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The Coordinate Bonding in Transition Metal Complexes of 2-Carbamoyldimedone. II. Metal Chelates of N-Substituted 2-Thiocarbamoyldimedones[1]

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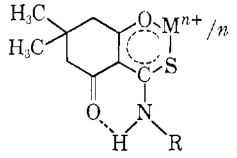
Received September 14, 1967

Six N-phenyl-2-thiocarbamoyldimedone and N-methyl-2-thiocarbamoyldimedone chelates of Co(III), Cu(II), Ni(II), and Zn(II) have been synthesized. The coordinate bonding has been investigated by spectral, magnetic, proton resonance, and electron resonance measurements. The findings are compared with the properties reported for complexes of 2-carbamoyldimedone. Introduction of sulfur into the carbamoyl moiety appears to reduce intermolecular bonding in the metal complexes and to enhance the covalency of the metal–ligand bonding. Nmr, spectral, and combustion analyses indicate that tris(N-phenyl-2-thiocarbamoyldimedonato)cobalt(III) combines with toluene in a 1:1 ratio.

Introduction

A few investigations of the metal-binding properties of tetracyclines have been reported.[3,4] On the basis of spectral and magnetic properties of cobalt(II) and nickel(II) complexes of three tetracyclines, Baker and Brown[4] concluded that the metal ions are coordinated to the tetracyclines through oxygen atoms and the diketoamide group is most likely the portion participating in the coordinate bonding. Prior to the report of Baker and Brown, we had carried out a study of metal complexes of a 2-carbamoyldimedone (2-carbamoyl-5,5-dimethylcyclohexane-1,3-dione), which is a simpler model system of the diketoamide group, and we presented evidence for the coordination of the oxygen rather than the nitrogen of the carbamoyl moiety to the metal ion in each chelate.[1] The magnetic and spectral data suggest that the bis(N-substituted 2-carbamoyldimedonato)metal complexes have a quasi-octahedral structure. The structure is attributed to intermolecular bonding involving the metal ion of one molecule and the nitrogens in the carbamoyl moieties of two neighboring molecules.

The study of monothio-β-diketones and their metal complexes by Chaston, Livingstone, *et al.*,[5] indicates that the replacement of one oxygen atom of a β-diketone markedly alters the metal-bonding properties of the ketone. As part of our investigation of 2-carbamoyldimedone chelates, we have prepared metal complexes of some N-substituted 2-thiocarbamoyldimedones of the general formula



R = C_6H_5, $n = 2$, M = Cu, Zn, Ni
$n = 3$, M = Co
R = CH_3, $n = 2$, M = Ni
$n = 3$, M = Co

The coordinate bonding in the compounds differs noticeably from that of the analogous 2-carbamoyldimedone derivatives but is similar to the bonding reported for metal chelates of monothio-β-diketones.[5]

Experimental Section

Chemicals.—Chloroform-*d* was supplied by Merck Sharp and Dohme of Canada. The calibrant for magnetic susceptibility measurements, mercury(II) tetrathiocyanatocobaltate(II), was obtained from Eastman Organic Chemicals.

Synthesis of Compounds. Ligands.—N-Phenyl-2-thiocarbamoyldimedone (5,5-dimethylcyclohexane-1,3-dione) was synthesized according to the procedure of Goerdeler and Keuser,[6] and N-methyl-2-thiocarbamoyldimedone was prepared as described by Dudek and Dudek.[7]

Complexes.—The divalent metal complexes of N-phenyl- and N-methyl-2-thiocarbamoyldimedone listed in Table I were prepared by the following general method. The 2-thiocarbamoyldimedone derivative (8 mmoles) dissolved in hot ethyl acetate was added to the hot aqueous solution of the metal acetate hydrate (4 mmoles). The two-phase mixture was stirred overnight, the complex forming as an insoluble product between the two phases. The mixture was filtered, and the precipitate washed with cold water and then dried *in vacuo* over phosphorus pentoxide. The material was recrystallized from the appropriate solvent.

The cobalt complexes in Table I were synthesized as follows. The ligand (12 mmoles) was dissolved in hot ethyl acetate and combined with a hot aqueous solution of cobalt(II) acetate tetrahydrate (4 mmoles). Air was drawn through the mixture overnight. The complex formed between the two phases was filtered, washed with cold water, dried *in vacuo* over phosphorus pentoxide, and recrystallized from the appropriate solvent.

