the UV cross section is sufficiently large that it should be possible to observe the change in electronic spectrum with temperature. The infrared spectrum presents more of a problem since the cross section for the bands of interest is relatively low, and since the minor rotamer will only be ~10% of the mixture. Nevertheless, the greatly increased sensitivity afforded by infrared diode lasers should permit the spectrum to be observed. Experiments of these types are planned.

8. Calculations

The ab initio calculations were carried out by using GAUSSIAN-86[34] along with standard basis sets. The calculations for the electronically excited states were carried out using the MELD package.[35]

Acknowledgment. This investigation was supported by a grant from the National Science Foundation. The calculations were carried out with a Trace computer made available via an NIH instrumentation grant. R.E.R. acknowledges an NSF predoctoral fellowship. We thank Prof. Davidson for making the MELD programs available to us, and we thank Prof Squillacote for providing the matrix isolated spectrum of butadiene.

Registry No. 1,3-Butadiene, 106-99-0; 1,3-butadiene-*2,3*-d_2, 1983-06-8; 1,3-butadiene-*1,1,4,4*-d_4, 10545-58-1; 1,3-butadiene-d_6, 1441-56-1.

Supplementary Material Available: Tables of internal coordinates of butadiene and F matrix from *trans*-butadiene, *cis*-butadiene, and *gauche*-butadiene (10 pages). Ordering information is given on any current masthead page.

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Lead Sequestering Agents. 1. Synthesis, Physical Properties, and Structures of Lead Thiohydroxamato Complexes

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Abstract: In an approach to the synthesis of ligands specific for Pb^{2+}, lead complexes with mono- and bis(thiohydroxamic acids) have been prepared and characterized on the basis of their elemental analyses and their infrared, NMR, and UV spectra. The structures of the two compounds bis(*N*-methylthiobenzohydroxamato)lead(II) (**2**) and bis(*N*-methylthioacetohydroxamato)lead(II) (**5**) have been determined by single-crystal X-ray diffraction using automated counter methods. The structure of **2** is based on a five-coordinate geometry in which the sulfur atoms and the stereochemically active electron lone pair on Pb^{2+} occupy the equatorial positions of a trigonal bipyramid. The axial positions are occupied by the oxygen atoms and weak, outer-sphere coordination occurs from ligation by the thiohydroxamate oxygen atoms of adjacent molecules. Compound **5** exists in a similar pseudotrigonal-bipyramidal geometry in the solid state, but the equatorial positions are occupied by the lone electron pair on lead, one oxygen atom, and one sulfur atom. Additional weak coordination is formed by two oxygen atoms and one sulfur atom from neighboring molecules. Bis(*N*-methylthiobenzohydroxamato)lead(II) (**2**) crystallizes in space group $C2/c$ with $Z = 4$, $a = 18.067$ (2) Å, $b = 12.518$ (2) Å, $c = 8.103$ (1) Å and $\beta = 101.93$ (1)°. Full-matrix least-squares refinement using 1805 reflections with $F_o^2 > 3\sigma(F_o)^2$, with all non-hydrogen atoms given anisotropic temperature factors, converged to unweighted and weighted R factors of 1.7 and 1.9%, respectively. Bis(acetothiohydroxamato)lead(II) (**5**) crystallizes in space group $P2_1/n$ with $Z = 4$, $a = 7.958$ (2) Å, $b = 7.445$ (1) Å, $c = 19.007$ (3) Å, and $\beta = 98.74$ (2)°. Full-matrix least-squares refinement using 1924 reflections with $F_o^2 > 3\sigma(F_o)^2$, with all non-hydrogen atoms given anisotropic temperature factors, converged to unweighted and unweighted R factors of 4.1 and 5.1%, respectively.

This paper is the first of a planned series for a research program with the goal of developing specific complexing agents for lead. To that end we will present here the background to the problems posed by lead intoxication and the chemical and biological parameters that form the boundary conditions for our ligand design.

Due to the increasing industrial uses of lead, huge amounts of lead and its compounds enter the environment each year.[1,2] It is estimated that ~3.5×10^9 kg of lead ores were mined in 1974.[3] Industrial uses of lead include storage batteries, alkyllead production, cable sheathing, pigments, and lead alloys.[2,4] Thus, even with precautions being taken, plants, animals, and humans are exposed to, and are contaminated with, lead.

Lead uptake by humans occurs through absorption of lead compounds or lead-contaminated food or drink from the gastrointestinal tract, through absorption of airborne particles through the lungs, and through absorption of lead through the skin.[5-7] Most lead compounds are insoluble in vivo, so only small amounts of lead are absorbed from the gastrointestinal tract. However, since it is slowly eliminated, lead accumulates in liver, kidneys, bones, and other parts of the body.[8] The inhalation of lead compounds as lead carbonate and lead sulfate dust results in the

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accumulation of these compounds in the lungs, which is followed by gradual disposal of lead to the blood and bones.[6] Tetraalkyllead compounds, which are lipid soluble, are easily absorbed from the respiratory and gastrointestinal tracts and through the skin; major fractions of these alkyllead compounds accumulate in the brain.[6]

