Lead(II)/Platinum(II) Complexes with and without Pb–Pt Interactions

Alan L. Balch,* Ella Y. Fung, Jeffrey K. Nagle,† Marilyn M. Olmstead, and Stephen P. Rowley

Department of Chemistry, University of California, Davis, California 95616

Received February 19, 1993

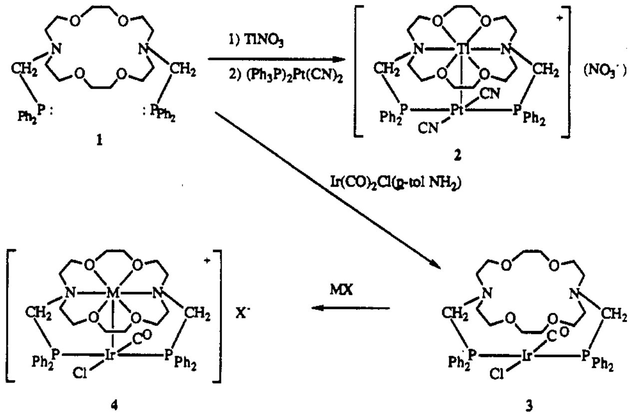
The possibility of obtaining complexes with Pb–Pt bonding that would be analogous to the Tl–Pt bonding in pseudooctahedral $Tl_2Pt(CN)_2$ and $[Tl(crown\text{-}P_2)Pt(CN)_2]^+$ (crown-P_2 is $Ph_2PCH_2N(C_2H_4OC_2H_4OC_2H_4)_2NCH_2PPh_2$) is examined. Treatment of $K_2[Pt(CN)_4]$ with $Pb(NO_3)_2$ in water produces pale yellow $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$, which crystallizes in the monoclinic space group $P2_1$ with a = 6.487(1) Å, b = 17.928(3) Å, c = 9.316(2) Å, and β = 107.76(1)° at 125 K with Z = 2. Refinement of 2371 reflections with $I > 2\sigma(I)$ and 134 parameters yielded R = 0.033, R_w = 0.038. The structure consists of zigzag columns of planar $[Pt(CN)_4]^{2-}$ units (Pt–Pt distances 3.267(1), 3.298(1) Å) with the lead and potassium ions and water molecules in channels between the columns of tetracyanoplatinates. No direct Pt–Pb interactions are present. Treatment of crown-P_2 with *trans*-$Pt(CN)_2(PPh_3)_2$ and $Pb(O_2CCH_3)_2$ yields colorless $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3){\cdot}1.5H_2O{\cdot}CH_3OH{\cdot}0.25CHCl_3$, which crystallizes in the monoclinic space group $P2_1/n$ with a = 13.483(4) Å, b = 24.125(10) Å, c = 16.212(4) Å, and β = 90.06(2)° at 130 K with Z = 4. Refinement of 5636 reflections with $F > 6.0\sigma(F)$ and 355 parameters yielded R = 0.074, R_w = 0.098. The structure consists of a planar $P_2Pt(CN)_2$ portion with a lead ion contained within the azacrown portion and positioned directly above the platinum center. One acetate ion is chelated to the lead, while the other is a noncoordinating counterion. The Pt–Pb distance is long (3.313(2) Å). Nevertheless, the observation of a small Pt–Pb coupling (J = 274 Hz) in the ^{195}Pt NMR spectrum indicates that a detectable Pt–Pb interaction is present within this binuclear complex.

Introduction

The planar anion $[Pt(CN)_4]^{2-}$ forms salts with a variety of cations in which the anions self-associate into stacks upon crystallization.[1,2] Five classes of such stacks have been recognized: linear chains with equidistant Pt–Pt spacing, linear chains with two distinct Pt–Pt spacings, zigzag chains with equidistant spacings, zigzag chains with two different spacings, and helical chains.[3] The cations that are involved in the formation of these columnar materials include alkali metal, alkaline earth metal, lanthanide, and guanidinium ions with charges that range from 1+ to 3+. With the simple columnar tetracyanoplatinates, the Pt–Pt distances range from 3.75 to 3.09 Å.[1,3] Partial oxidation of these chains results in shortening of these distances into the range 2.92–2.80 Å.[1,3,4]

In contrast, treatment of an aqueous solution of $K_2[Pt(CN)_4]$ with thallium(I) nitrate produces colorless $Tl_2Pt(CN)_4$. This has a discrete molecular structure in which the two thallium ions are positioned above and below the planar $Pt(CN)_4$ portion to give a pseudooctahedral unit.[5] The Pt^{II}–Tl^{I} distance is 3.14(1) Å. The intense blue luminescence of $Tl_2Pt(CN)_4$ has been the subject of several studies,[5–7] and a theoretical examination of the bonding within the Tl–Pt–Tl unit has revealed that the major bonding interaction within the molecule is electrostatic.[8] However, there is a significant covalent component to this bonding. This aspect of the bonding involves σ overlap between the filled $5d_{z^2}$ and the empty $6p_z$ valence orbitals on platinum and the filled 6s and empty $6p_z$ valence orbitals on thallium.

