

reference electrode. The source of the triangular wave potential used in the oscillographic measurements was designed by Drs. D. D. DeFord and D. E. Smith of this department. Conventional polarograms were traced on a Sargent Model SR recorder and oscillograms were displayed on a Tektronix Model 502 A oscilloscope and photographed with a Tektronix Model C-13 oscilloscope camera.

A Varian Associates A-60 instrument was used to obtain the nuclear magnetic resonance spectra of the compounds studied, and the chemical shifts were measured directly from the chart. Carbon tetrachloride was used for the solvent with 2% cyclohexane as internal reference and the concentration of each compound under investigation was 0.05 mole fraction.

Calculation of molecular quantities, *e.g.*, spin densities, bond orders, etc., was performed on an IBM 709 digital computer. The input data consisted of the elements of the H-matrix, which was then diagonalized by the Jacobi routine.

Acknowledgments. The authors especially wish to thank Dr. D. F. Shriver for the use of his computer program and Dr. D. E. Smith for the use of his polarographic equipment as well as for their many helpful discussions. The Northwestern University Computing Center generously provided computer time. This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

The Nature of the Solution of Sodium Tetracarbonylcobaltate(-I) in Various Solvents^{1,2}

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. Received February 1, 1965

The ν_{CO} of $\text{NaCo}(\text{CO})_4$ is shown to be subject to a substantial solvent shift. In pure THF, the salt shows three bands in the 5- μ region of the spectra, while only one band is observed in water and DMF solutions. Conductance data for the salt indicate that ion pairs as well as larger clusters are formed in pure THF. The shape of the Δ vs. \sqrt{C} curves for water or aqueous THF solutions is also characteristic of a solution in which ions are associated. The data are interpreted in terms of the effects of the cationic field and the interaction with the environment.

Introduction

In an extension of the studies of the infrared spectra of carbonylmetallate ions in this laboratory,⁴ it has been necessary to prepare the salt of $\text{Co}(\text{CO})_4^-$ in various solvents. It was soon observed that the carbonyl stretching frequency (ν_{CO}) of this ion in the 5- μ region of the infrared spectra is subject to a substantial solvent effect. This large shift raised the question of the factors which influence the amount of the shifts and of the nature of the solutions of carbonylmetallate ions. This paper reports the results of spectrographic and conductometric studies of the $\text{Co}(\text{CO})_4^-$ anion in solutions of various mixtures of piperidine and water, THF and water, DMF and water, and THF and DMF.

Results

Infrared Spectra. The infrared spectrum of $\text{NaCo}(\text{CO})_4$ in THF solutions was examined at 5 μ over the

concentration range from 2.0 to 0.0009 *M* with a high resolution spectrometer. The cell path length was increased with dilution to keep a similar amount of solute in the beam. The general nature of the results is shown in Figure 1. A concentrated solution of $\text{NaCo}(\text{CO})_4$ in pure THF exhibits two bands in the 5- μ region, *viz.*, at 1883 (s) and 1861 (m, sh) cm^{-1} . As the solution becomes more dilute, the dissymmetry on the high frequency side of the main band becomes very pronounced and appears to give rise to a separation into two overlapping bands (1886 and *ca.* 1890 cm^{-1}) in the most dilute solutions. At the same time, the side band at 1861 cm^{-1} seems to shift toward lower frequencies and becomes more clearly separated from the more intense absorption; it was observed at 1854 cm^{-1} in the 0.026 *M* solution.

When a small amount (8%) of water was added to a THF solution of $\text{NaCo}(\text{CO})_4$, both side bands disappeared, leaving the main band at 1886 cm^{-1} nicely symmetrical. The effect of DMF was the same but more gradual. It was not until DMF constituted about half of the solvent that the side bands disappeared completely. This is the only band observed at 5 μ in these solvents and appeared at ν_{CO} 1919 cm^{-1} in water and 1892 cm^{-1} in DMF. The band in water solution was broader than that in either DMF or THF solution.

