(12)	82.5 (8)	S(13)-Ti(2)-S(16)	79.9 (6)
S(13)-Ti(2)-S(17)	102.6 (8)	S(16)-Ti(2)-S(17)	99.8 (7)
S(13)-Ti(2)-S(20)	159.0 (7)	S(16)-Ti(2)-S(20)	79.3 (7)
S(17)-Ti(2)-S(20)	83.5 (7)	S(13)-Ti(2)-S(21)	102.3 (7)
S(16)-Ti(2)-S(21)	104.5 (9)	S(17)-Ti(2)-S(21)	147.7 (6)
S(20)-Ti(2)-S(21)	80.6 (8)	S(13)-Ti(2)-S(24)	80.4 (6)
S(16)-Ti(2)-S(24)	159.9 (8)	S(17)-Ti(2)-S(24)	80.6 (7)
S(20)-Ti(2)-S(24)	120.6 (6)	S(21)-Ti(2)-S(24)	83.6 (7)
C(30)-As(1)-C(36)	111 (1)	C(30)-As(1)-C(42)	108 (1)
C(36)-As(1)-C(42)	106 (1)	C(30)-As(1)-C(48)	109 (1)
C(36)-As(1)-C(48)	113 (1)	C(42)-As(1)-C(48)	110 (1)
C(54)-As(2)-C(60)	110 (1)	C(54)-As(2)-C(66)	109 (1)
C(60)-As(2)-C(66)	109 (1)	C(54)-As(2)-C(72)	107 (1)
C(60)-As(2)-C(72)	112 (2)	C(66)-As(2)-C(72)	110 (1)
C(78)-As(3)-C(84)	110 (1)	C(78)-As(3)-C(90)	109 (1)
C(84)-As(3)-C(90)	111 (1)	C(78)-As(3)-C(96)	112 (1)
C(84)-As(3)-C(96)	108 (1)	C(90)-As(3)-C(96)	107 (1)
C(102)-As(4)-C(108)	118 (1)	C(102)-As(4)-C(114)	105 (1)
C(108)-As(4)-C(114)	112 (1)	C(102)-As(4)-C(120)	108 (1)
C(108)-As(4)-C(120)	105 (2)	C(114)-As(4)-C(120)	108 (1)

fined isotropically, while the phenyl rings on the counterions were refined as rigid groups with a C-C bond length of 1.395 Å. The hydrogen atoms were placed in calculated positions 0.96 Å away from the attached carbon atom and were not refined. The final *R* indices are given in Table I.

The refined structure was plotted by using the SHELXTL graphics package. Figures 1 and 2 show the two anions in the asymmetric unit with labeling of the atoms, and the molecular packing of the anions is shown in Figure 3. All bond distances are given in Table II, but only selected bond angles are shown in Table III. Atom coordinates of the anions are given in Table IV. The remaining bond angles, cation positional parameters, hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material.

Results and Discussion

The syntheses of the tris complexes of Mn, Nb, and Ti differed vastly. The Mn complex, synthesized in an EtOH/H₂O mixture, required the presence of air although it was also extremely air sensitive in solution. If the product was not isolated quickly, total decomposition to a yellow solid was observed. The same results were noted in the synthesis of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}(\text{mnt})_3]$.²¹ The synthesis of the mnt^{2-} complex of Mn required an excess of Mn^{2+}

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) of $\text{Ti}(\text{DDDT})_3^{2-}$ Anions

