Amide Group Coordination to the Pb^{2+} Ion

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The binary and ternary (2,2′-bipyridine) complexes of dipositive lead formed by *N*-carbonyl and *N*-sulfonyl amino acids, which are ligands containing the peptide and the sulfonamide group, respectively, were investigated in aqueous solution by NMR and differential pulse polarography, and some were also characterized crystallographically. *N*-Tosylglycine, *N*-tosyl-β-alanine, and *N*-benzoylglycine behave as simple carboxylate ligands at acid pH, while around neutrality they switch to dianionic N,O-bidentate chelating ligands due to the involvement of the deprotonated amide nitrogen as an additional donor site. The same coordination behavior is maintained in the presence of 2,2′-bipyridine. The binary and ternary species formed in solution, and their stability constants were determined and compared with those of the homologous complexes of Pd^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}. The Pb^{2+} ion is the only dipositive metal which is effective in promoting peptide nitrogen deprotonation in benzoylglycine. The molecular structures of [Pb(*N*-tosylglycinato-*N*,*O*)(H_2O)] (**1**), [Pb(*N*-benzoylglycinato-*O*)$_2$(H_2O)$_2$]·$2H_2O$ (**2**), and [Pb(*N*-tosylglycinato-*O*)$_2$(bpy)] (**3**) were determined by X-ray crystallography (*O* and *N*,*O* refer to the ligands binding as carboxylates and as N,O-chelating dianions, respectively). These compounds are all polymeric with six- to eight-coordinate metals showing distorted coordination geometries indicative of a stereochemically active metal lone pair. Polymerization is invariably determined by a bidentate chelate carboxylate group with one oxygen bridging between two metals, and in **2** and **3** it occurs through the formation of chains of Pb_2O_2 square-planar rings. The binding set in **1**, involving a deprotonated amide nitrogen and a sulfonic oxygen, is unprecedented for the Pb^{2+} ion. This work provides new information on the solution and solid state chemistry of dipositive lead with ligands of biological interest, a research area that has received little attention in the past, although it is of great relevance for understanding the mechanisms of metal toxicity.

Introduction

Toxic metal ions of environmental origin may specifically bind to proteins, nucleic acids, and small metabolites in living organisms, causing either alteration or loss of the biological function, and may perturb the homeostatic control of essential metals to which they are related in terms of ionic radius and coordination chemistry.[1−3] The Pb^{2+} ion, a large-scale environmental pollutant, is known to obstruct heme biosynthesis, to inhibit several zinc enzymes such as carbonic anhydrase, acetylcholine esterase, and acid phosphatases, to interact with nucleic acids and transfer RNA affecting protein synthesis,[1,4−7] and to accumulate, also exchanging with Ca^{2+}, in the apatite structure of the bone. One of the determinants of Pb^{2+} toxicity is likely the borderline "hard-soft"character.[8] Lacking a marked donor atom preference, this metal ion may fit in the binding sites of several biomolecules and adapt to different coordination geometries (with the large ionic radius as a limiting factor). However, very little is known at present about specific interactions at a molecular level. Moreover, although the coordination chemistry of Pb^{2+} [1,9] is a key factor in determining the biological effects of this metal, only a relatively few studies have appeared concerning Pb^{2+} interactions with simple biomolecules. These include studies of amino acids, small peptides, and nucleotides for which stability constants of the complexes in aqueous solution have been reported.[5−7,10−14] Also, the X-ray structures of Pb^{2+} complexes with ligands containing donor groups of biological relevance have never been thoroughly investigated.

Metal coordination of the CONH group in small peptides may occur through either the carbonyl oxygen or the deprotonated amide nitrogen, provided the metal is initially coordinated by the terminal amino group.[15] Closure of the five-membered

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chelate ring involving the deprotonated peptide nitrogen provides a strong metal binding and occurs at acidic or slightly alkaline pH values *only* with Pd^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}.[15] *N*-Sulfonyl amino acids are low molecular weight ligands which were found to reproduce this coordination behavior and selectivity toward dipositive metals. In fact, at pH values close to neutrality, these compounds were shown to bind as dianions, i.e. through one carboxylate oxygen (acting as the primary binding site) and the deprotonated amide nitrogen, only to a few metals, namely Pd^{2+} and Cu^{2+} (like peptides) and also Cd^{2+}.[16-19] Hence they were used as models to probe for the factors determining metal effectiveness in promoting amide nitrogen deprotonation. In ternary 2,2′-bipyridine systems, the additional heteroaromatic ligand was found to favor Cu^{2+} and Cd^{2+}substitution for the sulfonamide nitrogen-bound hydrogen and to induce the binding of the these ligands as N,O-dianions also to the Zn^{2+} ion.[20-23]

In this paper, we describe the binding of the *N*-sulfonyl- and *N*-carbonyl amino acids to the Pb^{2+} ion, focusing on the structural characterization of the crystalline compounds and on the determination of the nature and stability of the species formed in aqueous solution in the pH range 4−10. Our goal is to characterize the interaction of the Pb^{2+} ion with the amide bond and to compare it with that of the other metals of biological interest previously investigated.[16-23] We found that the Pb^{2+} ion is effective in promoting peptide and sulfonamide nitrogen deprotonation in these ligands. Polymeric compounds with distorted coordination geometries indicative of a stereochemically active metal lone pair were invariably obtained in the solid state. We believe that this study provides new information on the metallobiochemistry of lead, which at present is still scarcely explored.

Experimental Section

Materials. *N*-Tosylglycine (tsgly), *N*-tosyl-*β*-alanine (ts*β*ala), and *N*-benzoylglycine (bzgly) (C. Erba) were twice recrystallized before use. Nanopure water was used throughout. Stock solutions of $Pb(NO_3)_2$ were standardized with EDTA. *N*-Tosylglycine ^{13}C-enriched at the carboxylic carbon was obtained by reacting the ^{13}C-enriched amino acid with tosyl chloride.[24]

Preparation of the Complexes. Pb(tsgly-*N,O*)·H$_2$O (1). (In what follows, *O* and *N,O* refer to the ligands binding as carboxylates and as N,O-chelating dianions, respectively.) A 20 mL portion of an aqueous $Pb(NO_3)_2$ solution (0.025 M) was added under continuous stirring to 30 mL of an aqueous tsgly solution (0.017 M) at pH 6.5. The pH was kept constant by adding small amounts of concentrated aqueous NaOH. After 12 h at 40 °C, white crystals appeared. They were collected by vacuum filtration and washed with ethanol. Anal. Calcd for $C_9H_{11}NO_5PbS$: C, 23.87; H, 2.45; N, 3.10. Found: C, 23.84; H, 2.45; N, 3.00. Yield = 20%.

