garding 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,
BROOKLYN COLLEGE OF THE CITY UNIVERSITY OF NEW YORK, BROOKLYN, NEW YORK

A Thermodynamic Study of the Coördination Compounds of Transition Metal Ions with 2-Pipecolylamine and 2-(2-Aminoethyl)-piperidine[1]

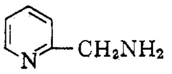
BY ROBERT P. HELD AND DAVID E. GOLDBERG

Received July 3, 1962

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.

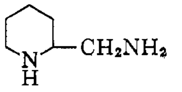
Introduction

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

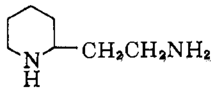


and its derivatives[4, 5] as well as the analogous amines with one more methylene group between the nitrogen atoms.[4,6]

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.

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TABLE I

THERMODYNAMIC PROPERTIES

	n	log K_n[a]				$-\Delta F^0_n$	$-\Delta H^0_n$[b]	ΔS^0_n[b]
		10°	20°	30°	40°	30°	10–40°	10°
2-Pipecolylamine complexes								
H^+	1	9.97 ± 0.05	9.70 ± 0.07	9.46 ± 0.04	9.21 ± 0.05	13.1	11	6
	2	6.54 ± 0.24	6.33 ± 0.04	6.12 ± 0.06	5.77 ± 0.15	8.5	10	−4
Cu^{2+}	1	10.12 ± 0.02	9.85 ± 0.04	9.60 ± 0.02	9.24 ± 0.14	13.3	12	5
	2	8.51 ± 0.04	8.21 ± 0.025	7.96 ± 0.07	7.58 ± 0.03	11.0	11	−1
Ni^{2+}	1	6.56 ± 0.21	6.37 ± 0.02	6.23 ± 0.03	6.02 ± 0.02	8.6	7	4
	2	5.39 ± 0.03	5.17 ± 0.025	4.98 ± 0.07	4.95 ± 0.025	6.9	7	1
	3	3.66 ± 0.03	3.36 ± 0.00	2.90 ± 0.02	3.16 ± 0.02	4.0	6	−5
Co^{2+}	1	4.99 ± 0.04	4.91 ± 0.025	4.81 ± 0.03	4.78 ± 0.04	6.7	3	1
	2	4.65 ± 0.04	4.49 ± 0.04	3.96 ± 0.04	4.17 ± 0.04	5.5	7	−6
2-(2-Aminoethyl)-piperidine complexes								
H^+	1	10.78 ± 0.08	10.37 ± 0.02	10.10 ± 0.06	9.87 ± 0.09	14.0	11	9
	2	8.79 ± 0.16	8.33 ± 0.07	8.07 ± 0.02	7.81 ± 0.02	11.2	12	−2
Cu^{2+}	1	9.14 ± 0.02	8.76 ± 0.00	8.60 ± 0.03	8.49 ± 0.025	11.9	8	12
	2	6.44[c]	5.94[c]	5.86[c]	5.77[c]	8.1	8	0
Ni^{2+}	1	5.45 ± 0.02	5.28 ± 0.02	5.28 ± 0.03	5.37 ± 0.00	7.3	1	21
	2	[d]	4.31 ± 0.06	4.42 ± 0.02	4.55 ± 0.03	6.1	−4[e]	5

[a] Values of K_n are *formation constants* defined as equilibrium constants for the equation $MA_{n-1}^{+x} + A \leftrightarrows MA_n^{+x}$. [b] Estimated from measurements of log K_n at temperatures from 10 to 40°. [c] Value doubtful, K varies slightly with $\bar{n}$. [d] Precipitation. [e] Averaged over 20–40°.

characteristic of the 2:1 diamine chelate with copper(II) was not obtained from the deep blue color of the 1:1 chelate upon addition of further 1,3-propanediamine. This same lack of color change was noted here. Second, Lane and Thompson[10] did report a second constant for 2-(2-aminoethyl)-pyridine which is comparable to the one found in this investigation. Their work was in 50 volume % dioxane.

No data are reported with silver(I) and 2-(2-aminoethyl)-piperidine due to the variation of log K with $\bar{n}$. This same result was noted by Goldberg[4] with 2-picolylamine, 2-picolylmethylamine, and 2-(2-aminoethyl)-pyridine. This behavior probably is due to the tendency of silver ion to form bimetallic complexes, as noted by Schwarzenbach.[11]

Attainment of equilibrium between 2-(2-aminoethyl)-piperidine and nickel(II) was slow for the first few additions of amine. This effect was noted for similar ligands by Goldberg[4] and by Bjerrum.[12] Apparently this behavior is not due to precipitation and there is no obvious reason for this slow attainment of equilibrium.

The values for the second formation constants for the nickel(II) and 2-(2-aminoethyl)-piperidine system are somewhat in doubt. Precipitation occurred at 10°, but reproducible values were obtained at 20, 30, and 40°. The stability constants increase with temperature, and the calculated ΔH is positive.

Discussion

Protonation Constants.—Both log K_1 and log K_2 are lower for 2-pipecolylamine (9.46 and 6.12 at 30°) than for N-methyl-1,2-ethanediamine[3] (9.90 and 6.63) but significantly higher than for 2-picolylamine[4] (8.51 and 3.1). The unsaturated nitrogen atom of the latter compound is weakly basic compared to the saturated nitrogen atoms of the former, bringing about this effect.

