CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Heteropoly Compounds. VII.[1] Triheteropoly Nickelates[2]

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The synthesis of the ammonium salts of all 6-heteropoly and 6-triheteropoly nickelates(II) corresponding to the general formula $(NH_4)_4[NiMo_{6-n}W_nO_{24}H_6]\cdot 5H_2O$ with $n = 0$ to 6 is described. All compounds are light blue in color. Free acids of these compounds were obtained by ion exchange. The charge on the free heteropoly anion, as determined from coagulation measurements, was found to be -4. Basicities of the free acids were obtained using a spectrophotometric technique. These were found equal to 4 over the concentration range investigated ($\sim 10^{-3}$–10^{-5} *M*).

Introduction

The most widely studied classes of heteropoly compounds are those in which the ratio of peripheral metal atoms to central atom is 6, 9, or 12; *i.e.*, 6-heteropoly, 9-heteropoly, and 12-heteropoly compounds. Species containing two or three different elements on the periphery, tri- and tetraheteropoly compounds, have been reported in the 12-heteropoly series by Kokorin[3,4] and more recently by Bulloff.[5] The compounds prepared by Bulloff contained P, As, Ge, Si, and B in the central position and various combinations of V, W, and Mo on the peripheral positions. Identification was carried out by X-ray diffraction and spectrophotometry. In addition, Simmons and Baker[6] have reported a heteropoly complex which contains two different central atoms.

In this paper we report the preparation of the 6-triheteropoly nickelates(II) of molybdenum and tungsten, corresponding to the general formula $R_4[NiMo_{6-n}W_nO_{24}H_6]\cdot 5H_2O$, where n may vary between 0 and 6. This formulation has been proposed by Baker[7] and will be discussed below. Experiments are described which have been designed to determine whether these preparations are true compounds or isomorphic mixtures of the diheteropoly compounds. We also have determined the anionic charge, basicity, and degree of polymerization in dilute aqueous solution by coagulation and spectrophotometry.

The diheteropoly end compounds, $R_4[NiMo_6O_{24}H_6]$ and $R_4[NiW_6O_{24}H_6]$, were first prepared by Barbieri[8] and Agarwala and Baker,[9] respectively. These compounds are sky blue. Earlier attempts to synthesize the molybdenum compound by Marckwald[10] and Hall[11] and the tungsten compound by Rosenheim, Pieck, and Pinsker[12] resulted in green compounds, indicating the presence of cationic nickel and casting doubt on the purity of the preparation. The only triheteropoly nickelate reported is that prepared by Fernandes,[13] a sky blue compound formulated by him as $K_6H_4[Ni(MoO_4)_2(WO_4)_4]\cdot xH_2O$.

Experimental

A. Preparation of Compounds. 1. Ammonium Heteropoly Nickelates(II).—The di- and triheteropoly nickelates(II) of molybdenum and tungsten were prepared by dissolving in 200 ml. of water a total of 60 mmoles of W and Mo in various ratios. For W, $Na_2WO_4\cdot 2H_2O$ was used and for Mo, MoO_3 except for mole ratios Mo:W of 6:0 and 5:1, for which $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Na_2MoO_4\cdot 2H_2O$, respectively, were used. This mixture was boiled to effect solution and the pH was adjusted to 6–7 by addition of NaOH or HCl as required. To this, another solution containing 2.6 g. of $NiSO_4\cdot 6H_2O$ was added dropwise with stirring (about one drop per second). The color changed from green to blue-green and finally to a yellowish green. The mixture was refluxed for about 10 min. and then filtered. Ten g. of NH_4Cl was added to the filtrate, whereupon a light blue salt precipitated. This salt was moderately soluble in cold water, soluble in boiling water, and insoluble in benzene, ethyl alcohol, and ether. It decomposed in strongly acidic and moderately alkaline solutions. The product was recrystallized from hot aqueous solution, washed, air dried, and analyzed. Each preparation and each analysis was duplicated at least once.

