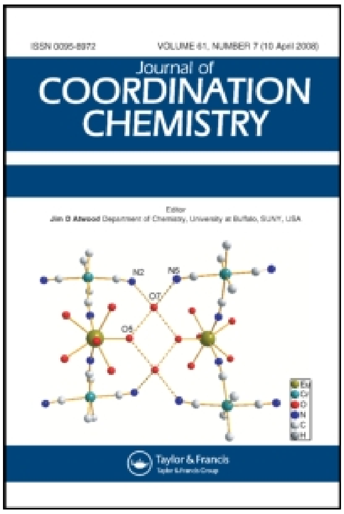

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Hexafluorophosphate salts of *bis* and *tetrakis*(2,2′-bipyridine)lead(II) complexes

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Both *bis*- and *tetrakis*-substituted 2,2′-bipyridine complexes of lead(II), $[Pb(bpy)_2](PF_6)_2$ and $[Pb(bpy)_4](PF_6)_2 \cdot bpy$, respectively, have been characterized by X-ray crystallography as hexafluorophosphate salts when three equivalents of bipyridine is combined with $Pb(NO_3)_2$ in aqueous solution prior to metathesis. The *tetrakis*-substituted product, $[Pb(bpy)_4](PF_6)_2 \cdot bpy$, shows an unusual combination of intramolecular and intermolecular π-stacking of two of the bipyridine ligands throughout the crystal. Incomplete metathesis also produces a catenated, mixed-anion complex, $[Pb(bpy)_2(\mu\text{-}NO_3)](PF_6)$, where the nitrate bridges lead(II) metal centers to form a 1-D coordination polymer. If metathesis is carried out using perchlorate, a known $[Pb(bpy)_2](ClO_4)_2$ analog is produced along with $[bpyH](ClO_4)$, which has not been previously characterized by X-ray crystallography.

Keywords: Lead; Diimine; Hexafluorophosphate; Coordination chemistry; Bipyridine

1. Introduction

During our investigations of new transition and post-transition metal diimine complexes [1–3], we required electrochemical standards for metal-centered oxidations of similar type complexes. $[Cd(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) is one example that is easily synthesized and well characterized [4–7], however, our attempts to produce similar bipyridine complexes of lead(II) produced mixtures that contain anything but the familiar *tris*-substituted type of metal complex. Herein, we report the addition of three equivalents of 2,2′-bipyridine with $Pb(NO_3)_2$ followed by metathesis with hexafluorophosphate and perchlorate salts that yield mixtures of crystalline products, including both *bis* and *tetrakis* bipyridine complexes that are not easily separable (all are clear/white blocks), but can easily be distinguished by single-crystal X-ray crystallography.

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2. Experimental

Crystallographic data were collected using Mo-Kα radiation on a Bruker SMART APEXII diffractometer. Cell constants were determined after integration from more than 7000 reflections [8]. Structures were solved by direct methods using SIR97 [9] and refined using SHELXL-97 [10]. Data reduction and refinement were completed using the WinGX suite of crystallographic software [11]. All hydrogens were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Table 1 presents additional crystallographic and refinement information.

Compound **4** was determined to be a non-merohedral twin, indexed using Cell_Now [12] and scaled using TWINABS [12] as a two-component twin. The hydrogen on the protonated bipyridine nitrogen in **4** was found from the difference map. The largest residual electron densities in the Pb structures reside next to heavy metal centers.

3. Results

Addition of $Pb(NO_3)_2$ to three equivalents of 2,2′-bipyridine in warm water, followed by metathesis with excess potassium hexafluorophosphate yielded a white precipitate. Extraction of the dried precipitate with acetonitrile and slow evaporation yielded a mixture of two crystalline products: the monoprotonated bypyridine ligand, $[bpyH](PF_6)$, which has previously been characterized by X-ray crystallography [13], and a new complex, $[Pb(bpy)_2(\mu\text{-}NO_3)](PF_6)$ (**1**). Complex **1** shows incomplete metathesis by hexafluorophosphate and results in a 1-D coordination polymer formed with bridging nitrates $[Pb(bpy)_2(\mu\text{-}NO_3)](PF_6)$ (figure 1). The lead has a distorted octahedral coordination environment and shows oxophilic character of lead when oxygen-containing anions are present. Oxygen O(1) has long Pb–O interactions of 3.03 and 3.30 Å, suggestive of a dual chelating coordination mode for nitrate, resulting in a pseudo seven-coordinate complex. The closest Pb–F contact in this structure is ~3.4 Å. Another mixed-anion structure of $[Pb(bpy)_2(\eta^2\text{-}CH_3COO)](ClO_4)$, including a chelating acetate, has previously been reported [14].

