[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Metal Complexes of Purine and Some of its Derivatives

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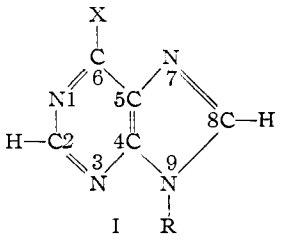
The acid dissociation constants of purine and some of its derivatives have been investigated and the reactions between these purines and certain divalent metal ions have been described. The stoichiometry of the metal complexes in the acid region has been determined; also, their formation constants have been evaluated.

The Calvin–Bjerrum[2] potentiometric titration technique and spectrophotometric measurements have been used to study the behavior of some divalent metal ions with purine and some of its derivatives.

This investigation is a part of a systematic study of the interactions of metal ions with purines and pyrimidines. Previous work[3] on the reaction between 6-aminopurine (adenine) and divalent metal ions indicated that the imino group of the imidazole ring was involved in the reaction. The present work shows that this is not the case with 6-mercapto-, 6-hydroxy- and 9-methyl-6-mercaptopurine but is so with purine, 6-chloro- and 6-methylmercaptopurine.

The compounds investigated in this study are conveniently represented by I



X	R	Compound
-H	-H	Purine
-SH	-H	6-mercaptopurine
-OH	-H	6-hydroxypurine (hypoxanthine)
$-SCH_3$	-H	6-methylmercaptopurine
$-NH_2$	-H	6-aminopurine (adenine)
-Cl	-H	6-chloropurine
-SH	$-CH_3$	9-methyl-6-mercaptopurine

Experimental

The titration apparatus, purification of 1,4-dioxane, standardization of sodium hydroxide and perchloric acid have been described previously.[4]

Potentiometric measurements of *p*H values were made with a Beckman Model "G" *p*H meter equipped with an external glass-saturated calomel electrode pair and standardized with Beckman buffers at *p*H 4 and 7.

Stock solutions of approximately 0.01 *M* metal ions were prepared by dissolving their reagent grade perchlorates, obtained from G. Frederick Smith Co., in water.

The nickel(II) solution was standardized by precipitation with dimethylglyoxime. The zinc(II) solution was standardized by precipitation with diammonium hydrogen phosphate. The lead(II) solution was standardized by precipitation as the sulfate.

6-Mercaptopurine hydrate, obtained from the Nutritional Biochemicals Corp., was recrystallized from boiling water with charcoal and dried at 110°.

Anal. Calcd. for $C_5H_4N_4S \cdot H_2O$: C, 35.28; H, 3.55. Found: C, 35.23; H, 3.34.

The equivalent weight found by titrating the mercaptide proton was 167 (theoretical 170.2).

6-Hydroxypurine (hypoxanthine), obtained from Nutritional Biochemicals Corp., was recrystallized according to the procedure of Hitchings.[5]

Anal. Calcd.: N, 41.2. Found: N, 41.7.

6-Chloropurine was obtained through the courtesy of Dr. G. H. Hitchings, The Welcome Research Laboratories, Tuckahoe 7, New York.

The equivalent weight found by titrating the imino proton was 155.0 (theoretical 154.6).

Anal. Calcd.: Cl, 22.9. Found: Cl, 22.4.

6-Methylmercaptopurine was prepared from 6-mercaptopurine according to the procedure of G. Elion, *et al.*[6]

Melting point: reported: 218–220°. Found: 216–218°.

6-Aminopurine (adenine) was obtained from Nutritional Biochemicals Corp. and dried at 110°.

Anal. Calcd.: C, 44.5; H, 3.7. Found: C, 44.4; H, 3.7.

Purine was obtained from Nutritional Biochemicals Corp. and dried at 110°. The equivalent weight found by titrating the imino proton was 119.1 (theoretical 120.1).

9-Methyl-6-mercaptopurine was obtained through the courtesy of Dr. Roland K. Robins, Department of Chemistry, Arizona State College, Tempe, Arizona.

Ultraviolet absorption spectrum: Reported[7]: λ_{max} 324 mμ; a = 19,600 at *p*H 1 in HCl. Found: λ_{max} 324 mμ; a = 19,100 at *p*H 1 in HCl.

The titration procedure has been described[3] previously for 6-aminopurine (adenine) and was used for purine, 6-chloro- and 6-methylmercaptopurine; for the remaining derivatives of purine the procedure differed in that 2.0 ml. of metal ion and 3.0 ml. of water were used instead of 5.0 ml. of metal ion.