2. Free Acids of Heteropoly Nickelates(II).—The free acids of the above salts, prepared from integral mole ratios of Mo and W, were obtained by ion exchange using Amberlite IR-120 as described previously.[14–16] Nickel could not be detected in the effluent of the solution which was used for the regeneration of the ion exchange column, indicating that no nickel in cationic form was present in the heteropoly salts exchanged on the same column. Solutions of the free acids showed the same optical absorption spectra as the ammonium salts from which they were prepared. Unlike the salts, concentrated solutions of the free acids became slightly turbid after several weeks, indicating decomposition. There was no apparent decomposition during shorter periods of time nor did very dilute solutions indicate decomposition for periods as long as 1 month. The free acids cannot be obtained by double decomposition of ammonium heteropoly nickelates with mineral acids, as can be done with some other heteropoly acids (12-tungstosilicic acid or tungstophosphoric acids).

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(1) Part VI: J. R. Keller, E. Matijević, and M. Kerker, *J. Phys. Chem.*, **65**, 56 (1961).

(2) Supported by the International Nickel Company, Inc.

(3) A. I. Kokorin, *Zh. Obsch. Khim.*, **27**, 549 (1957).

(4) A. I. Kokorin and N. A. Polotebnova, *ibid.*, **27**, 304 (1957), and cited literature.

(5) J. J. Bulloff, Proc. 7th International Conference on Coördination Chemistry, Stockholm, 1962, p. 195.

(6) V. E. Simmons and L. C. W. Baker, ref. 5, p. 195.

(7) L. C. W. Baker, "Advances in the Chemistry of the Coördination Compounds," The Macmillan Company, New York, N. Y., 1961, pp. 604–612.

(8) G. A. Barbieri, *Atti accad. Lincei*, **23**, [II] 357 (1914).

(9) U. C. Agarwala and L. C. W. Baker, presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, Abstract No. 43, p. 16-M.

(10) E. Marckwald, Dissertation, Basel, 1895.

(11) R. D. Hall, *J. Am. Chem. Soc.*, **29**, 692 (1907).

(12) A. Rosenheim, M. Pieck, and J. Pinsker, *Z. anorg. allgem. Chem.*, **96**, 139 (1916).

(13) L. Fernandes, *Gazz. chim. ital.*, **56**, 655 (1926).

(14) L. C. W. Baker, B. Loev, and T. P. McCutcheon, *J. Am. Chem. Soc.*, **72**, 2374 (1950).

(15) L. C. W. Baker, G. A. Gallagher, and T. P. McCutcheon, *ibid.*, **75**, 2493 (1953).

(16) E. Matijević and M. Kerker, *ibid.*, **81**, 5560 (1959).

B. Analyses.—Ammonia was determined using the usual Kjeldahl procedure. **Nickel** was determined by titration using Titriplex III (disodium salt of ethylenediaminetetraacetic acid) and Murexide (ammonium salt of purpuric acid) as the indicator.[17] **Tungsten** was determined gravimetrically as WO_3 after separation from molybdenum as described by Marbaker.[18] The total loss of NH_3 and H_2O was obtained by heating separate samples at 500° to constant weight.

C. Materials and Instruments.—All chemicals used were of the purest commercial grade. Solutions were prepared with doubly distilled water, the second distillation being carried out in an all-Pyrex still.

Absorption measurements were obtained using a Beckman DU spectrophotometer and calibrated silica cells. A Beckman Model G pH meter with glass electrodes was used for pH measurements.

D. Coagulation and Spectrophotometry.—A coagulation method was employed for the determination of the charge of heteropoly nickelate ions in solution. This method has been described in detail earlier.[16,19–21] In the present work, positive silver bromide sols *in statu nascendi* were coagulated with solutions of the ammonium salts and the free acids of all the diheteropoly nickelates(II) and the triheteropoly nickelates(II) corresponding to integral Mo:W ratios.

The basicity was determined by a spectrophotometric method described earlier.[16,22] Methyl orange was used as the indicator. Optical densities were obtained at 520 mμ.

Results

A. Synthesis and Characterization of Triheteropoly Nickelates.—The analyses of the ammonium salts of the heteropoly nickelates are summarized in Table I. Each preparation, corresponding to a particular mole ratio of Mo:W, was carried out at least in duplicate and each of these were analyzed in duplicate. Both the reproducibility of the preparations and the precision of the analyses were high. For example, the tungsten content for duplicate preparations was generally within 0.5% (*e.g.*, 40.0 ± 0.1%).