From the precipitate produced by the initial metathesis, some solubility was also observed in CH_2Cl_2/MeOH. Slow evaporation produced a small number of X-ray quality crystals of composition $[Pb(bpy)_2](PF_6)_2$ (**2**). Complex **2** (figure 2) binds only two 2,2′-bipyridine ligands and is essentially four coordinate and mononuclear (Pb–N bond distances are given in table 2). The structure has several relatively long lead–hexafluorophosphate interactions, however, with the shortest Pb–F contacts equaling 3.0 Å. This is the same stoichiometry reported previously for $[Pb(bpy)_2](ClO_4)_2$ and $[Pb(phen)_2](ClO_4)_2$ [14, 15], but is structurally different as the PF_6^- here have weaker cationic interactions. $[Pb(bpy)_2](ClO_4)_2$ is a dimer of $[Pb(bpy)_2]^{2+}$ units bridged by perchlorate. Replacement with the less coordinating anion, PF_6^-, in all of these cases produce significantly different structures than those determined when oxoanions are present, where at least one oxygen is always found coordinated to Pb(II).

If the filtrate from the initial metathesis reaction is allowed to concentrate, pale pink crystals of composition $[Pb(bpy)_4](PF_6)_2 \cdot bpy$ (**3**) were isolated. The structure of **3** shows an expanded coordination sphere, not unusual for lead(II), with four bpy ligands bound to the metal center (figure 3). Three of the bpy ligands have normal Pb–N bond

Table 1. Crystallographic and refinement data for [Pb(bpy)$_2$](μ-NO$_3$)(PF$_6$) (**1**), [Pb(bpy)$_2$](PF$_6$)$_2$ (**2**), [Pb(bpy)$_4$](PF$_6$)$_2$ · bpy (**3**), and [bpyH](ClO$_4$) (**4**).

	1	**2**	**3**	**4**
Empirical formula	$C_{20}H_{16}N_5O_3P_1Pb$	$C_{20}H_{16}F_{12}N_4P_2Pb$	$C_{50}H_{40}F_{12}N_{10}P_2Pb$	$C_{10}H_9ClN_2O_4$
Formula weight	726.55	809.50	1278.05	256.64
System	Bruker APEXII	Bruker APEXII	Bruker APEXII	Bruker APEXII
Temperature (K)	100(1)	100(1)	100(1)	100(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P 21/c*	*P 21/n*	*P 21/n*	*P c*
Unit cell dimensions (Å, °)				
a	13.3651(16)	9.9697(1)	15.8617(9)	5.960
b	11.2203(13)	24.4124(3)	14.1100(8)	12.850
c	16.4170(19)	20.1684(2)	22.7069(13)	7.070
α				
β	113.672(1)	99.241(1)	109.646(1)	100.41
γ				
Volume (Å^3), *Z*	2254.8(5), 4	4844.0(1), 8	4786.2(5), 4	532.6, 2
Calculated density (g cm^{-3})	2.140	2.220	1.774	1.600
Absorption coefficient (mm^{-1})	7.638	7.209	3.688	0.363
F(000)	1384	3072	2520	264
θ range for data collection (°)	2.26–25.00	1.96–25.00	1.73–26.40	3.17–25.00
Index ranges	±15; ±13; ±19	−15/18; −16/+16; −25/22	±19; ±17; ±28	−7/+6; 0/+15; 0/+8
Reflections collected	20,864	34,885	51,613	940
Independent reflection	3966	8521	9832	940
Observed reflections	3354	7782	8671	932
Max. and min. transmission	0.062 and 0.357	0.140 and 0.300	0.245 and 0.646	0.839 and 0.941
Restraints/parameters	0/325	0/703	0/676	2/158
Goodness-of-fit on F^2	1.048	1.044	1.015	1.102
Final *R* indices [$I > 2\sigma(I)$]	0.0227	0.0184	0.0194	0.0202
R indices (all data)	0.0523	0.0398	0.0438	0.0544
Largest difference peak and hole (e Å^{-3})	1.23 and −1.02	0.64 and −0.70	0.89 and −0.48	0.18 and −0.29