The maximum ionic strength μ was 0.01.

The method for the calculation of the formation constants has been described.[4]

Absorption spectra were obtained with a Beckman Model DU spectrophotometer using matched 1 cm. silica cells.

Results

The acid dissociation constants determined are summarized in Table I. pK_{a_1} refers to the dissociation of the protonated species, pK_{a_2} refers to the dissociation of the 6-substituent and pK_{a_3} refers to the dissociation of the imino hydrogen in the nine position.

The formation constants for purine and the substituted purine metal reactions are recorded in Table II. In the case of 6-mercapto- and 6-hydroxypurine, log K_2 could not be evaluated because precipitation of the metal complex occurred at the higher *p*H values. However, it was possible to obtain values of log K_{av} ($\bar{n}$ = 1.0 where $\bar{n}$ is the average number of donor groups bound per metal ion) before the onset of precipitation with these

(1) Department of Chemistry, University of Arizona, Tucson, Arizona.

(2)(a) M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945); (b) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(3) T. R. Harkins and H. Freiser, THIS JOURNAL, **80**, 1132 (1958).

(4) H. Freiser, R. G. Charles and W. H. Johnston, *ibid.*, **74**, 1383 (1952).

(5) G. H. Hitchings, *J. Biol Chem.*, **139**, 843 (1941).

(6) G. B. Elion, E. Burgi and G. H. Hitchings, THIS JOURNAL, **74**, 411 (1952).

(7) R. K. Robins and H. H. Lin, *ibid.*, **79**, 490 (1957).

TABLE I

ACID DISSOCIATION CONSTANTS OF PURINE AND ITS DERIVATIVES IN 50% V./V. DIOXANE–WATER AT 25.0°

Compound	pK_{a_1}	pK_{a_2}	pK_{a_3}
Purine	2	..	9.23
6-Aminopurine	3.54	..	10.65
6-Chloropurine	<2	..	8.21
6-Hydroxypurine	<2	9.66	...
6-Methylmercaptopurine	<2	..	9.50
6-Mercaptopurine	<2	8.67	11.9
9-Methyl-6-mercaptopurine	<2	9.19	...

two reagents, except for the case of cobalt(II) and 6-hydroxypurine.

The stoichiometry of the 6-mercaptopurine–copper(II) complex was determined by Job's method of continuous variations at *p*H 5.[8,9] These results which seem to indicate a 2:1 complex, 6-mercaptopurine to copper(II), are shown in Fig. 1. However, preliminary evidence has been obtained that 6-mercaptopurine reduces Cu(II) to Cu(I). A detailed investigation of this reaction now is being undertaken and will be reported later.

TABLE II

COMPLEX FORMATION CONSTANTS OF SOME SUBSTITUTED PURINES IN 50% V./V. DIOXANE–WATER AT 25.0°

Metal ion	log K_1	log K_2	2 log K_{av}
	6-Mercaptopurine		
Ni(II)	5.29	..	10.2
Co(II)	5.44	..	9.6[a]
Pb(II)	6.61	..	12.1
Zn(II)	5.90	..	11.6
	6-Hydroxypurine		
Cu(II)	7.55	..	14.8
Ni(II)	5.04	..	9.6
Pb(II)	5.04	..	9.2[a]
Zn(II)	6.03	..	11.9[a]
	6-Aminopurine		
Cu(II)	8.94	..	16.8
Ni(II)	6.18	..	12.0[a]
Zn(II)	6.42	..	12.4[a]
	6-Chloropurine		
Cu(II)	6.13	5.66	11.8
	6-Methylmercaptopurine		
Cu(II)	7.69	7.27	14.9
	Purine		
Cu(II)	6.90	6.44	13.5
Ni(II)	4.88		9.3
	9-Methyl-6-mercaptopurine		
Ni(II)	6.76	5.78	12.2

[a] Maximum rather than true values due to hydrolysis of metal ion.

The stoichiometry of the 6-chloropurine–copper(II) complex was investigated by the mole ratio method of Yoe and Jones.[10] The results obtained suggest a 2:1 complex, 6-chloropurine to copper(II) at *p*H 6.5. These results are presented in Fig. 2.

(8) P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

(9) W. C. Vosburgh and G. F. Cooper, THIS JOURNAL, **63**, 437 (1941).

