heptatrienone nucleus, some experiments were run with α-bromotropolone, *sym*-tribromotropolone and 2-aminotropone.

Experimental

α-Bromotropolone, m.p. 101–103°, and tribromotropolone, m.p. 118–120°, were prepared by the methods of Cook, *et al.*,[3] who report melting points of 103–106° and 122–123°, respectively. 2-Aminotropone, m.p. 105°, was prepared by the method of Doering and Knox[4] who report m.p. 100–101°. Nozoe and co-workers report[5] m.p. 106–107° for 2-aminotropone. *Anal.* Calcd. for C_7H_7ON: N, 11.57. Found: N, 11.80.

Potentiometric titrations in 50% aqueous dioxane were conducted in the manner described previously.[6] The bromo compounds were found to be appreciably stronger acids than unsubstituted tropolone. In the solvent used, for α-bromotropolone pK_D 6.95, and for tribromotropolone pK_D 4.48. Both materials showed limited solubilities in 50% aqueous dioxane. The metal derivatives all were only indifferently soluble. The complexes of tribromotropolone were so insoluble that no formation constants could be determined.

Previously[6,7] it was observed that several of the six-coördinate divalent metals (*i.e.*, zinc) react with basic solutions of tropolone and some of its derivatives to form complex anions of the type MCh_3^-. Such behavior was not observed with α-bromotropolone. From a titration of α-bromotropolone in the presence of $Zn(NO_3)_2$, a yellow powder, m.p >300°, was isolated. *Anal.* Calcd. for $Zn(C_7H_4O_2Br)_2$: C, 36.13; H, 1.72. Found: C, 36.31; H, 1.65. From the magnitude of the formation constants as shown in Table I, it can be deduced that a third α-bromotropolonate ion would be bound very weakly, if at all, by the metal ions which sometimes exhibit a coördination number of six.

TABLE I

FORMATION CONSTANTS OF METAL COMPLEXES OF α-BROMOTROPOLONE

Metal	Be	Pb	Zn	Ni	Mg
log K_1	8.1	7.5	6.9	6.5	4.9
log K_2	7.3	5.6	5.8	5.6	3.9

A solution of 2-aminotropone alone showed no acidic behavior. In the presence of $Cu(NO_3)_2$, however, it was found that two protons were released per copper ion. This release of protons was accompanied by the precipitation of the green copper derivative described by Nozoe, *et al.*[5]

Discussion

The order of stabilities of the metal complexes of α-bromotropolone is the same as that found for other tropolones containing no fused rings. The relationship between the acid dissociation constant and formation constant of the complex with a given metal ion is the same as for the alkyltropolones.[8]

The reaction of 2-aminotropone with copper ion indicates that this material behaves as a nitrogen analog of tropolone and not as a substituted amine. Infrared spectra[9,10] indicate the presence of a hydrogen bond between the amino and carbonyl groups. From the titration data it is obvious that one of the amino hydrogens is lost upon formation of the copper derivative. Although the loss of a proton with subsequent formation of a primary metal to nitrogen bond is not unknown for bidentate ligands[11] of the diamine type, it is felt that in the present situation the nitrogen atom is not behaving as a simple amine nitrogen.

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A Spectrophotometric Study of Copper Halide Complexes

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The spectrophotometric determination of thermodynamic data for complex ion formation has always been subject to the objection that there exists no satisfactory way of either incorporating or determining activity coefficients. The usual procedure is to make measurements at constant ionic strength in the hope that the variation in the activity function is negligible. Then mass action constants for a series of solutions can be determined; and indeed heats of formation may be derived since the ratio of the mass action constants at two temperatures is then approximately equal to the ratio of the corresponding thermodynamic equilibrium constants. Free energy and entropy of dissociation calculations must be regarded as only indicative.

This note concerns a problem arising in the spectrophotometric study of copper halide complexes. Lack of agreement between Näsänen[1] and Farrington[2,3] on $CuBr^+$, and between Näsänen[4] and McConnell[5] on $CuCl^+$, together with discrepancies between their data and those of the author prompted investigation (see Table II).