Infrared Spectra.—Spectra were obtained on a Perkin-Elmer Model 337 grating spectrometer using the potassium bromide pressed-disk method. The instrument was calibrated with a polystyrene film and the wavelengths are accurate to ± 5 cm^{-1}.

Ultraviolet Visible Spectra.—Spectra were taken on Perkin-Elmer 202 and Cary Model 14 recording spectrometers. Chloroform, which had been passed through a column of aluminum oxide to remove alcohol, was used as the solvent. All spectra were recorded at room temperature.

Proton Resonance Spectra.—The spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. The spectra were recorded at the ambient temperature of the probe, 31°, except for bis(N-phenyl-2-thiocarbamoyldimedonato)-

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TABLE I

CHARACTERIZATIONS OF SOME METAL COMPLEXES OF N-SUBSTITUTED 2-THIOCARBAMOYLDIMEDONES

R	M	n	Dec pt, °C[a]	Yield, %	Analysis, % C		H		N		S		Solvent(s) used in recrystallization
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
C_6H_5	Cu	2	180–181	75	58.86	58.99	5.27	5.39	4.58	4.64	10.47	10.45	Benzene–cyclohexane
C_6H_5	Zn[b]	2	197–198	75	57.00	57.53	5.42	5.40	4.43	4.39	10.15	10.32	Benzene–hexane
C_6H_5	Ni	2	285–286	75	59.32	59.53	5.31	5.50	4.61	4.47	10.56	10.74	Benzene
C_6H_5	Co[c]	3	158–160	40	64.11	64.36	5.79	5.98	4.31	4.16	9.89	9.93	Cyclohexane, then toluene–hexane
CH_3	Ni	2	250–251	70	49.70	50.04	5.84	5.86	5.80	5.86	13.27	13.35	Benzene
CH_3	Co	3	212–213	50	51.78	51.78	6.08	6.30	6.04	5.91	13.82	13.88	Toluene–hexane

[a] All compounds decomposed on melting. [b] Data for 1:1 bis(N-phenyl-2-thiocarbamoyldimedonato)zinc(II)–water. [c] Data for 1:1 tris(N-phenyl-2-thiocarbamoyldimedonato)cobalt(III)–toluene.

TABLE II

INFRARED BANDS (CM^{-1}) OF N-SUBSTITUTED 2-THIOCARBAMOYLDIMEDONES AND THEIR METAL CHELATES[a]

R	M	n	Uncoordinated ν(C=O)	ν(C=C)	Cross-conjugated system	ν(C=S)	ν(M—O)
C_6H_5	H	1	1610 vs	1540 m	1500 vs, 1400 s	1274 m, 1150 m	475 m
C_6H_5	Cu	2	1605 s	1550 s	1470 vs, d, 1380 s	1268 m, 1145 m	478 m
C_6H_5	Zn	2	1600 m	1550 m	1470 vs, 1360 s	1268 m, 1140 b	478 m
C_6H_5	Ni	2	1600 m	1550 m	1470 vs, d, 1380 s	1270 m, 1150 m	483 m
C_6H_5	Co	3	1590 m	1545 m	1475 vs, 1370 s	1268 m, 1140 m	486 m
CH_3	H	1	1600 vs	1540 sh	1520 vs, 1380 s	1262 m, 1146 m	475 m
CH_3	Ni	2	1600 m	1550 m	1480 vs, 1400 s	1272 m, 1145 m	488 m
CH_3	Co	3	1590 m	1550 m	1480 vs, 1370 s	1275 m, 1150 m	480 m

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; d, doublet.

nickel(II) the spectrum of which was run at 40, 50, and 60° owing to the low solubility of the complex. No change in chemical shifts was observed over this temperature range. The spectra were calibrated as previously described.[1] All compounds were studied in 10% w/w chloroform-d, except bis(N-phenyl-2-thiocarbamoyldimedonato)zinc(II) monohydrate which was also studied in dimethyl sulfoxide-d_6.

Magnetic Measurements.—Magnetic measurements were made by the Gouy method at room temperature (24 ± 2°). The calibrant was mercury(II) tetrathiocyanatocobaltate(II).[8] The magnetic moments were corrected for diamagnetic contributions.[9] The estimated error is ±2%.

Electron Paramagnetic Resonance Spectra.—Spectra were obtained with a Varian V-4502 epr spectrometer employing 100-kHz modulation and detection and operating at about 9.5 GHz. The klystron frequency was measured by a Hewlett-Packard 5245L electronic counter with a 5255-A frequency converter. The magnetic field was determined with a proton gaussmeter, the frequency of which was measured by the same electronic counter. The samples were 20% toluene–80% chloroform solutions, and the spectra were recorded at room temperature and at 77°K.