(10) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

In any titration, five ml. of 0.1 *N* sodium hydroxide is required to neutralize the excess perchloric acid and any protonated species which may be present; consequently, the displacement of the purine, perchloric acid and metal ion curve at 5 ml. of base from the purine and perchloric acid must be due to proton release, which in the absence of metal hydrolysis must depend on the reaction between the purine and the metal ion. All metal ions titrated in this study show an equivalent weight corresponding to one-half the molecular weight. Thus, it may be concluded that all complexes are 2:1, purine to metal ion.

Titration curves of 6-mercaptopurine in the presence of copper(II), nickel(II), zinc(II), lead(II) and cobalt(II) are presented in Fig. 3. Titration curves of hypoxanthine in the presence of copper(II), nickel(II), zinc(II) and lead(II) are given in Fig. 4.

The displacement of the 6-mercaptopurine–metal curves except cobalt at 7.5 ml. of base may be attributed to the dissociation of the imino hydrogen in the nine position of 6-mercaptopurine–metal complex and may well reflect the strength of metal ligand bonding since the weaker hypoxanthine metal complexes in Fig. 4 do not show this marked displacement. Further, the 6-mercaptopurine–metal complexes dissolve at this point whereas those of hypoxanthine do not.

Titration curves of 6-chloropurine in the presence of copper(II) are presented in Fig. 5. The displacement at 9 ml. of base is attributed to hydrolysis of the copper in the 2:1 complex.

Discussion

Dissociation Constants.—There are a number of nitrogen atoms which might act as basic centers in the purine system. Cochran[11] on the basis of X-ray crystallographic data concluded that the proton in 6-aminopurine (adenine) hydrochloride is bound to the number one nitrogen. Albert and Brown,[12] by comparing the basicities of imidazole, benzimidazole, pyrimidine, purine and adenine, also suggested that the principal basic center of adenine may be located in the pyrimidine ring. Harkins and Freiser[3] concluded that the basic center in adenine was the amino group. The present study is in accord with the conclusions of the latter authors.

A comparison of the pK_{a_1} values for the 6-substituted purines other than adenine, suggests that the absence of a basic group having a pK_{a_1} in the vicinity of three to four may be attributed to the absence of the amino group. It may be argued that this behavior is consistent with the assumption that the ring nitrogen in position 1 or 3 is the basic center and that the substituents in the 6-position reduce its basicity, inasmuch as there is such an effect upon the basicity of the nitrogen in the 9-position. Thus, when the amino group is successively replaced by methylmercapto, hydrogen and chloro groups there is a corresponding decrease in the basicity of the nitrogen atom, *i.e.*, an increase in the acidity of the imino hydrogen. The effect of substituents upon the 9 nitrogen may be understood readily in terms of a meso-

(11) W. Cochran, *Acta Cryst.*, **4**, 81 (1951).

(12) A. Albert and D. J. Brown, *J. Chem. Soc.*, 2061 (1954).

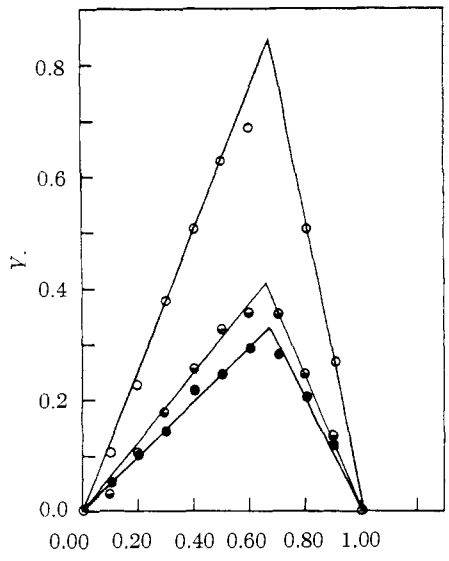


Fig. 1.—Job's method of continuous variations of copper(II) and 6-mercaptopurine; 9.53×10^{-5} mole per liter 50% v./v. dioxane–water. Y = calcd. absorptivity − obsd. absorptivity *vs.* mole fraction of 6-mercaptopurine: ○, λ 327 mμ; ◒, λ 312 mμ. Y = obsd. absorptivity − calcd. absorptivity *vs.* mole fraction of 6-mercaptopurine: ●, λ 284 mμ.