Since marked differences in the values of ν_{CO} were observed in various solvents, the value of ν_{CO} in mixed solvents was investigated. The values of ν_{CO} in various media are presented in Table I and are plotted in Figures 2 and 3. These solvent shifts are very much larger than those characteristic of neutral metal carbonyls.⁵ In all spectra examined, only one band was observed in the 5- μ region except those of the solutions in THF and in

(1) Abstracted from the Ph.D. thesis of M. T. Yang, Purdue University, 1962.

(2) Supported by a grant from the Atomic Energy Commission.

(3) Fulbright Postdoctorate Fellow, 1959-1961.

(4) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

(5) C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

Table I. Carbonyl Stretching Frequencies of $\text{NaCo}(\text{CO})_4$

Water-THF mixture			Water-DMF mixture		Water-piperidine mixture ^d	
THF, vol. %	ν_{CO} , ^a cm^{-1}	ν_{CO} , ^b cm^{-1}	DMF, vol. %	ν_{CO} , cm^{-1}	Piperidine, vol. %	ν_{CO} , cm^{-1}
0	1918.7		0	1918.7	0	1918.7
8	1917.5	1915.3	11	1915.5	9	1916.3
20	1908.2	1902.8	16.7	1914.9	17	1914.7
25		1895.8	20	1911.3	50	1894.7
40	1891.1		33.3	1906.1	67	1891.2
80	1890.8	1888.5	42.9	1902.2		
90		1887.8	50	1899.8		
95		1887.9	57.2	1898.1		
100		1887.5 ^c	66.7	1896.0		
			80	1895.7		
			83.3	1894.3		
			88.9	1893.3		
			100	1892.0		

^a This series was prepared by adding solvent to a water stock solution. ^b This series was prepared by adding solvent to a THF stock solution. ^c Side bands also appear. ^d Measured with a $\text{Ba}[\text{Co}(\text{CO})_4]_2$ solution.

the mixtures of THF and DMF containing less than 50% of DMF.

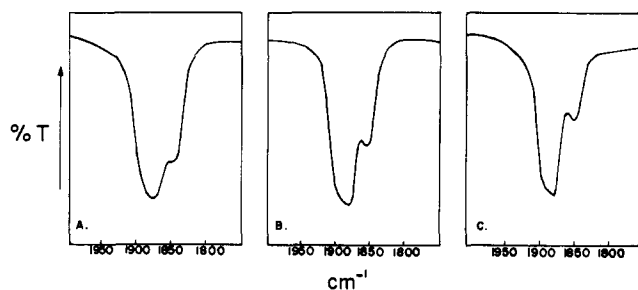


Figure 1. Infrared spectra of $\text{NaCo}(\text{CO})_4$ in THF, 5- μ region: A, 1.95 M; B, 0.20 M; C, 0.05 M.

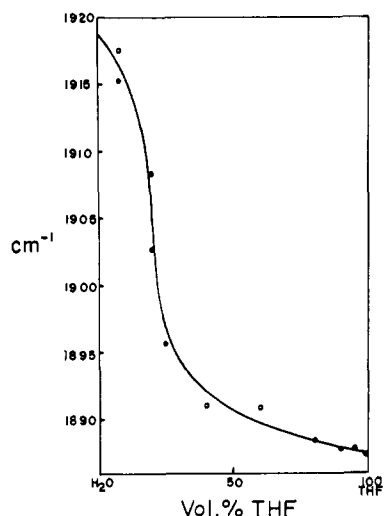


Figure 2. ν_{CO} of $\text{NaCo}(\text{CO})_4$ in THF-water mixtures.