Once lead enters the blood, most of it (~97%) is rapidly taken up by erythrocytes and is distributed to soft tissues, liver, and kidneys, with some going to the brain, spleen, and heart and ~3% of lead remaining in blood plasma.[3,9] Eventually 90% of the body lead is deposited in the bones. Alteration of acid–base metabolism of the body, which may mobilize calcium, may also mobilize lead from the bones into soft tissues.[3]

The toxicity of lead is well documented;[1,2,5-12] it affects the functioning of the blood, kidneys, liver, testes, brain, nervous system, and other organs of the body. The toxicity of lead is due, in general, to its binding affinity to thiol and cellular phosphate groups of numerous enzymes, proteins, and cell membranes,[9,11-13] thus inhibiting or interfering with the functions of those enzymes, which include acetylcholine esterase, acid phosphatase, ATPase, and carbonic anhydrase.[4] Lead also inhibits the biosynthesis of heme, disturbs the globin synthesis, and increases premature red cell destruction.[3,4,6,10] Lead is toxic to the central nervous system, especially in children.[3,11,12] Lead binding to functional groups in cell membranes of testes, kidneys, liver, and brain leads either to complete breakdown or to reduced functioning of these tissues;[6] one result of this is that kidneys excrete sugars and amino acids and their tubular uric acid excretion is depressed.[3]

Chelating agents have been evaluated in the therapy of lead poisoning in both humans and animals.[4] These include the following: EDTA or CaEDTA;[14] *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA);[15,16] a combination of EDTA and the thiol-containing ligand 2,3-dimercapto-1-propanol (BAL); sodium 2,3-dimercapto-1-propanesulfonate (DMPS);[17-21] penicillamine;[17,22] *N*-(2-mercaptopropionyl)glycine;[23] and 2,3-dimercaptoglycine.[23-25] Generally these drugs have been found to be nonspecific, relatively toxic, or both.[12] For example, EDTA strongly complexes essential trace-metal ions in the body, resulting in the removal of these metal ions as well as lead.

Our target is the synthesis of chelating agent ligands that are powerful, and selective, chelating agents for lead ion. We explore here the thiohydroxamato group, since thiohydroxamic acids form stable complexes with lead ion, as indicated by the stability constant of lead thiohydroxamato complexes ($\log \beta_2 \approx 20.7$ for *N*-phenylthiobenzohydroxamic acid in 70% aqueous dioxane)[26] compared with that of the lead EDTA complex ($\log \beta_1 = 16.5$).[27] This relative stability is quite different from the "harder" metal ions of principal concern as natural trace elements.

Table I. Summary of Crystallographic Data and Parameters for Bis(*N*-methylthiobenzohydroxamato)lead(II) (**2**) and Bis(*N*-methylthioacetohydroxamato)lead(II) (**5**)[a,b]

	2	**5**
formula	$Pb(C_8H_8NOS)_2$	$Pb(C_3H_6NOS)_2$
fw	539.62	415.49
space group	$C2/c$	$P2_1/n$
a, Å	18.067 (2)	7.958 (2)
b, Å	12.518 (2)	7.445 (1)
c, Å	8.103 (1)	19.007 (3)
β, deg	101.93 (1)	98.74 (2)
V, Å^3	1792.9 (7)	1113.1 (6)
Z	4	4
d_{calcd}, g/cm^3	2.00	2.48
d_{obsd}, g/cm^3	1.98[c]	2.47[c]
crystal size, mm	0.12 × 0.15 × 0.20	0.25 × 0.20 × 0.20
μ(Mo Kα), cm^{-1}	94.9	152.8
radiation	Mo Kα (λ = 0.70926 Å)	Mo Kα
reflcns measd	$\mp h,+k,\pm l$	$\mp h,+k,\pm l$
scan method	θ–2θ	θ–2θ
no. of total data	2061	2443
no. of unique data, $F^2 > 3\sigma(F_o)^2$	1805	1924
no. of params refined	106	118
R	0.017	0.041
R_w	0.019	0.051
GOF	0.96	1.67
p factor	0.02	0.05

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of 24 reflections with 2θ near 30°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses. [c] Measured by flotation in dibromoethane/methanol mixture.

We report here the synthesis of several lead thiohydroxamato complexes, including a lead complex with a bis(thiohydroxamato) ligand, the physical properties of these lead complexes, and the X-ray structural characterization of them.

Experimental Section

Lead nitrate (Fisher Scientific Co.) was used for the synthesis of the complexes. Reagent-grade solvents and chemicals were used throughout the syntheses without further purification. The bis(thiohydroxamic acid) 3,3′-(ethylenedioxy)bis(*N*-methylthiobenzohydroxamic acid) (**1**) was prepared as described elsewhere,[28] bis(*N*-methylthiobenzohydroxamato)lead(II) (**2**) was prepared by a literature procedure.[29] Infrared spectra were obtained as KBr pellets for lead complexes and in pure ligand form between NaCl disks for *N*-methyl(thioacetohydroxamic acid) (**3**), using a Nicolet 5/DX FT spectrometer. NMR spectra were collected on a custom-built 200-MHz FT spectrometer. Visible–UV spectra were recorded on a Hewlett-Packard 8450A UV/vis spectrometer. Melting points were obtained in open capillaries with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the Analytical Laboratory, University of California, Berkeley.