Pb(tsgly-*O*)$_2$. A 20 mL portion of aqueous lead acetate (0.02 M) was added to 40 mL of ethanolic or aqueous tsgly (0.02 M), and the pH was adjusted to 5 with NaOH. White platelets separated from the mixture after a few hours at room temperature. Anal. Calcd for $C_{18}H_{20}N_2O_8PbS_2$: C, 32.56; H, 3.04; N, 4.22. Found: C, 32.47; H, 3.14; N, 4.17. Yield = 70%.

Pb(bzgly-*O*)$_2$·4H$_2$O (2). The compound was prepared as described above for the corresponding species with tsgly. Separation of the crystals was achieved in the pH range 4.5−6.3. The crystals were dried on filter paper. Anal. Calcd for $C_{18}H_{24}N_2O_{10}Pb$: C, 33.99; H, 3.81; N, 4.41. Found: C, 33.13; H, 3.95; N, 4.24. Yield = 70%.

Pb(ts*β*ala-*O*)$_2$·2H$_2$O. The compound was prepared as described above for the corresponding species with tsgly and bzgly. Separation of the crystals was achieved in the pH range 4.5−6.7. At higher pH values, metal hydroxide precipitation occurred. Anal. Calcd for $C_{20}H_{28}N_2O_{10}PbS_2$: C, 32.99; H, 3.88; N, 3.85. Found: C, 33.47; H, 3.62; N, 3.86. Yield = 75%.

Pb(tsgly-*O*)$_2$(bpy) (3). A 20 mL quantity of a methanolic solution of bpy (0.025 M) was added to 30 mL of aqueous tsgly (0.017 M) at pH 6. A 20 mL solution of aqueous $Pb(NO_3)_2$ was then added dropwise to the resulting solution, adjusting the pH to 6 with NaOH. After a few days at room temperature, poor crystals of the binary species **1** appeared together with well-formed crystals of formula Pb(tsgly-*O*)$_2$(bpy). The solid was filtered off and washed with ethanol. The same compound was also obtained using a Pb^{2+}:tsgly molar ratio of 1:2. Anal. Calcd for $C_{28}H_{28}N_4O_8PbS_2$: C, 40.99; H, 3.43; N, 6.84. Found: C, 41.05; H, 3.41; N, 6.82. Yield = 40%.

Pb(ts*β*ala-*O*)$_2$(bpy). This compound was prepared with the procedure described above for the analogous species with tsgly. Separation of the solid complex was achieved in the pH range 4.5−6.5. Anal. Calcd for $C_{30}H_{32}N_4O_8PbS_2$: C, 42.47; H, 3.81; N, 6.61. Found: C, 42.61; H, 3.78; N, 6.66. Yield = 80%.

Polarography. Investigation of the binary systems was carried out on 1×10^{-4} M $Pb(NO_3)_2$ solutions with ligand-to-metal molar ratios in the range 2:1 to 20:1. The same metal ion concentration was used for the ternary (bpy) systems, with metal:bpy:ligand molar ratios from 1:1:2 to 1:1:20. Sodium nitrate was used as the base electrolyte, and the ionic strength was kept constant ($I = 0.1$ M). The pH of the solutions was adjusted by adding small amounts of concentrated aqueous HNO_3 or NaOH. Polarographic and differential pulse polarography (DPP) measurements were carried out with an Amel 472 Multipolarograph at 25 ± 0.1 °C using a scan rate of 2 mV s^{-1} and a pulse height of 35 mV. A saturated calomel electrode (SCE) was used as the reference and a platinum sheet as the counter electrode. All $E_{1/2}$ values were calculated according to the Parry−Osteryoung equation[25] and referred to the SCE. Quasi-reversible reduction processes were invariably observed for binary and ternary systems. The reversible $E_{1/2}$ values were determined according to Matsuda and Ayabe.[26] A Jenway 3045 ion analyzer equipped with an Ingold HA 405-60-K1 pH combination electrode was used for pH measurements.

Spectroscopy. ^1H and ^{13}C NMR spectra were obtained on a Bruker AMX-400 spectrometer operating at 400.13 and 100.30 MHz, respectively. Typical acquisition parameters were as follows. ^1H NMR: spectral bandwidth, 5 kHz; pulse width, 6.5 μs (90° pulse); pulse delay, 4 s; number of scans collected, 256−512. ^{13}C NMR: spectral bandwidth, 10 kHz; pulse width, 9 μs (90° pulse); pulse delay, 2 s; number of scans collected, 2000. Spectra were run on aqueous (D_2O) millimolar solutions of the crystalline complexes at 27 ± 0.1 °C and are referenced to tetramethylsilane. In the proton spectra the residual HDO peak was suppressed by a presaturation pulse from the decoupler. The pH was adjusted by adding small amounts of concentrated NaOH or $HClO_4$. pH-meter readings (pD values) are reported throughout the paper. Infrared spectra were recorded with a Perkin-Elmer FT-IR 1600 instrument as KBr pellets in the spectral range 4000−400 cm^{-1}.

X-ray Crystallography. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature (293 K). Crystal data and details of the data collection are listed in Table 1 and are available as Supporting Information. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction

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Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds

	$[Pb(tsgly\text{-}N,O)(H_2O)]$	$[Pb(bzgly\text{-}O)_2(H_2O)_2]\cdot 2H_2O$	$[Pb(tsgly\text{-}O)_2(bpy)]$
compd no.	**1**	**2**	**3**
empirical formula	$C_9H_{11}NO_5PbS$	$C_{18}H_{24}N_2O_{10}Pb$	$C_{28}H_{28}N_4O_8PbS_2$
M	452.45	635.59	819.87
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/a$	$Pccn$	$P\bar{1}$
a/Å	11.63(1)	40.16(2)	6.920(6)
b/Å	7.672(5)	6.847(4)	11.139(2)
c/Å	13.316(3)	8.255(1)	19.756(4)
α/deg	90	90	97.14(2)
β/deg	98.16(4)	90	96.77(4)
γ/deg	90	90	98.20(3)
V/Å^3	1176.1(8)	2269(1)	1481(1)
Z	4	4	2
D_c, D_m/g cm^{-3}	2.55, 2.40	1.86, 1.90	1.84, 1.90
μ/cm^{-1}	146.3	75.4	59.3
av transm factor	0.72	0.66	0.93
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.035	0.067	0.025
$R' = [\sum w(\Delta F^2)/\sum wF_o^2]^{1/2}$	0.033	0.074	0.025

based on a ψ scan[27] was applied. The structures were solved by conventional Patterson and Fourier techniques and refined with full-matrix least-squares calculations with $\Sigma w\,(|F_o| - |F_c|)^2$ being minimized. All non-hydrogen atoms were refined anisotropically, except four carbon atoms of the phenyl ring in **1**, which were found to be statistically distributed over two positions (A, B) and which were isotropically refined with site occupation factors of 0.5. For **2** and **3**, the hydrogen atoms, except those of water molecules, were located from the difference Fourier maps. They were introduced in the subsequent refinements as fixed atoms with isotropic thermal parameters 1.0 Å higher than those of the atoms to which they were bound. The hydrogen atoms of complex **1** were ignored. Unit weight was adopted in the refinement procedure of **1** and **3**, while for **2** the weighting scheme was $w = 3.5301/(\sigma^2(F_o) + 0.01305F_o^2)$. Complex neutral-atom scattering factors[28] were used throughout. All calculations were carried out on an IBM 486/sx personal computer with the CRYSRULER[29] crystallographic package. Final fractional coordinates are available as Supporting Information.

