EXPERIMENTAL

Compounds. The $[Co(NH_3)_6]Br_3$ used was the same material as previously described.(2) The $(NH_4)_2CoBr_4$ was prepared by heating a 2:1 molar mixture of ammonium bromide and cobalt (II) bromide for 30 min at 225°C.

Thermoanalytical techniques. The procedures used in the techniques of thermogravimetric analysis, high temperature magnetic susceptibility, and reflectance spectroscopy were the same as previously described.(1)

RESULTS AND DISCUSSION

The mass-loss and the percentage cobalt (III) ion reduced curves are given in Fig. 1. As can be seen, the $[Co(NH_3)_6]Br_3$ began to lose mass beginning at about 225°C. At about this same temperature, reduction of the cobalt (III) $\rightarrow$ cobalt (II) ion began also, indicating that intermediate compounds containing cobalt (III) were not formed in the reaction. This is contrary to the report by Viltange(3) in which cobalt (III) bromide was reported as an intermediate compound. Reduction of the cobalt (III) ion was completed at 280°C. From the mass-loss curve, only cobalt (II) bromide was found at 310°C which then oxidized to form the Co_3O_4 mass level beginning at 380°C. In an attempt to further detect any intermediate ammine complexes, the $[Co(NH_3)_6]Br_3$ was also heated for long periods of time isothermally at a temperature of 225°C. Again it was observed that the mass-loss and the reduction reactions began at the same time and proceeded at about the same rate. The stoichiometry of the product at the completion of the mass-loss corresponded to a 1:1 molar ratio of NH_4Br to $CoBr_2$.

The magnetic moment of the cobalt ion in the $NH_4Br:CoBr_2$ mixture was found to be 4·95 B.M. The average magnetic moment for the cobalt ion found in a synthetic 1:1 molar mixture of cobalt (II) bromide and $(NH_4)_2CoBr_4$ was 4·92 B.M., a value very close to that observed in the dissociation products of the initial compound. Since the moment for the cobalt ion is 5·18 B.M. in cobalt (II) bromide and 4·72 B.M. in $(NH_4)_2CoBr_4$, it is logical to conclude that both cobalt (II) bromide and $(NH_4)_2CoBr_4$ are formed as intermediates in the thermal dissociation of $[Co(NH_3)_6]Br_3$.

To further substantiate the presence of $(NH_4)_2CoBr_4$ and cobalt (II) bromide reaction intermediates, the reflectance spectra of the compounds were obtained as shown in Fig. 2. The decomposition products (obtained at 225°C) gave the same reflectance curve as that of a synthetic mixture of $(NH_4)_2CoBr_4$ and cobalt (II) bromide. Thus, the thermal dissociation of $[Co(NH_3)_6]Br_3$, using the stoichiometry data previously given by Wendlandt,(2) can be written as:

$$6[Co(NH_3)_6]Br_3 \rightarrow 3CoBr_2 + 3(NH_4)_2CoBr_4 + N_2 + 28NH_3$$

followed by:

$$3(NH_4)_2CoBr_4 \rightarrow 6NH_4Br + 3CoBr_2$$

The overall reaction is then:

$$6[Co(NH_3)_6]Br_3 \rightarrow 6CoBr_2 + 6NH_4Br + N_2 + 28NH_3$$

Acknowledgement—The support of this work by the United States Air Force, Office of Scientific Research, through Grant No. 23-63, is gratefully acknowledged.

Department of Chemistry
Texas Technological College
Lubbock
Texas 79409

E. L. Simmons
W. W. Wendlandt

(2) W. W. Wendlandt, *J. inorg. nucl. Chem.* **25**, 545 (1963).

(3) M. Viltange, *Mikrochim. Acta* 461 (1964).

