observed in iron(III) acetylacetonate which has been interpreted as resulting from the donation of a *negative* spin to the half-filled d shell leaving *positive* spin on the ligand.

Insofar as the contact shifts reflect the π-bonding properties of the complex, which they do if our earlier interpretations are correct, these results demonstrate the effect of a given ligand on the bonding properties of another ligand. It is just this kind of interaction which must be responsible for the specificity of certain transition metal complexes in homogeneously catalyzed reactions. Thus only the right combination of ligands on a given transition metal ion will provide the optimum bonding conditions for the substrate in a homogeneously catalyzed reaction. The detailed interpretation of the present results must await a more rigorous theoretical treatment of the type previously attempted for vanadium(III) acetylacetonates. However, one or two preliminary observations can be made at this point. The d^2 V(III) ion has one empty and two half-filled d orbitals which are available for π bonding even in strictly octahedral symmetry. In the complex with one aminotroponimine and two acetylacetonate ligands the negative spin on the aminotroponiminate indicates that this ligand is interacting with the empty d orbital since this is the only orbital which can accept a positive spin leaving negative spin on the ligand. On the other hand, in the complex with one acetylacetonate and two aminotroponimines it appears that the acetylacetonate is interacting with a half-filled orbital since positive spin is delocalized. This result can perhaps be rationalized if it is remembered that the metal-to-ligand charge-transfer interaction can only profitably involve a half-filled orbital; if the d orbital is empty, such interaction can lend neither to a gain in energy nor to observable contact shifts. Since metal-to-ligand π charge transfer is thought to be the most important interaction with the acetylacetonate ligand, it therefore seems plausible that this ligand will prefer to interact with a half-filled orbital. With aminotroponimine, on the other hand, since only ligand-to-metal π charge transfer need be considered, the preference could well be for interaction with an empty d orbital, donating an α electron to keep parallel spins in the d orbitals as much as possible and maximize the energy in this way. It is perhaps plausible that these preferences should only become apparent when there is only one ligand of a given type since with two or more identical ligands there may well be interactions with both filled and half-filled orbitals, and the over-all shifts will represent a combination of effects.

Turning to the mixed Mn(III) chelates, some fairly substantial changes are again apparent in the shifts of the mixed chelates. However, there is no drastic change in the pattern as there is for the V(III) complexes. If the π interactions are predominantly with those d orbitals available for π bonding even in octahedral symmetry, this result is understandable since all such orbitals are half-filled. It is interesting to note that in the mixed chelates some of the aminotroponiminate resonances are split, reflecting the expected nonequivalence of these protons in the lower symmetry.

Finally, it should be noted that the susceptibility measurements indicate that the tris aminotroponiminates of both Mn(III) and Fe(III) are low-spin complexes, whereas the tris acetylacetonates and the mixed complexes are high spin.

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Lanthanide and Actinide Complexes of Glycine. Determination of Stability Constants and Thermodynamic Parameters by a Solvent Extraction Method

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The first stability constants of the complexes formed between glycine and trivalent Ce, Pm, Eu, Am, and Cm at an ionic strength of 2.0 *M* ($NaClO_4$) have been determined by a solvent extraction technique. Under the conditions of the experiments (pH 3.64) complexation takes place between the metal cation and the zwitterion $NH_3^+CH_2CO_2^-$ while complexation by the free anion to form a chelate is negligible. Values for enthalpy and entropy for the formation of the monoligand complex have been determined by a temperature differential method. In all cases the enthalpy of complexation is endothermic, the complexes being stabilized by a relatively large positive entropy change. This indicates the formation of inner-sphere complexes similar to those formed between lanthanide and actinide ions and simple carboxylate ligands.

Introduction

In an earlier study of the complexation of light lanthanides by glycine and β-alanine, it was assumed that the ligand anion formed a chelate with the cation.[1] Preliminary investigations[2] using the method of pH titration raised serious doubts about this interpretation of the results. We have used a solvent extraction technique at constant pH to restudy the complexing by glycine. This ligand can exist in three forms

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[1] M. Cefola, A. S. Tampa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, **1**, 290 (1962).