Table 2. Logarithms of the Overall Stability Constants, β,[a] Determined in 0.1 M $NaNO_3$ at 298 K for Binary and Ternary (bpy) Pb^{2+} Complexes with *N*-Sulfonyl and *N*-Carbonyl Amino Acids

	L		
species	tsgly	tsβala	bzgly
$[PbHL]^+$	1.08	1.21	1.09
$[Pb(HL)_2]$[b]	2.03	2.13	2.06
$[PbL]$	6.43	6.50	6.70[c]
$[Pb(bpy)(HL)_2]$[b,d]	5.03	5.11	5.06
$[Pb(bpy)L]$[d]	9.11	9.21	9.51[c]

[a] The overall stability constants are relative to the equilibria $Pb^{2+} + n HL^-$ (or L^{2-}) = $[Pb(HL)_n]^{2-n}$ (or $[PbL_n]^{2-2n}$) for the binary complexes, and to the analogous equilibria for the ternary bpy species. Estimated standard deviation for log β is 0.07. [b] Observed only for ligand-to-metal molar ratios greater than 8:1. [c] Value obtained by assuming a pK_{NH} of 15 for uncomplexed bzgly (see text). [d] Value obtained by using a log β value of 2.9 for $[Pb(bpy)]^{2+}$.[33]

Results

Polarography. For all binary systems, only one quasi-reversible, two-electron, and diffusion-controlled reduction wave (wave I_b) is observed in the pH range 2.5−5.8. In particular, up to pH 4 the $E_{1/2}$ value is independent of ligand concentration and corresponds to that of the solvated Pb^{2+} ion. At higher pH the $E_{1/2}$ value moves toward more negative values with increasing ligand concentration. Above pH 5.8 a second quasi-reversible and bielectronic wave (wave II_b) appears, whose $E_{1/2}$ depends upon ligand concentration and, above pH 10, is also pH dependent. The two reduction waves coexist in the pH range 5.8−7.5, and the sum of their diffusion current is nearly constant. The current of wave II_b decreases above pH 10 due to metal hydroxide precipitation. *N*-Sulfonyl amino acids are known to bind to a number of metal ions acting either as simple carboxylate ligands at acid pH or as N,O-bidentate ligands through one carboxylate oxygen and the deprotonated amide nitrogen at higher pH values.[16−19] Therefore, waves I_b and II_b most probably correspond to the reduction of the above two types of complexes, respectively. This is confirmed by X-ray crystallography, which indicates that tsgly acts as a dianion in the complex which precipitates above pH 6 (see below). The overall stability constants (β) of the above low- and high-pH complexes, defined as

$$\beta_{Pb(HL)_n} = \frac{[Pb(HL)_n]}{[Pb][HL]^n} \quad \text{and} \quad \beta_{PbL_n} = \frac{[PbL_n]}{[Pb][L]^n}$$

respectively, where L is the fully deprotonated (dianionic) ligand (charges are omitted for clarity), were obtained with the DeFord−Hume method[30] and are listed in Table 2. Selection of the species to be included in the equilibrium calculations was based on the Lingane plots[31] which, for a given reduction wave at a given pH, yield the number of ligands bound to the metal in the prevailing species. The β values for the carboxylate species were determined between pH 6.3 and 7.5 (at these pH values the uncomplexed ligand in solution is the carboxylate monoanion) by following the change in $E_{1/2}$ ($\Delta E_{1/2}$) of wave I_b with ligand concentration. Those for the high-pH, nitrogen-deprotonated, complexes were calculated from $\Delta E_{1/2}$ values vs ligand concentration for wave II_b at pH values from 7.5 to 9, by using pK_{NH} values of 11.4 and 11.2 for free tsgly and tsβala.[21] For bzgly, for which an experimental pK_{NH} value is not available, the β values listed in Table 2 were calculated using a pK_{NH} of 15, which is that determined for the peptide group from equilibrium measurements and indirect kinetic methods for closely related molecules and is the pK_{NH} value assumed for the prototypic amide group in small peptides.[15] An uncertainty of ±1 unit in the above pK_{NH} value causes an uncertainty of ±0.5 unit in the β values of the binary and ternary complexes of the dianionic ligand. The species distribution

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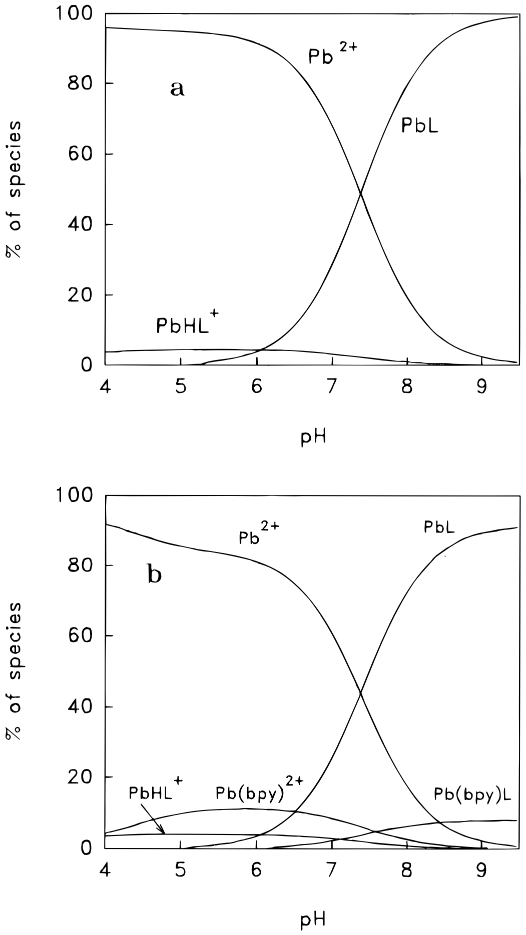

Figure 1. Species distribution curves for (a) the binary Pb−tsgly system and (b) the ternary Pb−tsgly−bpy system, with molar ratios of 1:20 and 1:20:1, respectively. $[Pb^{2+}] = 2 \times 10^{-4}$ M.

curves as a function of pH for tsgly, taken as a representative system, are reported in Figure 1a.