Ligand Synthesis. 3-Hydroxy-*N*-methylthiobenzohydroxamic acid (**4**) was prepared from 3-(hydroxyethyl)thiobenzoate and *N*-methylhydroxylamine in 90% yield by literature procedures,[30] mp 96–97 °C. Anal. Calcd (found) for $C_8H_9NO_2S$: C, 52.44 (52.61); H, 4.95 (5.30); N, 7.65 (7.74); S, 17.50 (17.39). *N*-Methylthioacetohydroxamic acid (**3**) was prepared from ethyl dithioacetate[31] and *N*-methylhydroxylamine by a literature procedure,[31] mp −7 °C. Anal. Calcd (found) for C_3H_7NOS: C, 34.26 (34.18); H, 6.70 (6.45); N, 13.32 (13.23); S, 30.49 (30.40).

Synthesis of Metal Complexes. (a) Bis(*N*-methylthioacetohydroxamato)lead(II) (5). An aqueous solution of lead nitrate (0.66 g, 2.0 mmol) in 20 mL was added to a stirred aqueous solution of sodium *N*-methylthioacetohydroxamate (0.51 g, 4.0 mmol) in 40 mL. The mixture was stirred for 20 min and then heated to 80 °C. The solution was filtered while hot and allowed to crystallize by slow cooling. The pale

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Table II. Positional Parameters and their Estimated Standard Deviations for Compound **2**[a]

atom	x	y	z	B, Å^2
Pb	0	0.02280 (1)	$^1/_4$	2.837 (3)
S	0.90265 (5)	0.18476 (7)	0.39953 (9)	3.83 (2)
O	0.0762 (1)	0.0839 (2)	0.0616 (3)	3.72 (4)
N	0.1035 (1)	0.1838 (2)	0.0783 (3)	3.31 (5)
C1	0.1247 (3)	0.2209 (4)	−0.0770 (5)	5.88 (9)
C2	0.1135 (2)	0.2364 (2)	0.2213 (4)	3.03 (5)
C3	0.1430 (2)	0.3476 (2)	0.2230 (4)	3.26 (6)
C4	0.2171 (2)	0.3693 (3)	0.3030 (4)	3.81 (7)
C5	0.2454 (2)	0.4718 (3)	0.3012 (6)	4.86 (8)
C6	0.1992 (2)	0.5526 (3)	0.2211 (5)	5.31 (8)
C7	0.1258 (3)	0.5316 (3)	0.1476 (6)	5.8 (1)
C8	0.0968 (2)	0.4287 (3)	0.1484 (5)	4.87 (8)
H4	0.2484	0.3136	0.3588	5.0*
H5	0.2963	0.4867	0.3547	6.3*
H6	0.2187	0.6228	0.2173	6.9*
H7	0.0941	0.5878	0.0952	7.6*
H8	0.0454	0.4147	0.0976	6.3*
H1A	0.1114	0.1681	−0.1622	7.6*
H1B	0.0986	0.2854	−0.1130	7.6*
H1C	0.1777	0.2332	−0.0563	7.6*

[a] Starred atoms were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$, where a, b, and c are real cell parameters, and $B(i,j)$ are anisotropic β's.

greenish-yellow crystals were filtered, washed with a small amount of cold water and dried in vacuum over P_2O_5, mp 190–191 °C. Anal. Calcd (found) for $Pb(C_3H_6NOS)_2$: C, 17.34 (17.37); H, 2.91 (2.90); N, 6.74 (6.72).

(b) Bis(3-hydroxy-*N*-methylthiobenzohydroxamato)lead(II) (6). An aqueous solution of lead nitrate (0.66 g, 2.0 mmol) in 20 mL was added to a stirred aqueous solution of sodium 3-hydroxy-*N*-methylthiobenzohydroxamate (0.82 g, 4.0 mmol) in 30 mL. The mixture was stirred for 20 min and the pale yellow precipitate was filtered, washed with water, and dried in vacuum over P_2O_5. The complex was recrystallized from dimethylformamide (DMF)/H_2O, mp 210–211 °C. Anal. Calcd (found) for $Pb(C_8H_8NO_2S)_2$: C, 33.62 (33.93); H, 2.82 (3.12); N, 4.90 (5.37).

(c) 3,3′-(Ethylenedioxy)bis(*N*-methylthiobenzohydroxamato)lead(II) (7). This complex was prepared from lead nitrate and disodium 3,3′-(ethylenedioxy)bis(*N*-methylthiobenzohydroxamate) by using a procedure similar to that used for the synthesis of **6**, with a lead to ligand mole ratio of 1:1. The complex was purified by extraction into chloroform, followed by the evaporation of the solvent or precipitation of the complex with hexane, mp 195–196 °C. Anal. Calcd (found) for $Pb(C_{18}H_{18}N_2O_4S_2)$: C, 36.17 (35.44); H, 3.04 (3.08); N, 4.69 (4.39).