Scheme I



Since little is known about the ability of other ions with an s^2 electronic configuration to interact with $[Pt(CN)_4]^{2-}$ (and other d^8 planar complexes), we have been studying systems in which such interaction might occur. In order to bring these rather different ions together, we synthesized the new ligand crown-P_2 (**1**).[9] This ligand can use the phosphorus atoms to bind to a soft d^8 metal center while the azacrown portion provides an environment that is suitable for enclosing a main group metal ion. Some chemistry that has previously been documented with this bridging ligand is summarized in Scheme I.[9–11]

Here we explore the possibility of obtaining Pt^{II}–Pb^{II} bonding with $[Pt(CN)_4]^{2-}$ and with (crown-P_2)$Pt(CN)_2$. The synthesis of crown-P_2 (**1**) is reported in detail, and the structure of **2** is compared to that of the new Pb^{II}/Pt^{II} complex that is formed with crown-P_2 as a bridge.

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† On leave from the Department of Chemistry, Bowdoin College, Brunswick, ME 04011.

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0020-1669/93/1332-3295$04.00/0

Table I. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$

	x	*y*	*z*	*U*
Pb	8211(1)	5622(3)	8775(1)	9(1)[a]
Pt(1)	6616(1)	7466(3)	3306(1)	7(1)[a]
Pt(2)	11575(1)	7737(3)	3155(1)	7(1)[a]
K(1)	10841(6)	7969(3)	8101(4)	19(1)[a]
K(2)	9223(5)	5125(3)	4592(4)	17(1)[a]
O(1)	5991(18)	5201(7)	6053(13)	16(2)
O(2)	11289(18)	5564(7)	7765(14)	19(2)
O(3)	4952(16)	4848(7)	9547(12)	11(2)
O(4)	14228(21)	6793(8)	8096(16)	29(3)
O(5)	10725(20)	5254(8)	1443(15)	24(3)
O(6)	7446(19)	8846(7)	8074(14)	20(2)
N(1)	12872(22)	8651(8)	6175(15)	15(3)
N(2)	12439(25)	6203(10)	4846(18)	25(3)
N(3)	10268(21)	6857(8)	133(16)	16(3)
N(4)	7342(22)	9079(8)	4674(15)	16(3)
N(5)	5193(23)	8187(8)	113(16)	14(2)
N(6)	5894(21)	5852(9)	1974(16)	18(3)
N(7)	7862(25)	6763(9)	6567(18)	22(3)
N(8)	10965(20)	9255(8)	1387(14)	11(2)
C(1)	12482(21)	8322(8)	5126(16)	11(3)
C(2)	12155(23)	6758(9)	4321(17)	12(3)
C(3)	10728(23)	7179(9)	1238(16)	10(3)
C(4)	7049(22)	8490(9)	4144(17)	10(3)
C(5)	5720(22)	7930(8)	1262(16)	10(3)
C(6)	6161(22)	6426(8)	2439(16)	9(2)
C(7)	7476(28)	7028(10)	5340(20)	21(3)
C(8)	11143(25)	8692(9)	2013(18)	14(3)

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

Results

Preparation and Structural Characterization of $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$. Slow diffusion of an aqueous solution that contains equimolar amounts of lead(II) nitrate and potassium cyanide into an aqueous solution of $K_2[Pt(CN)_4]{\cdot}3H_2O$ yields small, pale yellow crystals of $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$ (**5**). This procedure is similar to the one used for the preparation of $Tl_2Pt(CN)_4$.[5] Unlike $Tl_2Pt(CN)_4$, however, **5** contains a columnar structure.

Suitable crystals for an X-ray diffraction study were harvested from this simple process. The complex crystallizes with one lead ion, two potassium ions, two tetracyanoplatinate ions, and six water molecules in the asymmetric unit. Atomic coordinates are given in Table I. Selected interatomic distances and angles are presented in Table II.

Figure 1 shows a view of the zigzag chain of $[Pt(CN)_4]^{2-}$ ions that are present in the solid. Within this chain there are two individual Pt–Pt distances, 3.267(1) and 3.298(1) Å. The Pt–Pt–Pt angles are identical, 162.3(1)°. The angle between the planes of the tetracyanoplatinate ions is 1.1°, and these tetracyanoplatinate ions are staggered within the columns. The average C–Pt–Pt–C dihedral angle is 36.2°.

Figure 2 shows a view of the unit cell. The lead ions and the potassium ions sit in channels between the columns and do not interact directly with the platinum centers in the solid. Consequently, the shortest Pb⋯Pt distance is quite long, 5.491(1) Å. The lead ion is surrounded by four water molecules (with Pb–O distances ranging from 2.45(1) to 2.80(1) Å) and by two nitrogen atoms from the cyano groups (with Pb–N distances of 2.52(1) and 2.69(1) Å).

The structure of $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$ may be related to that of $K_2Sr[Pt(CN)_4]_2{\cdot}6H_2O$, which appears to be isomorphous.[13]

Preparation and Spectroscopic Characterization of Crown-P₂ and Its Complexes. Crown-P₂ (**1**) was obtained in 86% yield by condensation of diphenylphosphine, paraformaldehyde, and diaza-18-crown-6 in toluene at 60 °C. It was converted into $[Tl(crown\text{-}P_2)Pt(CN)_2](NO_3)$ (**2**) by treatment with *trans*-$Pt(CN)_2(PPh_3)_2$ and thallium(I) nitrate. The ^{31}P NMR spectrum of **2** in chloroform solution consists of a prominent doublet at 7.6 ppm that is due to coupling to thallium (^{205}Tl 70.5% natural abundance,

Table II. Selected Interatomic Distances and Angles for $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$[a]