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Ti(1)	2501 (9)	4932 (5)	884 (3)	38 (3)
S(1)	2060 (12)	5435 (7)	1599 (4)	41 (6)
C(1)	2455 (32)	5059 (24)	2074 (9)	51 (1)
S(2)	2246 (15)	5459 (7)	2629 (4)	57 (8)
C(2)	2548 (29)	4944 (24)	3093 (12)	51 (1)
C(3)	3248 (27)	4839 (19)	2926 (13)	51 (1)
S(3)	3383 (13)	4218 (8)	2474 (4)	61 (7)
C(4)	2911 (26)	4594 (22)	2022 (9)	51 (1)
S(4)	3078 (10)	4268 (7)	1459 (4)	43 (6)
S(5)	1627 (9)	5482 (7)	457 (5)	52 (6)
C(5)	1097 (19)	4876 (15)	257 (16)	51 (1)
S(6)	441 (12)	5146 (7)	-107 (5)	73 (7)
C(6)	-147 (23)	4561 (16)	84 (17)	51 (1)
C(7)	-76 (21)	3845 (17)	-107 (16)	51 (1)
S(7)	686 (14)	3572 (8)	197 (5)	96 (9)
C(8)	1196 (20)	4244 (15)	366 (17)	51 (1)
S(8)	1828 (9)	4004 (8)	735 (5)	49 (6)
S(9)	3246 (12)	4468 (8)	307 (4)	57 (7)
C(9)	3864 (18)	5036 (16)	223 (16)	51 (1)
S(10)	4528 (12)	4771 (8)	-136 (6)	80 (7)
C(10)	5184 (21)	5279 (16)	72 (17)	51 (1)
C(11)	4960 (25)	5953 (16)	-76 (15)	51 (1)
S(11)	4323 (10)	6324 (7)	299 (5)	61 (6)
C(12)	3799 (19)	5654 (15)	392 (16)	51 (1)
S(12)	3158 (11)	5879 (7)	757 (5)	46 (6)
Ti(2)	2487 (8)	26 (5)	941 (3)	32 (3)
S(13)	1910 (10)	668 (6)	1528 (4)	36 (5)
C(13)	2078 (26)	384 (22)	2101 (9)	51 (1)
S(14)	1575 (15)	744 (8)	2543 (4)	66 (8)
C(14)	1713 (26)	224 (20)	3055 (13)	51 (1)
C(15)	2446 (27)	138 (22)	3144 (14)	51 (1)
S(15)	2759 (15)	-454 (7)	2725 (5)	62 (8)
C(16)	2537 (32)	-73 (24)	2163 (9)	51 (1)
S(16)	2878 (13)	-458 (6)	1672 (4)	41 (5)
S(17)	1677 (11)	-777 (8)	706 (6)	51 (6)
C(17)	2123 (16)	-1448 (14)	570 (22)	51 (1)
S(18)	1579 (12)	-2132 (8)	525 (6)	70 (7)
C(18)	2087 (21)	-2851 (18)	468 (15)	51 (1)
C(19)	2670 (19)	-2678 (19)	160 (13)	51 (1)
S(19)	3252 (10)	-2188 (9)	463 (7)	68 (7)
C(20)	2789 (17)	-1465 (14)	578 (22)	51 (1)
S(20)	3244 (10)	-756 (9)	622 (6)	56 (6)
S(21)	3338 (11)	739 (8)	697 (6)	67 (7)
C(21)	2943 (16)	1419 (15)	489 (21)	51 (1)
S(22)	3510 (12)	2078 (8)	497 (6)	70 (7)
C(22)	3083 (23)	2822 (18)	356 (16)	51 (1)
C(23)	2487 (22)	2667 (18)	46 (15)	51 (1)
S(23)	1858 (12)	2107 (7)	228 (6)	77 (7)
C(24)	2281 (16)	1400 (14)	430 (20)	51 (1)
S(24)	1838 (11)	676 (8)	409 (5)	51 (6)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ions. This was not necessary for the DDDT^{2-} complex, in which an excess of ligand was employed. Attempts to recrystallize the product for crystal growth were unsuccessful due to the extreme air sensitivity of the complex in solution. The solid also undergoes slow decomposition.