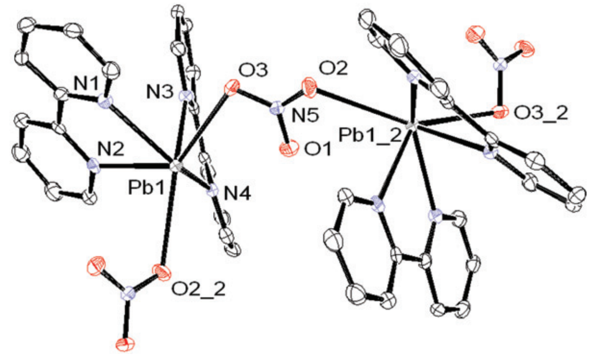

Figure 1. Thermal ellipsoid diagram (50%) of $[Pb(bpy)_2(\mu\text{-}NO_3)](PF_6)$ (**1**). The hydrogens and the PF_6 counteranions have been omitted for clarity.

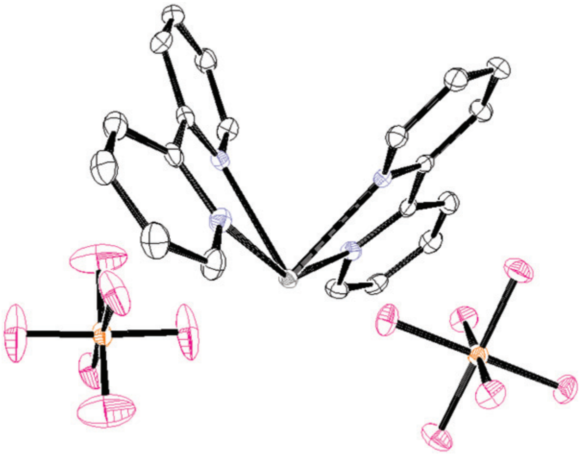

Figure 2. Thermal ellipsoid diagram (50%) of $[Pb(bpy)_2](PF_6)_2$ (**2**). Hydrogens have been omitted.

Table 2. Common bond lengths (Å) and angles (°) in Pb structures.

	1	**2**	**3**
Pb1–N1	2.543(4)	2.440(2)	2.663(2)
Pb1–N2	2.540(4)	2.489(2)	2.674(2)
Pb1–N3	2.517(4)	2.531(3)	2.573(2)
Pb1–N4	2.625(4)	2.535(3)	2.670(2)
Pb1–N5	–	–	2.760(2)
Pb1–N6	–	–	2.723(2)
Pb1–N7	–	–	2.960(3)
Pb1–N8	–	–	2.841(3)
Pb1–O2	2.805(4)	–	–
Pb1–O3	2.705(3)	–	–
O2–Pb1–O3	147.4(1)	–	–

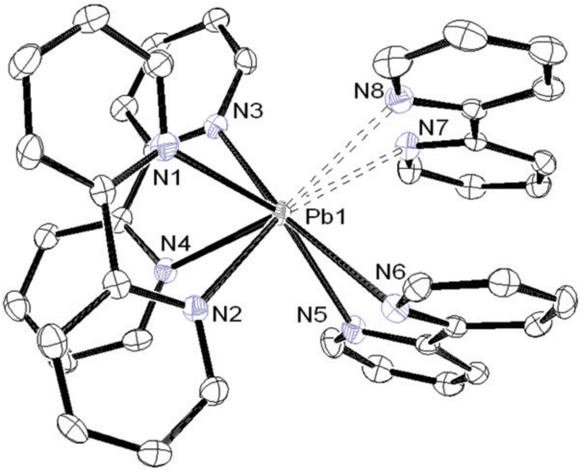

Figure 3. Thermal ellipsoid diagram (50%) of $[Pb(bpy)_4](PF_6)_2 \cdot bpy$ (**3**). BpyN5/N6 and bpyN7/N8 visibly π-stack. Hydrogens, PF_6 anions, and the uncoordinated bpy present in the structure have been omitted for clarity.