	Distances (Å)		
Pt(1)–Pt(2)	3.298(1)	$Pt(2)–Pt(1)^{v}$	3.267(1)
Pt(1)–C(4)	1.98(2)	Pt(1)–C(5)	1.99(1)
Pt(1)–C(6)	2.02(1)	Pt(1)–C(7)	1.97(2)
Pt(2)–C(1)	2.04(2)	Pt(2)–C(2)	2.04(2)
Pt(2)–C(3)	1.97(2)	Pt(2)–C(8)	1.99(2)
Pb–O(1)	2.62(1)	Pb–O(2)	2.45(1)
Pb–O(3)	2.80(1)	$Pb–O(5)^{iii}$	2.61(1)
$Pb–N(3)^{iii}$	2.69(1)	$Pb–N(8)^{i}$	2.52(1)
K(1)–O(6)	2.70(1)	K(1)–N(1)	2.81(2)
K(1)–N(7)	2.96(2)	$K(1)–N(3)^{iii}$	2.85(2)
$K(1)–N(5)^{iv}$	2.90(1)	K(2)–O(1)	2.83(1)
K(2)–O(2)	2.96(1)	K(2)–N(2)	2.80(2)
$K(2)–N(1)^{ii}$	2.96(1)	$K(2)–N(4)^{ii}$	2.83(1)
	Angles (deg)		
$Pt(1)–Pt(2)–Pt(1)^{v}$	162.3(1)		
C(4)–Pt(1)–C(6)	179.6(7)	C(4)–Pt(1)–C(5)	87.4(6)
C(4)–Pt(1)–C(7)	91.5(7)	C(5)–Pt(1)–C(6)	92.2(6)
C(6)–Pt(1)–C(7)	88.8(7)	C(5)–Pt(1)–C(7)	178.8(8)
C(1)–Pt(2)–C(3)	179.2(6)	C(1)–Pt(2)–C(2)	90.4(6)
C(1)–Pt(2)–C(8)	89.6(6)	C(2)–Pt(2)–C(3)	90.0(7)
C(3)–Pt(2)–C(8)	89.9(6)	C(2)–Pt(2)–C(8)	177.5(7)
O(1)–Pb–O(2)	83.6(4)	O(1)–Pb–O(3)	82.6(4)
$O(1)–Pb–O(5)^{iii}$	148.2(4)	$O(1)–Pb–N(3)^{iii}$	137.7(5)
$O(1)–Pb–N(8)^{i}$	74.1(4)	O(2)–Pb–O(3)	147.5(4)
$O(2)–Pb–O(5)^{iii}$	90.5(4)	$O(2)–Pb–N(3)^{iii}$	82.6(5)
$O(2)–Pb–N(8)^{i}$	74.0(5)	$O(3)–Pb–O(5)^{iii}$	86.0(4)
$O(3)–Pb–N(3)^{iii}$	126.3(5)	$O(3)–Pb–N(8)^{i}$	74.0(5)
$O(5)^{iii}–Pb–N(3)^{iii}$	71.6(5)	$O(5)^{iii}–Pb–N(8)^{i}$	74.2(5)
$N(3)^{iii}–Pb–N(8)^{i}$	138.0(6)		

[a] Symmetry codes: i = 2 − *x*, ¹/₂ + *y*, 1 − *z*; ii = 2 − *x*, *y* − ¹/₂, 1 − *z*; iii = *x*, *y*, 1 + *z*; iv = 1 + *x*, *y*, 1 + *z*; v = 1 + *x*, *y*, *z*.

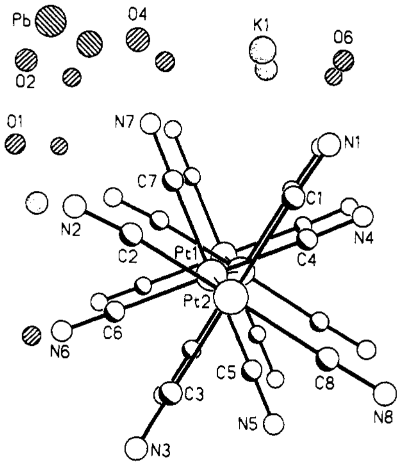

Figure 1. View down a column of tetracyanoplatinate ions in $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$ with 50% thermal contours for all atoms.

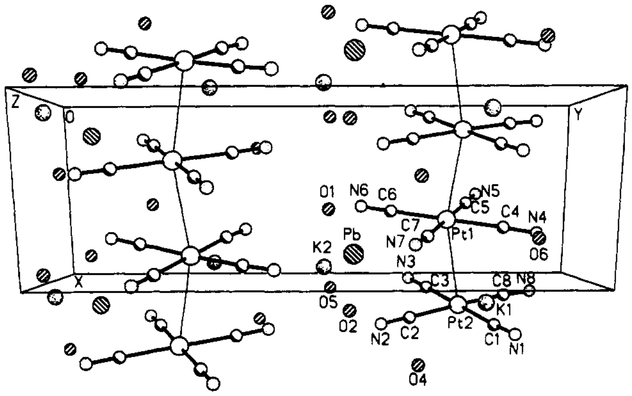

Figure 2. View of the unit cell in $K_2Pb[Pt(CN)_4]_2{\cdot}6H_2O$.

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(13) (a) $K_2Sr[Pt(CN)_4]_2{\cdot}6H_2O$: monoclinic $P2_1$ or $P2_1/m$; *a* = 9.373 Å, *b* = 17.957 Å, *c* = 6.653 Å, *β* = 108.2°. (b) Krogmann, K.; Stephan, D. *Z. Anorg. Allg. Chem.* **1968**, *362*, 290.