[2] J. L. Bear and G. R. Choppin, unpublished data, 1963.

$$NH_3{}^+CH_2CO_2H \overset{pK_1}{\rightleftarrows} NH_3{}^+CH_2CO_2{}^- \overset{pK_2}{\rightleftarrows} NH_2CH_2CO_2{}^-$$

The pH was chosen such that the predominant form in our solutions was the zwitterion. The temperature cofficient method was used to obtain thermodynamic data on the complexation.

Experimental Section

Exchanger.—The liquid cation exchanger used in the solvent extraction procedure was dinonylnaphthalenesulfonic acid (referred to as HD) obtained from R. T. Vanderbilt Co. Solutions were prepared in *n*-heptane (0.001–0.006 *M*).

Glycine Solutions.—Reagent grade glycine from Fisher Scientific Co. was recrystallized before use from a 1:1 by volume ethanol–water mixture. The crystals were dried in an oven at 120°. The stock solution was prepared by weighing the dried material and making up to a known volume with distilled water.

Ionic Strength.—In the strict definition, the zwitterion does not contribute to the ionic strength. However, it seems likely that its effect on the solvent medium would resemble that of a 1:1 electrolyte. Consequently, we adjusted the aqueous solutions to an "effective" ionic strength of 2.0 *M* by assuming 1:1 electrolyte behavior for the glycinate zwitterion and adding an appropriate volume of concentrated sodium perchlorate solution. Since the total zwitterion concentration varies from 0.01 to 0.1 *M*, it makes little if any practical difference whether we included the zwitterion concentration or not in the total ionic strength.

Tracers.—The ^{144}Ce, ^{147}Pm, $^{152-154}$Eu, ^{243}Am, and ^{244}Cm obtained from Oak Ridge National Laboratory were dissolved in 0.1 *M* perchloric acid and extracted into the organic phase prior to use.

Procedure.—Both organic and aqueous phases were preequilibrated by contact with portions of the opposite phases used in the solvent extraction experiments. The extraction technique was essentially the same as used previously.[3,4] After 8–14 hr of mixing, the phases were allowed to settle for 24 hr prior to sampling. For the γ-emitting nuclides, ^{144}Ce and $^{152-154}$Eu, sample phases were counted in liquid aliquots using an NaI (Tl) well-scintillation counter. Self-absorption in the solid and liquid samples made it impracticable to count the β emissions of ^{147}Pm or the α emissions of ^{243}Am and ^{244}Cm of the aqueous phase. These ions were added initially to the organic phase only and samples from this phase were counted before and after equilibration with the aqueous phase. Both α and β emitters were counted in a windowless 2π proportional counter.

All of the experiments were carried out in duplicate and two aliquots were taken at every concentration point. All temperatures were maintained to within ±0.1°. The data from a typical run are shown in Table I.[5]

The acid dissociation constants of glycine at $\mu = 2.0$ *M* were determined by pH titration with a Beckman research pH meter. The determinations were carried out at 2, 30, and 40°, the titration vessel being a double-walled glass container through which water from a constant-temperature bath was circulated. The pH meter was standardized using a solution of 0.01 *M* perchloric acid and 1.99 *M* sodium perchlorate solution. In all cases the pH of this solution was taken to be 2.00. In order to obtain the first acid dissociation constant, excess perchloric acid was added and the p*K* was calculated from the calculated half-titration point. The p*K* values are listed in Table II.

Results and Discussion

Aqueous solutions were adjusted to pH 3.64 before equilibrium with the organic phase containing the activity. At this pH about 90% of the glycine ligand is in the zwitterion form ($NH_3{}^+CH_2CO_2{}^-$).