X-ray Crystallography. (a) Compound 2. Single crystals were obtained from chloroform/ethanol solution by slow evaporation. The space groups $C2/c$ or Cc were established from precession photography; the choice of $C2/c$ was subsequently confirmed by the structure analysis. Cell parameters and other crystallographic data are summarized in Table I. A redundant data set ($\mp h,k,\mp l$) was collected and averaged to give 2061 unique data, which were converted to structure factor amplitudes.[32,33] Inspection of the list of intensity standards showed a 7% decomposition and hence a decay correction was applied. Absorption correction was made by the use of ψ-scan data.[34] The correction factors ranged from 1.4 to 1.0, with an average of 1.15. The structure was solved by standard heavy-atom procedures and refined by full-matrix least-squares methods.[32] The phenyl hydrogen atoms were introduced as fixed atoms (C–H distance = 0.95 Å, bisecting the C–C–C angles), and the methyl hydrogens were introduced as rigid groups (C–H distance = 0.95 Å, H–C–H angle = 109.5°) centered on the methyl carbon, with a C–H bond trans to N–C(phenyl) bond. Full-matrix least-squares refinement with 106 variables, using the 1805 reflection with $(F_o)^2 > 3\sigma(F_o)^2$, led to convergence with $R = 0.017$, $R_w = 0.019$. The positional and thermal parameters of the atoms are listed in Table II. Values of F_o and F_c, general temperature factor expressions (B's), and root-mean-square amplitudes of vibrations are listed in supplementary Tables S1–S3, respectively.[35]

Table III. Positional Parameters and Their Estimated Standard Deviations for Compound **5**[a]

atom	x	y	z	B, Å^2
Pb	0.21091 (4)	0.34971 (4)	0.28644 (2)	2.184 (6)
S1	0.1964 (4)	0.3542 (4)	0.4358 (1)	3.92 (6)
S2	0.5222 (4)	0.1853 (3)	0.2964 (1)	3.04 (5)
O1	0.3439 (9)	0.6096 (9)	0.3415 (3)	2.9 (1)
O2	0.3768 (9)	0.4773 (8)	0.2002 (4)	3.1 (1)
N1	0.344 (1)	0.6593 (9)	0.4095 (4)	2.4 (1)
N2	0.501 (1)	0.3813 (9)	0.1793 (4)	2.2 (1)
C1	0.290 (2)	0.630 (2)	0.5309 (5)	4.6 (3)
C2	0.284 (1)	0.560 (1)	0.4555 (5)	2.8 (2)
C3	0.430 (2)	0.834 (1)	0.4238 (6)	3.6 (2)
C4	0.724 (2)	0.158 (2)	0.1912 (8)	5.4 (3)
C5	0.581 (1)	0.254 (1)	0.2171 (5)	2.5 (2)
H11	0.2412	0.5437	0.5584	6.0*
H12	0.4040	0.6524	0.5512	6.0*
H13	0.2263	0.7390	0.5298	6.0*
H31	0.4619	0.8806	0.3811	4.6*
H32	0.3546	0.9172	0.4413	4.6*
H33	0.5284	0.8199	0.4584	4.6*
H41	0.7680	0.0685	0.2244	6.8*
H42	0.6844	0.1029	0.1464	6.8*
H43	0.8114	0.2415	0.1853	6.8*
H61	0.4726	0.5396	0.0937	5.1*
H62	0.6610	0.4887	0.1193	5.1*
H63	0.5380	0.3493	0.0785	5.1*

[a] Starred atoms were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\mathrm{B}(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ where a, b, and c are real cell parameters, and $B(i,j)$ are anisotropic β's.

(b) Compound 5. Single crystals were obtained from aqueous solution by slow cooling. The space group $P2_1/n$ (an alternate setting of $P2_1/c$) was established from precession photography. Cell parameters and other crystallographic data are summarized in Table I. A unique data set ($h,k,\mp l$) was collected. Because of substantial decomposition, reflections with $h > 8$ were excluded. The remaining 2443 unique intensity data were converted to structure factor amplitudes.[32,33] Inspection of the list of intensity standards showed a maximum 40% decomposition (nearly isotropic), so a decay correction was applied. Absorption correction was made by the use of ψ-scan data, with a range of correction factors from 2.0 to 1.0, and an average of 1.2.[34] The structure was solved by standard heavy-atom procedures. The methyl hydrogens of the two methyl groups CH_3C and CH_3N were introduced in their idealized positions, as described for the earlier structure. Full-matrix least-squares refinement with 118 variables, using the 1924 reflections with $F^2 > 3\sigma F^2$ converged to $R = 0.041$, $R_w = 0.051$. The positional and thermal parameters of the atoms are listed in Table III. Values of F_o and F_c, general temperature factor expressions (B's) and root-mean-square amplitudes of vibrations are listed in supplementary Tables S4–S6, respectively.[35]

Results and Discussion

The IR spectra of the lead complexes of **5–7** are in general similar to those of the uncoordinated ligands, although some of the ligand bands disappear or change positions upon coordination. Several bands in the region 900–1600 cm^{-1} correspond to the thiohydroxamato group, three of which previously have been assigned to the N—C═S group;[36,37] these appear at 1566, 1259, and 1106 cm^{-1} in the spectrum of compound **3** and are shifted to 1551, 1237, and 1096 cm^{-1}, respectively, in the spectrum of the lead complex. The positions of these bands in compound **4** and its lead complex **6** are similar to those previously reported for *N*-methylthiobenzohydroxamic acid and its lead complex.[29] The IR spectra of **1** and its lead complex **7** are more complicated;

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(32) For details regarding data reduction and processing, scattering factor tables, and the program ORTEP, please refer to: Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