Results

Infrared Spectra.—The band assignments listed in Table II are based on the infrared studies of monothio-β-diketones and their metal chelates by Chaston, Livingstone, *et al.*[10–12] The spectra of the 2-thiocarbamoyldimedone and the monothio-β-diketone compounds appear to be similar; however, vibrational coupling in the cross-conjugated system of 2-thiocarbamoyldimedones[7] renders assignment of bands in the 1600–1400-cm^{-1} region more difficult. The value of the carbon–sulfur stretching frequency is also uncertain. The nickel(II) chelates of N-substituted 2-thiocarbamoyldimedones exhibit two absorptions of moderate intensity at ~1270 and ~1150 cm^{-1} while the carbon–sulfur stretching frequency bands of the monothio-β-diketone–nickel chelates appear between 1260 and 1220 cm^{-1}.[10] According to the arguments of Chaston, Livingstone, *et al.*,[10] the bands in the 490–470-cm^{-1} region are attributed to metal–oxygen stretching frequencies. This assignment is questionable, however, since the band positions are independent of the nature of M, M being a proton or a divalent or trivalent metal ion.

Ultraviolet–Visible Spectra.—The increase in wavelength and intensities of the ultraviolet absorptions of N-phenyl- and N-methyl-2-thiocarbamoyldimedone upon complexation with metal ions is indicative of an enhancement of the electron delocalization in the conjugated systems of the ligands. The two bands in the visible region and the absence of any near-infrared absorption in the spectra of the nickel(II) chelates suggest a square-planar structure for these compounds. The absorptions at 16.3 and 20.4 × 10^3 cm^{-1} are tentatively assigned to the transitions $^1A_g \rightarrow {}^1B_{1g}$ and $^1A_g \rightarrow {}^1B_{3g}$, respectively, based on D_{2h} microsymmetry.[13]

Proton Magnetic Resonance Spectra.—The sharpness of the bands in the spectra and the absence of any noticeable contact shifts indicate that the nickel and cobalt complexes, as well as the zinc compound, are diamagnetic. The splitting by 5 Hz of the N-methyl resonance of each N-methyl-2-thiocarbamoyldimedone

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Table III

Ultraviolet–Visible Data (cm^{-1}) for N-Substituted 2-Thiocarbamoyldimedones and Their Metal Chelates[a]

R	M	n	$\tilde{\nu}_{max}$	$\tilde{\nu}_{max}$ (most intense)	$\tilde{\nu}_{max}$	$\tilde{\nu}_{max}$	$\tilde{\nu}_{max}$	$\tilde{\nu}_{max}$
C_6H_5	H	1		38,500 (4.32)	34,500 (4.20)			
C_6H_5	Cu	2		35,900 (4.73)	33,200 sh (4.52)	25,500 (4.08)		17,700 (2.72)
C_6H_5	Zn	2		37,000 (4.70)	32,400 (4.54)			
C_6H_5	Ni	2	42,300 (4.65)	32,200 (4.83)			20,600 (2.54)	15,900 sh (1.92)
C_6H_5	Co	3	41,400 (4.64)	33,700 (4.92)			16,400 (1.81)	
CH_3	H	1		39,800 (4.41)	37,000 sh (4.18)			
CH_3	Ni	2	42,500 (4.60)	32,800 (4.50)			20,100 (2.46)	16,300 (1.78)
CH_3	Co	3	41,200 (4.64)	35,200 (4.94)			16,600 (1.81)	

[a] Log values of molar extinction coefficients are given in parentheses; sh, shoulder.

Table IV

Proton Magnetic Resonance Data for Metal Complexes of N-Substituted 2-Thiocarbamoyldimedones[a]

R	M	n	Dimethyl	Methylene	R	N–H	O–H
C_6H_5	H	1	1.12	2.38 2.57	7.43	13.97[b]	17.37[b]
C_6H_5	Zn[c]	2	1.01	2.53 2.56	7.35	15.2	
C_6H_5	Ni	2	1.01	2.42 2.47	7.30	14.3	
C_6H_5	Co	3	1.00 1.07	2.35 (toluene) 2.43 2.65 2.75	7.18 (toluene) 7.28	14.7	
CH_3	H	1	1.05	2.42 2.50	3.14 (J = 4.8 Hz)	12.3[b]	17.11[b]
CH_3	Ni	2	1.00	2.38 2.47	3.21 (J = 5.0 Hz)	12.8	
CH_3	Co	3	1.00 1.01	2.42 2.62 2.68	3.24 (J = 5.0 Hz)	13.2	

[a] Chloroform-d solvent. In ppm downfield from tetramethylsilane. [b] Reference 7. [c] In dimethyl sulfoxide-d_6: dimethyl, 0.95; methylene, 2.40; water, 3.31; R, 7.33; N–H, 15.1.

complex (see Table IV and Figure 1) is due to the coupling with the NH proton. Thus removal of the amide hydrogen to produce an imine form on complexation is ruled out.