Those preparations for which integral ratios of Mo:W were used in the reaction mixture gave crystals whose analyses corresponded to a triheteropoly compound with the same mole ratio. The question may be posed as to whether these preparations are truly heteropoly compounds or isomorphous mixtures of the two diheteropoly end compounds, containing the same ratio of Mo:W as the reaction mixture. The various compounds of the 6-series are known to be isomorphous and there might possibly be the same correspondence between the mole ratio of Mo:W in the starting mixture and in the product. In order to explore this possibility, preparations were obtained in which half integral ratios of Mo:W were used in the reaction mixture. The W analyses for these runs also are reported in Table I. Only for Mo:W = 1.5:4.5 was the ratio in the product approximately the same as the starting ratio. In all other cases, the amount of W was rather close to that of a triheteropoly compound of integral ratio of Mo:W. Obviously there is not a simple correspondence between the composition of the product and the initial mixture.

TABLE I

PREPARATION AND ANALYSIS OF HETEROPOLY NICKELATES(II): $(NH_4)_4[NiMo_{6-n}W_nO_{24}H_6]\cdot 5H_2O$

Mole ratio Mo:W in reaction mixture		Ni	W	Mo	NH_3	$H_2O + NH_3$
	Calcd. for $n = 0$	4.95	..	48.5	6.08	20.9
6:0	Found	4.98	..	48.3	6.11	20.3
	Calcd. for $n = 1$	4.60	14.4	..	5.66	19.5
5.6:0.5	Found	..	15.7	..	..	..
5:1	Found	4.43	13.8	..	5.69	20.6
	Calcd. for $n = 2$	4.31	27.0	..	5.30	18.2
4.5:1.5	Found	..	25.6	..	..	..
4:2	Found	4.20	27.9	..	5.22	17.7
	Calcd. for $n = 3$	4.05	38.0	..	4.97	17.1
3.5:2.5	Found	..	36.0	..	..	..
3:3	Found	4.02	37.8	..	5.03	16.6
	Calcd. for $n = 4$	3.81	47.8	..	4.64	16.1
2.5:3.5	Found	..	47.4	..	..	..
2:4	Found	3.71	48.3	..	4.46	16.1
	Calcd. for $n = 5$	3.61	56.5	..	4.44	15.3
1.5:4.5	Found	..	51.5	..	..	..
1:5	Found	3.51	56.0	..	4.37	15.6
0.5:5.0	Found	..	58.2	..	..	..
	Calcd. for $n = 6$	3.42	64.4	..	4.21	14.5
0:6	Found	3.46	64.2	..	4.06	14.2

In a second experiment the preparations obtained with Mo:W = 3:3 and an equimolar mixture of the two diheteropoly compounds were recrystallized. The salts were rapidly dissolved in boiling water and the clear solution was immediately and rapidly cooled down in order to prevent possible reaction at the high temperatures. After five recrystallizations (in which 20 g. of salt was reduced to 4 g.) the 3:3 product analyzed precisely the same as the starting material, *viz.*, 37.8% W, compared to a calculated theoretical value of 38.0%. On the other hand the W composition of the equimolar mixture of the two diheteropoly salts changed from 37.8 to 39.0% after two recrystallizations (29 g. of salt reduced to 8.3 g.). This indicates that the 3:3 product is not simply a mixture of the two diheteropoly compounds.

Supporting evidence for the existence of triheteropoly anions was obtained from spectrophotometric data in the ultraviolet which are presented in Fig. 1. Here, absorption curves for solutions of the diheteropoly compounds $(NH_4)_4[NiMo_6O_{24}H_6]$ and $(NH_4)_4[NiW_6O_{24}H_6]$ and an equimolar mixture of these are compared with the preparation whose analysis corresponds to $(NH_4)_4[NiMo_3W_3O_{24}H_6]$. The pH of these solutions was carefully maintained at 4.92. The spectra were not found to be pH dependent in this range. In the case of the equimolar mixture, the smooth curve is calculated from the spectra of the pure diheteropoly compounds assuming Beer's law and the dots are the experimental points. These experiments were duplicated with completely independent preparations of the heteropoly compounds. Again, it is quite obvious that the preparation whose analysis corresponds to $(NH_4)_4$-

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[17] "Complexometric Assay Methods with Titriplex," published by E. Merck AG, Darmstadt.

[18] E. E. Marbaker, *J. Am. Chem. Soc.*, **37**, 86 (1915).

[19] E. Matijević and M. Kerker, *J. Phys. Chem.*, **62**, 1271 (1958).