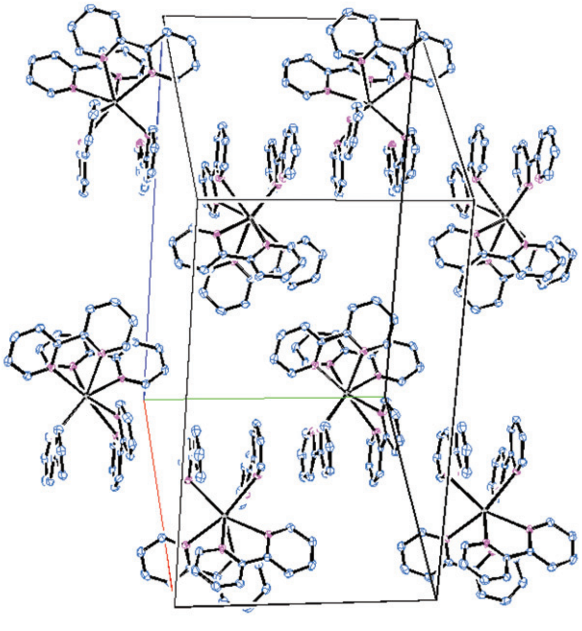

Figure 4. Crystal packing diagram of **3** showing infinite π-stacks along the 0 1 0 axis. Hydrogens, PF_6^-, and the uncoordinated bpyN9/N10 have been removed.

distances (table 2); however, the fourth bpy (bpyN5/N6) has longer Pb–N bonds. The reason for this is that two of the bpy ligands (bpyN5/N6 and bpyN7/N8) form an infinite π-stack through the crystal that averages 3.4–3.6 Å separation, typical of π–π distances, thus gaining increased crystal lattice energy. Two π-stacking bpy ligands

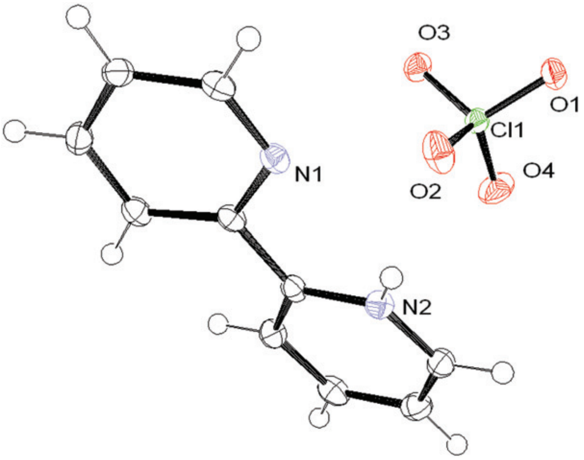

Figure 5. Thermal ellipsoid diagram (50%) of [bpyH](ClO_4) (**4**). Hydrogen bonds: N2–H99 $\cdots$ O3 = 2.909(3) Å; 149(4)°; N2–H99 $\cdots$ N(1) = 2.671(3) Å; 110(3)°.

within each complex (bpyN5/N6 and bpyN7/N8) π-stack with the same bpy pair of a neighboring complex (figure 4). This is much different from the previously characterized [Pb(phen)$_4$($OClO_3$)](ClO_4) complex where four phen ligands are equally bound to the lead which is also capped by a single perchlorate oxygen, making a nine-coordinate metal–ligand environment [16]. A fifth bipyridine ligand, bpyN9/N10 (not shown in figure 3), is also trapped within the crystal, unbound to lead. It is relatively flat with the nitrogens pointing away from each other. This uncomplexed bipyridine is found as a π-dimer with bpyN1/N2, but does not form an infinite π-stack throughout the crystal. Compound **3** also exhibits a weak yellow luminescence.

Finally, repeating the metathesis with sodium perchlorate, we were able to confirm the structure of [Pb(bpy)$_2$](ClO_4)$_2$ previously reported [16], but a second product, [bpyH](ClO_4) (**4**), was also discovered which has not been reported (figure 5). This is likely because **4** was found as a non-merohedral twin, which was indexed using Cell_Now. The structure of **4** is similar to that previously reported for [bpyH](PF_6) [13].

Supplementary material

The details of compounds **1**, **2**, **3**, and **4** are obtained in CCDC-767652, -767650, -767649, and -767651, respectively. Crystallographic files in CIF format can be obtained free of charge from the Cambridge Crystallographic Data Center, www.ccdc.cam.ac.uk/conts/retrieving.html.

Acknowledgments

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