It was intended to find the extent to which neglect of activity coefficients accounted for the discrepancies. The interesting result, however, is that the lack of agreement can be attributed wholly to the seemingly justifiable neglect of the dihalide complex, CuX_2. It will be shown that the usual criteria point to the existence of only the mono complex in these experiments, in spite of the presence of another complex absorbing at the same wave length. Easily attained circumstances give rise to a system containing comparable amounts of two complex species whose behavior is consistent with the assumption that only one is present. When this is considered the discordant results are reconciled.

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[1] R. Näsänen, *Acta Chem. Scand.*, **4**, 816 (1950).

[2] P. S. Farrington, THIS JOURNAL, **74**, 967 (1952).

[3] Although Farrington observes that at similar ionic strengths there is favorable agreement between the *K* he and Näsänen determined, he seems not to have noticed that Näsänen's *K* is for the reverse of the reaction he (Farrington) considers.

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[5] H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).

Experimental

The absorption spectra of the series of solutions in Table I were measured with a Beckman DU spectrophotometer.

TABLE I

Series	Formal concentrations		μ^a	T, °C.
I	$C_{Cu^{++}} = 0.001$	$C_{Cl^-} = 0.10, 0.25, 0.50, 0.75$	1.0	22.0
II	$C_{Cu^{++}} = 0.005$	$C_{Br^-} = 0.40, 0.48, 0.64, 0.96$	1.6	27.2 34.4 41.4
III	$C_{Cu^{++}} = 0.001$	$C_{Br^-} = 0.32, 0.40, 0.64, 0.96$	1.6	27.2
IV	$C_{Br^-} = 0.001$	$C_{Cu^{++}} = 0.20, 0.32, 0.40, 0.48$	1.6	27.2

[a] Ionic strength.

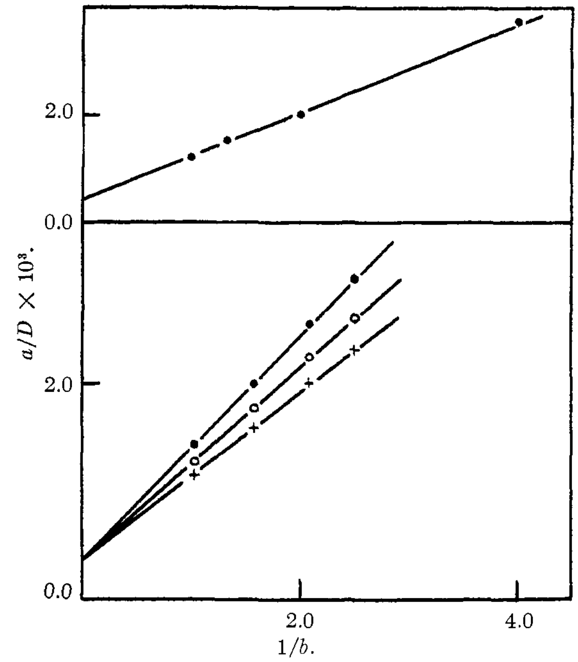

Fig. 1.—Experimental data for series II at 27.2°, ●; at 34.4°, O; at 41.4°, +; and for series I (upper graph). Optical densities used are those at the absorption maximum, 2500 Å. for $CuCl^+$, and 2840 Å. for $CuBr^+$. The intercepts are $1/\epsilon_1^{max.}$ in equation 1.

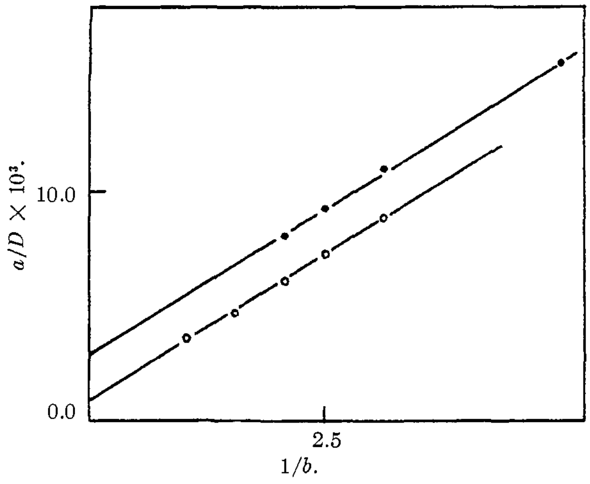

Fig. 2.—Experimental data for series III, O; and series IV, ●.