The ternary 2,2′-bipyridine systems show a peculiar polarographic behavior. At acid pH values a single wave is still observed (wave I_t), which shows $E_{1/2}$ values and overall electrochemical properties very similar to those of wave I_b. Two new quasi-reversible and bielectronic waves, wave II_t and wave III_t, appear simultaneously above pH 6. The former is nearly identical to wave II_b in the binary systems, while the latter falls at more negative $E_{1/2}$ values. We assign wave I_t to the reduction of binary and ternary carboxylate species and waves II_t and III_t to the reduction of binary and ternary nitrogen-deprotonated complexes, respectively. This equilibrium between binary and ternary species over the entire pH range investigated provides the best fit to the experimental data. The overall stability constants for the ternary complexes, still selected on the basis of Lingane plots, were calculated according to Shaap and McMasters[32] using a log β value of 2.9 for $[Pb(bpy)]^{2+}$ [33] and are collected in Table 2. The distribution curves as a function of pH for the ternary Pb−tsgly−bpy system are shown in Figure 1b.

NMR Spectroscopy. The pD dependence of the chemical shift of the ^1H NMR methylene peak(s) of tsgly, bzgly, and tsβala for the free ligands and for binary and ternary (bpy) Pb^{2+} systems are reported in Figures 2a, 3, and 4, respectively. In all cases, no additional resonances were observed in the presence of the metal in the pH range investigated, a result of the fast exchange of the amino acid between free and metal-bound states on the NMR time scale. pK_a values of 3.9, 3.8, and 4.7 for the deprotonation of the carboxylic group in the free ligand were determined for tsgly, bzgly, and tsβala, respectively. A further

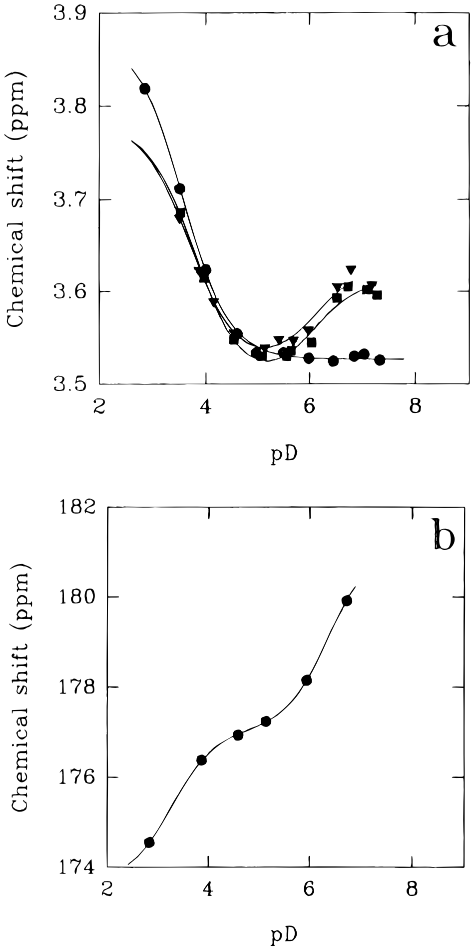

Figure 2. (a) pD dependence of the chemical shift of the methylene resonance in the ^1H NMR spectrum of tsgly in D_2O: (●) free ligand; (▼) saturated solution of $[Pb(tsgly\text{-}N,O)(H_2O)]$ (**1**); (■) saturated solution of **1** plus bpy in a 1:1 molar ratio with the metal. $T = 300$ K. $[Pb^{2+}] = 2 \times 10^{-3}$ M. (b) pD dependence of the chemical shift of the ^{13}C NMR resonance of the isotopically enriched carboxylic carbon of tsgly in the presence of the Pb^{2+} ion in a 2:1 ligand-to-metal molar ratio. $T = 300$ K. $[Pb^{2+}] = 1 \times 10^{-3}$ M.

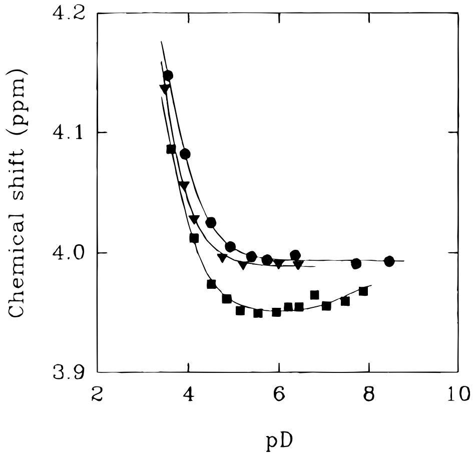

Figure 3. pD dependence of the chemical shift of the methylene resonance in the ^1H NMR spectrum of bzgly in D_2O: (●) free ligand; (▼) saturated solution of $[Pb(bzgly\text{-}O)_2(H_2O)_2]\cdot 2H_2O$ (**2**); (■) saturated solution of **2** plus bpy in a 1:1 molar ratio with the metal. $T = 300$ K. $[Pb^{2+}] = 1 \times 10^{-3}$ M.

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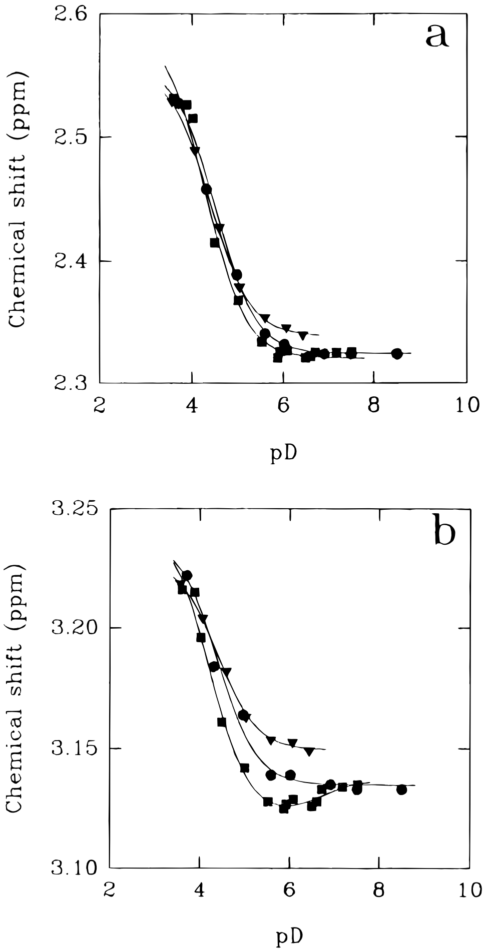

Figure 4. pD dependence of the chemical shift of the central peak of the two methylene triplets in the ^{1}H NMR spectrum of tsβala in D_2O: (a) α-CH_2; (b) β-CH_2; (●) free ligand; (▼) saturated solution of the crystalline compound $[Pb(ts\beta ala\text{-}O)_2]\cdot H_2O$; (■) saturated solution of the crystalline compound $[Pb(ts\beta ala\text{-}O)_2]\cdot H_2O$ plus bpy in a 1:1 molar ratio with the metal. $T = 300$ K. $[Pb^{2+}] = 1 \times 10^{-3}$ M.