The Nb complex was synthesized under Ar in THF by a procedure analogous to the monoanionic vanadium complex¹⁵ with two exceptions. First, an excess of NbCl_5 was used to give a metal to ligand ratio of 2:5. Second, isolation of the product and recrystallization were carried out under an Ar atmosphere. The Nb species is sensitive to air in solution but stable as a solid. This complex was isolated with five different counterions ranging in size from tetramethylammonium to tetraphenylarsonium. The larger counterions yielded single crystals of sufficient size for structure determination, yet the diffraction of X-rays was poor and crystallographic analysis was not possible.

The dianionic Ti species was prepared under Ar in 100% EtOH. An excess of TiCl_3 was used resulting in a metal to ligand ratio of 2:3. Recrystallization yielded green crystals from purple solutions, and these colors were also observed for $[(\text{C}_6\text{H}_5)_4\text{As}]_2$

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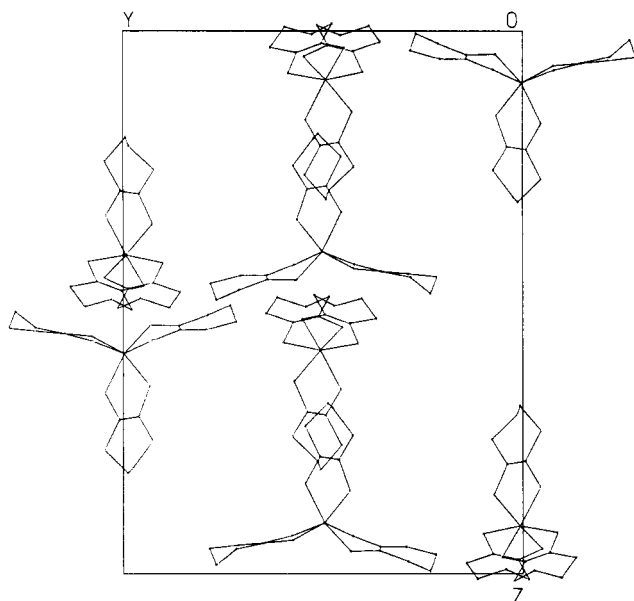


Figure 3. Cell packing diagram for $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$. Cations are not shown.

Table V. IR Band Positions (cm^{-1})

	Mn	Nb	Ti
C-C	1445	1400	1435
C-S	1165	1170	1155
$\begin{array}{c} S \\ \\ R-C=S \end{array}$	830	880	840
M-S	355 325	430 370	420 345

$[Ti(mnt)_3]$.¹⁶ Solutions of the Ti complex are sensitive to air whereas the solid is air stable. After many attempts at crystal growth with different cations as described for the Nb complex, suitable crystals for X-ray structure determination were obtained with the tetraphenylarsonium cation.

Similarities between the Ti and Nb complex syntheses include an excess of metal reactant and reaction carried out under Ar atmosphere. Both the Mn and Ti complex syntheses required the presence of the cation in solution upon complex formation. This indicates a transient stability of the metal complex in solution.

The infrared spectra of all three tris complexes contain the characteristic bands observed for transition-metal dithiolenes. These are listed in Table V. The dianionic complexes of Mn and Ti show C=C bands at higher energies and C=S and S=C(R)→S absorptions at lower energies than the Nb monoanion. This is evidence of more dithiolate character of the ligands for the dianions as compared to the monoanion.

The 1H NMR spectra of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$ and $[(C_6H_5)_4N][Nb(DDDT)_3]$ exhibit the expected singlet due to the ligand protons and resonances characteristic of the cations. The presence of these signals indicates that these complexes are diamagnetic. In contrast, the 1H NMR spectrum of $[(C_2H_5)_4N]_2[Mn(DDDT)_3]$ showed broad resonances that appear to be a singlet at 1.2 ppm and a multiplet centered around 3.15 ppm. Due to the broadening, absolute assignments cannot be made although the large singlet resulting from the ligand protons is definitely absent. This is evidence of a paramagnetic species. The resonances observed are most likely those of the tetraethylammonium ion that is not in close contact with the paramagnetic Mn complex. Magnetic moments of 3.85 and 3.97 μ_B have been reported for $[(C_6H_5)_4As]_2[Mn(mnt)_3]$ and $[(C_4H_9)_4N]_2[Mn(S_2C_6Cl_4)_3]$, respectively.^{16,22} These moments correspond to three unpaired electrons and a Mn(IV) metal center. The dianionic Ti complexes of these two ligands are reported as diamagnetic.^{16,22} Therefore, the proposed paramagnetism and diamagnetism of $Mn(DDDT)_3^{2-}$

