expression[30] was employed. With the value of g fixed at 2.137, use of 52 data points in the temperature range 6.7-299.7 K leads to a value of -2.316 (5) cm^{-1} (correlation coefficient 0.999 983) for the exchange coupling constant J of the antiferromagnetically coupled dimer **4**.[31]

When the $1/\chi$ vs T data for **7** is fitted to Curie-Weiss law, a small positive value is obtained for the constant Θ. For example, the set of data collected at 5-kG field yields a Θ value of +1.085. This indicates a ferromagnetically coupled ground state for **7**. Weak ferromagnetic interaction between adjacent copper(II) centers has been reported for mono(μ-chloro)-bridged copper(II) chain complexes of caffeine and 2-(2-(methylamino)ethyl)-pyridine.[1c,21] Ferromagnetic ground states have also been observed in bis(μ-chloro)-bridged dimeric[32] and chain complexes[33] of divalent copper. A complete report on the magnetic properties of **7** will be reported later, following the acquisition of a good data set at extremely low temperatures.

Summary. The following are the principal results and conclusions of this investigation:

(1) A set of novel halo-bridged copper(II) complexes (**4**-**7**) of two peptide ligands, PypepH and PmpepH, have been synthesized, and the crystal structures of **4** and **7** have been determined. These complexes constitute a rare class of halo-bridged peptide complexes of bivalent copper.

(2) In **4**, two copper centers are bridged by two Cl^- ions, giving rise to a centrosymmetric dimer. A similar structure is predicted for **5**. In **7**, two adjacent Cu(Pmpep)Br units are bridged by a single Br^- ion and the pattern continues to give rise to a novel mono(μ-bromo)-bridged chain compound. A mono(μ-chloro)-bridged structure is assumed for **6**. Steric constraints, imposed by PmpepH, are responsible for the formation of the unusual mono(μ-halo)-bridged structures.

(3) When dissolved in water, methanol, or DMF, the halo-bridged complexes readily dissociate into monomeric tetragonal copper(II) species.

(4) The EPR parameters for each of the monomeric copper(II) species are characteristic of the particular peptide ligand it is derived of. The coordinated halide ion has minor influence on these values.

(5) Variable-temperature magnetic susceptibility studies demonstrate that the two copper(II) centers in **4** are antiferromagnetically coupled with an exchange coupling constant (J) value of -2.32 cm^{-1}. Similar measurements suggest a ferromagnetic ground state for **7**.

Acknowledgment. This research was supported by a Faculty Research Grant and the donors of the Petroleum Research Fund, administered by the American Chemical Society, at the University of California, Santa Cruz, CA, and by the NSERC of Canada at the University of Windsor, Ontario, Canada. We thank Drs. William Armstrong, Angelica Stacy, and Karl Hagen for help with susceptibility measurements.

Registry No. **4**, 113403-58-0; **5**, 113403-59-1; **6**, 113403-60-4; **7**, 113403-61-5.

Supplementary Material Available: Crystal structure data for [Cu(Pypep)Cl]$_2$·2H$_2$O (**4**) and [Cu(Pmpep)Br]$_\infty$ (**7**) including thermal parameters for non-hydrogen atoms (Table S1) and hydrogen atom parameters (Table S2) (3 pages); observed and calculated structure factors (Table S3) for **4** and **7** (12 pages). Ordering information is given on any current masthead page.

(28) We are aware of the use of the more general magnetization expression[2b,2c,29] for a pair of $S = {}^1/_2$ ions in cases where the singlet-triplet splitting is comparable to (or smaller than) the Zeeman energy $g\mu_B B$ (B = magnetic field strength). As mentioned in the text, theoretical treatment of the susceptibility data will be reported in detail at a later date.
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Effectiveness of the Cadmium(II) Ion in Promoting Sulfonamide Nitrogen Deprotonation. ^{113}Cd NMR, Polarographic, and pH-Metric Investigations on the Cadmium(II)-*N*-Tosylglycinate and Cadmium(II)-*N*-Dansylglycinate Systems in Aqueous and Methanolic Solutions

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^{113}Cd NMR, polarographic, and pH-metric investigations reveal the ability of the Cd^{2+} ion in substituting for the nitrogen-bound hydrogen of the amino acids N-protected by a sulfonic group. In aqueous and methanolic solution, *N*-tosylglycine and *N*-dansylglycine interacting with the Cd^{2+} ion show a pH-dependent binding mode, at increasing pH changing from simple carboxylate to N,O-bidentate ligands. The overall equilibria involving the prevailing complexes are similar to those previously found with the Cu^{2+} ion, but the stability of the cadmium complexes is lower by factors ranging from 10 to 10^4. Two binary complexes of formula $[CdL_2(H_2O)_4]$ (L = *N*-tosylglycinate, *N*-dansylglycinate) were separated in the solid state. X-ray powder spectra and IR data for the complex of *N*-tosylglycine show that it is isomorphous and isostructural with the analogous complexes with Zn^{2+}, Co^{2+}, and Ni^{2+}, in which the ligand is monodentate through the carboxylate group.