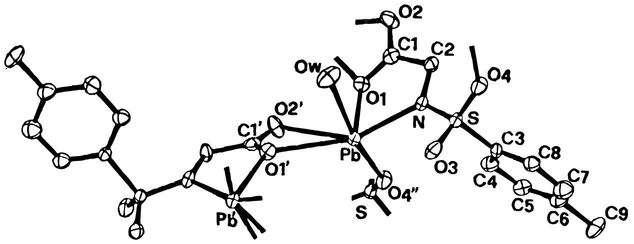

Figure 5. ORTEP view of the Pb atom environment in $[Pb(tsgly\text{-}N,O)(H_2O)]$ (**1**) with the atom-numbering scheme.

equilibrium, due to the deprotonation of the sulfonamide nitrogen, is observed with pK_a values in the range 10.7−11 (not shown). The same pH titrations performed on millimolar aqueous (D_2O) solution of the crystalline binary complexes for all of the above ligands yielded apparent pK_a values for the carboxylic group very similar to the pK_a of the free ligands (4.0, 3.3, and 4.8 for tsgly, bzgly, and tsβala, respectively). At pD values above 5.5 the chemical shift of the methylene peak of tsgly clearly increases up to pH ~7. Metal hydroxide precipitation occurs thereafter. For the other ligands, $Pb(OH)_2$ precipitates slightly above pH 6. Comparison with the polarographic data indicates that the above chemical shift change observed for tsgly is most probably due to the Pb^{2+}-promoted amide nitrogen deprotonation of the ligand (the increase in frequency of the methylene peak, opposite to the frequency decrease caused by deprotonation of the amide nitrogen in the free ligand, suggests that the metal itself affects the chemical shift of the methylene group). For all ligands no apparent pK_a value for the equilibrium $Pb^{2+} + HL^- = PbL + H^+$ can be obtained, since metal hydroxide precipitation occurs at a pH value much lower than the theoretical high-pH limit of the titration (i.e., the pH above which all the metal is present as PbL), which turns out to be about 9, as indicated by the species distribution curves calculated for the concentration of the reactants employed in the NMR spectra. This problem cannot be avoided either by using more diluted solutions, since the end of the titration moves at higher pH and is still preceded by metal hydroxide precipitation, or by increasing the ligand-to-metal molar ratio, which reduces the spectral changes due to amide nitrogen deprotonation of the ligand. The pD titration of the ^{13}C NMR resonance of the isotopically enriched carboxylic carbon of the ligand in the same binary Pb−tsgly system (Figure 2b) closely reproduces the above ^{1}H NMR titration. The increase in frequency of the first step with a pK_a value of 3.9 corresponds to the deprotonation of the carboxylic group of the ligand, while the additional frequency increase can, as above, be attributed to the formation of the nitrogen-deprotonated complexes. Carboxylic groups are known to undergo shielding effects on the ^{13}C NMR resonance upon metal binding.[34−38]

The pD profiles of the ^{1}H NMR methylene resonances of the amino acid ligands in the ternary systems containing a Pb^{2+}:bpy:ligand molar ratio of 1:1:2 (Figures 2a, 3, and 4), are invariably very similar to that of the binary Pb−tsgly system. Hence, the titration step around pH 4 corresponds to the deprotonation of the carboxylic group, whose pK_a is almost unmodified as compared to those of the free ligands, followed by a frequency increase due to deprotonation and metal binding of the amide nitrogen of the amino acid ligand. Consistently, for tsβala such an equilibrium is clearly detected only for the β-CH_2 group which is adjacent to the amide nitrogen (Figure 4b).

Description of the Structures. Drawings of the structures and selected interatomic distances and angles for **1**−**3** are shown in Figures 5−7 and reported in Tables 3−5, respectively.

$[Pb(tsgly\text{-}N,O)(H_2O)]$ (1). The Pb atom is coordinated at short distances by N, O1, and Ow atoms (in the range 2.314(8)−2.423(9) Å) and at longer distances by the chelating carboxylate oxygens O1′ and O2′ and the sulfonic O4″ oxygen (in the range 2.683(8)−2.827(5) Å). Each tsgly dianion coordinates three Pb^{2+} atoms giving rise to a three-dimensional polymeric arrangement. The shortest Pb···Pb separation is 4.748(2) Å. The Pb−N bond within the glycine-like chelate ring (2.38(1) Å) is, as expected, remarkably shorter than Pb−N bonds involving amino, pyridyl, and imino nitrogens (2.470−2.668 Å)[39−42] and longer than Pb−N bonds in Pb^{2+} complexes with dialkylamides (2.22−2.26 Å).[43] The Pb−O1 bond (2.314-

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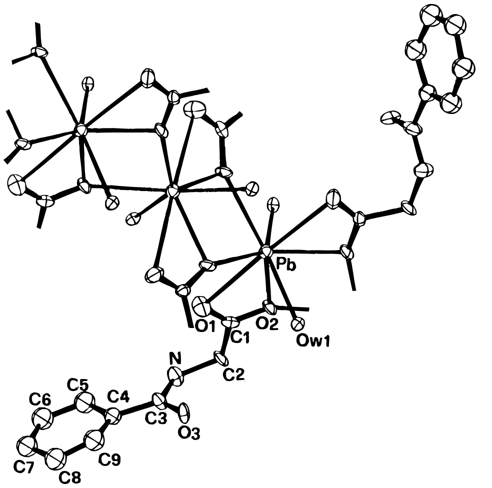

Figure 6. ORTEP view of the Pb atom environment in [Pb(bzgly-*O*)$_2$(H$_2$O)$_2$]·2H$_2$O (**2**) with the atom-numbering scheme.