J. inorg. nucl. Chem., 1966, Vol. 28, pp. 2439 to 2441. Pergamon Press Ltd. Printed in Northern Ireland

Some chelates of 4-hydroxy-1, 5-naphthyridine

(*Received* 21 *March* 1966)

It has been demonstrated(1) earlier that 4-hydroxy-1,5-naphthyridine (HNTD) forms 1:1 and 1:2

(1) A. Albert and A. Hampton, *J. chem. Soc.* 505 (1954).

complexes with Fe(III), Fe(II), Cu(II), and Ni(II) in aqueous solution. We wish to report the observations of 1:1 complexes with other metal ions in acid solution, as well as the isolation of some solid 1:2 complexes of HNTD.

Evidence for the formation of 1:1 complexes between HNTD and Cd(II), Zn(II), Ni(II), and Cu(II) was obtained by JOB's method(2) at pH = 1. Also, it was observed that Al(III) and Mg(II) do not chelate with HNTD at pH = 1. The Zn(II)–HNTD chelate was found to be fluorescent at pH = 1. An irregular JOB's plot was observed for the Ni–HNTD chelate, having two maxima, one at a nickel-to-ligand ratio of 0·57 and the other at 0·40. This is interpreted as the superposition of two curves resulting from the formation of 1:1 (mole ratio 0·50) and 1:2 (mole ratio 0·33) complexes in solution.

The solid chelates of HNTD prepared had the formula $M(HNTD)_2$ and their properties are summarized in Table 1. Attempts to prepare Cd(II), Pb(II), and Ba(II) using the same procedure were unsuccessful. A yellow–white precipitate was obtained when preparation of the Zn(II) chelate was attempted. Analyses on the product showed 47·1 C, 4·1 H, 13·0 N, and 14·5% Zn as compared with values of 54·1 C, 2·8 H, 15·8 N, and 18·4% Zn, calculated for $Zn(HNTD)_2$. Several batches of the zinc chelate consistently gave the same analyses, and attempts at purification were unsuccessful.

TABLE 1.—METAL CO-ORDINATION COMPLEXES OF 4 HNTD(a)

Metal ion	Colour	M.p.	Calc. (%)				Found (%)			
			C	H	N	M	C	H	N	M
Cu(II)	Green	>325°C	54·3	2·8	15·8	17·9	54·6	3·4	16·0	17·9
Ni(II)	Lt. green	>325°C	55·1	2·9	16·1	16·8	55·2	3·2	16·2	16·7
Co(II)	Brown(b)	>325°C	55·1	2·9	16·1	16·9	54·8	3·0	16·0	16·8

(a) All compounds have the formula $Me(C_8H_5N_2O)_2$.

(b) The Co(II) chelate was yellow when freshly precipitated from solution and turned brown on drying.

Attempts to prepare the Cd(II), Zn(II), Pb(II), and Ba(II) chelates by other procedures were unsuccessful. This included fusion of salts with HNTD, precipitation of the chelates from dimethyl formamide and precipitation from aqueous solutions. Although some precipitates were obtained from these syntheses, the C, H, and N analyses did not correspond to any reasonable stoichiometry.

EXPERIMENTAL

Materials

3-Aminopyridine was purchased from Reilly Tar and Chemical Co. and was recrystallized from a benzene–ligroine mixture according to the procedure of ALLEN and WOLF(3) (m.p. 63–64°C). Diethyl ethoxymethylenemalonate was purchased from Kay-Fries Chemicals, Inc. and was vacuum distilled immediately prior to use. 4-Hydroxy-1,5-naphthyridine was prepared by modifying the procedures of PRICE and ROBERTS(4) and of ADAMS *et al.*(5) Our modification is reproduced in detail because insufficient experimental details are given in the PRICE and ROBERTS paper(4) and very low yields of 4HNTD were obtained using the ADAMS *et al.* procedure.(5)

Ethyl β-(3-pyridylamino)-α-carbethoxyacrylate (I). An equimolar mixture of 3-aminopyridine and diethyl ethoxymethylenemalonate was heated in a Claisen flask until ethanol ceased to be evolved. (150–180°C). After allowing it to solidify, the reaction mixture was extracted with boiling ligroine. Upon cooling, a white precipitate of (I) formed, (m.p. 65–66°C). It was noted that the yield of (I) depended sharply on the purity of the starting materials and that the yield of subsequent steps depended on the purity of (I).