Introduction

Metal coordination of a peptide or sulfonamide nitrogen may only occur upon the substitution of the metal ion for the bound hydrogen.[1,2] The transition-metal ions exhibit different abilities in such a displacement: the order $Pd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$ has been found in peptide hydrogen substitution,[1] while

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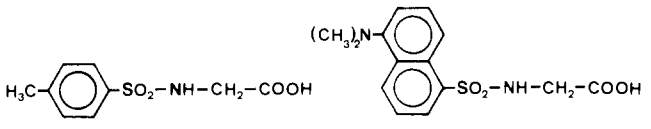
only the first two metal ions are found to be effective in substituting for the nitrogen-bound hydrogen of amino acids N-protected by an $ArSO_2$ group (Ar = aryl).[1-6]

With the aim of gaining a deeper understanding of the metal–$ArSO_2$–amino acid interactions, we have investigated the coordinative behavior of this class of ligands toward the Cd^{2+} ion. It is well-known that the metal substitution for the nitrogen-bound hydrogen suffers competition with metal hydroxide precipitation in neutral or basic solution. Since the cadmium hydroxide has a lower stability with respect to those of the above metal ions,[7] the effect of this competition should be lowered, and pH values in which the above substitution does occur could in principle be reached. So, the interaction of the Cd^{2+} ion with these sulfonamide nitrogen containing ligands is worth testing also for comparative purposes: in fact, recent ^{13}C and ^{113}Cd NMR studies[8] suggest the failure of the Cd^{2+} ion to promote the peptide nitrogen deprotonation.

In this paper we report an investigation on the solution and solid-state behavior of Cd^{2+}–*N*-tosylglycinate and Cd^{2+}–*N*-dansylglycinate systems. The solution study was performed over



N-tosylglycine *N*-dansylglycine

a wide pH range in aqueous and methanolic solution through ^{113}Cd NMR, polarographic, and pH-metric measurements with the aim to reveal the species present in solution and to determine their stability constants. The characterization of the solid complexes was also performed in order to obtain further evidence of the proposed solution coordinative behavior of the ligands.

Experimental Section

Materials. Reagent grade $Cd(ClO_4)_2 \cdot 6H_2O$ (Alfa Chemicals) and *N*-dansylglycine, *N*-tosylglycine, and *N*-benzoylglycine (Sigma) were twice recrystallized before use. Cadmium-113 oxide (91.67 atom % ^{113}Cd), obtained from Oak Ridge National Laboratory, was converted to the perchlorate for use in the NMR study in aqueous solution. Doubly distilled water and anhydrous methanol (C. Erba) were used throughout.

Polarographic Analysis. In aqueous solution measurements were performed on 1×10^{-4} M cadmium(2+) perchlorate solutions with ligand-to-metal molar ratios in the range (2:1)–(10:1). $NaClO_4$ was used as the base electrolyte, and the ionic strength was kept constant ($I = 0.1$ M). In order to characterize the electronic transfer process, concentrations of Cd^{2+} ion ranging from 1×10^{-4} to 5×10^{-4} M and dropping times of 2, 3, 4, and 6 s were used. The same experimental conditions were maintained in methanolic solution: $Cd(ClO_4)_2 \cdot 6H_2O$ and $NaClO_4$ were recrystallized from this solvent before use. The pH of the solutions was adjusted by adding small amounts of concentrated NaOH in the same solvent. Polarographic measurements were carried out with an Amel 472 Multipolarograph at 25 ± 0.1 °C. A saturated calomel electrode (SCE) was used as reference for the aqueous solution and an $Ag/AgNO_3$ (0.1 M) electrode for the methanolic solution. However, all

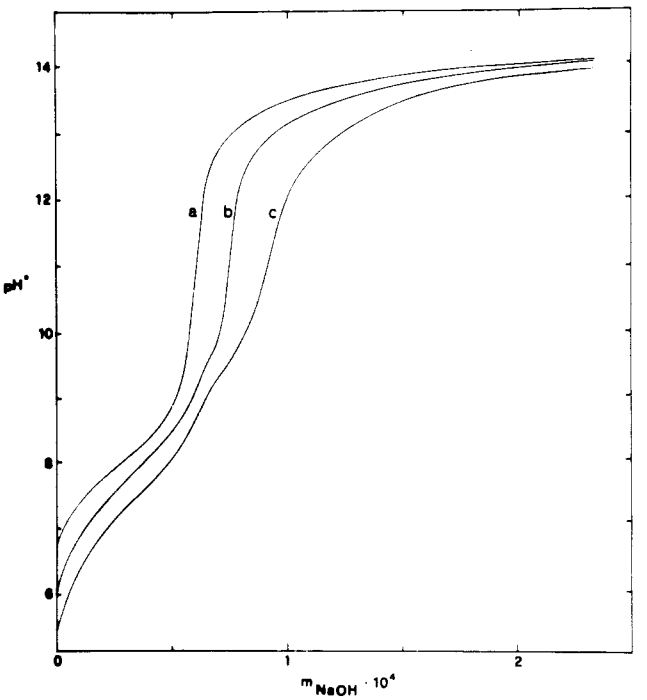


Figure 1. Neutralization curves of *N*-dansylglycine in the presence of Cd^{2+} in methanolic solution ($m_{dnsgly} = 6 \times 10^{-5}$): (a) $m_{Cd^{2+}} = 0$; (b) $m_{Cd^{2+}} = 1.5 \times 10^{-5}$; (c) $m_{Cd^{2+}} = 3 \times 10^{-5}$. m = number of moles. A 5×10^{-5} M NaOH solution in anhydrous methanol was used as titrant. *N*-tosylglycine shows identical behavior.