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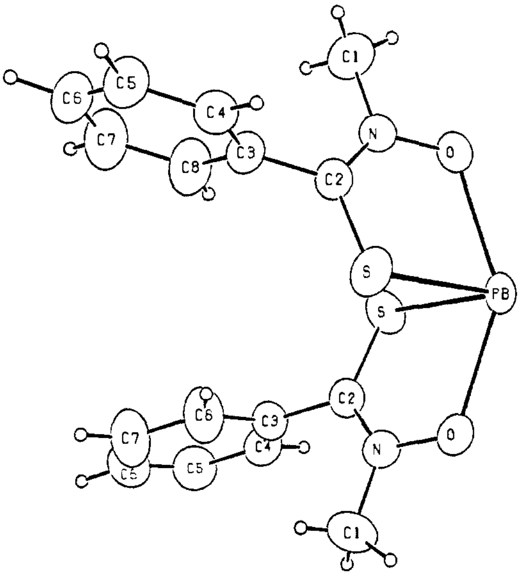
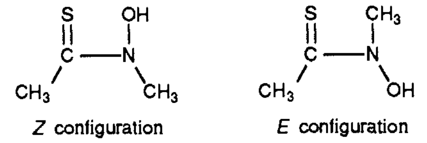


Figure 1. Perspective view of compound **2** with the numbering scheme of the non-hydrogen atoms. The crystallographic and molecular 2-fold axis is horizontal while the vertical axis is what would be the 3-fold axis of a trigonal-bipyramidal geometry. The non-hydrogen atoms are drawn at 50% probability contours of the thermal motion, while the hydrogen atoms have an arbitrary size. The vacant coordinate position to the right is interpreted as being occupied by the nonbonding electron pair of Pb^{2+}.

two of the three N—C=S bands appear at 1542 cm^{-1} and as a split band at 1310 and 1280 cm^{-1}; these are shifted to 1534 and 1289 cm^{-1}, respectively, in the spectrum of the lead complex. The third band, which appears at 1075 cm^{-1} in the spectrum of **1**, is tentatively assigned as the 1070-cm^{-1} band in the spectrum of the lead complex **7**.

The proton NMR spectra of the lead complexes are similar to those of the uncoordinated ligands. The NMR spectrum of **3** shows two singlets in $CDCl_3$ solution at δ 3.609 (NCH_3) and 2.568 (CCH_3); however, four singlets appear in the spectrum of **3** in $DMSO/D_2O$ at δ 3.721, 3.62 (NCH_3), and 2.539, 5.529 (CCH_3), indicating the presence of both the *Z* and *E* configurations in the more polar solvent:



Z configuration *E* configuration

The NMR spectrum of the lead complex **5** shows two singlets for the NCH_3 protons in DMSO solution at δ 3.332 and 3.388, indicating the presence of two geometric isomers or complexes in solution. Similarly the NMR spectrum of **2**, which shows one singlet at δ 3.514 (NCH_3) in $CDCl_3$,[29] shows two singlets at δ 3.338 and 3.404 in DMSO. The NMR spectrum of **1** shows one singlet at δ 3.556 (NCH_3) in DMSO solution, while its lead complex **7** shows two singlets for NCH_3 protons at δ 3.332 and 3.388 in DMSO solution. The former is similar to the NMR spectra of *N*-methylthiobenzohydroxamic acid and its lead complex **2**; the latter supports the assignment of two complexes, as determined from the IR spectra of the complexes.

The UV/vis spectrum of **3** shows two maxima in the region of 200–280 nm, which are assigned to n → π* transitions;[37,38] the positions of these bands change with change in polarity of the solvent: λ, nm (log ε, M^{-1} cm^{-1}) in water 265 (4.08), 213 (3.70); and in acetonitrile 269 (4.08), 212 (3.70). The spectrum of the lead complex **5** is even more sensitive to the solvent; both the maxima and extinction coefficients change: λ, nm (log ε) in water 265 (4.23), and nonresolved shoulder at 215 (4.28); and in acetonitrile 275 (3.93) and a shoulder at 228 (4.30). These changes in spectra are assigned to the presence of two isomers or complexes in solution, which vary in proportion depending upon the polarity of the solvent used. The UV/vis spectra of other complexes were not obtained due to the lack of solubility in appropriate solvents.

Table IV. Intermolecular Distances (Å) and Angles (deg) for Compound **2**[a]

	Distances		
Pb–S	2.7462 (8)	C_3–C_4	1.389 (4)
Pb–O	2.383 (2)	C_3–C_8	1.372 (5)
Pb–O*	2.935 (2)	C_4–C_5	1.382 (5)
S–C_2	1.694 (3)	C_5–C_6	1.385 (5)
N–C_1	1.464 (4)	C_6–C_7	1.363 (7)
N–C_2	1.312 (4)	C_7–C_8	1.391 (6)
C_2–C_3	1.490 (4)		
	Angles		
S–Pb–O	70.46 (5)	O–N–C_1	111.4 (3)
S–Pb–S	84.83 (4)	C_2–N–C_1	125.9 (3)
S–Pb–O′	81.97 (6)	C_2–C_3–C_4	119.7 (2)
O–Pb–O′	142.53 (10)	C_2–C_3–C_8	120.2 (3)
O*–Pb–O*′	125.85 (5)	C_4–C_3–C_8	120.0 (3)
Pb–O–N	119.0 (2)	C_3–C_4–C_5	120.0 (3)
Pb–S–C_2	97.4 (1)	C_4–C_5–C_6	119.6 (4)
S–C_2–N	123.2 (2)	C_5–C_6–C_7	120.1 (4)
S–C_2–C_3	119.4 (2)	C_6–C_7–C_8	120.7 (4)
N–C_2–C_3	117.4 (3)	C_3–C_8–C_7	119.5 (4)
O–N–C_2	122.5 (3)		
	Dihedral Angles		
(S,S′,O)/(S,S′,O′)	59.0		
(Pb,S,O)/(Pb,S′,O′)	84.1		
(Pb,S,S′)/(Pb,O,O′)	81.2		

[a] A 2-fold related atom is denoted by (e.g.) S′; an atom from an adjacent molecule is denoted (e.g.) by O*.