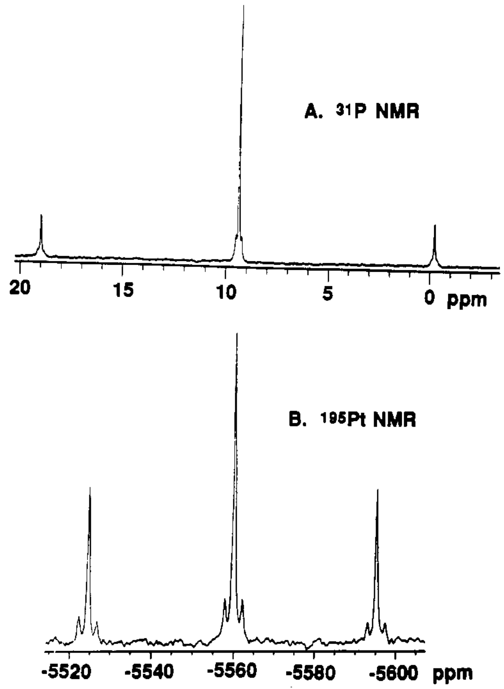
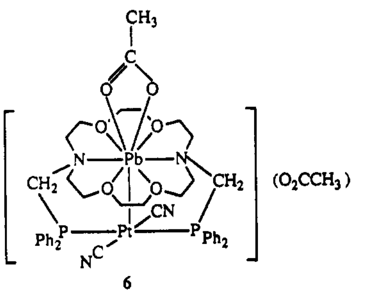


Figure 3. NMR spectra of $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3)$ in chloroform–methanol solution: A, 121.7-MHz $^{31}P\{^1H\}$ spectrum; B, 64.3-MHz $^{195}Pt\{^1H\}$ spectrum.

^{203}Tl 39.5% natural abundance, both spin $^1/_2$) with $J(Tl,P) = 41$ Hz. Pairs of satellites that come from coupling to ^{195}Pt are also present with $^1J(Pt,P) = 2293$ Hz. The $^{195}Pt\{^1H\}$ NMR spectrum consists of a doublet of triplets with $\delta = -4684$ ppm, $^1J(Pt,P) = 2293$ Hz, and $^1J(Pt,Tl) = 3825$ Hz.

Treatment of *trans*-$Pt(CN)_2(PPh_3)_2$ with crown-P_2 in a mixture of toluene and methanol followed by the addition of diethyl ether yields white (crown-P_2)$Pt(CN)_2$. This complex shows a singlet at 2.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum with satellites due to coupling to ^{195}Pt (spin $^1/_2$; 33.4% natural abundance) with $^1J(Pt,P) = 2225$ Hz and a cyanide stretch at 2126 cm^{-1} in the infrared spectrum. Addition of lead(II) acetate in methanol to a chloroform solution of (crown-P_2)$Pt(CN)_2$ yields $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3)$ (**6**), which may be obtained with difficulty as colorless crystals through the slow diffusion of diethyl ether into the mixture.



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NMR spectra of $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3)$ are shown in Figure 3. The $^{31}P\{^1H\}$ spectrum shown in panel A consists of a singlet at 9.4 ppm with a pair of satellites due to coupling to ^{195}Pt with $^1J(Pt,P) = 2270$ Hz. Each line in the spectrum shows an additional pair of satellites due to coupling to ^{207}Pb (spin $^1/_2$, 22.6% natural abundance) with $J(Pb,P) = 27.5$ Hz. The ^{195}Pt NMR spectrum is shown in panel B of this figure. The spectrum consists of a triplet that is due to coupling to the two equivalent phosphorus atoms with $^1J(Pt,P) = 2270$ Hz. The chemical shift is −5560 ppm. Each line of the triplet possesses satellites that are due to coupling to lead with $^1J(Pb,Pt) = 274$ Hz.

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3)\cdot 1.5H_2O\cdot CH_3OH\cdot 0.25CHCl_3$[a]

	x	*y*	*z*	*U*(eq)[b]
Pt	8389(1)	1998(1)	4610(1)	21(1)
Pb	8571(1)	1162(1)	2997(1)	20(1)
N(1)	8445(15)	3046(8)	3498(13)	44(7)
N(2)	8266(15)	856(8)	5540(12)	40(7)
N(3)	6532(12)	1366(7)	3188(10)	23(5)
N(4)	10545(12)	1295(7)	3561(9)	22(5)
O(1)	7436(10)	296(6)	3275(8)	27(5)
O(2)	9308(10)	311(5)	3923(8)	22(4)
O(3)	9816(11)	1658(6)	2010(8)	30(5)
O(4)	7861(10)	1996(5)	2071(8)	26(4)
O(5)	8044(12)	810(6)	1607(9)	37(5)
O(6)	9420(11)	441(6)	2111(9)	36(5)
P(1)	6665(4)	1956(2)	4680(3)	21(2)
P(2)	10083(4)	2100(2)	4761(3)	25(2)
C(1)	8431(16)	2662(9)	3920(12)	27(5)
C(2)	8338(16)	1290(9)	5229(12)	29(5)
C(27)	6138(15)	1417(8)	4028(11)	24(5)
C(28)	10851(15)	1837(8)	3903(12)	25(5)
C(29)	6088(16)	870(8)	2757(12)	25(5)
C(30)	6372(16)	332(9)	3215(13)	31(5)
C(31)	7779(17)	−162(9)	3789(13)	36(6)
C(32)	8874(18)	−201(10)	3698(15)	47(7)
C(33)	10316(17)	288(9)	3913(14)	37(6)
C(34)	10725(16)	864(8)	4153(12)	26(5)
C(35)	11111(16)	1187(9)	2784(12)	29(5)
C(36)	10884(16)	1625(9)	2115(12)	29(5)
C(37)	9499(16)	2157(9)	1582(13)	33(5)
C(38)	8413(16)	2079(10)	1319(13)	36(6)
C(39)	6818(15)	1912(9)	1862(12)	29(5)
C(40)	6265(16)	1860(8)	2671(12)	26(5)
C(41)	8745(18)	497(10)	1561(14)	38(6)
C(42)	8836(21)	173(12)	747(16)	58(8)