Both log K_1 and log K_2 are lower for 2-(2-aminoethyl)-piperidine (10.10 and 8.07) than for 1,3-propanediamine (10.32 and 8.33), but significantly higher than those for 2-(2-aminoethyl)-pyridine (9.52 and 3.84), analogous to the above situation.

Protonation constants of the aminoethylpiperidine are greater than those for the pipecolylamine because of the greater separation of the two nitrogen atoms. This observation is in agreement with data for 1,2-ethanediamine[3] and 1,3-propanediamine[6] and for 2-picolylamine[4] and aminoethylpyridine.[4]

Formation Constants.—The formation constants of 2-pipecolylamine are lower than those of 1,2-ethanediamine, due to the lower base strength and the greater steric effects in the former. The same can be said for 2-(2-aminoethyl)-piperidine compared with 1,3-propanediamine. However, a comparison of the formation constants of 2-pipecolylamine with 2-picolylamine and 2-picolylmethylamine, and of 2-(2-aminoethyl)-piperidine with 2-(2-aminoethyl)-pyridine, indicates that some other factor has to be considered, since the pyridines have a much higher stability than indicated from their base strengths. This stability is attributed to their ability to form dative π-bonds in their coordination compounds.

Formation constants of 2-pipecolylamine are uniformly higher than those for 2-(2-aminoethyl)-piperidine. This effect is in full agreement with the higher stability with divalent metal ions of saturated five-membered chelate rings over six-membered chelate rings.[2,13]

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TABLE II

VALUES OF THE RATIO $\Delta F_i/[(\Delta F_H)_1 + (\Delta F_H)_2]$[a,b]

	i	Cu	Ni	Co
2-Pipecolylamine	1	0.62	0.40	0.31
	2	.51	.32	.25
	3		.19	
2-(2-Aminoethyl)-piperidine	1	.47	.29	
	2	.32	.24	

[a] $t = 30°$; ionic strength → 0. [b] Equivalent data for similar ligands are given in ref. 4.

Interpretations.—The relative stability of different coördination compounds per unit of base strength for the ligand is shown in Table II. Goldberg and Fernelius,[4] in an attempt to estimate the π-bonding contribution to the over-all stability, compared the ratio $\Delta F/[(\Delta F_H)_1 + (\Delta F_H)_2]$ for ligands which could form π-bonds to the ratio for ligands which could not. Systems were chosen to minimize other differences in ligands. Steric effects were not too dissimilar and base strength was taken into account in the analysis. This investigation yields data by which 2-picolylamine can be compared to a ligand with closer (though still not identical) steric properties. This comparison shows slightly lower to equal ratios for 2-pipecolylamine compared to ethylenediamine and 2-(2-aminoethyl)-piperidine compared to 1,3-propanediamine, and indicates that the π-bonding contribution of 2-picolylamine and 2-(2-aminoethyl)-pyridine is at least as great as originally supposed.[4]

Acknowledgment.—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell research grant in support of this work, and to Dr. W. C. Fernelius for his many suggestions.

CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Partial Resolution of Some Copper(II) and Nickel(II) β-Ketoimine Compounds by Means of a Chromatographic Technique

BY TONG-MING HSEU, DEAN F. MARTIN, AND THERALD MOELLER

Received November 19, 1962

Adsorption of some copper(II) and nickel(II) β-ketoimines on a column of D-lactose, followed by elution with benzene–petroleum ether, effects partial resolution of the compounds into optically active fractions. In all systems, complete recovery of solute was characteristic. The optically active fractions were subject to racemization at rates inversely related to the degree of steric hindrance present in the β-ketoimine. Negative results were obtained in attempts to resolve bis-(4-iminopentane-2-ono)-copper(II) although attempts to resolve the analogous nickel(II) compound were partially successful.

In connection with studies of the kinetics and mechanisms of chelate- and amine-exchange reactions involving β-ketoimine–metal compounds, it was of interest to obtain optically active samples of these compounds. The successful partial resolution of certain trivalent metal acetylacetonates by means of a chromatographic technique using D-lactose[1-3] suggested a possible application to bivalent metal derivatives of β-ketoimines. The existence of enantiomers of the type $M[RCOCHC(=NR'')R']_2$ was expected to arise from one of several possible causes: distortion from a planar configuration because of steric interaction of the terminal groups (R, R′, and R″), the existence of a tetrahedral configuration, or the existence of an octahedral configuration due to association either with other complex molecules or with solvent.

A few chelating agents capable of forcing a tetrahedral disposition of metal valences have been devised. The most successful of these are 2,2′-bis-(salicylideneamine)-6-6′-dimethyldiphenyl and 2,2′-bis-(salicylideneamino)-diphenyl for which the copper(II), but not the nickel(II), derivatives have been prepared.[4] The resolution of the copper(II) derivatives by a chromatographic technique was suggested, but the results seem never to have been reported.

The third possible cause of optical activity might be expected for nickel(II) compounds. Most nickel chelate compounds suspected of being examples of tetrahedral compounds have been shown to have an octahedral disposition of nickel–donor atom bonds either as a result of inclusion of other ligands within the coördination sphere[5] or as a result of molecular association.[6] It is interesting to note that Craig and Mellor[7] have suggested that tetracoördinate nickel(II) chelate compounds involving O and N donor atoms have a planar distribution of metal valences. Recent studies[8,9] of nickel–salicylaldimine compounds confirmed the

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