The larger chemical shift of the NH proton in bis(N-phenyl-2-thiocarbamoyldimedonato)zinc(II), δ 15.2 ppm, than in bis(N-phenyl-2-carbamoyldimedonato)zinc(II), δ 12.9 ppm, suggests that for the zinc chelates, as for the free ligands,[7] the hydrogen bonds involving the NH proton are stronger in the sulfur derivatives. Also the chemical shift data denote stronger hydrogen bonding of the NH group in the metal complexes than in the corresponding free ligand, the order of increasing hydrogen bonding being ligand < Ni(II) < Co(III) < Zn(II) complex. The N–H chemical shift exhibited by the zinc compound is the same for both chloroform and dimethyl sulfoxide solutions. Apparently, even in strongly coordinating solvents such as dimethyl sulfoxide, the hydrogen bond of the NH group is not perturbed. The independence of the NH chemical shift of solvent, temperature, and concentration indicates that the hydrogen bonding is intramolecular rather than intermolecular.

The existence of the zinc complex as the monohydrate, which is suggested by the elemental analysis, was corroborated by the nmr spectrum of the compound in dimethyl sulfoxide-d_6. This particular solvent was used to locate the water resonance, since proton exchange in dimethyl sulfoxide is slow.[14] The resonance at 3.31 ppm shown by the zinc complex coincides with the absorption which appears in a spectrum of the pure solvent on addition of water.

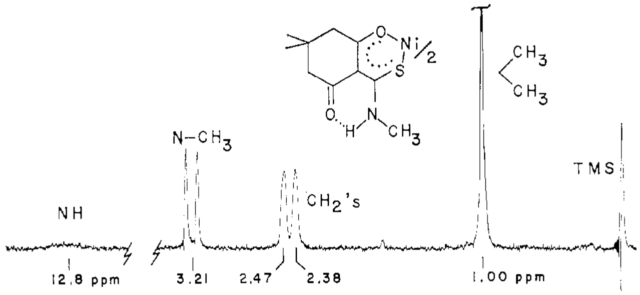

Figure 1.—Pmr spectrum ($CDCl_3$ solution) of bis(N-methyl-2-thiocarbamoyldimedonato)nickel(II).

The resonance of the methyl protons occurs as a singlet for each of the complexes except the cobalt(III) chelates where the resonance is a doublet. Also, as shown in Figure 2, the spectrum of each cobalt(III) complex contains three methylene resonances in the ratio 2:1:1 unlike the 1:1 doublet exhibited by the other 2-thiocarbamoyldimedone chelates. The *trans* isomer of the tris chelates or a mixture of *cis* and *trans* isomers may be responsible for the multiplicity of bands in the spectra of the cobalt(III) complexes.[15]

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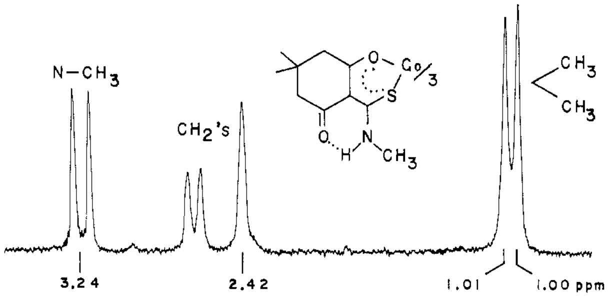

Figure 2.—Pmr spectrum ($CDCl_3$ solution) of tris(N-methyl-2-thiocarbamoyldimedonato)cobalt(III). The NH signal is not shown.