[a] Coordinates for phenyl carbons, anion atoms, and solute atoms omitted: see supplementary material for these. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystal Structure of $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3)\cdot 1.5H_2O\cdot CH_3OH\cdot 0.25CHCl_3$ and Comparison with $[Tl(crown\text{-}P_2)Pt(CN)_2](NO_3)$. The lead/platinum complex crystallizes with one cation, one acetate counterion, one disordered methanol molecule, two sites with water molecules at fractional occupancy, and one partially occupied site that contains a chloroform molecule. Selected atomic coordinates are given in Table III. A set of important distances and angles is given in Table IV. A drawing of the cation is shown in Figure 4. For comparison, a view of the thallium/platinum complex **2** is shown in Figure 5, and bond distances and angles are also given in Table IV. For this complex, there are two independent cations in the asymmetric unit. Other crystallographic data for **2** have been reported earlier.[9]

The cation in **6** consists of a nearly planar $P_2Pt(CN)_2$ portion with a lead ion positioned directly above the platinum center. The structure is thus similar to that of **2** (Figure 5) and to related iridium complexes, **4**.[10,11] The Pt–Pb distance is 3.313(2) Å. This is significantly longer than the Pt–Tl distances in both cations in **2** (2.911(2) and 2.958(2) Å). It is also longer than the Pb–Ir distance (3.117(1) Å) in $[ClPb(crown\text{-}P_2)Ir(CO)Cl]^+$.[10]

The coordination about the lead ion consists of the azacrown macrocycle and a chelating acetate ligand. Both oxygen atoms of this acetate form bonds of similar lengths (2.51(1) and 2.53(1) Å) to lead. The range of Pb–O distances that involve the azacrown portion is 2.61(1)–2.83(2) Å. The two Pb–N distances are 2.81(2) and 2.83(2) Å. These distances within the azacrown portion are all shorter than the corresponding distances in $[ClPb(crown\text{-}P_2)Ir(CO)Cl]^+$.[11] The positioning of the lead ion may be influenced by the presence of the chelating acetate. This ligand may serve to position the lead ion further from the platinum center than is the case in $[ClPb(crown\text{-}P_2)Ir(CO)Cl]^+$, where the lead is closer to the corresponding iridium atom.[11] The azacrown portion of the crown-P_2 ligand has the nitrogen atoms oriented so that their lone pairs point inward toward the lead ion.

Table IV. Selected Interatomic Distances and Angles in $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2]^+$ and $[Tl(crown\text{-}P_2)Pt(CN)_2]^+$

	$[(CH_3CO_2)Pb\text{-}(crown\text{-}P_2)Pt(CN)_2]^+$	$[Tl(crown\text{-}P_2)Pt(CN)_2]^{+\,a}$ cation 1	cation 2
	Distances (Å)		
Pt–M	3.313(2)	2.911(2)	2.958(2)
Pt–P(1)	2.329(6)	2.343(8)	2.312(11)
Pt–P(2)	2.310(6)	2.329(8)	2.333(10)
Pt–C(1)	1.95(2)	2.03(3)	1.99(3)
Pt–C(2)	1.98(2)	1.99(3)	1.98(3)
M–N(3)	2.81(2)	3.14(2)	3.05(2)
M–N(4)	2.83(2)	3.01(2)	2.98(2)
M–O(1)	2.63(1)	2.75(2)	2.77(3)
M–O(2)	2.73(1)	2.76(2)	2.91(2)
M–O(3)	2.61(1)	2.77(2)	2.77(2)
M–O(4)	2.53(1)	2.76(2)	2.87(2)
M–O(5)	2.51(1)		
M–O(6)	2.53(1)		
	Angles (deg)		
P(1)–Pt–P(2)	170.4(2)	171.0(3)	172.0(3)
C(1)–Pt–C(2)	175.4(8)	174.4(14)	175.9(17)
P(1)–Pt–C(1)	95.4(6)	93.3(8)	97.7(11)
P(1)–Pt–C(2)	84.4(6)	85.4(7)	79.9(11)
P(2)–Pt–C(1)	86.8(6)	85.0(8)	81.4(11)
P(2)–Pt–C(2)	94.2(6)	95.4(7)	100.5(13)
M–Pt–P(1)	95.0(1)	92.8(2)	92.4(2)
M–Pt–P(2)	94.2(1)	96.2(2)	95.5(3)
M–Pt–C(1)	92.5(6)	89.1(9)	94.9(10)
M–Pt–C(2)	82.9(6)	85.4(7)	88.6(13)
N(3)–M–O(1)	63.3(5)	62.7(14)	59.5(17)
N(3)–M–O(4)	65.3(5)	63.2(15)	63.9(16)
N(4)–M–O(2)	64.3(5)	62.0(14)	63.8(17)
N(4)–M–O(3)	62.7(5)	65.9(15)	61.5(17)
O(1)–M–O(2)	61.3(4)	59.4(14)	63.3(17)
O(3)–M–O(4)	62.8(4)	60.7(12)	62.6(16)
O(5)–M–O(6)	52.1(5)		
P(1)–C(27)–N(3)	117.2(14)	113(2)	111(2)
P(2)–C(28)–N(4)	115.4(14)	109(2)	111(2)

[a] Atom labeling follows that in Figure 4.