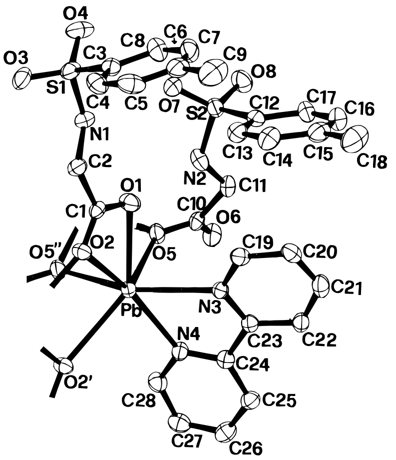

Figure 7. ORTEP view of the Pb atom environment in [Pb(tsgly-*O*)$_2$(bpy)] (**3**) with the atom-numbering scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **1**[a]

Pb−O1	2.314(8)	Pb−O4″	2.683(8)
Pb−N	2.38(1)	Pb−Ow	2.423(9)
Pb−O2′	2.78(1)	Pb−O1′	2.827(9)
S−O3	1.450(9)	S−O4	1.436(9)
S−N	1.56(1)	S−C3	1.77(1)
O1−C1	1.30(1)	O2−C1	1.28(1)
N−C2	1.46(1)		
N−Pb−Ow	82.7(3)	O4″−Pb−Ow	156.1(3)
O4″−PbN	89.2(3)	O2′−Pb−Ow	81.9(3)
O2′−Pb−N	138.3(3)	O2′−Pb−O4″	89.7(3)
O1′−Pb−Ow	69.8(3)	O1′−Pb−N	151.4(3)
O1′−Pb−O4″	119.2(3)	O1′−Pb−O2′	46.7(3)
O1−Pb−Ow	79.9(3)	O1−Pb−N	68.3(3)
O1−Pb−O4″	76.3(3)	O1−Pb−O2′	71.0(3)
O1−Pb−O1′	112.5(3)	Pb−O1′−Pb′	134.7(4)
Pb−O1−C1	119.2(7)	N−C2−C1	107(1)
Pb−N−S	119.6(5)	S−N−C2	120.0(9)
Pb−N−C2	120.4(8)	O1−C1−O2	120(1)
O2−C1−C2	118(1)	O1−C1−C2	123(1)

[a] Key: $' = -x + {}^1/_2,\ y - {}^1/_2,\ -z + 1;\ '' = x + {}^1/_2,\ -y + {}^1/_2,\ z.$

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **2**[a]

Pb−O1	2.75(1)	O1−C1	1.22(2)
Pb−O2′	2.46(1)	O2−C1	1.27(2)
Pb−O2″	2.75(1)	C3−O3	1.26(3)
Pb−Ow1	2.62(1)	N−C3	1.32(2)
C2−N	1.45(2)		
O1−Pb−O1′	141.3(4)	O2−Pb−O2‴	119.3(3)
O2‴−Pb−Ow1′	140.3(3)	O2−Pb−O2″	139.5(3)
O2‴−Pb−Ow1	76.8(3)	O2−Pb−O2′	80.1(3)
O2″−Pb−O2‴	70.5(3)	O1−Pb−Ow1′	92.2(3)
O2−Pb−Ow1′	73.8(3)	O1−Pb−Ow1	87.0(4)
O2−Pb−Ow1	76.8(3)	O1−Pb−O2‴	76.2(3)
O1−Pb−O1′	177.6(3)	O1−C1−O2	122(1)
O1−Pb−O2″	105.9(3)	C2−N−C3	123(2)
O1−Pb−O2′	128.7(3)		
O1−Pb−O2	48.9(3)		

[a] Key: $' = {}^1/_2 - x,\ {}^1/_2 - y,\ z;\ '' = {}^1/_2 - x,\ y,\ {}^1/_2 + z;\ ''' = x,\ {}^1/_2 - y,\ {}^1/_2 + z.$

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex **3**[a]

Pb−O1	2.627(4)	S1−C3	1.769(6)
Pb−O2	2.827(5)	S2−O7	1.438(5)
Pb−O2′	2.745(4)	S2−O8	1.428(5)
Pb−O5″	2.649(3)	S2−N2	1.599(6)
Pb−O5	2.523(5)	S2−C2	1.775(5)
Pb−N3	2.612(4)	O1−C1	1.260(8)
Pb−N4	2.609(5)	O2−C1	1.249(8)
S1−N1	1.617(5)	O5−C10	1.274(7)
S1−O3	1.426(5)	O6−C10	1.236(7)
S1−O4	1.428(5)		
N3−Pb−N4	62.6(1)	O2−Pb−O5	121.2(1)
O5−Pb−N4	80.4(1)	O2−Pb−O5″	97.3(1)
O5−Pb−N3	79.8(1)	O2−Pb−O2′	89.1(1)
O5″−Pb−N4	101.0(1)	O1−Pb−N4	143.4(1)
O5″−Pb−N3	146.4(2)	O1−Pb−N3	85.4(1)
O5″−Pb−O5	68.1(1)	O1−Pb−O5	76.6(2)
O2′−Pb−N4	82.3(1)	O1−Pb−O5″	96.3(1)
O2′−Pb−N3	129.3(1)	O1−Pb−O2′	134.1(1)
O2′−Pb−O5	131.3(1)	O1−Pb−O2	47.6(1)
O2′−Pb−O5″	71.2(1)	S1−N1−C2	117.3(4)
O2−Pb−N4	156.0(2)	S2−N2−C11	123.5(5)
O2−Pb−N3	108.0(1)	O1−C1−O2	123.5(6)
O5−C10−O6	125.3(5)		

[a] Key: $' = -x + 1,\ -y,\ -z;\ '' = -x,\ -y,\ -z.$

(8) Å) is much shorter than Pb−O$_{carboxylate}$ bonds (2.40−3.11 Å).[44−46] The coordination geometry can be described as distorted bicapped square-pyramidal with O4″, N, Ow, and O1′ atoms acting as equatorial ligands (with deviations from the mean plane of ±0.3 Å) and O1 and O2′ atoms as apical ligands. The vacancy of a coordination position in *trans* to O1 and O2′ suggests that the metal lone pair is stereochemically active. The five atoms of the glycine-like ring are almost planar, with deviations from the mean plane from −0.077 to 0.156 Å. Bond distances and angles within the ligand fall in the typical range for metal complexes of tsgly dianions.[47] Crystal packing is mainly due to contacts involving the oxygen atoms (in the range 2.66(1)−2.98(1) Å).

[Pb(bzgly-*O*)$_2$(H$_2$O)$_2$]·2H$_2$O (2). The Pb atom lies on the binary axis, and only one bzgly anion is crystallographically independent. The ligand coordinates one Pb atom through the chelate carboxylate group and a second Pb atom through the carboxylate O2 atom, which thus acts as a monoatomic bridge. A further bond is formed by the Ow1 atom of one water molecule. Each Pb−O bond is duplicated by symmetry transformation, thus originating a polymeric chain of Pb$_2$O$_2$ square-planar rings with Pb···Pb distances of 4.127(1) Å. The

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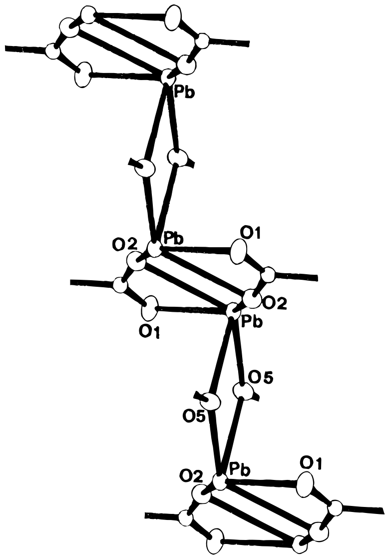