$E_{1/2}$ values are referred to the SCE. The pH measurements were performed with an Amel 337 pH meter using, in aqueous solution, an Ingold HA 405-60-K1 pH combination electrode and, in methanolic solution, an Ingold B7213 glass electrode as the indicator electrode and an $Ag/AgNO_3$ (0.1 M) electrode as the reference electrode. For pH measurements in methanolic solution two buffers at pH 5.79 ± 0.05 and pH 7.53 ± 0.05 referred to the pH scale in methanol were used.[9] All pH (and pK_a) values in methanolic solution, reported in this paper, refer to this pH scale[10] (pH*).

^{113}Cd NMR Spectra. All measurements were made at 44.385 MHz on a Varian XL-200 spectrometer equipped with a multinuclear broadband probe. Spectra were obtained by using 10 mm o.d. tubes and are externally referenced to 0.1 M aqueous $Cd(ClO_4)_2$ solution at 23 °C. Positive chemical shifts correspond to lower shielding. Natural abundance 0.1 M $Cd(ClO_4)_2$ was used for spectra in methanolic solution (CD_3OD) at ambient temperature. In aqueous solution, due to the high T_1 value for the ^{113}Cd nucleus in D_2O,[11] spectra were obtained with the minimal amount of D_2O required for internal spectrometer lock. For solubility problems of the ligands, the temperature was raised to 60 °C and 7×10^{-3} M ^{113}Cd-enriched perchlorate solutions were used. A ligand-to-metal molar ratio of 2:1 was used throughout. Standard acquisition parameters were as follows: spectral width, 4 kHz; pulse delay, 6–8 s; acquisition time, 2 s; pulse width, 10 μs (45° pulse); collected number of scans, 200–2000. Due to the negative gyromagnetic ratio of the ^{113}Cd nucleus, all spectra were obtained with no decoupling. No correction for diamagnetic susceptibility was applied.

Preparation of Solid Complexes. Crystals of formula $CdL_2(H_2O)_4$ (L = *N*-tosylglycinate, *N*-dansylglycinate) were obtained by slow evaporation at room temperature of aqueous methanolic 1:1 solutions containing cadmium(2+) hydroxide and amino acid in a 1:2 molar ratio.

X-ray Powder Spectra. X-ray data were obtained with a Philips PW 1050 diffractometer at 298 K with a Cu Kα source.

Results and Discussion

Solution Behavior. pH-Metric Data. The glycine moiety of *N*-tosyl- and *N*-dansylglycine (abbreviated tsgly and dnsgly, respectively) behaves as a bifunctional acid, due to the slightly

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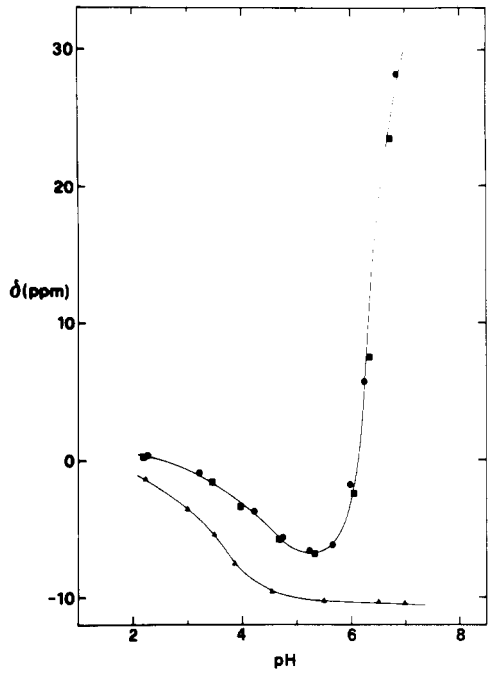

Figure 2. ^{113}Cd chemical shift of 7×10^{-3} M ^{113}Cd-enriched $Cd(ClO_4)_2$ with 1.4×10^{-2} M ligands vs pH in aqueous solution: (■) *N*-tosylglycine; (●) *N*-dansylglycine; (▲) *N*-benzoylglycine. $T = 60$ °C. The chemical shift of the solvated $^{113}Cd^{2+}$ ion at pH 2.5 is found to be 1.80 ppm.

protonic character of the sulfonamide hydrogen (in water, $pK_{NH}^{tsgly} = 11.6$ and $pK_{NH}^{dnsgly} = 11.7$; in methanol, $pK_{NH}^{tsgly} = 13.5$ and $pK_{NH}^{dnsgly} = 13.7$).[4a,6a] The Cd^{2+} ion exerts some influence on the ligand dissociation equilibria (Figure 1), as previously observed for the Cu^{2+} ion.[6a] Two steps appear in the pH-metric titrations in methanol: the first and the second require amounts of titrating NaOH according to eq 1 and 2, respectively, where m = number

$$m_{NaOH} = m_L \quad (1)$$

$$m_{NaOH} = m_L + m_{Cd^{2+}} \quad (2)$$

of moles and L = ligand. The first step may be confidently assigned to the formation of Cd^{2+} complexes in which the ligands coordinate through the carboxylate group,[6a,12] and the second step, having an apparent pK_a value about 9.6, markedly lower than the pK_{NH} of the free ligand, may be tentatively attributed to the Cd^{2+}-promoted amide deprotonation. For the ligand-to-metal molar ratios investigated, eq 2 suggests the coordination with the Cd^{2+} ion of only one N,O-bidentate amino acid molecule. In aqueous solution, the incipient precipitation of cadmium hydroxide at pH near 9 makes the observation of the second step quite doubtful, also in the presence of high ligand-to-metal molar ratios.