TABLE I

EXPERIMENTAL RESULTS OF SOLVENT EXTRACTION OF ^{144}Ce[a]

Zwitterion concn, *M*	$1/K_D$	Zwitterion concn, *M*	$1/K_D$
0.000	0.905	0.0546	1.167
0.0091	0.933	0.0637	1.202
0.0182	0.931	0.0729	1.276
0.0273	1.052	0.0820	1.288
0.0364	1.090	0.0910	1.360
0.0455	1.085		

[a] Temperature 40.0 ± 0.1°; initial volume of each phase, 3.0 ml; aliquot taken, 1.0 ml of each phase; concentration organic phase, 0.006 *M* HD in *n*-heptane.

TABLE II

ACID DISSOCIATION CONSTANTS OF GLYCINE AT IONIC STRENGTH 2.0 *M* ($NaClO_4$)[a]

Temp, °C	pK_1	pK_2
2	2.79 ± 0.02	9.64 ± 0.03
25	2.76 ± 0.05	9.56 ± 0.08
40	2.72 ± 0.05	9.59 ± 0.12

[a] $K_1 = [H^+][NH_3{}^+CH_2CO_2{}^-]/[NH_3{}^+CH_2CO_2H]$; $K_2 = [H^+][NH_2CH_2CO_2{}^-]/[NH_3{}^+CH_2CO_2{}^-]$.

Assuming that the zwitterion complexes with the metal ion the stability constant was calculated from the equation

$$\frac{1}{K_D} = \frac{1}{K_D{}^0} + \frac{\beta_1}{K_D{}^0}[NH_3{}^+CH_2CO_2{}^-] + \frac{\beta_2}{K_D{}^0}[NH_3{}^+CH_2CO_2{}^-]^2$$

where K_D is the concentration of nuclide in the organic phase divided by the concentration in the aqueous phase. $K_D{}^0$ is the distribution coefficient in the absence of the complexing ligand and β_1 and β_2 are the over-all stability constants for the formation of the first and second complexes.

The value of β_1 was computed from the above equation after assuming that β_2 was negligibly small. The plot of $1/K_D$ against $[NH_3{}^+CH_2CO_2{}^-]$ showed no sign of curvature indicating that the β_2 could indeed be neglected.

To verify the assumption that, with the rare earths, the ligand complexed in the form of the zwitterion, an experiment on europium was carried out at pH 5.82. As compared to the other runs this involves an increase in zwitterion concentration of about 10%, whereas the concentration of the anion increased by a factor of about 100. At this pH assuming that complexing was due to the zwitterion only, a value of $K_1 = 6.2 \pm 0.3$ was obtained at 40°. This result is in good agreement with the value obtained at pH 3.64 given in Table III. No such agreement was found when calculations were made on the assumption that complexation of the anion was taking place. Moreover, the stability constants calculated on the bases of anion concentration are quite unreasonable (*e.g.*, 6.3×10^6 for the data in Table I). From Raman spectroscopy, Krishman and Plane have concluded that glycine forms monodentate complexes *via* the zwitterion with Zn(II), Cd(II), and Be(II) at low pH values (*ca.* 2.0–4.0).[6]

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(5) Material supplementary to this article has been deposited as Document No. NAPS-00015 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 W. 34 St., New York, N. Y. 10001. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

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TABLE III

STABILITY CONSTANTS OF THE MONOGLYCINATE COMPLEXES

	Temp, °C				
Ion	0	11	25	40	55
Ce	2.2 ± 0.5[a]	...	3.4 ± 0.4	5.0 ± 0.6	5.7 ± 0.6
Pm	2.8 ± 0.3	3.3 ± 0.7	4.7 ± 0.3	6.2 ± 0.5	...
Eu	4.1 ± 0.3		5.0 ± 0.3	6.0 ± 0.4	8.0 ± 0.3
Am	3.0 ± 0.4	3.7 ± 0.1	4.9 ± 0.2	6.0 ± 0.3	...
Cm	4.2 ± 0.2	4.6 ± 0.6	6.4 ± 0.2	8.9 ± 0.3	...

[a] The error assigned is twice the standard deviation (2σ).