Figure 8. Arrangement of the polymeric square-planar Pb_2O_2 rings in **3**.

bond distances involving the metal are in the range 2.46(1)−2.75(1) Å. The benzoylglycinate anion acts as an asymmetric bidentate chelate and a bridging ligand through the carboxylate group. This group behaves analogously to that observed in **1**. The metal coordination polyhedron in this compound cannot be unambiguously defined, as well as the direction of lone-pair stereochemical activity. Crystal packing is mainly due to O···O contacts involving a lattice water molecule. Bond distances and angles within the ligand fall in the range of literature data.[47]

[Pb(tsgly-*O*)$_2$(bpy)] (3). The Pb atom is coordinated by the N3 and N4 atoms of the bpy molecule, two symmetry-related carboxylate O5 oxygens of two bridging tsgly ligands, the O1 and O2 atoms of an anisobidentate chelating carboxylate group, and the carboxylate oxygen O2′. Overall, the metal is seven-coordinated with bond distances in the range 2.523(5)−2.827(5) Å. Each tsgly monoanion bridges two Pb atoms forming a polymeric chain running along the *x* axis. The chain is formed by exactly planar Pb_2O_2 rings, nearly orthogonal to one another (Figure 8). The Pb···Pb′ distance is 4.285(3) Å, and Pb···Pb″ is 3.970(2) Å. The coordination polyhedron can be described as a distorted octahedron where N3, N4, O5″ and the midpoint O1, O2 are coplanar and the normal to this plane forms angles of 14.9 and 34.6° with the Pb−O5 and Pb−O2′ bonds, respectively. The value of the latter angle suggests that the lone pair is stereochemically active in the direction opposite to that of the Pb−O5 bond. Bond distances and angles within the ligand and the bpy molecule fall in the range of literature data.[47] Crystal packing is mainly due to interchain ring stacking interactions (in the range 3.39−3.88 Å) involving bpy molecules.

Infrared Spectroscopy. For all compounds, the asymmetric and symmetric stretching modes of the carboxylate group fall in the ranges 1574−1546 and 1408−1384 cm^{-1}, respectively, with $\Delta\nu$ values ($\Delta\nu = \nu(COO)_{as} - \nu(COO)_s$) between 170 and 146 cm^{-1}. This is in line with the small difference in C−O bond lengths within the carboxylate group among **1**−**3** and suggests that the carboxylate group binds in the same way also in the complexes not structurally characterized. In **1**, the deprotonation of the sulfonamide nitrogen causes the expected high energy shift of the stretching vibrations of the SO_2 and S−N bonds as compared to the case of the free ligand.[16]

Discussion

Binary Systems. The pH dependence of the ^1H and ^{13}C chemical shifts of the ligand in the Pb−tsgly system unequivocally indicate that above pH 6 a change in the coordination mode of the ligand occurs. This is confirmed by the X-ray structure of the complex separated in the solid state from solutions at these pH values, which shows that the ligand behaves as an N,O-bidentate dianion. As a consequence, the polarographic waves I_b and II_b can be confidently attributed to the reduction of the complexes in which tsgly acts as simple carboxylate and as an N,O-bidentate ligand, respectively. The same pH-dependent coordination behavior can be proposed for the other two ligands, which show identical electrochemistries and very similar pH dependences of the NMR spectra. Since the $E_{1/2}$ values of the polarographic wave II_b are independent of pH in all binary systems, the chemical shift change above pH 6 cannot be due to the formation of a mixed hydroxy−carboxylate complex. Overall, these observations indicate that the Pb^{2+} ion is effective in promoting amide nitrogen deprotonation in these ligands.

The same prevailing species are observed for the three ligands (Table 2). Due to the electron-withdrawing effect of the sulfonyl and carbonyl groups, the log β values of the $[Pb(HL)]^+$ and $[Pb(HL)_2]$ complexes are slightly lower than those for Pb^{2+} complexes with monocarboxylate ligands (in the ranges 1.1−2.68 and 2.0−3.5, respectively).[48,49] The stability constants for bzgly are in good agreement with values previously determined electrochemically for the same ligand[50] and for acetylglycine.[48,51] As expected, the log β values for the nitrogen-deprotonated PbL species are greater than those for Pb^{2+} complexes with amino acids with noncoordinating side chains (from 4.0 to 5.5),[14] due to the greater donor strength of the deprotonated amide nitrogen as compared to the amino nitrogen. Comparison with other binary metal−*N*-substituted amino acidate systems reveals the following: (i) The magnitude of the step constants K^{MHL}_{ML} relative to the formation of the nitrogen-deprotonated species from the precursor carboxylate complex, which follows the order $Pd^{2+} \gg Pb^{2+} > Cu^{2+} \geq Cd^{2+}$,[18,19] indicates that metal effectiveness in substituting for the sulfonamide nitrogen-bound hydrogen upon closure of the five-membered ring closely follows the order of "softness" of the acidic character, namely $Pd^{2+} \gg Pb^{2+} > Cu^{2+} > Cd^{2+}$.[8] This correlation can hardly be considered accidental and may indicate that metal affinity for nitrogen as the donor atom plays a role in determining the binding selectivity of these ligands and, by analogy, that of peptides toward dipositive metals.[15] Of course, the overall metal ability to promote amide nitrogen deprotonation in these ligands also depends on the stability of the precursor carboxylate complex (and of the complex formed by the primary ligating amino group in peptides), as well as on the solubility of the metal hydroxide. However, the relevance of the above factor emerges clearly if we consider that Co^{2+}, Ni^{2+}, and Zn^{2+}, which are "harder" acids than the above metal ions, are indeed ineffective in promoting nitrogen deprotonation in the present sulfonamide ligands and less effective than Pd^{2+} and Cu^{2+} in peptides. (ii) The Pb^{2+} ion is the only metal found so far to substitute for the proton of the NHCO group in binary complexes with *N*-carbonyl amino acids. The greater stability of the corresponding [PbL] species as compared to the *N*-sulfonyl amino acids (Table 2) must be ascribed to the greater

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basicity of the peptide nitrogen as compared to a sulfonamide nitrogen. In the light of the observations in the previous point, the existence of a stable [PbL] complex for bzgly is somewhat surprising, given that the Pd^{2+} ion was found unable to form the same complex.[18,19] One may speculate that the Pb^{2+} ion, possessing a greater affinity for oxygen donors than the Pd^{2+} ion, forms more stable carboxylate precursors and, hence, sets up a stronger interaction with the primary binding group (or "anchoring group"), which is essential for successive peptide nitrogen deprotonation. (iii) Comparison between the stability constants for the [PbL] complexes of tsgly and tsβala indicates that stability is not affected by the chelate ring size. Most probably the remarkable donor strength of the deprotonated amide nitrogen strongly reduces the effects of the greater strain[52] of a six-membered ring as compared to a five-membered ring in Pb^{2+} chelate complexes. Analogous behavior was observed previously for the same complexes of the Cd^{2+} ion.[53] The greater basicity of the carboxylate group in tsβala as compared to the *N*-substituted α-amino acids justifies the increase in stability of the corresponding carboxylate complexes.