Two bands are found⁶ in the long wave length region at 553 (s) and 528 (w) cm^{-1} . They were not appreciably affected by the solvents of different constitution. It

(6) W. F. Edgell, J. R. Huff, M. Yang, P. Cecchi, N. Koizumi, and R. Summitt, "The Infrared Spectra of the $\text{Co}(\text{CO})_4^-$ Ion in Various Compounds and Solvents. Vibrational Assignments and Force Constant Calculations. Bonding Considerations in $\text{Co}(\text{CO})_4^-$ and $\text{Ni}(\text{CO})_4$ with Extensions to Other Metal Carbonyl Derivatives," to be published.

should be noted, however, that when water was a component of the solution, only solutions with a moderate per cent of water could be studied.

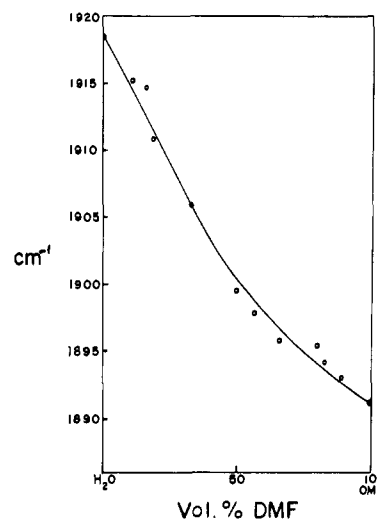


Figure 3. ν_{CO} of $\text{NaCo}(\text{CO})_4$ in DMF-water mixtures.

Conductance Measurements. The equivalent conductance (Λ) of $\text{NaCo}(\text{CO})_4$ was determined in THF, in water, and in THF-water mixtures. The results are listed in Table II and are plotted against \sqrt{C} in Figures 4 and 5.

Discussion

The conductance data for $\text{Na}^+[\text{Co}(\text{CO})_4]^-$ (Table II and Figures 4 and 5) are typical of those found with pronounced association of the anion and the cation.⁷ From the shape of the Λ vs. \sqrt{C} curve, one concludes that ion-pair formation occurs in dilute THF solutions. The deep minimum ($\sqrt{C} \approx 0.1$) and the inflection point ($\sqrt{C} \approx 0.3$) in the conductance curve for pure THF solutions (Figure 4) suggest the formation also of cluster ions, e.g., triplets and quadruplets, in the more concentrated solutions. The formation of clusters is

(7) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, Chapters XV-XVIII.

Table II. Equivalent Conductance Data of $\text{NaCo}(\text{CO})_4$ at 25°^a

THF		80% THF-20% water		20% THF-80% water		Water	
$c \times 10^2$	Λ	$c \times 10^2$	Λ	$c \times 10^2$	Λ	$c \times 10^2$	Λ
14.73	14.36	7.26	41.69	3.19	50.05	19.58	56.33
11.89	13.73	1.81	46.96	0.80	53.69	9.72	55.00
8.992	12.86	0.454	46.70	0.20	63.30	4.77	62.02
5.718	12.39	0.113	59.6	0.05	73.91	2.06	77.78
2.993	10.04	0.0284	56.4	0.0125	88.34	1.12	68.38
1.538	9.02	0.00715	84.1	0.00312	124.7	0.544	84.01
0.7476	9.56					0.276	85.52
0.4891	10.42					0.139	89.16
0.3083	11.84					0.0612	117.78
0.2089	12.53					0.0299	125.08
0.1342	14.38					0.0170	116.76

^a Units: moles/liter and mho/mole.

also evidenced by the high viscosity of the THF solution when the concentration is high. The slope of the conductance curves for the salt in aqueous THF mixtures and even in pure water itself is that commonly associated with the presence of ion pairs.

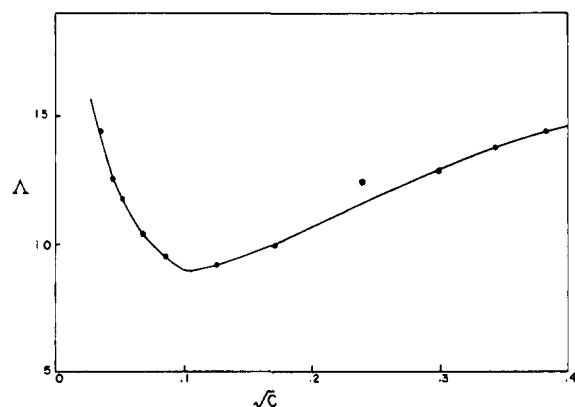


Figure 4. Equivalent conductance of $\text{NaCo}(\text{CO})_4$ in THF.