Table V. Intermolecular Distances (Å) and Angles (deg) for Compound **5**

	Distances		
Pb–S_1	2.859 (2)	O_2–N_2	1.331 (8)
Pb–S_2	2.744 (2)	N_2–C_2	1.287 (10)
Pb–O_1	2.371 (5)	N_1–C_3	1.479 (9)
Pb–O_2	2.448 (5)	N_2–C_5	1.295 (9)
Pb–S*	3.358 (2)	N_2–C_6	1.463 (9)
Pb–O_1*	2.996 (5)	C_1–C_2	1.520 (10)
Pb–O_2*	2.880 (5)	C_4–C_5	1.493 (12)
S_1–C_2	1.705 (8)		
S_2–C_5	1.723 (7)		
O_1–N_1	1.345 (7)		
	Angles		
S_1–Pb–O_1	68.6 (1)	S_1–C_2–N_1	123.2 (6)
S_2–Pb–O_2	69.3 (1)	S_1–C_2–C_1	117.8 (6)
S_1–Pb–S_2	96.26 (7)	N_1–C_2–C_1	119.0 (7)
S_1–Pb–O_2	140.17 (14)	S_2–C_5–N_2	121.8 (6)
S_2–Pb–O_1	89.77 (15)	S_2–C_5–C_4	118.0 (6)
O_1–Pb–O_2	74.27 (17)	N_2–C_5–C_4	120.2 (7)
O_1*–Pb–O_2*	59.33 (14)	O_1–N_1–C_2	123.3 (6)
O_1*–Pb–S*	93.52 (10)	O_1–N_1–C_3	110.5 (6)
O_2*–Pb–S_2*	129.33 (12)	C_2–N_1–C_3	126.0 (6)
Pb–S_1–C_2	98.7 (2)	O_2–N_2–C_5	123.6 (6)
Pb–S_2–C_5	99.8 (3)	O_2–N_2–C_6	112.4 (6)
Pb–O_1–N_1	125.6 (4)	C_5–N_2–C_6	123.9 (6)
Pb–O_2–N_2	119.6 (4)		
	Dihedral Angles		
(S_1,S_2,O_1)/(O_1,O_2,S_2)	43.1		
(Pb,S_1,S_2)/(Pb,O_1,O_2)	51.7		
(Pb,O_1,S_2)/(Pb,O_2,S_1)	87.4		

[a] Atoms from adjacent molecules are denoted (e.g.) by O*.

X-ray Crystallography. Both complexes **2** and **5** exist as essentially monomeric species in the solid state; the minimum Pb–Pb distance is 4.09 Å in **2** and 4.05 Å in **5**. However, in both complexes the lead ion is weakly coordinated by additional ligands. The Pb^{2+} in **2** is weakly complexed by two additional oxygen atoms from neighboring molecules, while in **5**, coordination is from three weak bonds to two oxygen atoms and one sulfur atom from neighboring molecules. Figures 1 and 2 show perspective views

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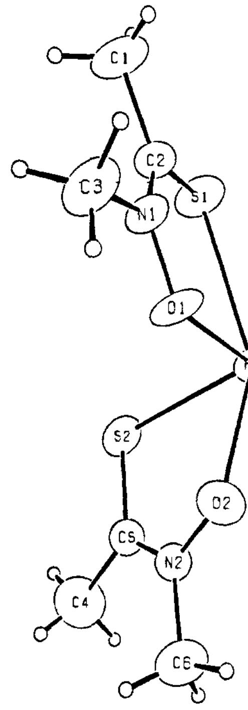

Figure 2. Perspective view of compound **5** with the numbering scheme of the non-hydrogen atoms. The horizontal axis is the approximate 2-fold axis of a trigonal-bipyramidal geometry as described for compound **2**. Similarly, the vertical axis is what would be the idealized 3-fold axis. The vacant coordination position to the right is interpreted as being occupied by the nonbonding electron pair of Pb^{2+}. The non-hydrogen atoms are drawn at 50% probability contours of the thermal motion, while the hydrogen atoms have an arbitrary size.

of complexes **2** and **5**, respectively. Table IV gives selected bond lengths, bond angles, and dihedral angles for **2**, and Table V gives the corresponding parameters for **5**. Bond distances and angles within the thiohydroxamato rings are similar to those observed for other thiohydroxamato complexes;[39,40] however, the large size of Pb^{2+} makes the bite angle (S–Pb–O) for these lead complexes (~70°) smaller than the bite angles for transition-metal complexes.[39] They are instead similar to the bite angle in the complex of hafnium(IV).[40]