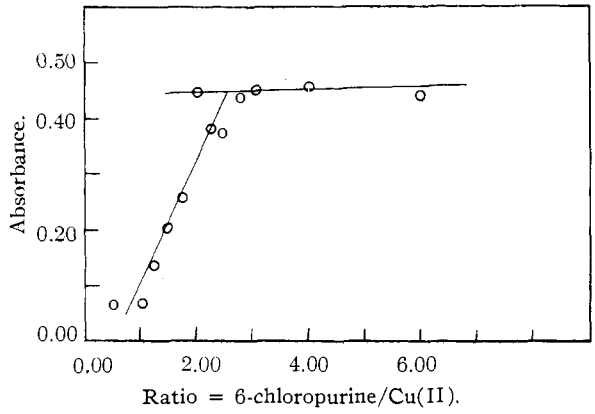


Fig. 2.—Mole ratio method of 6-chloropurine and copper(II) in 50% v./v. dioxane–water at *p*H 6.5 adjusted with sodium hydroxide; λ 578 mμ.

meric effect[13] whereby the amino group has a greater tendency than the methylmercapto and chloro groups to supply electrons *via* the +M mechanism to the unsaturated purine system. However, the +M effects of the –OH and $-NH_2$ groups are sufficiently close to warrant a comparison of the pK_{a_1} values of hypoxanthine (pK_{a_1} = 1.98 in water)[12] and adenine (pK_{a_1} = 4.22 in water).[3,12] The great difference in these pK_{a_1} values is a strong indication that different basic centers are involved in these two compounds. It has been shown by Pullman and Berthier[14] that the $-NH_2$ group in adenine has a greater electron density than any other nitrogen atom in

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. 2.
(14) B. Pullman and G. Berthier, *Compt. rend.*, **243**, 380 (1956).

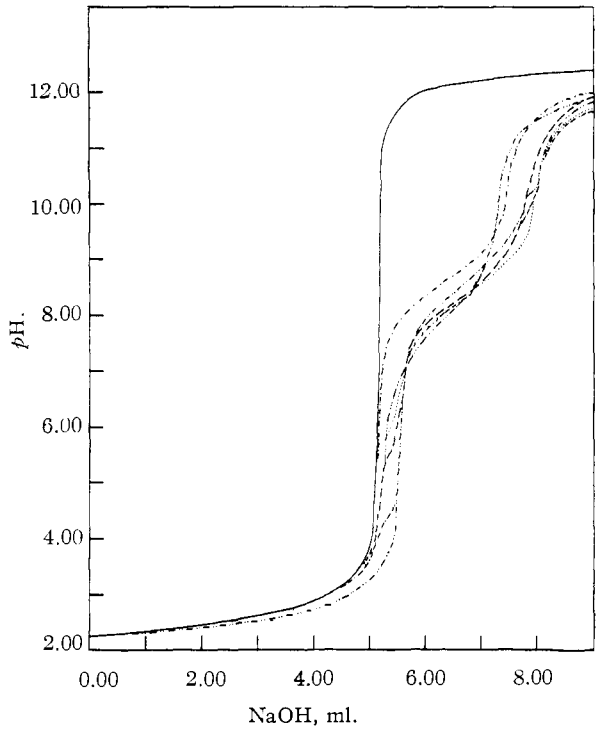


Fig. 3.—Titration curves of 6-mercaptopurine (0.22 mmole) + $HClO_4$ (0.50 mmole) in 50% v./v. dioxane–water: ———, perchloric acid *vs.* sodium hydroxide; –·–·–·, 6-mercaptopurine; —··—, copper(II); – – ·– – · lead(II); – – – –, zinc(II); ....., nickel(II); –···– cobalt(II). Metal = 0.02 mmole.