TABLE IV

THERMODYNAMIC PARAMETERS FOR THE MONOGLYCINATE COMPLEXES AT 25.0° AND $\mu = 2.0\ M$ ($NaClO_4$)

Ion	ΔG, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, cal deg^{-1} mol^{-1}
Ce	0.75 ± 0.03	3.3 ± 0.4	14 ± 2
Pm	0.91 ± 0.03	3.5 ± 0.4	15 ± 2
Eu	0.99 ± 0.02	2.3 ± 0.4	11 ± 2
Am	0.93 ± 0.02	2.9 ± 0.4	13 ± 2
Cm	1.12 ± 0.02	3.3 ± 0.4	15 ± 2

The results of the calculation of enthalpy values from the temperature differential method are given in Table IV with values of ΔG and ΔS. In all cases the enthalpy is positive and, hence, opposed to complexation. These endothermic values are larger than for the monoacetate complexing[7] and comparable to the monoisobutyrate data.[8] The driving force for the complex formation is the positive entropy which is comparable to that of the monocarboxylate complexes. The similarity of the ΔH and ΔS values to those for the simple carboxylate anions, in contrast to the disagreement with the values for the α-hydroxycarboxylate complexes,[7,9] leads to the conclusion that the glycinate zwitterion forms inner-sphere, monodentate complexes with the trivalent lanthanide and actinide ions. The agreement between the entropy values of the acetate and glycinate complexing indicates that the effect on the hydration of the cation is comparable. Consequently, the lower stability of the glycinate complexes as determined by the more endothermic enthalpy is probably due to decreased ionic attraction in the zwitterion complex $M^{3+}\cdots{}^{-}O_2CCH_2NH_3^+$ than in the acetate where the ligand positive charge is absent, $M^{3+}\cdots{}^{-}O_2CCH_3$.

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Metal Complexes of Nonamethylimidodiphosphoramide

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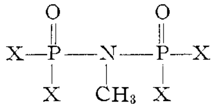
Complexes of nonamethylimidodiphosphoramide, $[(CH_3)_2N]_2P(O)N(CH_3)P(O)[N(CH_3)_2]_2$, with both transition and non-transition metal perchlorates have been prepared. The coordinating ability of nonamethylimidodiphosphoramide (NIPA) is quite similar to that of octamethylpyrophosphoramide (OMPA). Infrared evidence is in agreement with the formation of a six-membered chelate ring between the phosphoryl oxygens of NIPA and the metal ions. The *Dq* value of NIPA toward Ni(II) is the same as that for OMPA (726 *vs.* 727 cm^{-1}) while the $\beta°$ value for NIPA with Ni(II) is lower (9.7 *vs.* 11.1%). The substitution of the N-methyl group for the bridge oxygen of OMPA appears to have little effect on the stability of the complexes.

Introduction

Donoghue and Drago[2] prepared a series of metal complexes of hexamethylphosphoramide (HMPA). The infrared data for these complexes are in support of coordination of the metal ions to the phosphoryl oxygen atom of the ligand. The transition metal perchlorate complexes isolated by them were generally four-coordinate and spectral data were indicative of tetrahedral geometry.

We have found that octamethylpyrophosphoramide (OMPA) is a very versatile bidentate ligand.[3] This ligand can be pictured as two HMPA molecules combined through a P–O–P linkage which has replaced one dimethylamino group on each HMPA molecule. OMPA acts as a bidentate ligand utilizing both phosphoryl oxygen atoms. Recent X-ray studies[4] have confirmed the previously proposed[3] six-membered chelate ring which is formed between the metal ions and the pyrophosphate linkage of OMPA. The high stability of these complexes was attributed to the chelate effect.

The purpose of the present study was to examine the coordinating ability of the ligand obtained by replacing the P–O–P oxygen atom with an N-methyl group. The resulting ligand, nonamethylimidodiphosphoramide (NIPA)



$$X-\underset{X}{\overset{O}{\overset{\|}{P}}}-\underset{CH_3}{N}-\underset{X}{\overset{O}{\overset{\|}{P}}}-X$$

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