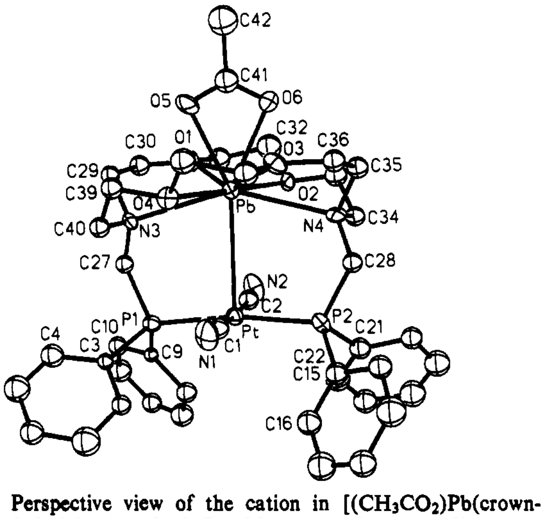

Figure 4. Perspective view of the cation in $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](O_2CCH_3)\cdot1.5H_2O\cdot CH_3OH\cdot0.25CHCl_3$ with 50% thermal contours for all atoms.

The orientation of the lead ion within the azacrown portion differs markedly from that seen in the simple adduct $(C_{12}H_{26}N_2O_4)\text{-}Pb(SCN)_2$ where the lead is surrounded by an essentially planar array of four oxygen atoms and two nitrogen atoms.[14]

Discussion

The results described here indicate the difficulty in obtaining significant bonding between Pt^{II} and Pb^{II} centers. Under conditions where $Tl_2Pt(CN)_4$ crystallizes, we have found that the $Pb(NO_3)_2$–$K_2Pt(CN)_4$ reaction produces $K_2Pb[Pt(CN)_4]_2\cdot6H_2O$. This salt possesses a structure that consists of zigzag columns of $[Pt(CN)_4]^{2-}$ ions with the lead and potassium ions set off to the side of the columns so that there is no direct Pb^{II}–Pt^{II} interaction.

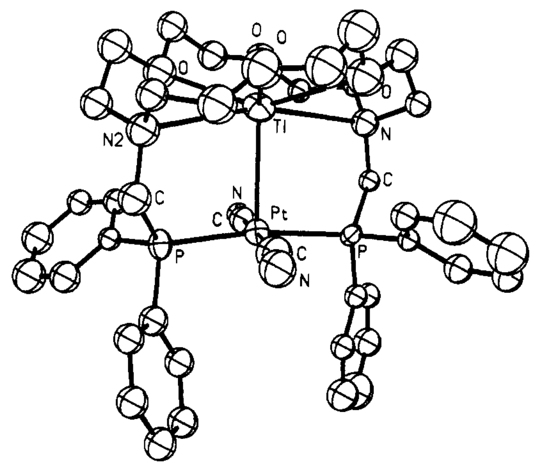

Figure 5. Perspective view of the cation in $[Tl(crown\text{-}P_2)Pt(CN)_2](NO_3)$.

Through the use of the bridging ligand crown-P_2, it is possible to position Pb^{II} and Pt^{II} ions close to one another. In **6** the Pt–Pb distance of 3.313(2) Å is long enough to lead to questions about the existence of any bonding between these two entities. Notice that the K···Ir distance in $[K(crown\text{-}P_2)Ir(CO)Cl]^+$ is only slightly longer (3.331(6) Å) and the electronic spectrum of the $Ir(CO)ClP_2$ portion in that complex is unaffected by the presence of the potassium ion.[11]

Nevertheless, the NMR spectral data do suggest that there is some bonding between the two metal ions in **6**. The observation of $J(Pb,Pt)$ = 274 Hz in the ^{195}Pt NMR spectrum of **6** can be compared to analogous coupling in a related complex. The planar Pt^{II} complex *cis*-$Pt(PPh_3)_2Ph(PbPh_3)$ has a true unbridged Pb–Pt single bond and a Pb–Pt distance (2.698(8) Å)[15] that is considerably shorter (by 0.615 Å) than the corresponding Pb–Pt distance in **6**. The ^{195}Pt NMR spectrum of *cis*-$Pt(PPh_3)_2Ph(PbPh_3)$ shows that $^1J(Pb,Pt)$ is 18 380 Hz. Related complexes with Pt–$PbPh_3$ bonds have $^1J(Pb,Pt)$ values that range from 14 200 to 18 515 Hz.[16] Thus the Pb–Pt interaction in **6** is extremely weak: 2 orders of magnitude weaker than a normal single Pb–Pt bond. Measurements of $^1J(Pb,Pt)$ should find general utility in assessing the nature of Pb–Pt bonding in other compounds.

In the context of this work, the recent discovery of a Pt^{II}–Pb^{II}–Pt^{II} chain (in $[Pb\{Pt(C_6F_6)_4\}_2]^{2-}$) with short Pt–Pb distances (2.769(2) and 2.793(2) Å) is remarkable.[17] The short contact between the lead ion and the ortho fluoro substituents on the pentafluorophenyl groups along with a significant ionic component to the Pb–Pt bonding may facilitate the bond shortening within the Pt^{II}–Pb^{II}–Pt^{II} unit.