The copper solutions were made by diluting a standard solution of cupric perchlorate. Hydrochloric acid and lithium bromide were used as sources of halide. Ionic strength was adjusted with perchloric acid. Temperature regulation to 0.5° was effected by Beckman Thermospacers. Data are shown in Figs. 1 and 2. The method of least squares was used to obtain the best values of slopes and intercepts. Copper ion absorption was corrected for in each case. Calculated results are in Table II.

TABLE II

	$CuBr^+$		
	II at 27.7°[a]	II at 34.4°	II at 41.4°
ϵ_1^{max}	1200	1200	1200
K_1	0.31	0.38	0.44
	IV	Näsänen	Farrington
ϵ_1^{max}	340	1480	200
K_1	1.14	0.94	2.08
	$CuCl^+$		
	I	Näsänen	McConnell
ϵ_1^{max}	3800	1480	1000
K_1	0.27	1.10	1.30

[a] Results for III are virtually the same as these.

Discussion

All the investigations whose results are in Table II employ virtually the same method. The only difference is in whether the copper to halide concentration ratio is large or small. Farrington's and McConnell's work are at large values, Näsänen's at small values, and this work at both large and small values of the ratio. If it is assumed that only CuX^+ is formed and that the small absorption of Cu^{++} has been corrected for, then

$$a/D = 1/\epsilon_1 K_1 b + 1/\epsilon_1 \qquad (1)$$

where D is the corrected optical density, $K_1 = K_{10}F = (CuX^+)/(Cu^{++})(X^-)$, and ϵ_1 is the molar extinction coefficient for CuX^+. K_{10} is the equilibrium constant and F the activity function. The letters a and b represent the formal concentrations of cupric and halide ion. Since the experiments are usually done with a large excess of one of the ions present it is convenient always to denote the concentration of the ion in excess as b and the other as a. In the succeeding application a is constant; and it is safely assumed that the equilibrium concentration of the ion in excess is b. Näsänen's calculations for $CuBr^+$ are in error on this point because of the false assumption that the concentration of complex in his experiments is negligible with respect to the formal copper ion concentration.

So long as F is constant a plot of a/D *versus* $1/b$ is linear if only the mono complex is formed. Conversely a linear plot is used to infer the presence of mono complex to the practical exclusion of others; and higher complexes are normally not considered except for non-linearity. Since a continuous variation experiment using mixtures of 0.005 F Cu^{++} and X^- clearly indicated 1:1 complexes and since the plots for all series of solutions were linear, (1) was used to calculate the values of ϵ_1 and K_1 listed in Table II. Results for series II and III not only disagreed with Farrington but with the results for series IV. Series I and McConnell's results disagreed. An inexplicable feature of the disagreement between III and IV was the two different values given for the extinction coefficient of $CuBr^+$.

It seems difficult to reconcile results obtained by the straightforward application of a method for which there is apparently more than adequate justification. One is led to inquire, then, if this be due to variation in F at constant ionic strength, or if it be possible to obtain a linear plot in the presence of a higher complex absorbing in the same region. The first explanation need not be pursued since it would require plots with different slopes but the same intercept. If a second complex, CuX_2, is present then (1) reads

$$a/D = 1/(\epsilon_1 + \epsilon_2 K_2 b)K_1 b + (1 + K_2 b)/(\epsilon_1 + \epsilon_2 K_2 b) \quad (2)$$

where $K_2 = (CuX_2)/(CuX^+)(X^-)$ and ϵ_2 is the molar extinction coefficient for CuX_2. In order that a plot of a/D *vs.* $1/b$ be linear in the presence of CuX_2 it is necessary that the second derivative of a/D with respect to $1/b$ be zero, which requires that

$$\epsilon_2 = \epsilon_1(1 \pm \sqrt{1 - 4R})/2R \quad (3)$$

where $R = K_2/K_1$. This condition need be considered only if $R \leqslant 1/4$. Equation 2 becomes

$$a/D = 1/\epsilon_1 K_1 b + (1 \mp \sqrt{1 - 4R})/2\epsilon_1 \quad (4)$$

and the interesting result is that the slope of such a plot is the same as for (1) where it was assumed no higher complex was present. Thus linearity must not be considered as proof of the absence of higher complexes, even in appreciable amounts.