^{113}Cd NMR Data. The ^{113}Cd chemical shift has been found to be remarkably sensitive to the nature of the donor atoms as well as to the coordination number, geometry, and solvent in a wide variety of Cd-containing systems like simple inorganic salts, metal complexes, and biological macromolecules.[13] In the case under investigation, ^{113}Cd NMR is particularly suitable in detecting the proposed change in the ligand coordination at increasing pH since oxygen and nitrogen donor ligands exert opposite effects on the ^{113}Cd resonance: the former shield the cadmium nucleus and the latter cause a deshielding effect.[14] Of interest is the comparison between the behavior of our ligands ($ArSO_2$–glycines) and that of *N*-benzoylglycine, which has been previously found to coordinate the Cd^{2+} ion, as well as Zn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+},

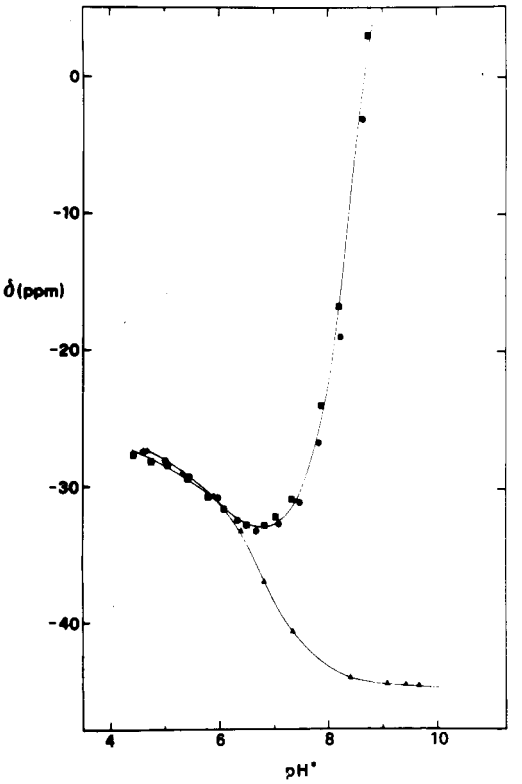

Figure 3. ^{113}Cd chemical shift of 0.1 M $Cd(ClO_4)_2$ with 0.2 M ligands vs pH in methanolic (CD_3OD) solution: (■) *N*-tosylglycine; (●) *N*-dansylglycine; (▲) *N*-benzoylglycine. $T = 21$ °C. The chemical shift of the solvated $^{113}Cd^{2+}$ ion at pH* 3.50 is found to be −27.44 ppm.

only through the carboxylate group in aqueous and alcoholic media.[4b,15]

Plots of ^{113}Cd chemical shifts vs pH for Cd^{2+} interacting with *N*-tosylglycine, *N*-dansylglycine, and *N*-benzoylglycine are reported in Figures 2 and 3. Only upfield shifts are observed for all ligands up to pH 5.4 and pH* 6.5 in aqueous and methanolic solution, respectively; in these pH ranges only a single time-averaged resonance is observed, indicative of a fast chemical exchange on the NMR time scale. At increasing pH, while *N*-benzoylglycine further shifts the cadmium resonance to lower frequencies with no changes in the line widths, the $ArSO_2$–glycines give rise to an "inversion" of the shielding effect, causing shifts to more deshielded values and increasing broadening of the signals (detectable up to pH 7 in water and pH* 8.2 in methanol). The upfield shift may be confidently considered as a result of cadmium complexation through the carboxylate group of the ligands,[16,17] while the subsequent downfield shift detected for $ArSO_2$–glycines may only be due to an involvement of a nitrogen in metal complexation. Since an amide nitrogen can coordinate only if deprotonated,[1] this behavior clearly indicates a change of the binding mode of the $ArSO_2$–glycines at increasing pH from an interaction through the carboxylate group to a bidentate coordination through the carboxylic oxygen and the deprotonated amide nitrogen, leading to the formation of a five-membered chelate ring. The comparison with the behavior of the Cd^{2+}–*N*-benzoylglycine system strengthens the above interpretation since, as expected, only the effect of the ligand coordination through the carboxylic group is detected. The pH dependence of the ^{113}Cd chemical shift given by the $ArSO_2$–glycines is qualitatively similar to that observed for simple amino acids[17] and peptides,[8] in which, however, the deshielding effect is due to the involvement of the amino group in metal coordination. The Cd^{2+} ion seems unable to promote