Table VI. Uv/Vis/Near-IR Absorption Maxima^a (cm^{-1})

$Mn(DDDT)_3^{2-}$	$Nb(DDDT)_3^-$	$Ti(DDDT)_3^{2-}$
17 900 (1800)	13 900 (11 000)	16 000 (6600)
25 200 (9000)	21 500 (10 000)	18 500 (6800)
29 900 (13 000)	29 500 sh	20 800 (5400)
		29 500 (10 000)

^a Measured in DMF. Molar absorptivities in units of $M^{-1} cm^{-1}$.

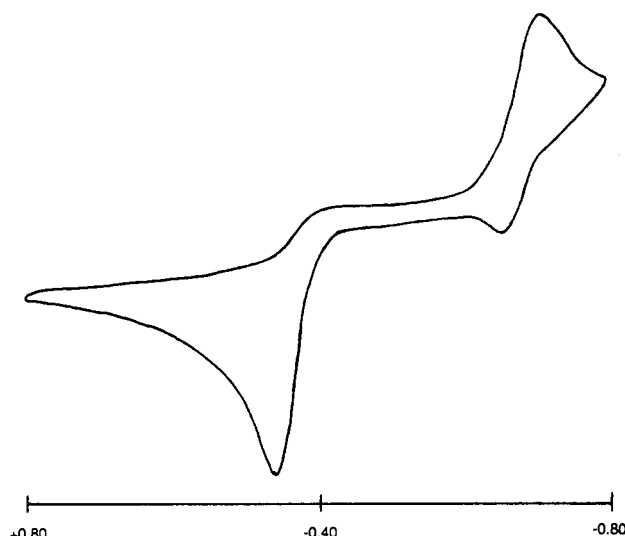


Figure 4. Cyclic voltammogram of $[(C_2H_5)_4N]_2[Mn(DDDT)_3]$. $E_i = -0.40$ V.

and $Ti(DDDT)_3^{2-}$ respectively, are consistent with previously studied complexes.

The UV/vis/near-IR absorption maxima for the three tris(dithiolenes) are given in Table VI. There are four reports of spectral results for dianionic tris(dithiolenes) of Mn.^{16,21-23} Three are with the mnt^{2-} ligand and differ significantly among themselves. The spectrum of the Mn complex of $DDDT^{2-}$ does not correlate well with any of those reported. The spectrum of the Ti complex, again, shows no distinct correlation to reports^{16,17,22} of other Ti species or to the isoelectronic complex $V(DDDT)_3^-$.¹⁵ This latter dissimilarity could be an indication of different electronic structures and thus coordination geometries. The V monoanion is trigonal prismatic. The poor correlation between complexes of different ligands is not surprising and has been previously noted.²² The spectrum of $Nb(DDDT)_3^-$ differs from two other reports,¹⁷ but one similarity is an intense low-energy absorption, which is indicative of highly delocalized bonding and, consequently, trigonal-prismatic coordination.²⁴ The Nb complex of benzenedithiolate does exhibit trigonal-prismatic geometry.²⁵ Although there are pitfalls in utilizing electronic spectra as a structural probe, their diagnostic value is valid for second- and third-row transition metals.¹⁷