[20] E. Matijević, D. Broadhurst, and M. Kerker, *ibid.*, **63**, 1552 (1959).

[21] B. Težak, E. Matijević, and K. F. Schulz, *ibid.*, **55**, 1557 (1951).

[22] J. R. Keller, E. Matijević, and M. Kerker, *ibid.*, **65**, 56 (1961).

$[NiMo_3W_3O_{24}H_6]\cdot 5H_2O$ is not a simple equimolar mixture of the two diheteropoly compounds.

In still another experiment the solution consisting of the equimolar mixture of the diheteropoly compounds was heated in a closed bottle for several hours at 90° and the spectrum taken after cooling to room temperature. This time the spectrum was identical with that obtained for the preparation with Mo:W = 3:3.

The spectrophotometric experiments eliminate the possibility that the preparations are isomorphous mixtures of diheteropoly compounds and along with the analytical work constitute strong evidence for the existence of the triheteropoly species. The question still remains as to whether we are dealing with a mixture of all the triheteropoly and the two diheteropoly species, or whether those preparations for which the analyses correspond to a particular compound do consist primarily of that compound. Indeed, even if a single triheteropoly species were synthesized, it might be argued that this would upon dissolution then equilibrate into a mixture of several species. Such equilibration would depend on the lability of the Mo–O and W–O bonds. The evidence presented here cannot definitively decide this question. However, in the last experiment described above, the equimolar mixture of end compounds reacted to give the spectrum of the 3:3 compound only when heated at 90°. This demonstrates that the Mo and W ligands are labile only at elevated temperatures.

The high stability at room temperature is consistent with Shoemaker's[23] finding that the enantiomorphic 9-molybdomanganate(IV) ion, $[Mn^{IV}O_6Mo_9O_{26}]^{-6}$, retains optical activity in solution. Furthermore, Tsigdinos[24] has shown by potentiometric titration that whereas there is no sign of complex formation between Ni^{+2} and $[Mo_7O_{24}]^{-6}$ at room temperature, the reaction proceeds at a measurable rate at about 60°. Accordingly, if a pure triheteropoly compound were formed, the evidence indicates that upon dissolution at room temperature it would not equilibrate to a mixture but rather would remain metastable.

It is quite likely that the reaction mixture, at the elevated temperatures at which synthesis is carried out, consists of an equilibrium mixture of all species and that those species with Mo:W ratios closest to the ratio of starting materials would predominate. In such a case, if the distribution of species is "frozen in" upon cooling, there would be an enrichment of such species upon precipitation and the crystals might even consist primarily of a single species. The fact that integral ratios of Mo:W were obtained in most cases, even when the starting ratio was half integral, is quite consistent with the possibility that the preparations consist of a single predominant species.

B. Basicity and Ionic Charge.—Eriks, *et al.*,[25] have shown, by single crystal X-ray work, that the 6-molybdo- and 6-tungstonickelates(II) have the Anderson[26]–Evans[27] structure so that the acids must be formulated as $[H_{10}NiMo_6O_{24}]_m$ and $[H_{10}NiW_6O_{24}]_m$. Agarwala and Baker[9] and Tsigdinos[24] have established the monomeric formulation ($m = 1$) by fused hydrate cryoscopy in Glauber's salt. Also, they have reported that the anions contain water of constitution, *i.e.*, there is non-ionizable H in the anion. Baker[7] has formulated these anions as $[NiO_6W_6O_{18}H_6]^{-4}$ and $[NiO_6Mo_6O_{18}H_6]^{-4}$, placing the non-ionizable H on the O atoms surrounding Ni. Tsigdinos[24] prepared the free acid by ion exchange of the ammonium salt and attempted to determine the basicity by potentiometric titration with NaOH. An end point was not obtained until the addition of twelve equivalents of NaOH. Tsigdinos concluded from the shape of the titration curve that decomposition of the acid had taken place.