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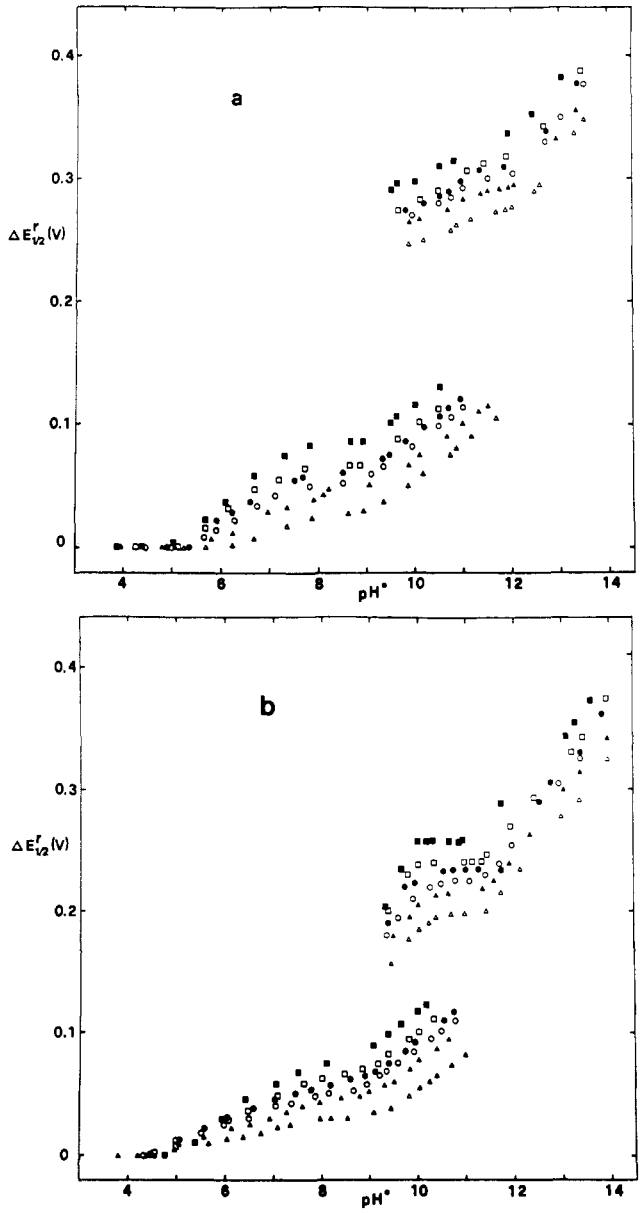

Figure 4. Plots of $\Delta E_{1/2}{}^r$ vs pH at increasing ligand concentrations in methanolic solution: (a) *N*-tosylglycine; (b) *N*-dansylglycine. $[Cd^{2+}] = 5 \times 10^{-4}$ M. Ligand concentrations: (△) 10^{-3} M; (▲) 2×10^{-3} M; (○) 3×10^{-3} M; (●) 4×10^{-3} M; (□) 5×10^{-3} M; (■) 10^{-2} M. $\Delta E_{1/2}{}^r = E_{1/2}{}^r(M) - E_{1/2}{}^r(C)$, where $E_{1/2}{}^r(M)$ is the reversible half-wave potential of the uncomplexed metal ion and $E_{1/2}{}^r(C)$ that of the complexed metal ion. $T = 25$ °C.

peptide nitrogen deprotonation,[8] even though definitive evidence has not been found; thus, its ability in substituting for the amide hydrogen in $ArSO_2$–amino acids may be reasonably ascribed to the more acidic character of this hydrogen as compared to that of the peptide hydrogen.

The results obtained confirm the above assignments of the pH-metric steps. In methanolic solution, the difference of 3 units between the pK_{NH} value of the metal-coordination ligand and the "inversion" pH value (pHi) is justified, under fast chemical exchange conditions, by the highly deshielded chemical shift values for the Cd^{2+} complexes containing nitrogen donor atoms.[18] In aqueous solution, the difference between the pK_{NH} value of the free ligands and pHi is similar to that observed for glycine.[17]

Polarographic Data. The polarographic parameters of *N*-tosylglycine and *N*-dansylglycine are fully comparable and are dramatically solvent-dependent (Figures 4 and 5). In methanolic solution, at pH* lower than 5, only one reversible wave is present,

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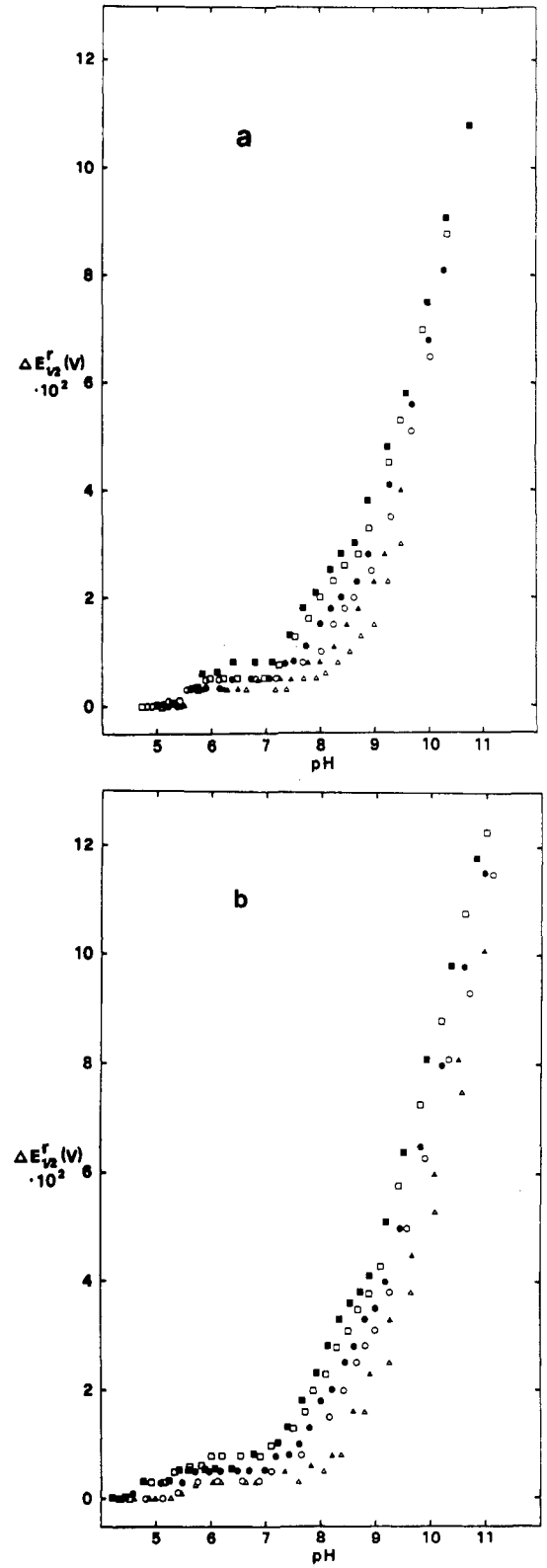