Cyclic voltammograms for the tris(dithiolenes) of Mn, Nb, and Ti are shown in Figures 4-6, respectively. The voltammogram of the Mn complex shows an irreversible oxidation at 0.13 V and a quasi-reversible redox wave centered at -0.55 V. This redox wave most likely corresponds to the $-2 \leftrightarrow -3$ couple. Figure 5 shows two reversible redox waves for $Nb(DDDT)_3^-$ with $E_{1/2} = 0.63$ and -1.66 V and an irreversible oxidation at 0.53 V. The reversible waves correspond to the $-1 \leftrightarrow -2$ and $-2 \leftrightarrow -3$ couples, respectively. The Ti complex yields a complicated cyclic voltammogram. There is a reversible redox wave with $E_{1/2} = -1.42$ V for the $-2 \leftrightarrow -3$ couple and three oxidations at 0.08, 0.28, and 0.55 V. The reduction peaks at -0.59 and -1.14 V are the direct result of these oxidations. This can be seen in Figure 7, which

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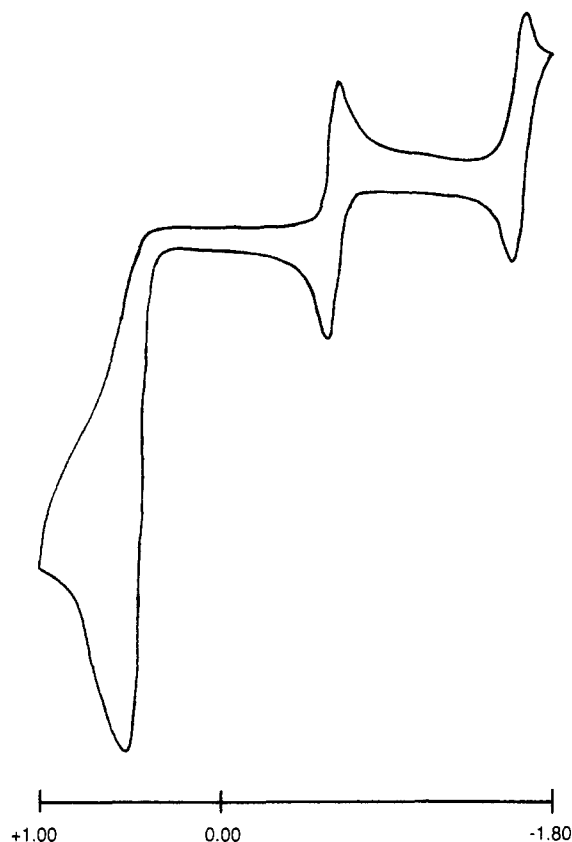


Figure 5. Cyclic voltammogram of $[(C_4H_9)_4N][Nb(DDDT)_3]$. $E_i = 0.00$ V.

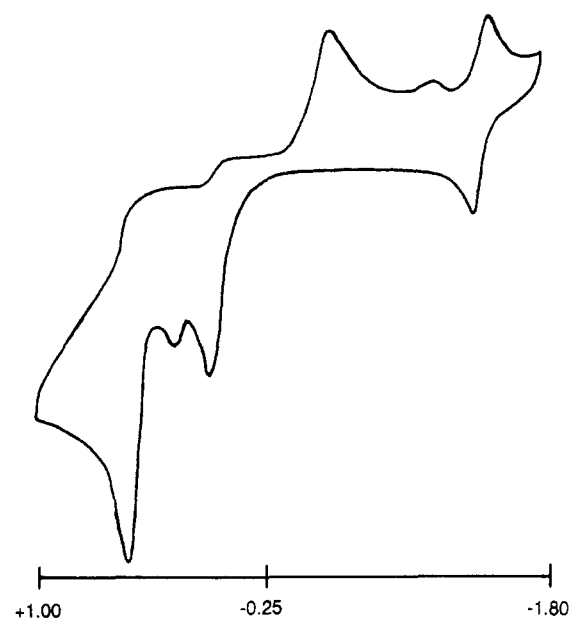


Figure 6. Cyclic voltammogram of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$. $E_i = -0.25$ V.

shows the cyclic voltammogram of the Ti complex scanned from -0.25 to -1.80 V, where only the reversible wave is observed. The process or processes corresponding to the irreversible waves observed in the cyclic voltammograms of $DDDT^{2-}$ complexes have not been elucidated. Irreversible waves are also found in the voltammograms of $V(DDDT)_3^{2-}$ and $[Co(DDDT)_2]^{2-}$.^{14,15} Voltammetric data on other dithiolenes of Mn, Nb, and Ti are scarce and make comparison difficult at this time.