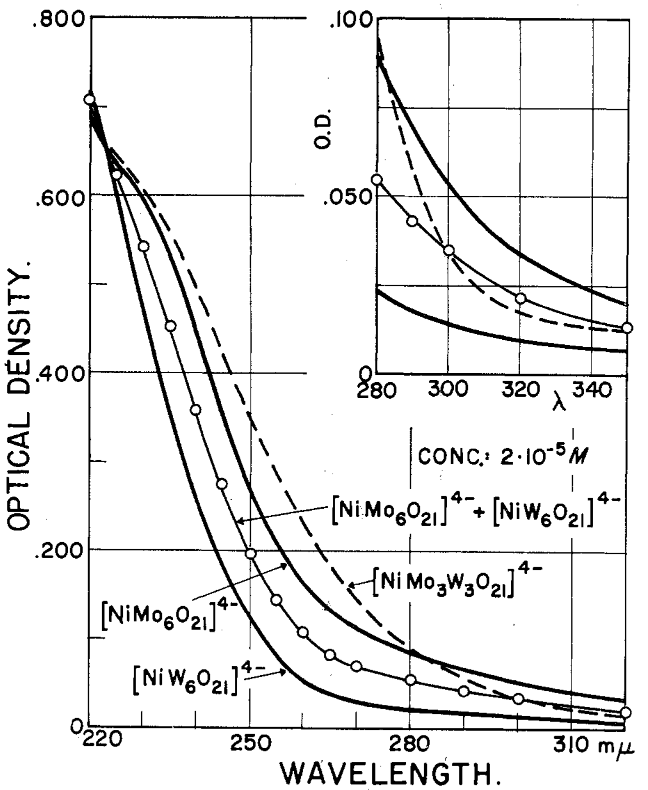

Fig. 1.—Optical densities of 2×10^{-5} molar solutions of $(NH_4)_4[NiMo_6O_{24}H_6]$, $(NH_4)_4[NiW_6O_{24}H_6]$ (heavy full lines), $(NH_4)_4[NiMo_3W_3O_{24}H_6]$ (dashed line), and of an equimolar mixture of $(NH_4)_4[NiMo_6O_{24}H_6]$ and $(NH_4)_4[NiW_6O_{24}H_6]$ (this line calculated, circles experimental).

We also have studied this problem utilizing a spectrophotometric and a coagulation technique to investigate the basicity and the degree of polymerization of the 6-heteropoly nickelic(II) acids. These techniques have been successful in elucidating this problem in connection with other heteropoly compounds[19,20,22] of the 12-series (12-tungstophosphoric, 12-tungstosilicic, 12-molybdoceric(IV) acids), the 9-series (9-tungstophosphoric acid), and the 6-series (6-molybdochromic(III) and 6-molybdocobaltic(III) acids).

The spectrophotometric method used gives the degree of ionization as a function of concentration. Since it does not require titration with alkali, it does not subject

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[23] D. P. Shoemaker, private communication, 1957; cited in ref. 24.

[24] G. A. Tsigdinos, Ph.D. Dissertation, Boston University, 1961.

[25] K. Eriks, N. F. Yannoni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Cryst.*, **13**, 1139 (1961).

[26] J. S. Anderson, *Nature*, **140**, 850 (1937).

[27] H. Evans, Jr., *J. Am. Chem. Soc.*, **70**, 1291 (1948).

Table II

Basicity of Heteropoly Nickelates(II)

$H_4[NiMo_6O_{24}H_6]$			$H_4[NiMo_3W_3O_{24}H_6]$			$H_4[NiW_6O_{24}H_6]$		
Molarity × 10^4	Optical density	Basicity	Molarity × 10^4	Optical density	Basicity	Molarity × 10^4	Optical density	Basicity
7.15	0.2845	4.1	8.62	0.290	4.0	6.28	0.279	4.1
6.44	.280	4.0	6.76	.2825	4.0	5.56	.270	3.9
5.72	.275	4.0	4.83	.268	4.0	5.03	.265	4.0
5.01	.271	4.2	3.86	.2565	4.0	4.40	.260	4.1
4.29	.2635	4.0	2.90	.242	3.9	3.77	.245	4.1
2.86	.245	4.1	1.93	.2185	3.8	2.51	.235	4.1
1.43	.2185	4.05	0.965	.1875	3.9	1.26	.200	4.0
0.715	.1825	4.0	.862	.1845	3.9	0.629	.1565	4.2
.572	.170	4.0	.483	.137	4.1	.503	.142	4.1
						.314	.115	4.0