A tetrahedral tetracarbonylcobaltate(-I) ion in a spherical field would belong to the point group T_d . In this case, there are two C-O stretching frequencies, an A_1 frequency ν_2 and the F_2 frequency ν_8 . Only the latter is infrared active. If the symmetry of the ion itself is reduced, the triple degeneracy of the F_2 mode may be partially or completely lifted and the A_1 mode (ν_2) becomes infrared active. The same thing occurs if the ion finds itself in an external field whose variation with the deformation of the ion reflects a lower symmetry than that of the ion (T_d) itself. The extent of the splitting of the F_2 band and the intensity of the A_1 mode are measures of the effective dissymmetry of the ion.

The solutions of $\text{NaCo}(\text{CO})_4$ in water, DMF, water-DMF, and most of the water-THF mixtures show one band in the 5- μ (C-O stretching) region of the spectra. Consequently, it must be concluded that the deformation variation in the potential energy and the electrical field at the ion is effectively tetrahedral in these cases.

In pure THF, the salt shows a main band at 1886 (vs) with a shoulder at about 1889 (s, sh) cm^{-1} and a moderately intense band at 1858 (m) cm^{-1} . These latter bands disappear upon the addition of water or sufficient DMF. It must be concluded that the carbonylmetallate species present in THF have an effective symmetry lower than T_d . It has been shown recently

that ν_8 of $\text{Co}(\text{CO})_4^-$ appears in water at a higher frequency than ν_2 .⁶ All these data are consistent with the assignment of the 1886- cm^{-1} band and the 1889- cm^{-1} shoulder to vibrations arising from the F_2 mode ν_8 and the 1858 cm^{-1} band to the A_1 mode ν_2 .

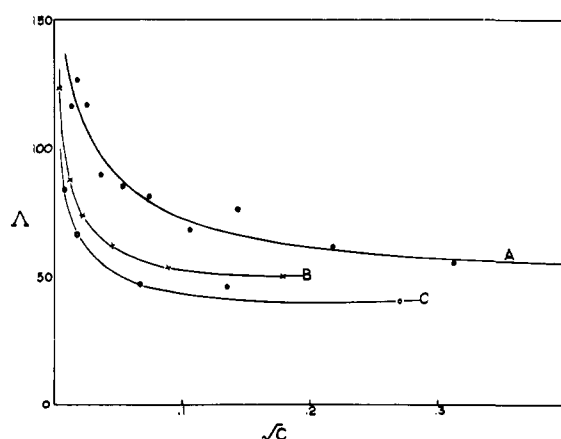
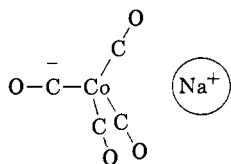


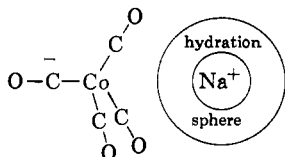
Figure 5. Equivalent conductance of $\text{NaCo}(\text{CO})_4$ in aqueous solutions: A, water; B, 80% water-20% THF; C, 20% water-80% THF.

Further light is shed on the nature of the THF solutions from the spectra obtained over the concentration range of the conductivity data plotted in Figure 4. The "extra" bands are present over the whole range but are clearly differentiated in the dilute solutions in marked contrast to the situation for the concentrated solutions. Conductance measurements show that triple and quadruple ions are present in substantial amounts in the more concentrated solutions, while ion pairs are predominant in the most dilute solutions on the low concentration side of the minimum. Yet it is just these latter solutions where the "extra" bands show most distinctly. Consequently, it must be concluded that the ion pairs in THF have an effective symmetry less than that of T_d .