The Tl^{I}–Pt^{II} bonding in **2** is certainly more significant than the Pb^{II}–Pt^{II} bonding in **6**. The Tl^{I}–Pt^{II} bond is 0.40–0.35 Å shorter than the Pb^{II}–Pt^{II} bond. This shortening is especially significant because the ionic radius of Tl^{I} (1.64 Å for coordination number 6) is larger than that of Pb^{II} (1.43 Å for coordination number 8).[18] Thus comparison of M–N and M–O distances in **2** and **6** confirms that the Pb^{II} has the shorter M–O and M–N distances and hence smaller size. Despite this, the lead ion is further from the platinum center in **6** than the thallium ion is in **2**. No doubt the higher positive charge on the Pb^{II} ion leads to a contraction of the $6s^2$ orbital that results in its lesser ability to overlap covalently with orbitals on platinum. Additionally, the higher

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charge results in less 6s/6p overlap (a so-called "hybridization defect") and hence weaker bonding to the adjacent platinum.[19]

Unfortunately, there is no compound with a true Tl^I–Pt^{II} single bond available to compare to **2**. However, it is possible to compare the Tl^I–Pt^{II} and Pb^{II}–Pt^{II} couplings seen in the ^{195}Pt NMR spectra. To do that, the reduced coupling constants $K(A,B)$ ($K(A,B) = 1/h(2\pi/\gamma_A)(2\pi/\gamma_B)J_{AB}$ where γ_A and γ_B are the gyromagnetic ratios for nuclei A and B) need to be considered.[20] For the Tl^I/Pt^{II} complex **2** $K(Tl,Pt)$ is 2570×10^{20} cm^{-3} while for **6** $K(Pb,Pt)$ is 507×10^{20} cm^{-3}. Thus the NMR spectral results confirm the greater degree of metal–metal bonding that is present in the Tl^I/Pt^{II} complex **2** relative to the Pb^{II}/Pt^{II} complex **6**.

Experimental Section

Preparation of Compounds. Crown-P_2 [1,10-Bis((diphenylphosphino)methyl)-1,10-diaza-4,7,13,16-tetraoxaoctadecane (1)]. Under a dinitrogen atmosphere, diphenylphosphine (0.35 g, 1.9 mmol) was added to a stirred mixture of 0.5 g of paraformaldehyde and 0.25 g (0.95 mmol) of diaza-18-crown-6 in 30 mL of toluene at 60 °C. After 3 h, the mixture was cooled to room temperature and filtered through Celite, and the solvent was removed in vacuo. The yellowish, oily solid was dissolved in 8 mL of dichloromethane, and 20 mL of hot ethanol was added. The solution was evaporated under vacuum until small, colorless crystals began to form. The mixture was then cooled to –20 °C under a dinitrogen atmosphere and stored at –20 °C for 16 h. The colorless, crystalline solid that formed was collected on a glass frit, washed with ethanol, and vacuum-dried. Yield: 0.54 g (86%). $^{31}P\{^1H\}$ NMR: $\delta = -26$ ppm (s). ^1H NMR: $\delta = 2.96$ ppm (t), $\delta = 3.55$ ppm (t), $J(H,H) = 5.7$ Hz; $\delta = 3.43$ ppm (d), $J(P,H) = 3.7$ Hz; $\delta = 3.53$ ppm(s). Mp: 110–112 °C dec.

[Tl(crown-P_2)$Pt(CN)_2$](NO_3). Toluene (25 mL) was added to a stirred slurry of 100 mg (0.15 mmol) of crown-P_2 and 39 mg (0.15 mmol) of thallium(I) nitrate in 25 mL of methanol. $Pt(CN)_2(PPh_3)_2$ (119 mg, 0.15 mmol) in a mixture of 20 mL of toluene and 20 mL of methanol was added dropwise over the course of the next hour to the resulting clear solution, which was then stirred for 3 h. The volume of the resulting pale yellow solution was reduced by rotary evaporation to 15 mL, and diethyl ether was added until the solution turned cloudy. The solution was stored at –20 °C for 16 h, at which time colorless needles had formed. These were collected on a glass frit, washed with ether, and vacuum-dried. Yield: 154 mg (81%). $^{31}P\{^1H\}$ NMR: $\delta = 7.6$ ppm, $J(Pt,P) = 2293$ Hz, $J(Tl,P) = 41$ Hz. ^{195}Pt NMR: $\delta = -4684$ ppm, $J(Tl,Pt) = 3825$ Hz, $J(P,Pt) = 2293$ Hz. IR (mineral oil mull): ν(CN) 2133 cm^{-1}.

[(CH_3CO_2)Pb(crown-P_2)$Pt(CN)_2$](O_2CCH_3) (6). A colorless solution of 126.9 mg (0.1674 mmol) of *trans*-$Pt(CN)_2(PPh_3)_2$ in 25 mL of toluene–methanol (1:1, v/v) was added over a period of 30 min to a solution of 110.0 mg (0.1671 mmol) of crown-P_2 in 10 mL of toluene. After the reaction mixture was stirred for 3 h, diethyl ether was added to the solution until it became cloudy. The solution was stored at –20 °C for 12 h. The white crystalline product, (crown-P_2)$Pt(CN)_2$, was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 107.1 mg (71%). (crown-P_2)$Pt(CN)_2$ is soluble in chloroform and dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum in dichloromethane is a singlet at 1.9 ppm with satellites due to ^{195}Pt with $^1J(Pt,P) = 2223$ Hz. The infrared spectrum (mineral oil mull) shows ν(CN) at 2126 cm^{-1}. A solution of 34.6 mg (0.0912 mmol) of lead(II) acetate in a minimum volume of methanol was added to a solution of 81.2 mg (0.0897 mmol) of (crown-P_2)$Pt(CN)_2$ in 5 mL of chloroform. Slow diffusion of diethyl ether into this solution produced colorless crystals of the product.

