the reaction of the fully protonated N-bonded sulfinamide isomer were obtained.

Product Distribution. In typical experiments, cobalt complexes were dissolved in appropriate media and after specific lengths of time the product solutions were sorbed onto SP-Sephadex C25 cation-exchange resin and eluted with either $NaClO_4$ (pH < 1 or ca. 6), NaCl (pH 7), or 0.23 M Na^+ (0.1 M $H_2PO_4^-$, 0.1 M HPO_4^{2-}, 0.2 M Cl^-; pH 6.88). Products were identified and quantified by absorption spectra, using ϵ and λ values reported.

For the reaction of $[(NH_3)_5CoNHSOCH_3]^{2+}$ in 0.1 M $HClO_4$ (I = 1.0 M, $NaClO_4$), after 93.7% reaction (10 min, 22 °C) recoveries were as follows: N-bonded isomer, 6.3% (R_f = 6.5); $[Co(NH_3)_5OH_2]^{3+}$, 4.5% (R_f = 3.5); O-bonded isomer, 89.2% (R_f = 2.5). For the O-bonded isomer in 0.1 M NaOH (I = 0.1 M) after 72% reaction (60 s, 20 °C), recoveries were as follows: N-bonded isomer, 6.1% (R_f = 5.7); $[Co(NH_3)_5OH_2]^{3+}$, 66.0% (R_f = 3.7); O-bonded isomer, 27.9% (R_f = 1.7).

For the reaction of the O-bonded isomer in 0.1 M NaMES buffer (pH 6.2), after 88% reaction (69 h, 25 °C), recoveries were as follows: N-bonded isomer, 19.8% (R_f = 7.5); $[Co(NH_3)_5OH_2]^{3+}$, 63.8% (R_f = 4.5); O-bonded isomer, 12% (R_f = 2.3); $[Co(NH_3)_6]^{3+}$, 4% (R_f = 1.5).

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Equilibria and Spectra of Mono- and Polynuclear Bromocuprate(I) Complexes in Aqueous Solution

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The spectra of $CuBr_2^-$ and $CuBr_3^{2-}$ were resolved in aqueous solution at 1 and 5 M ionic strengths, in neutral and 1 M H^+ concentration. The spectra revealed the presence of CTTS absorption bands centered at about 277 nm for the 5 M ionic strength solutions. The tris complex exhibits a higher molar extinction than does the bis complex in each solution, and increasing ionic strength causes a blue shift in this band. Such spectral behavior bears a very strong resemblance to that of the chlorocuprate(I) complexes. At increasing copper concentrations, spectral and solubility data confirmed that polynuclear complexes form, and freezing-point depression studies indicated that these complexes are $Cu_2Br_5^{3-}$ and $Cu_3Br_7^{4-}$. Concentration stability constants were calculated for these complexes at 5 M ionic strength, yielding $\beta_{25} = 4.80 \times 10^{15}$ and $\beta_{37} = 1.75 \times 10^{24}$. Spectral studies indicated that $Cu_2Br_5^{3-}$ exhibits a maximum at 277 nm, with nearly twice the extinction coefficient of $CuBr_3^{2-}$, while $Cu_3Br_7^{4-}$ showed a red-shift of this band to about 291 nm with almost a 3-fold increase in extinction coefficient compared to that of the monomer.

Introduction

The chlorocuprate(I) complexes in aqueous solution have been extensively studied in terms of equilibria,[3,4] spectra,[5-9] and photochemistry.[5,6,9-11] Such studies have indicated that the monomeric complexes, $CuCl_2^-$ and $CuCl_3^{2-}$, are the primary species in aqueous solutions of 0.01 M CuCl and at ligand concentrations up to 5 M and that the absorption spectra of both complexes, occurring only in the ultraviolet region, exhibit charge-transfer-to-solvent (CTTS) bands at about 274 nm, the intensities of which are higher for the tris- than for the bis-coordinated complex.

On the other hand, the analogous bromocuprate(I) complexes have received much less attention. Several equilibrium studies[3,12] in aqueous solution have shown that the complexes, $CuBr_2^-$ and $CuBr_3^{2-}$, are formed similarly to the chloro complexes, with somewhat higher stability constants, but no published spectra of these complexes are known. A comparison of the spectra of the chloro- and bromocuprates, as well as the analogous iodocuprates, could give some valuable insights into the effects the ligand has on the nature of the CTTS transition. This study, then, considers the equilibria and spectra of these bromocuprate complexes, and a subsequent paper will consider their photochemical properties.

In the course of this investigation, we discovered that, in contrast to the chlorocuprates, the bromocuprates tend to form dimers and trimers at relatively low copper concentrations (ca. 0.01 M), complicating the resolution of the equilibria and spectra. We have been successful, however, in separating the monomer spectra from those of the polynuclear complexes by carrying out the studies at low enough copper concentrations where only monomers exist. The spectra of the polynuclear species were then determined from solutions of higher copper concentrations using stability constants determined from solubility data.