The Pb–S distance of 2.746 (2) Å in **2** is slightly longer than Pb–S bond distances (2.55–2.72 Å) reported for lead complexes of mercaptan-containing ligands[41–45] (where the sulfur donor atom carries a full negative formal charge) and is comparable or slightly shorter than Pb–S distances reported for bis(*O,O'*-diisopropylphosphorodithionato)lead(II)[46] (2.76 and 2.77 Å), bis(ethylxanthinato)lead(II)[47] (2.79 Å), and bis(*N,N*-dimethyldithiocarbamato)lead(II)[48] (2.779 and 2.873 Å). Two Pb–S bond distances are observed for **5**, 2.744 and 2.859 Å, the shorter (equatorial) distance is comparable to the Pb–S distance in **2**, while the axial Pb–S distance is significantly longer. Similarly, the shorter equatorial Pb–O bond distance of 2.371 Å in **5** is less than the Pb–O distance of 2.444 Å reported for bis(D-penicillaminato)lead(II),[45] while the axial Pb–O bond distance of 2.448 Å in **5** is comparable.

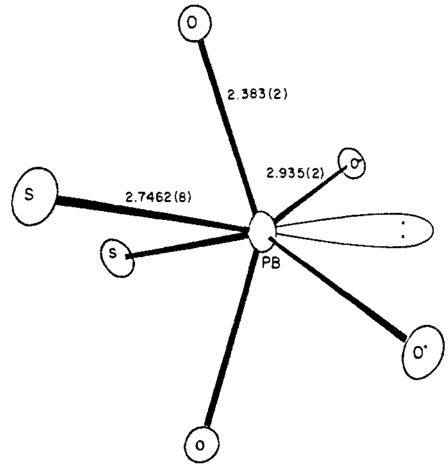

Figure 3. Perspective view of the coordination geometry of Pb^{2+} in compound **2**, which includes the "outer-sphere" ligands. Starred atoms are from neighboring molecules.

The primary coordination geometry of both **2** and **5** is clearly five-coordinate, with the fifth coordinate site occupied by the lone electron pair of Pb^{2+}. Both structures can be interpreted in terms of distorted trigonal-bipyramidal geometries, although neither conforms to the C_{2v} symmetry of an intermediate on the reaction path from a square pyramid to a trigonal bipyramid.[49] Compound **2** has crystallographically imposed 2-fold symmetry, with the lone pair and two sulfur atoms in the equatorial plane. The view in Figure 1 shows the stereochemical effect of the lone pair, which lies along the horizontal 2-fold axis to the right of the lead ion. The following parameters (with the corresponding values for an idealized[49] trigonal pyramid in parentheses) show the relationship to the trigonal bipyramid (TBP): angles O–Pb–O' 142.5 (180)°, S–Pb–S' 84.8 (120)°, S–Pb–O 70.5 (90)°, and S–Pb–O' 82.0 (90)°; dihedral angles (S,S',O)/(S,S',O') 59.0 (53.1), P,S,O)/(Pb,S',O-) 84.1 (60), and (Pb,S,S')/(Pb,O,O') 81.2 (90)°. Since the lone pair repels the ligand atoms, the O–Pb–O angle is nearly 40° smaller than the TBP value of 180°. This also results in the 35° compression of the S–Pb–S' bond angle. The angle between the equatorial plane of the TBP and the 3-fold axis remains 90° for the C_{2v} symmetry intermediates on the reaction path to the square pyramid. The corresponding dihedral angle (Pb,S,S')/(Pb,O,O') is 81.2° in **2**, which displays the distortion from C_{2v} to C_2 symmetry (which can be viewed as a twist of one plane relative to the other around the C_2 axis). This distortion of the structure, which is due to the small bite angle of the thiohydroxamate group, generates a marked polarity relative to a tetrahedral coordination. This in turn results in further weak or "outer-sphere" coordination by two symmetry-related oxygen atoms of adjacent molecules with a Pb–O* distance of 2.935 (2) Å and a O*–Pb–O*' angle of 125.85 (5)°. This complete coordination environment, including a representation of the lone pair, is shown in Figure 3.

Compound **5** is a geometric isomer of the idealized structure of **2** in that, while based on a TBP geometry, the positions of one of the thiohydroxamate groups has the S and O atoms interchanged such that the complex has no molecular symmetry and the two thiohydroxamate groups are inequivalent. As shown in Figure 2, the axial ligand atoms are S$_1$ and O$_2$. The equatorial positions are occupied by atoms O$_1$ and S$_2$ and by the lone electron pair, which occupies the vacant coordination site to the right of the lead ion. The stereochemical effect of the lone-pair/ligand repulsion can be seen in the longer axial, relative to equatorial, bond lengths of 2.86 versus 2.74 Å for Pb–S and 2.45 relative to 2.37 Å for Pb–O. Consistent with the Gillespie–Nyholm theory,[50] the closer axial ligands interact with the lone pair more than the