The above results lead to a conclusion that the ion pairs in pure THF differ significantly from the forms (ion pairs or otherwise) which exist in the aqueous THF solutions or in water. It is interesting to speculate on the nature of this difference. The most likely possibilities for the origin of dissymmetry are the anisotropic complexing of the ion with a THF molecule and the close proximity of the sodium ion in the ion pair. The latter is illustrated diagrammatically as



The fact that a small amount of water (8%) is able to destroy this species of ion pair seems much easier to understand if the asymmetry has its origin in the sodium ion. This water may be pictured as forming a hydration sphere around the sodium ion. The hydrated ion may also associate with the $\text{Co}(\text{CO})_4^-$ in THF as illustrated. Because of the presence of the solvation



sphere, the distance between the anion and the cation in this situation is greater than that in the first case. The close proximity of the sodium ion in the first ion pair is presumed to distort the effective electrical symmetry of the $[\text{Co}(\text{CO})_4]^-$ ion with the resulting appearance of "extra" bands in the infrared spectra. It is presumed that no effective distortion of the symmetry of the $[\text{Co}(\text{CO})_4]^-$ ion occurs in the second case because of the greater separation of the sodium ion from the anion and the presence of the hydration sphere.

The data in Table I show that the ν_{CO} of the $\text{Na}^+[\text{Co}(\text{CO})_4]^-$ is subject to a substantial solvent shift. This shift takes place continuously with the variation of the composition of the solvent. This fact associates the shift with a general solvent-solute interaction rather than the existence of two species, one of which would be characteristic of the ion in one of the pure solvents while the other would be characteristic of the ion in the other pure solvent. The solvent-solute interaction includes the effect of the reaction field of the environment of the ion pair and the more specific near-neighbor interaction of atoms of the solvent and of the ion pair. Recent spectroscopic studies have emphasized the importance of the latter type of interaction for solutes which are neutral molecules,⁸ and it is presumed that the same thing is true for the solutions studied in this work.

The magnitude of the solvent shifts reported here is many times that which is characteristic of the C-O stretching frequencies of neutral metal carbonyls, *i.e.*, $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, etc.⁵ The increase in the frequency shifts is presumed to be related to the presence of the charge on the ion and is rather likely to be the consequence of the increased participation of the antibonding π -orbitals of CO in the bonding of the CO groups to the metal in the ion as compared to that in the neutral metal carbonyls.^{4,9} A simple mechanism for this effect exists in that the dipole moment localized in a CO bond is larger in the $\text{Co}(\text{CO})_4^-$ ion than in $\text{Ni}(\text{CO})_4$ as shown by the charge distributions calculated by Nieuwpoort.¹⁰

(8) See for example, W. C. Price, W. F. Sherman, and G. R. Wikinson *Proc. Roy. Soc. (London)*, **A255**, 1 (1960).

(9) W. F. Edgell, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1958, p. 32S; 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p. 29M.

(10) W. C. Nieuwpoort, private communication.

Experimental

$\text{NaCo}(\text{CO})_4$, particularly in solution, is extremely sensitive to atmospheric oxygen. All preparations and handling of carbonyl compounds were performed with rigorous exclusion of air. Organic solvents were dried and distilled in a current of nitrogen immediately before use. Distilled water and conductivity water were boiled vigorously for 30 min., after which a stream of nitrogen was passed through them for at least 2 hr. prior to use.