Experimental Section

Materials. Reagent grade NaBr, HBr, $NaClO_4$, and $HClO_4$ were used for preparation of all stock solutions, from which solutions of a given hydrogen ion concentration, ligand concentration, and ionic strength could be prepared. CuBr was prepared from reagent grade copper powder and copper(II) sulfate by the same method described earlier[5] for the preparation of CuCl.

Procedures. For the determination of spectra of monomers, solutions of the desired ionic strength, ligand, and hydrogen ion concentration were prepared and bubble-degassed with argon. Exactly 3.0 mL of this solution was placed in a 1-cm quartz cuvette situated in an HP-8451 photodiode array spectrophotometer and the reference base line recorded. With a micropipet, 30 μL of a stock solution containing 0.01 M CuBr and 5 M NaBr was added so that the final concentration of CuBr was 9.8×10^{-5} M. This was quickly stirred by gently bubbling with He gas and the spectrum taken within 20 s of mixing to minimize oxidation by traces of air in the solutions. In spite of these precautions and because the copper concentrations were so small, occasionally the absorbance

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(3) Ahrland, A.; Tagesson, B. *Acta Chem. Scand.* **1977**, *A31*, 615.
(4) Sugasaka, K.; Fujii, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 82.
(5) Davis, D. D.; Stevenson, K. L.; Davis, C. R. *J. Am. Chem. Soc.* **1978**, *100*, 5344.
(6) Stevenson, K. L.; Kaehr, D. M.; Davis, D. D.; Davis, C. R. *Inorg. Chem.* **1980**, *19*, 781.
(7) Davis, C. R.; Stevenson, K. L. *Inorg. Chem.* **1982**, *21*, 2514.
(8) Kurtz, K. S.; Stevenson, K. L. *Proc. Indiana Acad. Sci.* **1985**, *94*, 187.
(9) Stevenson, K. L.; Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472.
(10) Horvath, O.; Papp, S. *J. Photochem.* **1985**, *30*, 47.
(11) Horvath, O.; Papp, S. *J. Photochem.* **1985**, *31*, 211.
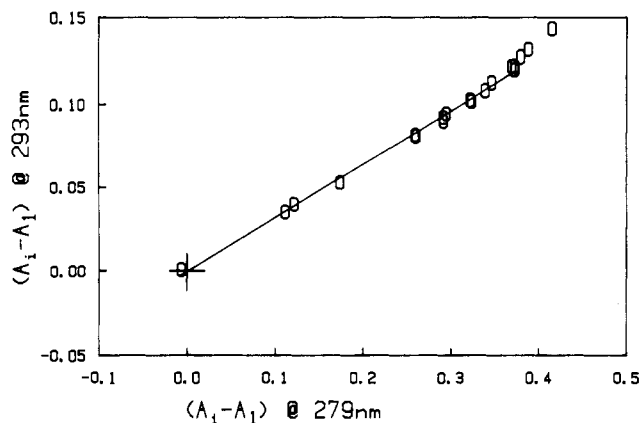(12) Peters, D. G.; Caldwell, R. L. *Inorg. Chem.* **1967**, *6*, 1478.

Figure 1. Matrix-rank plot for two species taken from 20 spectra in the solvent system: 5 M ionic strength, 1 M hydrogen ion concentration. The reference spectrum, spectrum 1, was that for the lowest [Br⁻], 0.0495 M; the highest [Br⁻] was 1.5346 M.

maximum would decay by 10–20% after several minutes. Therefore, the most reproducible spectrum was obtained by taking a series of spectra at time intervals of 30 s and extrapolating the absorbance back to the time of mixing to correct for any oxidation that occurred during the measurement of the spectra. These spectra were recorded on floppy disks for later calculation and analysis using HP-86 computers.

For the determination of dimer and trimer spectra, solutions of varying, high CuBr concentration at 1.5 M free ligand concentration, 5 M ionic strength, and 1 M H⁺ concentration were prepared from stock solutions. The correct total concentrations of ligand and perchlorate were calculated beforehand by using published stability constants or ones determined by solubility measurements in this work. Spectra were run in a 0.001-cm quartz cuvette (Hellma Cells) on a Beckman ACTA M-VI spectrophotometer, and stored digitally for later computation.