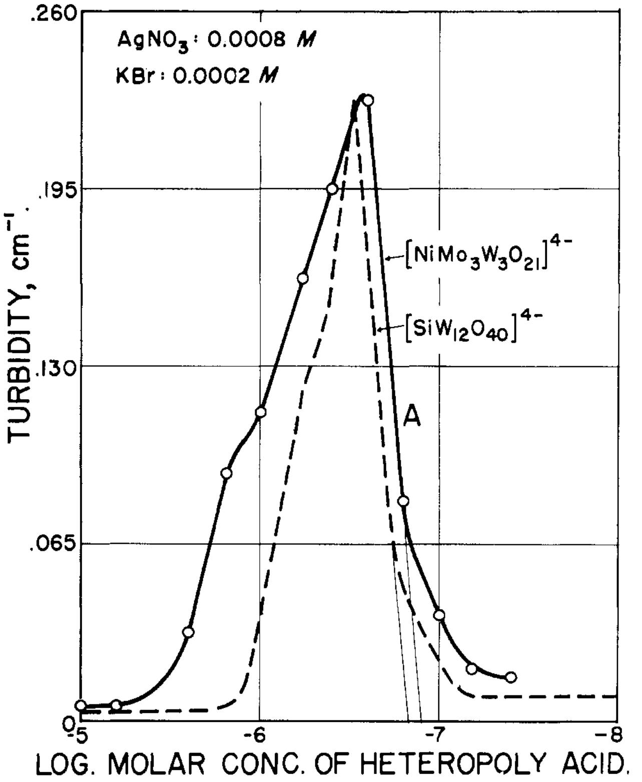

Fig. 2.—Coagulation curves for $H_4[NiMo_3W_3O_{24}H_6]$ and $H_4[SiW_{12}O_{40}]$ for a positive silver bromide sol *in statu nascendi*. Turbidities were obtained 60 min. after mixing the reacting components.

the compound to possible decomposition. The coagulation method leads to the actual charge of the prevalent ionic species in solution by using the latter as the coagulating ion for a lyophobic colloid. The combination of these two techniques on solutions of comparable concentration permits determination of the degree of polymerization of the species in question in the aqueous medium.

The coagulation experiments were performed with both the diheteropoly acids and the five preparations corresponding to integral Mo : W ratios. As an example of the results, the coagulation curve of the 3 : 3 preparation is given in Fig. 2. The coagulation curve for 12-tungstosilicic acid obtained earlier also is included.[19] The "coagulation limit" denoted by A in the diagrams is dependent on the charge of the counter ion, in this case the heteropoly ions. The agreement between the coagulation limits for the 12-tungstosilicic acid and the 3 : 3 preparation is excellent. Since there is little doubt that the 12-tungstosilicate ion has a charge of -4, the same charge must be assigned to the triheteropoly nickelate(II) ion used in this experiment. All of the other heteropoly and triheteropoly nickelates gave similar results, in agreement with the formulation $H_4[NiMo_{6-n}W_nO_{24}H_6]$. In view of the sensitivity of the coagulation limit to the charge of heteropoly anions (see Fig. 5, ref. 19) there is little doubt that all of these solutions contain primarily quadruply charged anions at high dilutions.

Basicity experiments were carried out for the two diheteropoly acids and for the preparation with a Mo : W ratio of 3 : 3. The results are given in Table II. Optical densities are for 10-cm. cells at 520 mμ. From these the indicator ratio is obtained, and the number of hydrogen ions per formula unit of heteropoly acid is calculated and reported as basicity. The basicity remains constant over the more than 10-fold dilution, which would indicate that the acids are completely ionized at these concentrations. Thus, they appear to be comparable in acid strength to the tribasic 6-molybdochromic(III) acid, tetrabasic 12-tungstosilicic acid, and hexabasic 9-tungstophosphoric acid, all of which also are completely ionized over this concentration range.

The dilute solutions of the acids (10^{-3}–10^{-5} *M*) were stable as evidenced by no changes in either pH or the visible and ultraviolet absorption spectra over a period of 2 months from the time of the preparation of the solutions. In addition, the basicity was determined repeatedly over a period of 1 month and identical results were obtained over the entire concentration range.

The basicity experiments alone do not permit one to draw conclusions regarding the degree of polymerization, *e.g.*, a basicity of four is consistent with eight hydrogen ions from a dimer. However, the fact that the ionization is complete at the concentrations under consideration, combined with the coagulation experiments which indicate that the prevalent anionic species has a -4 charge, unambiguously demonstrates that in dilute aqueous solution these acids are tetrabasic and monomeric.