The dicobalt octacarbonyl used in the preparation of the salts of $\text{Co}(\text{CO})_4^-$ was supplied by Union Carbide Chemical Co., Charleston, W. Va. Cobalt carbonyl mercury was prepared according to the method described by Hieber, *et al.*¹¹

Infrared Spectra of the Solutions of $\text{NaCo}(\text{CO})_4$. The infrared spectra in the $5\text{-}\mu$ region were studied using a Perkin-Elmer Model 112G grating infrared spectrometer. A potassium bromide or a sodium chloride prism was used with a $6\text{-}\mu$ grating. In some cases, a Perkin-Elmer Model 421 spectrometer with an automatically interchanging double grating monochromator was used in the same region. For the region between 400 and 700 cm^{-1} , a Perkin-Elmer Model 12B spectrometer with cesium bromide optics was used. The absorption bands of atmospheric moisture were used as calibration standards of wave length. Demountable KBr cells were used for the solutions in organic solvents. For the aqueous solutions, BaF_2 cells were used in the $5\text{-}\mu$ region, and KRS-5 cells were used for the long wave length region. Various cell spacers were used freely to obtain sharp, well-defined absorption bands.

The aqueous $\text{Ba}[\text{Co}(\text{CO})_4]_2$ solution (0.1 *M*) was prepared by allowing $\text{Co}_2(\text{CO})_8$ to react with a saturated $\text{Ba}(\text{OH})_2$ solution.¹² The spectra in a series of water-piperidine mixtures were taken with this solution and its mixtures with piperidine. For the water-DMF and water-THF mixtures, the aqueous $\text{NaCo}(\text{CO})_4$ (1.5 *M*) was prepared by the reaction of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and 10% excess of aqueous $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ solution.^{11,13} One volume of this stock solution was diluted with a fivefold diluent of the various solvent compositions to maintain constant concentration throughout the series. Solutions of $\text{NaCo}(\text{CO})_4$ in THF and DMF (1.5 *M*) were prepared by the reaction of $\text{Co}_2(\text{CO})_8$ and 20% excess of sodium amalgam (1.2%) in the respective solvents.^{6,14,15}

A series of 16 spectra of $\text{NaCo}(\text{CO})_4$ in THF solution, in the concentration range of 2 to 0.001 *M*, was taken. The concentration of $\text{Co}(\text{CO})_4^-$ was determined by the weight of the precipitate formed with an excess of 0.1 *M* aqueous tris(*o*-phenanthroline)cobalt(II) chloride solution.

Conductance Measurement. An inductively coupled, ratio-arm bridge was constructed by N. K. The initial capacitance balance of the bridge was performed with two variable air condensers (maximum capacitance 130 $\mu\text{mf.}$) in each side of the bridge. The range of con-

(11) W. Hieber, E. O. Fischer, and E. Brockly, *Z. anorg. allgem. Chem.*, **269**, 308 (1952).

(12) W. Hieber, W. Abeck, and J. Sedlmeier, *Angew. Chem.*, **64**, 480 (1952).

(13) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1259, 1270 (1957).

(14) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **74**, 1216 (1952).

(15) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

ductance measurement was extended to 10^{-2} mho with an extension decade conductance box. The extension conductor was coupled with a General Radio Co. polystyrene decade capacitor (Type 1419-A) and a General Radio Co. variable air precision capacitor (Type 722-CB) for extended capacitance balance. An R-C oscillator (Type 1210-C) and an amplifier and null detector (Type 1231-B), both of General Radio manufacture, were used as the signal source and the detector, respectively. Power was supplied by a General Radio Co. power supply (Type 1203-B). The conductance was measured at 1 kc.

Two conductance cells consisting of two parallel, bright platinum electrodes sealed into a spherical glass bulb were used. Two glass outlets, one at the bottom and one at the top of the bulb, were used to facilitate flushing with nitrogen. The cell constants were 0.1671 and 0.1084, respectively. The cells were placed in a water thermostat maintained at $25.0 \pm 0.1^\circ$.

The specific conductance of the water used was $K = 2.062 \times 10^{-6}$ mho cm^{-1} . THF, Baker Analyzed reagent grade, was distilled over lithium aluminum hydride in a current of nitrogen. It had $K = 4.02 \times 10^{-10}$ mho cm^{-1} . The value of K for the mixture of 80% water and 20% THF was 1.685×10^{-8} and that for the mixture of 20% water and 80% THF was 6.695×10^{-7} mho cm^{-1} .