Figure 5. Plots of $\Delta E_{1/2}{}^r$ vs pH at increasing ligand concentrations in aqueous solution: (a) *N*-tosylglycine; (b) *N*-dansylglycine. $[Cd^{2+}] = 1 \times 10^{-4}$ M. Ligand concentrations: (△) 1×10^{-4} M; (▲) 2×10^{-4} M; (○) 4×10^{-4} M; (●) 6×10^{-4} M; (□) 8×10^{-4} M; (■) 10^{-3} M. $T = 25$ °C.

bielectronic and diffusion controlled (wave I), corresponding to the solvated Cd^{2+} reduction. When the pH and ligand concentration are increased, the reduction process becomes quasi-reversible: the $E_{1/2}$ value of this wave decreases (that is, shifts toward more negative values) while the diffusion current, i_d, remains constant. A new quasi-reversible wave at more negative $E_{1/2}$ values (wave II) begins to appear at pH* about 9: as the pH is increased,

Table I. log β of the Complexes Present in Aqueous and Methanolic Solution at Different pHs[a]

species	H_2O ΔpH	H_2O dnsgly	H_2O tsgly	CH_3OH ΔpH	CH_3OH dnsgly	CH_3OH tsgly
$[CdLO]^+$	5–7	b	...	5–9	3.70	3.60
$[Cd(LO)_2]$		...	...		6.78	7.30
$[Cd(LO)OH]$		...	...	9–11	8.83	9.00
$[Cd(LO)_2OH]^-$		...	...		11.92	11.89
$[CdLNO]$	7–10	4.90	4.90	9–12	11.00	12.54
$[Cd(LNO)_2]^{2-}$		6.14	6.00		12.17	13.30
$[CdLNO(OH)]^-$		9.17	8.84		13.25	14.00
$[Cd(LNO)_2OH]^{3-}$		12.52	11.84		15.98	16.45
$[CdLNO(OH)_2]^{2-}$	>10	12.77	11.95	>12	14.60	15.25
$[Cd(LNO)_2(OH)_2]^{4-}$		15.83	14.90		17.60	18.70

[a] For concentration ranges where single species predominate, see text and Figures 4–7. Abbreviations: dnsgly = *N*-dansylglycinate; tsgly = *N*-tosylglycinate; LO = ligand coordinating through the carboxylate group; LNO = N,O-bidentate ligand. [b] Unreliable value (see text).

the i_d value of the wave increases to the detriment of that of wave I, but their sum remains constant. These waves coexist up to pH* 11, when wave I disappears. The $E_{1/2}$ value of wave II decreases on increasing the pH* and ligand concentration. Since each wave is diffusion-controlled, the species reduced in wave I give rise to those reduced in wave II in the bulk of the solution. The reversible half-wave potentials ($E_{1/2}^r$) were determined by the method of Matsuda and Ayabe.[19] With the same ligands the Cu^{2+} ion shows a quite similar polarographic behavior.[6a]

In aqueous solution, only one reversible and bielectronic wave is observed. Up to about pH 5 the $E_{1/2}$ value corresponds to that of the solvated Cd^{2+} ion reduction. The decreasing of $E_{1/2}$ at increasing pH is characterized by two steps separated by a plateau (Figure 5); i_d remains constant up to pH 9.5. At higher pH the $E_{1/2}$ value decreases linearly and also i_d decreases due to the precipitation of the cadmium hydroxide. Significantly, only the first step has been previously detected for the Cd^{2+}–*N*-benzoylglycine system.[15]

The comparison of this polarographic behavior with the pH-metric and ^{113}Cd NMR data allows us to reasonably assign the first wave and the first step in methanolic and aqueous solution, respectively, to the reduction of species in which the ligands coordinate through the carboxylate group, while the second wave and the second step are to be assigned to the reduction of species in which the ligands are bidentate through the carboxylic oxygen and the deprotonated amide nitrogen.