---

(2) P. JOB, *Annls Chim.* **9**, 113 (1928); W. C. VOSBURG and G. R. COOPER, *J. Am. chem. Soc.* **63**, 437 (1941).

(3) C. F. H. ALLEN and C. N. WOLF, *Org. Synth.* **30**, 3 (1950).

(4) C. C. PRICE and R. M. ROBERTS, *J. Am. chem. Soc.* **68**, 1204 (1946).

(5) J. T. ADAMS, C. K. BRADSHER, D. S. BRESLOW, S. T. AMORE and C. R. HAUSER, *J. Am. chem. Soc.* **68**, 1317 (1946).

3-Carbethoxy-4-hydroxy-1,5-*naphthyridine* (II). Purified (I) was suspended in Dowtherm A so that the resulting concentration was 0·12 M *or less.* While stirring vigorously the mixture was heated at 245–250°C* (no higher—danger of fire!) for 4–5 hr, using an air condenser. The mixture was cooled and filtered yielding a brown solid which, when washed with large volume of ligroine, became a light tan powder.†

3-Carboxy-4-hydroxy-1,5-*naphthyridine* (III). This was prepared from (II) by saponification.(5)

4-*Hydroxy*-1,5-*naphthyridine* (IV). This was prepared from (III) by simultaneous decarboxylation and vacuum sublimation at 300–325°C. (overall yield of crude material was 18–31 per cent). Crude (III) was purified by alternately vacuum subliming and recrystallizing from boiling water. Repeating this cycle seven times gave a white powder. *Anal.* Calc.; C, 65·74; H, 4·14; N, 19·17. Found; C, 65·69; H, 4·23; N, 19·27%.

Preparation of chelates

(IV) was dissolved in hot absolute ethanol (solubility: 0·16 g/l and a small excess of piperidine added. A solution containing the stoichiometric amount of anhydrous metal chloride was added, and the piperidine concentration reduced by distillation while adding fresh ethanol to keep at constant volume. After precipitation occurred, the solution was cooled and the precipitate filtered and washed with ethanol. Chelates of Cu(II), Co(II), and Ni(II) were successfully prepared by this procedure.

Analysis of chelates

Carbon, hydrogen and nitrogen analyses were obtained by conventional means. The metal content was determined polarographically (standard addition method). The chelates were digested in a hot 5:1 mixture of concentrated sulphuric and nitric acid for several hours. The solution was neutralized and diluted for analysis. Replicate runs gave a precision of ±0·5 per cent.

Acknowledgements—We wish to thank DENNIS BUZZARD and DAVID BAILEY for assistance in some phases of the work. We also thank Research Corporation for financial support.

Department of Chemistry
Juniata College
Huntingdon, Pennsylvania
and Lehigh University
Bethlehem, Pennsylvania

T. D. ECK
EARL L. WEHRY, JR.
DAVID M. HERCULES‡

---

* Heating the reaction mixture above 250°C causes large amounts of impurities to be formed and increases the danger of igniting the Dowtherm A.

† It was found that allowing the brown solid to stand in the filter paper for two days before washing improved ease of purification.

‡ Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., 02139.

J. inorg. nucl. Chem., 1966, Vol. 28, pp. 2441 to 2443. Pergamon Press Ltd. Printed in Northern Ireland

Magneto-chemistry of some amine complexes of copper (II) succinimide

(*Received* 29 *March* 1966)

THE MAGNETISM of copper (II) succinimide complexes with primary aliphatic amines are discussed in terms of the proposed structures.

The preparation, absorption spectra and configuration of some amine complexes of copper (II) succinimide have been characterized.(1) The present paper deals with the magneto-chemistry of the same series of the complexes. It is also the purpose of this paper to point out the distinction between a square planar and a tetrahedral configuration of the copper (II) complexes on the basis of magnetism.

(1) G. NARAIN and P. SHUKLA, *Z. Anorg. allg. Chem.* **342**, 221 (1966).