The structure of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$ belongs to the same space group as $[(C_4H_9)_4N][V(DDDT)_3]$ and also contains eight cations and eight anions in the asymmetric unit. The coordination of the six sulfurs around each Ti atom is best described as a

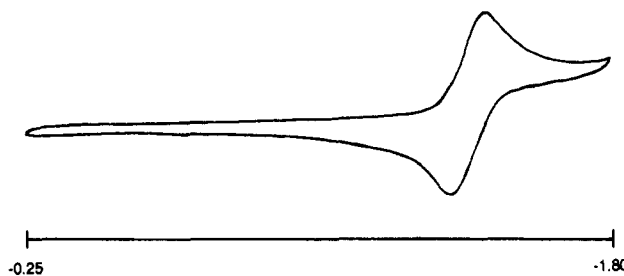


Figure 7. Reversible redox wave of $[(C_6H_5)_4As]_2[Ti(DDDT)_3]$. $E_i = -0.25$ V.

Table VII. Descriptive Angles (deg) of Coordination in Tris(dithiolenes)

	anion 1	anion 2	both anions
chelate bite angle	82.7 (8)	82.3 (7)	82.5 (8)
corrected octahedral limit	172.7	172.3	172.5
S-M-S trans angle	162 (1)	155.5 (8)	159 (1)

distorted octahedron with an average Ti-S bond length of 2.42 (2) Å. The average length of S-C bonds within the five-member coordination ring is 1.74 (5) Å, while S-C bond lengths in the outer ring of the ligand average 1.81 (5) Å. These numbers are not statistically different given their large standard deviation and show the predominantly single-bond character of the S-C bonds in the coordination ring and thus dithiolate character of the ligand. The C=C and C-C average bond lengths are 1.37 (8) and 1.54 (8) Å, respectively. The tetraphenylarsonium cations exhibit the expected tetrahedral structure with an average As-C bond length of 1.91 (3) Å.

An important criterion used to describe coordination in tris(dithiolenes) is the S-M-S trans angle. In trigonal-prismatic complexes, the value is observed to be approximately 136° . Pure octahedral coordination would exhibit an S-M-S trans angle of 180° , but due to the chelate bite angle in bidentate ligands, this value cannot be realized. Instead, a corrected octahedral limit is calculated to be the supplement of the complement of the chelate bite angle. The average values are shown in Table VII for anion 1 and anion 2, and the overall average of both anions is also shown. These values show that the S-M-S trans angles are intermediate between the trigonal-prismatic value and the corrected octahedral limit. Although the average trans angle for anion 2 is almost exactly midway between the two limits, the average trans angle for both anions is closer to the octahedral value. Thus, the coordination in $Ti(DDDT)_3^{2-}$ is accurately described as a distorted octahedron.

Dihedral angles were calculated between the plane containing the Ti atom and the two coordinating sulfurs and the plane of the corresponding ligand. The latter plane calculation excluded the two carbon atoms in the periphery of the ligand. It has been shown that the ligand planes bend with respect to the MS_2 plane in trigonal-prismatic structures whereas, in complexes approaching the octahedral limit, these two planes are essentially coplanar. The dihedral angles for anion 1 are 7, 6.8, and 8° , and those for anion 2 are 5.5, 15.8, and 26.9° . While the values are small, as expected in anion 1, the average for anion 2 is 16.1° . This could be the result of packing forces or an indication of the greater tendency of this anion toward trigonal-prismatic coordination in conjunction with the S-M-S trans angles previously discussed. Some of the values for trigonal-prismatic complexes are 20.5° for $V(DDDT)_3^{15}$, 18° for $Mo(S_2C_2H_2)_3$,¹ 21.4° for $Mo(bdt)_3$,²⁶ and 22.4° for $Nb(bdt)_3$.²⁵