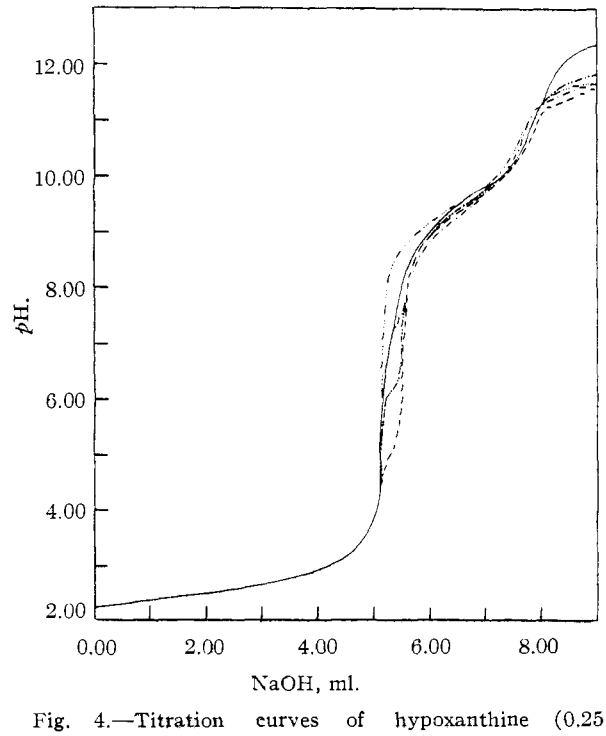


Fig. 4.—Titration curves of hypoxanthine (0.25 mmole) + $HClO_4$ (0.50 mmole) in 50% v./v. dioxane–water: –···–, hypoxanthine; – – – –, copper(II); –·–·–, zinc(II); –·–·–·, nickel(II); ———, lead(II). Metal = 0.02 mmole.

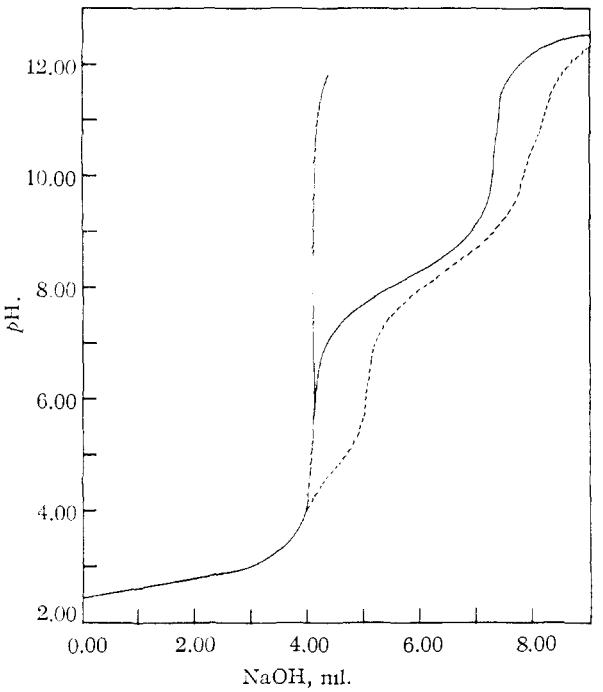


Fig. 5.—Titration curves of 6-chloropurine (0.33 mmole) + $HClO_4$ in 50% v./v. dioxane–water: ———, $HClO_4$; ———, 6-chloropurine + $HClO_4$; - - - -, copper(II) (0.05 mmole).

the molecule. Mason[15] in a molecular orbital study of purine predicted that the basic center would be the nitrogen atom with the greater charge density. Hence, from this study and the preceding arguments, we conclude that the $-NH_2$ group in adenine is more basic than any of the purine nitrogens.

Strong evidence that pK_{a_2} in 6-mercapto- and 6-hydroxypurine refers, respectively, to the mercapto and hydroxy group is the fact that methylation of 6-mercaptopurine with methyl iodide in the presence of one equivalent of sodium hydroxide results in the formation of 6-methylmercaptopurine with no methylation taking place in the 9-position.[6] Also, the increase in the value of pK_{a_2} for 9-methyl-6-mercaptopurine (9.19) over that for 6-mercaptopurine (8.67) may be attributed to the inductive effect of the methyl group which should lower the acidity of the mercapto group. This is consistent with the above interpretation of electronic interaction between the substituent in the six position with the nitrogen in the nine position and the assignment of pK_{a_2} to the mercaptan dissociation.

The decrease in acidity on going from 6-mercapto- to 6-hydroxypurine parallels results obtained for *o*-aminobenzenethiol and *o*-aminophenol[16] for mercapto and hydroxyl groups.