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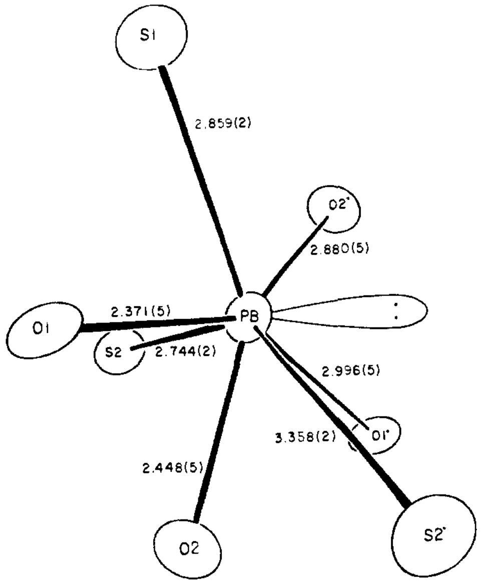

Figure 4. Perspective view of the coordination geometry of Pb^{2+} in compound **5**, which includes the "outer-sphere" ligands. Starred atoms are from neighboring molecules.

most distant equatorial ligands. The angle parameters also show the resultant distortion from a TBP geometry (in parentheses): angles S_1–Pb–O_2 140.2 (180)°, O_1–Pb–S_2 89.8 (120)°, S_1–Pb–S_2 96.3 (90)°, and O_1–Pb–O_2 74.3 (90)°; dihedral angles (S_1,S_2,O_1)/(O_1,O_2,S_2) 43.1 (53.1)°, (Pb,S_1,S_2)/(Pb,O_1,O_2) 51.7 (60)°, and (Pb,O_1,S_2)/(Pb,O_2,S_1) 87.4 (90)°. As in **2**, the lone pair causes the axial–axial angle to decrease nearly 40° from linearity. The larger sulfur atoms show a resultant S–Pb–S inter-ring bond angle that is greater than the corresponding O–Pb–O angle. However, as measured by the angle between the equatorial plane (Pb,O_1,S_2) and the axial plane (Pb,S_1,O_2) of 87.4°, there is less of a twist from a C_{2v} intermediate geometry than in **2**, although the thiohydroxamate groups still span the axial and equatorial positions. There is also a difference between **5** and **2** in the outer-sphere coordination. As shown in Figure 4, there is additional weak coordination from atoms S and O_1 and O_2 of neighboring molecules.

Given their solubility, it is probable that these complexes are monomeric species in solution and may exist in both geometries described for **2** and **5** (ignoring the weak Pb–O and Pb–S bonds), which would explain the change in the UV/vis spectra of these complexes with change in polarity of the solvent. This may also explain the presence of two singlets for the NCH_3 protons in the NMR spectra of these complexes in polar solvents. If so, this represents a surprisingly slow rate of isomerization.

In conclusion, lead complexes with mono(thiohydroxamato) and bis(thiohydroxamato) ligands have been prepared and characterized. The structures of compounds **2** and **5**, determined by X-ray crystallography, will serve as models for the design of lead-chelating agents incorporating thiohydroxamato groups.

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Supplementary Material Available: Listings of general temperature factor expressions (*B*'s) and root-mean-square amplitudes of vibration (Tables S2, S3, S5, and S6) (4 pages); observed and calculated structure factors (Tables S1 and S4) (27 pages). Ordering information is given on any current masthead page.

Isolation and Structural Characterization of the Copper–Barium–Alkoxide Cluster $Ba_2Cu_2(OR)_4(acac)_4{\cdot}2HOR$ ($R = CH_2CH_2OCH_3$) from Precursor Solutions to $YBa_2Cu_3O_7$ Thin Films

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Abstract: Attempts to identify intermediates in a solution route to thin films of the high-temperature superconductor $YBa_2Cu_3O_7$ have led to the isolation of the mixed-metal cluster $Ba_2Cu_2(OR)_4(acac)_4{\cdot}2HOR$ ($R = CH_2CH_2OCH_3$) (**1**). This compound, which is the first example of a molecular barium–copper cluster, was isolated from the reaction of the copper dimer $[(acac)Cu(OCH_2CH_2OCH_3)]_2$ with barium 2-methoxyethoxide, the first stage in the preparation of the thin-film precursor solution. Crystallographic data for **1** are as follows: formula = $Ba_2Cu_2O_{20}C_{38}H_{72}$, FW = 1250.5 g/mol, D_x = 1.57 g/cm^3, space group = $P\bar{1}$, a = 10.797 (3) Å, b = 11.269 (1) Å, c = 12.109 (1) Å, α = 106.18 (1)°, β = 100.93 (2)°, γ = 102.98 (2)°, Z = 1, R = 0.031 for 4059 reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 50°$, μ = 23.5 cm^{-1}, $\lambda(\mathrm{Mo}\,K\alpha_1)$ = 0.70930, $F(000)$ = 630. Data were collected at 23 °C. The metals are arranged in a rhomboid with triply bridging alkoxide oxygens above and below the two triangular planes defined by two barium atoms and one copper atom. Each metal atom is also bound to an acac ligand, and the barium is further coordinated by the methoxy oxygen of the triply bridging alkoxides and a 2-methoxyethanol. Thin films prepared from this route showed superconducting transition temperatures of 85 K, only small amounts of impurity phases by X-ray powder diffraction, and ≤0.1 atom % carbon as determined by nuclear reaction analysis.

Thin films of the new high-temperature superconductors, e.g., $REBa_2Cu_3O_7$, are needed for a range of technological applications. While several methods such as laser ablation, chemical vapor deposition, and electron beam evaporation are available for depositing these ceramic materials as thin films,[1-5] they require specialized equipment or facilities. In contrast, routes based on

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