The THF solution of $\text{NaCo}(\text{CO})_4$ (*ca.* 0.15 M) used in the conductance measurements was prepared as indicated above. The aqueous $\text{NaCo}(\text{CO})_4$ solution (*ca.* 2 M) was prepared by the reaction of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with 10% less than the required amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. The solution in the mixture of 80% THF and 20% water was prepared by mixing 4 volumes of the THF solution with 1 volume of water. It was subsequently diluted with the premixed diluent. The solutions in the mixture of 20% THF and 80% water were prepared likewise starting from the aqueous solution.

The concentrations of the $\text{Co}(\text{CO})_4^-$ solutions were determined photometrically with the color developed by nitroso-R-salt and cationic cobalt. An aliquot was withdrawn from each conductance measurement solution. It was allowed to decompose in air. After evaporating the organic solvent, it was treated according to a standard procedure.¹⁶ The volume of the sample solution was adjusted so that the cobalt content of the final 50 ml. of color-developed solution fell in the range of 0.03 to 0.15 mg. A calibration curve was constructed using Baker Analyzed reagent grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The absorbance was measured at 520 $m\mu$ with a Bausch and Lomb Spectronic 20 spectrophotometer.

(16) "ASTM Methods for Chemical Analysis of Metals," American Society for Testing Materials, Philadelphia, Pa., 1960, p. 185.

New Multidentate Ligands. III. Amino Acids Containing Methylenephosphonate Groups¹

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Contribution from the Departments of Chemistry, Clark University, Worcester, Massachusetts, and Illinois Institute of Technology, Chicago 16, Illinois. Received January 23, 1965

Syntheses, properties, and metal chelate formation constants are reported for the new ligands nitriloaceticdi(methylenephosphonic) acid (NADMP), nitriloacetic- β -propioniomethylenephosphonic acid (NAPMP), and N,N,N',N'-ethylenediaminetetra(methylenephosphonic) acid (ENTMP). The stoichiometries of their acid-base and metal ion interactions are deduced from potentiometric data, and the probable structures of the metal chelates formed are inferred by comparison of their metal ion affinities with those of analogous ligands.

Since the report by Schwarzenbach and co-workers² of the high affinity of the anion of nitrilodiaceticmethylenephosphonic acid for the Ca(II) ion, it appeared that the phosphonate group might be as effective or even more effective than the carboxylate group in contributing to the chelating tendencies of polyfunctional amino

acids.³ It was the purpose of this research, therefore, to prepare additional analogs of the well-known chelating agents nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). The method of Schwarzenbach, *et al.*,² was employed for the synthesis of nitriloaceticdi(methylenephosphonic) acid (NADMP), nitriloacetic- β -propioniomethylenephosphonic acid (NAPMP), and N,N,N',N'-ethylenediaminetetra(methylenephosphonic) acid (ENTMP).³ This paper describes the synthesis and properties of these new ligands and a potentiometric study of their proton and metal ion affinities in aqueous solution.

Experimental

Nitriloaceticdi(methylenephosphonic) Acid. A 0.10-mole sample of chloromethylphosphonyl chloride was added dropwise to 100 ml. of water, 0.40 mole of NaOH was added, and the solution was allowed to stand overnight. The sodium chloride was filtered off, an equivalent (0.10 mole) of glycine was then added, and the solution was heated on a steam bath at pH 10-11 for

(1) This work was supported in part by The Dow Chemical Co., Eastern Research Laboratories, Framingham, Mass., and by the Atomic Energy Commission under Research Grant No. AT(11-1-1020).

(2) G. Schwarzenbach, H. Ackermann, and P. Ruchstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

(3) S. Westerback and A. E. Martell, *Nature*, **178**, 321 (1956).