Ternary Systems. Both ligand coordination modes, namely as carboxylate O-donors and chelating N,O-dianions, are maintained in the presence of 2,2′-bipyridine as an additional ligand (Table 2). The binding of the dianionic ligands to the $[Pb(bpy)]^{2+}$ species is to some extent disfavored as compared to the aquo ion, as indicated by negative values of $\Delta \log K$ ($=\log K^{M(bpy)}_{M(bpy)L} - \log K^{M}_{ML}$) for all ligands ($\Delta \log K = -0.22$, -0.19, and -0.09 for tsgly, tsβala, and bzgly, respectively). Thus, the heteroaromatic base appears not to favor amide nitrogen deprotonation in this class of ligands, at variance with previous observations for the same ternary systems with Cu^{2+}, Cd^{2+}, and Zn^{2+} ions, for which pK_{NH} values 0.4−3 units lower than those for the binary systems and positive $\Delta \log K$ values were determined.[20−22,54] This effect was attributed to a preferential binding of the carboxylate group, acting as primary ligating group, to the $[M(bpy)]^{2+}$ species as compared to the solvated metal ion and possibly to a favorable influence of π-conjugation between the aromatic system of bpy and that of the aromatic moiety of the N-protecting group of the amino acid ligand in the nitrogen-deprotonated species. Due to the two-step mechanism of the formation of the nitrogen-deprotonated species, with the involvement of the carboxylate species as precursors, $\Delta \log K$ can be factored as follows:

$$\Delta \log K = (\log K^{M(bpy)}_{M(bpy)(HL)_2} - \log K^{M}_{M(HL)_2}) + (\log K^{M(bpy)(HL)_2}_{M(bpy)L} - \log K^{M(HL)_2}_{ML})$$

The above two effects determine an increase in the first and the second term of this equation, respectively. Average values of 0.1 and −0.26 for the first and second terms are obtained for the present Pb^{2+} systems, against corresponding values of 0.1 and 0.4 determined for the same ternary (bpy) complexes of dipositive copper.[19,54] Hence, it is apparent that the carboxylate ligands bind more strongly to both metals in the ternary systems, but while for the Cu^{2+} ion the stabilizing effect of a π-delocalization on the ternary nitrogen-deprotonated species is also operative, this is not the case for the Pb^{2+} ion, for which the change in the coordination mode of the ligand from carboxylate O-donor to N,O-bidentate dianion appears unfavored in the presence of a metal-coordinated bpy. The molecular bases for this effect are not obvious. It can be proposed that the likely distorted coordination geometry around the Pb^{2+} ion in these nitrogen-deprotonated ternary species (see below) would prevent the above π-conjugation. It may also be relevant to note that the Pd^{2+} ion, which shows negative $\Delta \log K$ values for homologous systems,[55] shares with the Pb^{2+} ion a "softer" acidic nature than Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}, for which the favorable effect of bpy on nitrogen deprotonation of this class of ligands has been observed.[22,56] It is apparent that, with Pb^{2+} and Pd^{2+}, which are remarkably active in nitrogen deprotonation in the binary systems, this effect is overcome possibly by structural factors related to coordination geometry and mechanistic factors,[55] respectively.

X-ray Structures. The large ionic radius, the remarkable ionic character of metal−ligand bonding, and the presence of a nonbonding pair of electrons most often possessing stereochemical activity cause the coordination geometry of the Pb^{2+} ion to be dominated by high coordination numbers and distorted geometries, the latter strongly affected by the nature and steric requirements of the ligands.[4,9] In all of the present compounds, the carboxylate group chelates to one Pb atom, with one oxygen bridging between two metals. This simultaneous chelation and bridging, leading to polymerization, is typical of lead(II) carboxylates, as well as the formation of chains of Pb_2O_2 square planar rings.[44−46] In particular, lead(II) formate is a three-dimensional polymer and the metal shows a distorted dodecahedral eight-coordination.[44] In the monodimensional polymers lead(II) bis(pentafluorobenzoate)−bis(methanol),[44] lead(II) acetate trihydrate,[44,46] and the pyridine adduct of lead(II) benzoate[4] the metal shows a square-antiprismatic geometry, being eight-coordinate in the first two cases and showing a seven-coordination plus one unoccupied site in the last complex. The lower metal coordination number in **1** might be related to the remarkable binding strength of the deprotonated nitrogen. In all cases, the distorted geometries indicate a stereochemically active nonbonding metal electron pair.

Compound **1** is the first example of a structurally characterized Pb^{2+} N,O-chelate complex. The Pb−N bond (2.38(1) Å) is 0.4 Å longer than the average Cu−N bond in analogous complexes of the five-coordinate Cu^{2+} ion.[47] Since the ionic radius of a six-coordinate Pb^{2+} ion is 0.53 Å greater than that of a five-coordinate Cu^{2+} ion,[57] it turns out that the deprotonated amide nitrogen has a stronger affinity for dipositive lead than for the copper ion, consistent with the greater step constant for the formation of the nitrogen-deprotonated species from the precursor carboxylate complex. The N−Pb−O1 angle in the five-membered N,O-chelate ring of **1** (68.3(3)°) is, as expected, much smaller than the corresponding angle in analogous Cu^{2+} and Pd^{2+} complexes (average value of 82.9°). This determines a remarkable opening of the two adjacent angles, M−O1−C1 and M−N−C2, as compared to the cases of the analogous copper and palladium complexes. The metal binding of a sulfonic oxygen in **1**, which creates a three-dimensional polymeric structure, is a novel feature in the coordination chemistry of dipositive lead. Compound **3** is one of the few ternary carboxylate Pb^{2+} complexes with a heteroaromatic base reported to date, in addition to $Pb(phen)(O_2CCH_3)_2 \cdot 2H_2O$[4] and $Pb(O_2CPh)_2 \cdot py$.[4] The phenanthroline complex shows the short-

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est Pb−Pb distances detected in lead(II) carboxylates (4.05 and 3.73 Å). One of the two Pb···Pb contacts in **3** (4.285 and 3.97 Å) is very short as well. This common feature may well be accidental, but the heteroaromatic base may also play a role, possibly through ring stacking interactions, which in **3** occur between the aromatic rings of adjacent chains.

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Supporting Information Available: Listings of IR data and elemental analyses, tables of full crystallographic data collection and reduction and structure refinement parameters, fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, complete bond lengths and angles, and mean least-squares planes for **1**−**3**, and tables of hydrogen atom parameters for **2** and **3** (19 pages). Ordering information is given on any current masthead page.

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