A molecular orbital scheme presented by Gray et al.²⁴ was based on trigonal-prismatic coordination and describes the distortion toward octahedral geometry on the basis of the number of electrons in bonding versus antibonding orbitals. The Ti complex is iso-electronic with the V monoanion, yet the latter is trigonal prismatic. Therefore, the structural differences cannot be explained

by differences in electron occupation of the molecular orbitals. Instead, the varying coordination geometries can be rationalized by the increase of d-orbital energies. An analogy can be made to the structures of $\text{Mo}(\text{bdt})_3$, $\text{Nb}(\text{bdt})_3^-$, and $\text{Zr}(\text{bdt})_3^{2-}$, which vary from trigonal prismatic to a distorted octahedron.²⁵⁻²⁷ The increase in the energies of the metal d orbitals is paralleled by a structural change. This can be related to the $4e'$ molecular orbital of Gray's scheme, which consists of metal and ligand character. As the d metal orbitals increase in energy, the $4e'$ orbital becomes more ligand in character and the ligands assume more dithiolate character. Thus, the relationship between coordination type and metal d-orbital energies is applicable to first-row transition-metal dithiolenes.

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Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank Dr. Charles F. Campana with the Nicolet Instrument Corp. for his assistance with the final refinement of the titanium structure and the National Science Foundation for funds toward upgrading our diffractometer (Grant CHE-8307022).

Registry No. $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Mn}(\text{DDDT})_3]$, 124022-58-8; $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Nb}(\text{DDDT})_3]$, 124022-60-2; $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Ti}(\text{DDDT})_3]$, 124022-62-4; $[\text{Mn}(\text{DDDT})_3]^{3-}$, 124022-63-5; $[\text{Nb}(\text{DDDT})_3]^-$, 124022-64-6; $[\text{Nb}(\text{DDDT})_3]^{3-}$, 124022-65-7; $[\text{Nb}(\text{DDDT})_3]^{3-}$, 124022-66-8.

Supplementary Material Available: Tables SI-SV, listing crystallographic data, cation positional parameters, remaining bond angles, anisotropic thermal parameters, and hydrogen coordinates (9 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal and Molecular Structures of Potassium Bis(μ -hydroxo)bis[dinitritoplatinate(II)] Sesquihydrate and Potassium *cyclo*-Tris(μ_3 -oxo-1:2:4;1:3:4;2:3:4)tris[dinitritoplatinate(II)]trinitritoplatinate(IV) Trihydrate

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Received April 25, 1989

The reaction of $\text{K}_2\text{Pt}(\text{NO}_2)_4$ with dilute sulfuric acid has been investigated. At least two polynuclear complexes are formed in the reaction. The first, $\text{K}_2[\text{Pt}_2(\text{NO}_2)_4(\text{OH})_2] \cdot 1\frac{1}{2}\text{H}_2\text{O}$, is a hydroxo-bridged dimer of Pt(II). Crystal data are space group *Ibca*, $a = 11.879$ (6) Å, $b = 13.094$ (4) Å, $c = 32.060$ (11) Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 4987$ (4) Å³, $Z = 16$, $R = 0.065$, and $R_w = 0.058$. The second, $\text{K}_5[\text{Pt}_4(\text{NO}_2)_9\text{O}_3] \cdot 3\text{H}_2\text{O}$, is a mixed-valence tetranuclear complex with a trinitritoplatinate(IV) unit oxo bridged to three *cyclo*-(μ_3 -oxo)dinitritoplatinate(II) units. Crystal data are space group *P* $\bar{1}$, $a = 9.940$ (2) Å, $b = 10.069$ (2) Å, $c = 15.206$ (3) Å, $\alpha = 72.15$ (1)°, $\beta = 74.69$ (1)°, $\gamma = 72.24$ (1)°, $V = 1354.9$ (4) Å³, $Z = 2$, $R = 0.032$, and $R_w = 0.032$.