The great increase in basicity of the imino group of 6-mercaptopurine over that of purine, adenine, 6-chloro- and 6-methylmercaptopurine is readily rationalized on the basis that further dissociation from an anion is involved. The fact that pK_{a_1} is too high to be estimated potentiometrically for 6-hydroxypurine is consistent with the greater +M effect of $-O^-$ compared with that of $-S^-$.[13]

Formation Constants.—The optimum *p*H range for an accurate evaluation of formation constants by the Calvin–Bjerrum technique is between 3 and 6 for the solvent medium employed in this study.[4] A comparison of *p*H values for the beginning of complex formation, $\bar{n} = 0.1$, complex formation at $\bar{n} = 1.0$, and the beginning of metal hydrolysis is presented in Table III. It would have been desirable to determine formation constants at higher reagent to metal ion ratios and thereby lower the *p*H range for complex formation, below the hydrolysis region of the metal ion concerned. Unfortunately, for 6-mercapto- and 6-hydroxypurine the maximum ratio of purine to metal ion obtainable was 9:1 and 15:1, respectively, because of the low solubility of the purines.

TABLE III

THE INTERFERENCE OF METAL HYDROLYSIS IN REACTIONS OF METAL IONS WITH 6-SUBSTITUTED PURINES

Metal	*p*H at $\bar{n} = 0.1$	*p*H at $\bar{n} = 1.0$	*p*H at start of metal hydrolysis in 50% v./v. dioxane–H_2O at 25°
	6-Mercaptopurine		
Ni(II)	5.9	6.5	7.3
Co(II)	4.4	6.6	5.8
Zn(II)	4.9	5.8	6.4
Pb(II)	4.2	5.5	6.2
	6-Hydroxypurine		
Cu(II)	4.3	4.6	5.2
Ni(II)	6.6	7.6	7.3
Zn(II)	6.2	6.4	6.4
Pb(II)	7.0	7.7	6.2
	6-Aminopurine		
Cu(II)	4.0	4.8	5.2
Ni(II)	6.3	7.1	7.3
Zn(II)	6.2	6.9	6.4

From Table III it may be seen that hydrolysis of the metal ion interferes to some extent in complex formation for the following reactions. Cobalt(II) with 6-mercaptopurine; lead(II) with 6-hydroxypurine, zinc(II) with both 6-hydroxy- and 6-aminopurine, and nickel(II) with 6-hydroxypurine. For these particular cases, the values of 2 log K_{av} shown in Table II must be regarded as maximum rather than true values. Hydrolysis did not interfere in other purine–metal reactions.

Two important conclusions concerning 6-mercapto- and 6-hydroxypurine may be drawn from Table II and Table IV. First, the metal stability sequence with the mercaptopurine seems unusual. Second, the mercaptopurine forms more stable chelates than the hypoxanthine despite its weaker basicity (*i.e.*, proton affinity).

The usual empirical stability sequence for divalent metal ions is: Cu > Ni > Pb > Co > Zn as has been pointed out by Mellor and Maley[17] holds with minor variations for many oxygen and nitrogen type ligands. In this study the stability sequence was found to be for 6-mercaptopurine:

(15) S. F. Mason, "The Chemistry and Biology of Purines," Little, Brown and Co., Boston, Mass., 1957, pp. 72–75.

(16) R. G. Charles and H. Freiser, THIS JOURNAL, **74**, 1385 (1952).

(17) D. P. Mellor and L. Maley, *Nature*, **159**, 370 (1947); **161**, 436 (1948).

TABLE IV

SUMMARY OF DIFFERENCES IN 2 LOG K_{av} FOR Ni(II), Pb(II) AND Zn(II) WITH A NUMBER OF REAGENTS

Reagent	Metal ions compared and relative stability order	Difference in 2 log K_{av} at 25.0°
6-Mercaptopurine	Pb > Zn	0.5
6-Hydroxypurine	Zn > Pb	0.6[a]
o-Aminobenzenethiol[14]	Pb > Zn	1.3
o-Aminophenol[14]	Zn > Pb	0.7
6-Mercaptopurine	Zn > Ni	1.4
6-Hydroxypurine	Zn ≥ Ni	2.3[a]
o-Aminophenol[14]	Ni ≥ Zn	0.2
Mercaptoacetic acid[16]	Zn > Ni	1.5[b]
β-Mercaptopropionic acid[19]	Zn > Ni	3.2[b]
6-Aminopurine	Zn ≥ Ni	0.4[a]
Ammonia[2]	Zn > Ni	1.2[b,c]

[a] Hydrolysis interferes. [b] In water. [c] At 30° in water.

Pb > Zn > Ni > Co and for 6-hydroxypurine: Cu > Zn, Ni > Pb.