The overall stability constants (β), calculated by the method of Shaap and McMasters,[20] are reported in Table I. In methanolic solution wave I corresponds to simple carboxylate and mixed monohydroxy–carboxylate complexes. The Lingane plots[21] of Figure 6 (the slope of the straight lines is given by JRT/nF, where J is the ligand coordination number) show that two carboxylate anions bind the metal ion on increasing pH and ligand concentration. The linear increase of $\Delta E_{1/2}^r$ that follows the sigmoidal trend of wave I (Figure 4) indicates the prevalence of the mixed monohydroxy–carboxylate complexes only above pH* 9; Figure 4 also indicates that these complexes are involved in the ligand deprotonation equilibria that give rise to the species corresponding to wave II. These latter species, in which the ligands act as N,O-bidentate dianions, are simple and mixed hydroxy complexes containing one and two coordinated ligand molecules (Table I); in particular, Figure 6 shows that two ligand molecules are coordinated to the Cd^{2+} ion, except for low ligand-to-metal ratios (up to 4:1) at low pH* (≤9.75). In aqueous solution, the very small values of $\Delta E_{1/2}^r$ ($\Delta E_{1/2}^r$(max) = 7 mV) of the first step do not allow the calculation of reliable stability constants for these carboxylate complexes; we can only estimate values ranging around a few units. Such a weak interaction is typical of the Cd^{2+} ion

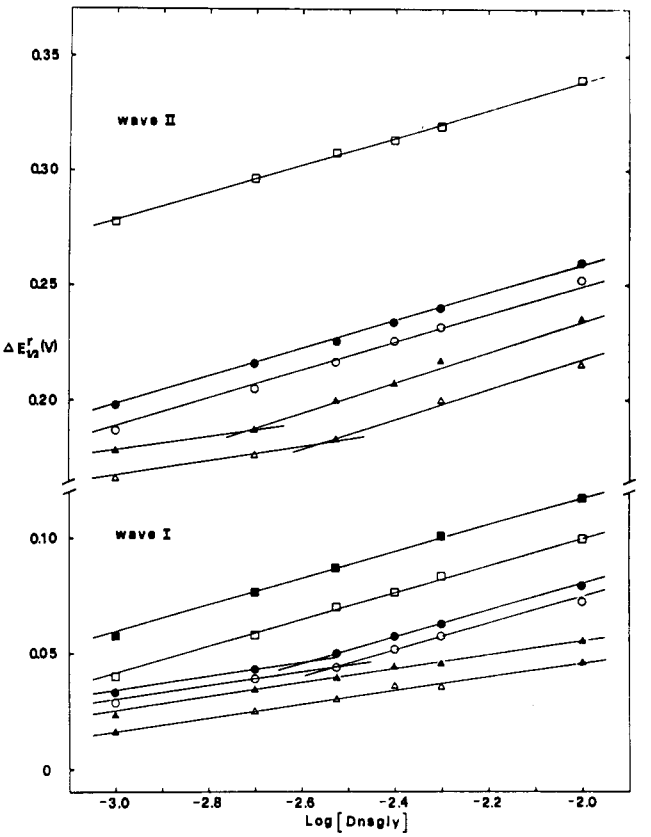

Figure 6. Plots of $\Delta E_{1/2}^r$ vs log [dnsgly] in methanolic solution at different pH* values: wave I, pH* 6.50 (△), 7.00 (▲), 7.50 (○), 8.00 (●), 9.50 (□), 10.00 (■); wave II, pH* 9.50 (△), 9.75 (▲), 10.00 (○), 11.00 (●), 13.00 (□). Identical qualitative trends are observed for *N*-tosylglycine.

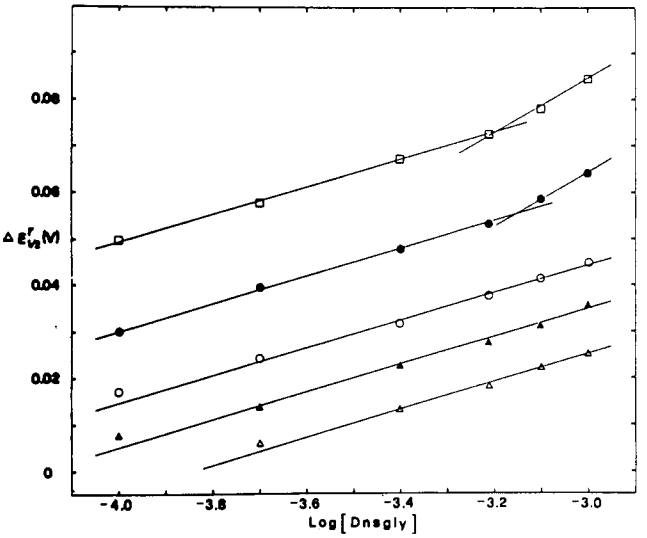

Figure 7. Plots of $\Delta E_{1/2}^r$ vs log [dnsgly] in aqueous solution at different pH values: (△) pH 8.00; (▲) pH 8.50; (○) pH 9.00; (●) pH 9.50; (□) pH 10.00. Identical qualitative trends are observed for *N*-tosylglycine.

interacting with monocarboxylate ligands.[22] The reduction processes corresponding to the second step involve the same complexes of wave II in methanol; the two ligands give rise to species of about the same stability and show a prevailing tendency to coordinate with the Cd^{2+} ion with only one N,O-bidentate molecule (Figure 7). The overall stability constants of the simple N,O-bidentate complexes (not mixed hydroxy) are fully comparable to those of Cd^{2+}–amino acidate complexes.[22] The lowering

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(20) Shaap, W. B.; McMasters, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 4699.
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effect of water on the stability constants, due to the higher solvation capability with respect to that of methanol, is reduced from 10^7 to 10^2 on increasing pH, that is, on increasing the coordination number of the complexes. In both solvents, the different steric hindrances of the N-protecting groups seem to exert no influence on the stability and the stoichiometry of the complexes.