Solubility of CuBr was determined as a function of total bromide ion concentration, at 1 M hydrogen ion concentration and 5 M ionic strength. Of these three concentration variables, only the ionic strength was indeterminate in such measurements, but by estimating the correct amount of sodium perchlorate to be added from the known stability constants and then by iterating several measurements at the high copper and ligand concentrations as trial values of stability constants of the polymers became more certain, we could hold the ionic strength to within 4% of the predetermined value for the final set of measurements. Degassed solutions were placed in stoppered flasks with excess CuBr and copper turnings and shaken in a constant temperature bath for at least 8 h. Aliquot samples were withdrawn through the rubber stopper into a syringe and passed through a microfilter into a flask containing water vigorously bubbled with argon, where they were titrated with standard cerium(IV) sulfate.

Freezing point measurements were used to determine the formulas of the dimer and trimer complexes. A large test tube was fitted with a rubber stopper containing a smaller sealed glass tube into which could be inserted the thermistor probe of a Digitec Model 5810 electronic thermometer. Twenty-five milliliters of 5 M NaBr was placed into the test tube, and the entire unit was placed into an ethanol bath cooled to about −40 °C. Alternately moving the tube in and out of the bath allowed the temperature to slowly be brought to the freezing point and held there as minute crystals of ice formed. Weighed portions of CuBr were added, and the freezing point was again determined in this way. Calibration of the freezing point depression constant was achieved by repeating the freezing point measurements by the addition of weighed portions of NaBr, instead of CuBr, to the 5 M NaBr solution.

All equilibrium constants are in terms of molar concentrations rather than activities, and it is assumed that activity coefficients do not vary in the solutions of constant ionic strength in this study.

Results and Discussion

Spectra of Mononuclear Complexes. The effect of ligand concentration on the absorption spectrum of CuBr solutions at constant ionic strength and hydrogen ion concentration is an increase to a maximum absorbance with increasing bromide ion concentration at all wavelengths. All spectral data for these determinations are contained in the supplementary material. A matrix-rank analysis[13] of these spectra for two species is shown

Table I. Equilibrium Constants and Spectral Features of $CuBr_2^-$ and $CuBr_3^{2-}$ in Four Aqueous Solvent Systems at 25 °C

μ, M	[H⁺], M	K	complex	λ_{max}, nm	ϵ_{max}, L mol⁻¹ cm⁻¹
1.0	10⁻⁷	5.4 ± 1.0	$CuBr_2^-$	275	1750
			$CuBr_3^{2-}$	281	9170
1.0	1.0	5.3 ± 1.0	$CuBr_2^-$	271	1070
			$CuBr_3^{2-}$	281	9260
5.0	10⁻⁷	9.5 ± 1.9	$CuBr_2^-$	273	2000
			$CuBr_3^{2-}$	277	9450
5.0	1.0	12.1 ± 2.4	$CuBr_2^-$	275	1760
			$CuBr_3^{2-}$	277	8640
2.0	10⁻⁷	10.2 ± 0.9[12]			
5.0	0.1	14.8 ± 2.6[3]			

in Figure 1 for the solvent system consisting of 5 M ionic strength and 1 M hydrogen ion. Since the points arrayed from left to right are in the order of increasing ligand concentration, it is clear that in the region of lower ligand concentrations the good linearity and the intersection with the origin confirm that only two species are in equilibrium. The curvature at the higher ligand concentrations (between 1 and 1.5 M Br⁻) could be attributed to the possibility that more than three species are in equilibrium, but it is more likely that the changing ionic medium, from perchlorate to bromide anion, affects the individual spectra of the species in equilibrium since these bands are CTTS in nature. For this reason, the resolution of the spectra of the two monomers is considered valid only at bromide concentrations at or below 1.0 M.

The spectral resolution procedure has been described previously for the chlorocuprates.[5,9] In view of the similarity of these complexes to the chlorocuprates and from the equilibrium studies by others,[3,12] it is quite reasonable to assume that the two monomers are defined by the equilibrium

$$CuBr_2^- + Br^- = CuBr_3^{2-} \qquad (1)$$
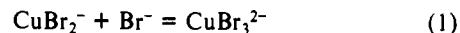
The dependence of absorbance, A, on the individual extinction coefficients of the di- and tribromocuprates, ϵ_2 and ϵ_3, is

$$A = c_0 l \{ \epsilon_3 + (\epsilon_2 - \epsilon_3)/(1 + K[Br^-]) \} \qquad (2)$$

where K is the equilibrium constant for reaction 1 at constant ionic strength, c_0 is the net copper concentration (mol L⁻¹), and l is the path length (cm).[5,14] At a group of wavelengths in the vicinity of the absorbance maximum, the value of K that gave the best linear fit to A vs $1/(1 + K[Br^-])$ was determined at each wavelength and the average computed. This average K was then used to compute ϵ_2 and ϵ_3 from eq 2, resulting in the resolved spectra. Table I lists the values of K and individual absorption features obtained for the two complexes in four aqueous solvent systems at 1 and 5 M ionic strengths and 1 M H⁺ and neutral solution (see the supplementary materials for the complete spectra of the two complexes in these systems). Also listed for comparison are values of K obtained from studies by others. The resolved spectra of $CuBr_2^-$ and $CuBr_3^{2-}$ in the 5 M ionic strength, 1 M hydrogen ion system are shown in Figure 5. Considering the error limits on all of these values of K, it appears that the values obtained in this work are in reasonable agreement with those obtained by other groups.[3,12]