Introduction

Recently, it has been demonstrated that $\text{K}_2\text{Pt}(\text{NO}_2)_4$ reacts with concentrated sulfuric or phosphoric acids to give respectively sulfate^{1,2} or phosphate^{2,3}-bridged dimeric metal-metal-bonded Pt(III) anionic complexes. This and other work has led to the recognition that there is a large class of relatively stable binuclear Pt(III) compounds with metal-metal bonds. It has been known for more than a century that $\text{K}_2\text{Pt}(\text{NO}_2)_4$ also reacts with dilute acids to give polynuclear products.⁴ These compounds have not been extensively investigated except that chemical studies of a red metallic appearing species have resulted in the suggestion that it is an ordered stacking of oxo-bridged trimeric molecules.⁵

Herein, we report the structures of two different polynuclear platinum complexes that result from the reaction of $\text{K}_2\text{Pt}(\text{NO}_2)_4$ with dilute sulfuric acid.

Experimental Section

Preparation of Compounds. In a 5-mL round-bottom flask, 0.050 g of $\text{K}_2\text{Pt}(\text{NO}_2)_4$ was dissolved in 1.0 mL of 0.22 M H_2SO_4 . The solution was stirred for 20 min at 85 °C, during which time the solution changed

Table I. Crystallographic Data

Potassium Bis(μ -hydroxo)bis[dinitritoplatinate(II)] Sesquihydrate	
$\text{K}_2[\text{Pt}(\text{NO}_2)_4(\text{OH})_2] \cdot 1\frac{1}{2}\text{H}_2\text{O}$	fw = 713.44
$a = 11.879$ (6) Å	space group <i>Ibca</i> (No. 73)
$b = 13.094$ (4) Å	$T = 24$ °C
$c = 32.060$ (11) Å	$\lambda = 0.71069$ Å (Mo K α)
$\alpha = \beta = \gamma = 90^\circ$	$\rho_{\text{calcd}} = 3.80$ g cm ⁻³
$V = 4987$ (4) Å ³	$\mu = 234$ cm ⁻¹ (Mo K α)
$Z = 16$	transm coeff = 0.06-0.59
$R(F_o) = 0.065$	$R_w(F_o) = 0.058$
Potassium	
<i>cyclo</i> -Tris(μ_3 -oxo-1:2:4;1:3:4;2:3:4)tris[dinitritoplatinate(II)]trinitritoplatinate(IV) Trihydrate	
$\text{K}_5[\text{Pt}_4(\text{NO}_2)_9\text{O}_3] \cdot 3\text{H}_2\text{O}$	fw = 1491.96
$a = 9.940$ (2) Å	space group <i>P</i> $\bar{1}$ (No. 2)
$b = 10.069$ (2) Å	$T = 24$ °C
$c = 15.206$ (3) Å	$\lambda = 0.71069$ Å (Mo K α)
$\alpha = 72.15$ (1)°	$\rho_{\text{calcd}} = 3.66$ g cm ⁻³
$\beta = 74.69$ (1)°	$\mu = 217$ cm ⁻¹ (Mo K α)
$\gamma = 72.24$ (1)°	transm coeff = 0.006-0.165
$V = 1354.9$ (4) Å ³	$R(F_o) = 0.032$
$Z = 2$	$R_w(F_o) = 0.032$

from colorless to blue to dark green. The solution was then evaporated to dryness by evacuation. The solid was dissolved in 0.5 mL of 0.22 M H_2SO_4 to form a red solution, the solution evaporated to dryness, the solid redissolved in 1 to 2 mL of water, and the new solution neutralized to pH 7.0 with K_2CO_3 . The resulting yellow solution was allowed to evaporate to dryness in a cold room, yielding solid material containing colorless and yellow crystals. The colorless crystals were presumed to

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