The present work is unable to provide evidence regarding the presence of six non-ionizable hydrogens included in the coördination sphere as waters of constitution. However, the formulation $[Ni_6OMo_nW_{6-n}O_{18}H_6]^{-4}$ has been used since it is consistent with recent X-ray and dehydration experiments in the solid state.[6]

Acknowledgment.—The financial support and advice of the International Nickel Company, Inc., which made this work possible is greatly appreciated. We are indebted to Dr. George L. Jones for the determination of basicities.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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A Thermodynamic Study of the Coördination Compounds of Transition Metal Ions with 2-Pipecolylamine and 2-(2-Aminoethyl)-piperidine[1]

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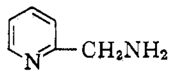
Formation constants were determined by the use of potentiometric titrations for 2-pipecolylamine with copper(II), nickel(II), and cobalt(II) ions and for 2-(2-aminoethyl)-piperidine with copper(II) and nickel(II) ions over the temperature range 10 to 40°. These values were used to estimate the dative π-bonding in the analogous unsaturated compounds.

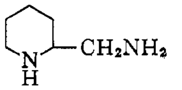
Introduction

Formation constants have been determined for a wide variety of amines with transition metal ions,[2] as for example ethylenediamine and its derivatives[3] and 2-picolylamine

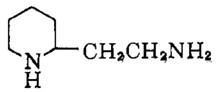


and its derivatives[4, 5] as well as the analogous amines with one more methylene group between the nitrogen atoms.[4,6]

In the present study data have been extended to include 2-pipecolylamine and 2-(2-aminoethyl)-piperidine.



2-Pipecolylamine



2-(2-Aminoethyl)-piperidine

The above ligands, with saturated rings, are of interest for comparison with their unsaturated analogs since differences can be interpreted in terms of dative π-bonding involving the aromatic rings in coördination compounds of the latter. Comparisons of the effects of ring size, base strengths, inductive effects, and steric effects also can be made using these data and existing data for known compounds. Stability constants were evaluated at temperatures of 10 to 40° under conditions of low ionic strength which could be calculated to zero ionic strength in harmony with previous work[3]—so that valid comparisons could be made.

Experimental

All procedures, except the preparations of amines, have been described previously.[4]

Amines.—2-Pipecolylamine and 2-(2-aminoethyl)-piperidine were prepared by the reduction with sodium and alcohol[7] of 2-picolylamine (Aldrich Chemical Co., Inc.) and 2-(2-aminoethyl)-pyridine (L. Light and Co., Colnbrook, England), respectively. 2-Pipecolylamine, obtained in 40% yield, boiled at 81–83° (24 mm.) [lit.[8] 80–81° (18 mm.)] and had a neutral equivalent of 113.8; calculated 114.19. 2-(2-Aminoethyl)-piperidine, obtained in 40% yield, boiled at 115–116° (15 mm.) and 106° (10 mm.) [lit.[9] 106–107° (10 mm.)]. The neutral equivalent was 131.1; calculated 128.22.

Results

Table I lists the protonation constants and formation constants determined in this investigation. The 95% confidence intervals are given with each value. Formation constants were not obtained for zinc(II), cadmium(II), and silver(I) with 2-pipecolylamine and for zinc(II), cadmium(II), and cobalt(II) with 2-(2-aminoethyl)-piperidine due to formation of precipitates. A third constant for nickel(II) and 2-(2-aminoethyl)-piperidine was not obtained. This same result was noted for 1,3-propanediamine by Bertsch[6] and for 2-(2-aminoethyl)-pyridine by Goldberg.[4]

Both Bertsch[6] and Goldberg[4] report no second constant for the 1,3-diamines with copper(II). A second ligand was coördinated with 2-(2-aminoethyl)-piperidine, although the constants obtained did vary somewhat with $\bar{n}$. It is interesting to note two items in this respect; first Bertsch[6] reported that the violet color

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[1] A portion of a thesis presented by Robert P. Held for the degree of Master of Arts, June, 1962.

[2] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, I. Organic Ligands," Special Publication No. 6, The Chemistry Society, Burlington House, London W 1, 1957.

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[4] D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, **63**, 1246 (1959).

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