That these conditions are not infrequently met is evident from the fact that the constant for a complex is often several times smaller than that for the next lower complex, and the value of ϵ_2 given by (3) is such that $\epsilon_1 \leqslant \epsilon_2 \leqslant 2\epsilon_1$ (if the minus sign is used). This raises a question as to the use of continuous variation experiments for ruling out the existence of all but the indicated species.

Equation 3 provides the basis for explaining equal slopes and different intercepts for the plots of series III and IV. Moreover if McConnell's results for $CuCl^+$ and $CuCl_2$ are accepted, it is seen that they are very nearly the values that make (3) applicable. In the solutions he uses for study of $CuCl^+$ it is far less likely that $CuCl_2$ is present than in series I. Using his K_1, K_2 and ϵ_1 at 2500 Å., one calculates that ϵ_2 should be 4300 to make (3) apply, and McConnell's experimental value of ϵ_2 is 4000.

Assuming that (3) will explain the difference between series III and IV with equal success, one obtains the following estimates of ϵ_2 and K_2 for $CuBr^+$ at 27°: $\epsilon_2 \sim 300$ or 1200, $K_2 \sim 0.25$. Since McConnell finds for $CuCl_2$ that $\epsilon_2 \sim 4\epsilon_1$, the value 1200 should probably be chosen for ϵ_2.

In conclusion, the assumption is found to be reasonable but incorrect that only the monocomplex is present in the case of low copper to halide ratios. The discrepancy between results at the two extremes of copper to halide concentration ratios is due to the unsuspected presence of CuX_2. When this is accounted for general agreement, even between experiments at different ionic strengths, is obtained. One is cautioned not to view as unequivocal continuous variation results or linearity in plots of extinction data.

The enthalpy change for the dissociation of $CuBr^+$ was calculated from series II and the van't Hoff equation. For $CuBr^+$, $\Delta H = -4.8 \pm 2.0$ kcal., which is a considerably larger enthalpy change than McConnell reports for $CuCl^+$.

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Binding of the Cobaltous Ion by Native and Modified Bovine Serum Albumins

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As a part of our general investigations on metal–protein interactions, we have studied the binding of the cobaltous ion by bovine serum albumin and by its methyl ester and N-acetylated derivative in an acetate buffer (*p*H 6.5 and ionic strength 0.2). Esterification and acetylation of the protein were carried out by the methods of Fraenkel-Conrat,[1,2] *et al.* Analyses showed 100% esterification of the free carboxyl groups in the former derivative and 83% acetylation of the free amino groups in the latter.

The addition of the methyl ester to cobalt chloride solution did not alter its absorption spectrum in the range studied (440–540 mμ). The native and acetylated albumins, however, increased its absorption, the latter having a more pronounced effect; the wave length of maximum absorption remained unaltered at 515 mμ (Fig. 1).

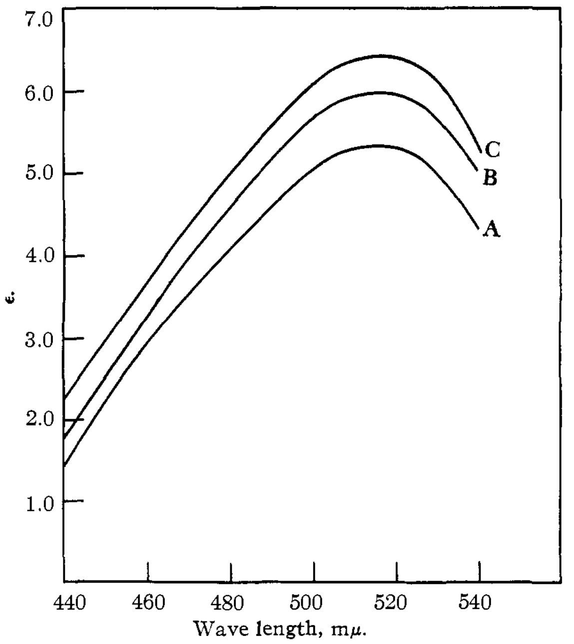

Fig. 1.—Absorption spectra in acetate buffer (*p*H 6.5, ionic strength 0.20): A, 0.057 *M* $CoCl_2$; B, 0.057 *M* $CoCl_2$ + 2% bovine serum albumin; C, 0.057 *M* $CoCl_2$ + 2% acetylated bovine serum albumin.

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