On recrystallization from toluene–hexane or benzene–hexane, tris(N-phenyl-2-thiocarbamoyldimedonato)cobalt(III) retains one molecule of the aromatic solvent per molecule of complex. Initially the crude product isolated from the reactant mixture was recrystallized once from cyclohexane to yield a crystalline solid with a decomposition point of 210° and no solvent band in its nmr spectrum. The solid, however, was no longer soluble in cyclohexane. Recrystallization of the material from toluene–hexane lowered the decomposition point to 160°. After being dried at 80° in an evacuated drying pistol for 18 hr, a sample still exhibited two solvent bands at 2.35 and 7.18 ppm in close agreement with the chemical shifts of 2.32 and 7.17 ± 0.03 ppm reported for toluene by Varian Associates.[16] The relative peak intensities suggested a ratio of one molecule of toluene to one molecule of cobalt(III) complex. The ratio was confirmed by combustion analyses. Benzene also was found to behave as a solvent of crystallization in the same molar ratio.

Magnetic Moments.—All of the metal complexes of N-substituted 2-thiocarbamoyldimedone which have been prepared in this investigation are diamagnetic except for bis(N-phenyl-2-thiocarbamoyldimedonato)copper(II). The magnetic moment of 1.87 BM recorded for the copper(II) complex is normal for a Cu(II) compound, the majority of Cu(II) compounds having magnetic moments of about 1.9 BM at room temperature.[17]

Electron Paramagnetic Resonance Spectra.—The g values obtained from room-temperature measurements are $g_0 = 2.11$ and 2.14 for the copper(II) complexes of N-phenyl-2-thiocarbamoyldimedone and N-phenyl-2-carbamoyldimedone, respectively. To obtain a good glass at liquid nitrogen temperature, the solvent mixture of 20% toluene–80% chloroform was used.[18,19] The 77°K spectra of the glasses were typical of copper(II) complexes of D_{2h} symmetry.[18] Analysis of the parallel absorptions yields $g_{\parallel} = 2.14$, $a_{\parallel}$ (Cu hyperfine splitting) $= -182 \times 10^{-4}$ cm^{-1} for bis(N-phenyl-2-thiocarbamoyldimedonato)copper(II) and $g_{\parallel} = 2.30$, $a_{\parallel} = -197 \times 10^{-4}$ cm^{-1} for bis(N-phenyl-2-carbamoyldimedonato)copper(II). The presence of "extra absorptions"[18] requires the use of a computer to obtain $g_{\perp}$ and $a_{\perp}$ values. Furthermore, evaluation of the parameters would not add significantly to the comparison of the thiocarbamoyldimedone and carbamoyldimedone chelates.[19] Consequently the values of $g_{\perp}$ and $a_{\perp}$ were not determined.

The absence of any nitrogen hyperfine splitting even at 77°K, although the line width at half-peak height was 10 gauss, indicates that the amide nitrogen is not bonded to the copper. Low values of $g_{\parallel}$ denote a high degree of covalency in the coordinate bonding of copper(II) complexes.[20] Apparently, in the 2-thiocarbamoyldimedone complex, the copper–sulfur bond is more covalent than the copper–oxygen bond in the analogous 2-carbamoyldimedone compound owing possibly to the greater polarizability of sulfur. From epr studies of copper diethyldithiocarbamate, Reddy and Srinivasan[21] reached a similar conclusion, namely, that the copper–ligand binding is more covalent with sulfur as the coordinating atom than with oxygen (or nitrogen).

Conclusion

The spectroscopic data indicate that in chelates of N-substituted 2-thiocarbamoyldimedone the sulfur atom is bonded to the metal ion. First, there is no nitrogen hyperfine splitting in the epr spectrum of bis(N-phenyl-2-thiocarbamoyldimedonato)copper(II). Second, the nmr data establish a hydrogen on the amide nitrogen which is strongly hydrogen bonded. Third, the differences betwen the 2-thiocarbamoyl- and 2-carbamoyldimedone complexes parallel the differences between metal complexes of monothio-β-diketones and β-diketones.[5] The exchange of sulfur for oxygen in the 2-carbamoyldimedone ligands changes the nickel(II) chelates from paramagnetic, associated, quasi-octahedral species to diamagnetic, square-planar complexes and converts the paramagnetic, associated, quasi-octahedral cobalt(II) complexes to diamagnetic, octahedral cobalt(III) compounds. The removal of the intermolecular association of the N-phenyl-2-carbamoyldimedone complexes on substitution of sulfur for oxygen is reflected in the increase in solubility of the compounds in organic solvents.

The oxidizing agent in the Co(II)–Co(III) transition is presumably molecular oxygen. The oxidation occurred on mixing the reagents and stirring without drawing air through the solution; however, a higher yield of the Co(III) complex was obtained using the stream of air. No bis(N-substituted 2-thiocarbamoyldimedonato)cobalt(II) was isolated. To identify the oxidizing agent, further studies are being carried out.