The change in the relative position of lead and zinc in these two compounds is similar to that which was reported by Charles and Freiser with *o*-aminobenzenethiol and *o*-aminophenol,[14] and would seem to reflect a general trend in sulfur-containing reagents.

Concerning the relative positions of zinc and nickel in the 6-mercaptopurine sequence the order may also be attributed to the participation of the sulfur atom in the bonding of the purine–metal complex. Further evidence that zinc(II) forms a stronger complex than nickel(II) when sulfur is involved in the ligand metal bond has been presented by Leussing[18] on the stabilities of mercaptoacetic acid–metal complexes and by Fernando and Freiser[19] on the stabilities of β-mercaptopropionic acid–metal complexes.

Acknowledgment.—The authors gratefully acknowledge the financial assistance of the U. S. Public Health Service.

(18) D. L. Leussing, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1958.

(19) Q. Fernando and H. Freiser, THIS JOURNAL, **80**, 4928 (1958).

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Synthesis and Spectra of Some Chromium(III) Complexes with 2-Methyl-1,2-propanediamine[1a,b]

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Conventional methods for the synthesis of tris-(ethylenediamine)-chromium(III) compounds (and some propylenediamine analogs), when isobutylenediamine (ibn) is used instead of ethylenediamine, generally have been found either to give no reaction or to yield bis-(ibn) complexes. Five new complex compounds have been isolated and characteriz d by chemical analyses and spectral methods: *trans*-$[Cr(ibn)_2(NCS)_2]SCN$, ox(ibn)Cr-ox-Cr(ibn)ox, $[H_2O(ibn)_2Cr\text{-}O\text{-}Cr(ibn)_2H_2O](SO_4)_2\cdot 7H_2O$, $[(ibn)_2Cr\text{-}(OH)_2\text{-}Cr(ibn)_2](ClO_4)_4$ and $[(ibn)_2Cr\text{-}(OH)_2\text{-}Cr(ibn)_2]Cl_4$. Spectral studies have shown that the latter complex undergoes interesting spectral transformations in aqueous solutions made weakly basic, similar to changes exhibited in the rapid conversion of the acidic rhodo cation to basic rhodo cation and the slower subsequent change to the erythro ion. Evidence was obtained for the existence of the $Cr(ibn)_3^{+3}$ ion. Chromium(III) forms complexes with ibn much less readily than with ethylenediamine or propylenediamine. The tendency of chromium(III) amines to form "ol" or "diol" bridges is greatly accentuated with ibn.

Chromium(III) complexes with ibn are of interest because this unsymmetric, optically inactive 1,2-diamine ligand implies the possible existence of eight diacidobis-(ibn) isomers (2 *trans* and 3 pairs of *d*- and *l*-*cis* isomers), possibly permitting a distinction among different mechanisms of substitution and isomerization reactions of chromium complexes. Apparently no such complexes have been reported in the literature, although compounds of Co(III),[2,3] Ni(II),[4] Cu(II),[4] Pd(II)[5,6] and Pt(II)[6,7] with ibn have been described. From studies[8–11] of some chromium(III) and many cobalt(III) complexes with en, C-substituted en and diamines with three or more methylene groups between the two amine groups, the stability of the complexes with five-membered chelate rings is known[11–13] to be much greater than for complexes with six or more atoms in the ring. Alkyl substitution at the carbon atoms usually affects only slightly the complexing properties of the 1,2-diamines (evidence mainly from cobalt complexes), whereas large effects are sometimes encountered with similar C-substitutions in 1,3-diamines, as for 2,2-dimethyl-1,3-propanediamine (neopentanediamine), a much

(1) (a) Abbreviations used: ibn = 2-methyl-1,2-propanediamine (isobutylenediamine); pn = 1,2-propanediamine (propylenediamine); en = ethylenediamine; py = pyridine; ox = oxalato. (b) Work partly supported under Contract AT(11-1)-34, Project 12, between the U. S. Atomic Energy Commission and the University. (c) On leave of absence from the Technical University of Denmark, Copenhagen.

(2) F. Basolo, THIS JOURNAL, **75**, 227 (1953).

(3) R. G. Pearson, C. R. Boston and F. Basolo, *ibid.*, **75**, 3089 (1953).

(4) F. Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954).

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(9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952.

(10) J. C. Bailar, Jr. (editor), "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956.

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