For both ligands the following amide deprotonation equilibria are suggested (LO = ligand coordinating through the carboxylate group; LNO = N,O-bidentate ligand):

$$[Cd(LO)_2] + OH^- \rightleftharpoons [Cd(LO)_2OH]^- \rightleftharpoons [CdLNO] + LO^- + H_2O \quad (3)$$

$$[Cd(LO)_2] + OH^- \rightleftharpoons [Cd(LO)_2OH]^- \rightleftharpoons [Cd(LNO)LO]^- + H_2O \quad (4)$$

$$[Cd(LO)_2] + 2OH^- \rightleftharpoons [Cd(LNO)_2]^{2-} + 2H_2O \quad (5)$$

In methanolic solution equilibrium 3 reasonably prevails only at pH* lower than 9.75 for the lowest ligand-to-metal ratios; practically it may only occur at the beginning of the nitrogen deprotonation, with low ligand concentration. At higher pH*, equilibria 4 and 5 are the prevailing ones: in particular, for ligand-to-metal ratios up to 4:1, the presence of two ligand molecules coordinated to the Cd^{2+} ion, as indicated by the Lingane plots, only one of which is deprotonated, as obtained from the pH-metric titrations, suggests the existence of the mixed species $[Cd(LNO)LO]^-$ with a stability constant comparable to that of $[Cd(LO)_2OH]^-$. For higher ligand-to-metal ratios, for which reliable potentiometric data are not available, equilibrium 5 cannot be excluded as an additional deprotonation mechanism. In aqueous solution, the same equilibria probably take place, as previously observed for the interaction with the Cu^{2+} ion;[6a] in particular, the Lingane plots suggest the general prevalence of equilibrium 3, except for high ligand-to-metal ratios ($\geq$6:1) at high pH ($\geq$9.5), where equilibria 4 and 5 can both take place.

The same ligands interacting with the Cu^{2+} ion give rise to practically the same types of complexes, which were found more stable than the corresponding cadmium complexes by factors varying from 10 to 10^4; in addition, reasonably due to the higher tendency of the Cu^{2+} ion with respect to that of the Cd^{2+} ion to form hydroxy species,[7] the mixed hydroxy complex was found to prevail at lower pH. Since the effectiveness of the Cu^{2+} and Pd^{2+} ions[1,6a] and, on the other hand, the inability of Zn^{2+}, Co^{2+}, and Ni^{2+} in assisting the sulfonamide nitrogen deprotonation correlates with the higher tendency for the former metal ions to form hydroxy species at low pH,[7] it is possible to hypothesize the metal-bound hydroxy group to be involved in the amide deprotonation mechanism as acceptor of the nitrogen-bound hydrogen. From this point of view, the effectiveness of the Cd^{2+} ion could be explained by considering that, though it forms a MOH^+ species (M = metal ion) with the same stability as those given by Zn^{2+}, Co^{2+}, and Ni^{2+},[7] the cadmium(2+) hydroxide $Cd(OH)_2$ has a lower stability than the others, thus allowing the attainment of higher pH in which the metal substitution for the amide hydrogen via the metal-bound hydroxy group may occur without suffering competition from the metal hydroxide precipitation.

Solid-State Behavior. We tried to separate solid complexes from solutions at different pHs. Two crystalline compounds of formula $[CdL_2(H_2O)_4]$ (L = *N*-tosylglycinate, *N*-dansylglycinate) were obtained from aqueous methanolic solutions at pH lower than 7.5;[23] at higher pH no solid complexes separated, owing to the competitive precipitation of the cadmium hydroxide, which, having a stability[20] comparable to that of the cadmium complexes at these pH values, separates in the course of a few hours.

The X-ray powder spectrum for the complex of *N*-tosylglycine shows that it is isomorphous with the previously investigated bis(*N*-tosylglycinato)tetraaquometal(II) complexes (metal = Co, Ni, Zn),[5] in which the metal ion lies on the center of symmetry and is bonded to two amino acid molecules through a carboxylic oxygen atom and to four water molecules in a slightly tetragonally distorted octahedral geometry. The more relevant IR bands for both cadmium complexes, very similar to one another in shape and position, are indicative of a ligand coordination only through the monodentate carboxylate group;[4a,5,6b,24] furthermore, the absorption frequencies of the SO_2 group are unchanged from those of the free ligand, excluding the involvement of this group in metal coordination. These data and preliminary results on the crystal and molecular structure of bis(*N*-tosyl-β-alaninato)tetraquaocadmium(II)[25] allow us to reasonably assign to both cadmium complexes the above structure.

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Registry No. $CdL_2(H_2O)_4$ (L = *N*-tosylglycinate), 113218-93-2; $CdL_2(H_2O)_4$ (L = *N*-dansylglycinate), 113218-94-3; ^{113}Cd, 14336-66-4.

Supplementary Material Available: Tables of electrochemical parameters in aqueous and methanolic solutions and of elemental analyses and IR data for the solid complexes (5 pages). Ordering information is given on any current masthead page.

(23) The pH measurements in aqueous methanolic solution, up to a water/methanol ratio of 1:1, were performed with a pH combination electrode standardized in aqueous solution, according to ref 10.
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