The epr results suggest greater covalency in the coordinate bonding of the N-phenyl-2-thiocarbamoyldimedone chelate of copper(II) than in the analogous carbamoyldimedone complex. The shift of the nickel(II) complex from high spin to low spin on exchange of

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(16) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif, 1962, spectrum no. 157.

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sulfur for oxygen indicates that sulfur produces a stronger ligand field than does oxygen in the nickel(II) chelates. This finding is in accord with the ligand-exchange studies[22] and stability constant measurements of monothio-β-diketone–nickel(II) chelates[23] which reveal that nickel(II) in a square-planar environment binds sulfur more strongly than oxygen. The high-frequency values of the first spin-allowed band in the spectra of the N-phenyl- and N-methyl-2-thiocarbamoyldimedone complexes of nickel(II) place these ligands higher in the spectrochemical series than the monothio-β-diketones investigated by Chaston and Livingstone.[22] Conjugation with the second carbonyl group in the dimedone ring may contribute to the crystal field stabilization energy.

Acknowledgment.—We thank Dr. Gerald O. Dudek for helpful suggestions. We are indebted to Harvard University for the use of various instruments. Acknowledgment is made to the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for partial support of this research.

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Notes

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The Dipolar Ion Structure of Phosphoramidic Acid. Heats of Ionization[1]

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Received November 7, 1967

Although there is conclusive evidence that amino acids exist in solution as dipolar ions, there is no completely definitive evidence concerning the structure of phosphoramidates in solution. The phosphoramidate anion, $[NH_3^+PO_3^{2-}]^-$, is believed to have a tripolar ion structure in crystals of the sodium salt.[2] This conclusion is based upon X-ray diffraction studies showing trigonal symmetry of the N–P axis with three N–O hydrogen bonds of equal length and with equal ONP angles. Although the positions of the hydrogen atoms were not determined, it is probable that if one of the hydrogen atoms were contributed by oxygen, the symmetry would be measurably disturbed.

This crystallographic study is the primary basis on which phosphoramidates are taken to have the tripolar ion structure in solution. The second ionization constant of phosphoramidic acid was found to increase in the presence of formaldehyde;[3] the first was not investigated. This result suggests and favors the dipolar ion structure of phosphoramidic acid, but it is also consistent with the "uncharged" formulation because it is quite reasonable to consider that the formaldehyde adduct of the uncharged form would be more acidic than the original structure.

The dipolar ion structure has been postulated in the treatment of hydrolysis and reactions of nucleophiles with phosphoramidic acid.[3–7]

In this work we have endeavored to obtain additional information bearing on the structure of phosphoramidic acid in solution by evaluating the heats of ionization of the first and second ionizations of phosphoramidic acid. The rationale of this method is based upon data presented in Table I. The heats of ionization of phosphoric acid at 25° involving the ionization of hydroxyl groups are numerically small for both the first and second ionizations. Therefore, we must expect that those ionizations of phosphoramidic acid which correspond to the ionization of hydroxyl groups will have numerically low heats of ionization. The heat of ionization of an ammonium function in phosphoramidic acid, on the other hand, might well be expected to have a large positive value if its ionization were the second ionization, *i.e.*, the one with $pK_a = 8.6$.

Results and Discussion

The ionizations of phosphoramidic acid can be represented as

$$\begin{array}{ccc}
\begin{matrix}[NH_3{}^+PO_3H^-]^0,\\ NH_2PO_3H_2\end{matrix} & \underset{}{\overset{-H^+,\ K_1}{\rightleftarrows}} & \left\{\begin{matrix}[NH_3{}^+PO_3{}^{2-}]^-,\\ NH_2PO_3H^-\end{matrix}\right\} \\
 & & \Big\uparrow\Big\downarrow{\scriptstyle -H^+,\ K_2} \\
 & & NH_2PO_3{}^{2-}
\end{array}$$

Values for ionization constants K_1 and K_2 were obtained from titration curves at different temperatures and ionic strengths. The ionization constants at infinite dilution (Table I) were obtained for 25° by extrapolation of the lines obtained by plotting pK *vs.* $\sqrt{\mu}/(1 + 1.15\sqrt{\mu})$ (Figure 1) in accordance with eq 1, where A and B are functions of the temperature and have the values of 0.509 and 0.329 at 25°.[8] The sym-

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[1] This research was supported by National Institutes of Health Fellowship 5F1-GM-25,555-02 and Grant NB 00573-16 and by National Science Foundation Grant 18926.

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