$K_2Pb[Pt(CN)_4]_2 \cdot 6H_2O$ (5). A 1.5-mL portion of an aqueous solution that contained 0.155 M $Pb(NO_3)_2$ and 0.155 M KCN was layered over a 1.5-mL portion of a 0.077 M aqueous solution of $K_2[Pt(CN)_4] \cdot 3H_2O$ in a 4 mm inner diameter tube. Small pale yellow crystals formed from this mixture after several hours.

X-ray Data Collection. [(CH_3CO_2)Pb(crown-P_2)$Pt(CN)_2$](O_2CCH_3)·$1.5H_2O \cdot CH_3OH \cdot 0.25CHCl_3$ (6). Colorless needles were obtained by slow diffusion of diethyl ether into a solution of the complex in a mixture of chloroform and methanol. The crystals were coated with a light hydrocarbon oil, and a selected crystal was placed in the 130 K dinitrogen stream of a Siemens R3m/v diffractometer that was equipped with a low-temperature apparatus. The two check reflections showed only random (<2%) fluctuations in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table V.

Table V. Crystal Structure Data

	$K_2Pb[Pt(CN)_4]_2 \cdot 6H_2O$	[(CH_3CO_2)Pb(crown-P_2)-$Pt(CN)_2$](O_2CCH_3)·$1.5H_2O \cdot CH_3OH \cdot 0.25CHCl_3$
	$C_8H_{12}PbN_8O_6K_2Pt_2$	$C_{45.25}H_{61.25}Cl_{0.75}N_4O_{10.5}P_2PbPt$
fw	991.8	1313.0
	$P2_1$, monoclinic	$P2_1/n$, monoclinic
a, Å	6.487(1)	13.483(4)
b, Å	17.928(3)	24.125(10)
c, Å	9.316(2)	16.212(4)
β deg	107.76(1)	90.06(2)
V, Å^3	1031.8(3)	5274(3)
Z	2	4
T, K	125	130
λ(Mo Kα), Å	0.710 69	0.710 69
μ, mm^{-1}	2.231	6.024
d_{calc}, Mg/M^3	3.19	1.649
transm factors	0.04–0.02	0.38–0.60
$R(F)^a$	0.033	0.074
$R_w(F)^b$	0.038	0.098

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

$K_2Pb[Pt(CN)_4]_2 \cdot 6H_2O$ (5). Yellow crystals were obtained as described above and coated with a light hydrocarbon oil, a selected crystal was mounted, and data were collected as described for **6**.

Solution and Refinement of Structures. [(CH_3CO_2)Pb(crown-P_2)$Pt(CN)_2$](O_2CCH_3)·$1.5H_2O \cdot CH_3OH \cdot 0.25CHCl_3$ (6). The calculations were performed on a Micro VAX 3200 computing system with the Siemens SHELXTL PLUS software package. The positions of the platinum and lead atoms were located from a Patterson map. The positions of other atoms were determined through the use of Fourier difference maps. Anisotropic thermal parameters were assigned to the platinum, lead, nitrogen, oxygen, and phosphorus atoms of the cation and anion. All other atoms were assigned isotropic thermal parameters. Hydrogen atoms were fixed at calculated positions through the use of a riding model in which the C–H vector was fixed at 0.96 Å and the isotropic thermal parameter for each hydrogen atom was fixed at a value of 0.04 Å^2 during refinement. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[21] The final stages of refinement included an absorption correction with a method that obtains an empirical absorption tensor from an expression that relates F_o and F_c.[22] There are two water molecules in the unit cell; the one involving O(9) had 100% occupancy while that involving O(10) had 50% occupancy. There is chloroform molecule in the structure with 0.25 occupancy. The C–Cl distances were fixed at 1.76 Å, and the Cl···Cl distances were constrained to 2.90 Å. A disordered methanol molecule is also present. The oxygen atom, O(11), of this methanol molecule had a refined occupancy of 100% while there was disorder in the carbon positions with C(46A) with 34% refined occupancy and C(46B) with 66% occupancy. The largest peak (3.25 e Å^{-3}) in the final difference Fourier map was located 0.952 Å from the platinum atom.

$K_2Pb[Pt(CN)_4]_2 \cdot 6H_2O$ (5). The structure was solved by the use of Patterson methods. The original choice of hand of the structure was found to be incorrect, and the structure was inverted. Extinction and absorption corrections[21] were applied. In the final cycles of refinement, anisotropic thermal parameters were assigned to the lead, platinum, and potassium ions. The largest peak (3.71 e Å^{-3}) in the final difference Fourier map was 1.04 Å from the lead ion. There were other spurious features in the difference map. They were due to truncation errors or to the very high absorption of this crystal.

Acknowledgment. We thank the National Science Foundation (Grant CHE 9022909) for support and Johnson Matthey, Inc., for a loan of platinum salts. J.K.N. thanks Bowdoin College for a faculty study leave.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and crystal refinement data for $K_2Pb[Pt(CN)_2]_2 \cdot 6H_2O$ and [(CH_3CO_2)Pt(crown-P_2)$Pt(CN)_2$](O_2CCH_3)·$1.5H_2O \cdot CH_3OH \cdot 0.25CHCl_3$ (15 pages). Ordering information is given on any current masthead page.

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