On the other hand, it is difficult to assign meaningful error limits to some of the spectral properties of these complexes. The wavelength maxima and extinction coefficients of $CuBr_3^{2-}$ are much more reliable than those for $CuBr_2^-$ owing to the much higher certainty in the intercept than the slope in eq 2, which results from the much greater difficulty in preparing and measuring spectra of solutions containing sizable $[CuBr_2^-]/[CuBr_3^{2-}]$

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(13) Coleman, J. S.; Varga, L. P.; Mastin, S. H. *Inorg. Chem.* **1970**, *9*, 1015.

(14) At the suggestion of a referee, it is noted here that ref 5 has typographical errors that should be corrected. Since the net absorbance of the equilibrated system, as in eq 1, above, is $A = l\epsilon c_0 = l(\epsilon_2 c_2 + \epsilon_3 c_3)$, and since $c_0 = c_2 + c_3 = c_2(1 + K[Br^-])$, where c_2 and c_3 are the concentrations of the two equilibrated complexes, it follows that the solution molar extinction coefficient is $\epsilon = (\epsilon_2 + \epsilon_3 K[Br^-])/(1 + K[Br^-])$ $= \epsilon_3 + (\epsilon_2 - \epsilon_3)/(1 + K[Br^-])$. Thus eq 2 in ref 5 should read, on the basis of the definitions in that paper, $\epsilon = \epsilon_2 + (\epsilon_1 - \epsilon_2)/(1 + \beta[Cl^-])$.

ratios. The uncertainty in the $CuBr_3^{2-}$ extinction coefficients is probably about 5%, while that for $CuBr_2^-$ could be as high as 50%. Nevertheless, it is possible to generalize that the two complexes have the same absorption band at 271–277 nm, but that the intensity is greater for the tris- compared to the bis-coordinated copper.

A separate experiment revealed that changing the solvent from H_2O to D_2O caused a 1.3-nm blue-shift in the maximum in the spectrum of 0.01 M CuBr in 1 M NaBr. Moreover, Table I shows that increasing ionic strength from 1 to 5 M also caused a blue-shift in the maximum for $CuBr_3^{2-}$. Both of these shifts are expected of a CTTS transition.[15]

It is worth comparing the spectra of the bromocuprate(I) complexes to those of the corresponding chlorocuprate(I) complexes.[5,9] Both systems show the CTTS band in the 272–280-nm region, with the band in tribromocuprate shifted toward the red about 3–4 nm compared to that of the chloro complexes. The oscillator strength increases when the coordination number increases from 2 to 3 for both systems, but it also increases when the ligand is changed from chloro to bromo, by almost 2-fold for the tris complexes and by more than 3-fold for the bis complexes. The chloro complexes also exhibit a band or shoulder at 235 nm, a region slightly out of the measurable wavelength range for these bromocuprate monomers due to the slight absorption by bromide ion, which is magnified by the extremely high ligand to copper concentration ratios (ca 10^4). However, this band can be seen at 235 nm in the series of spectra (Figure 4) taken at much lower ligand/copper ratios. Thus it is apparent that the energies of these electronic transitions in analogous complexes are not significantly affected by substitution of chemically similar ligands, lending support to the suggestion[9] that what has been characterized as a CTTS transition may be initiated by the atomic transition, $d^{10} \rightarrow d^9s^1$, the energy of which would not be greatly affected by halo ligand substitution.

Solubility Studies. Previous reports[3,12] of studies of the solubility of CuBr in solutions of varying bromide ion concentration did not extend into the high ligand concentration range where dimers or trimers were detected. The problem with such studies is that at high copper concentrations it becomes difficult to determine the free ligand concentrations needed to calculate stability constants and to ensure that the ionic strength remains constant in a series of ligand variations. This problem can be overcome by considering the solubility as a function of *total* added ligand concentration. A polynomial expression relates the molar solubility, S, to the free halide concentration, i.e.

$$S = K_s/x + K_s\sum\beta_i x^{i-1} + 2K_s^2\sum\beta_{2i}x^{i-2} + 3K_s^3\sum\beta_{3i}x^{i-3} + \dots \tag{3}$$

where K_s is the solubility product, β_i is the stability constant (in terms of concentration) of a monomeric halocuprate complex with i ligands, β_{2i} is a dimer stability constant with i ligands, β_{3i} is a trimer constant, etc., and x is the concentration of free halide ion ligand. The analytical or total halide ion concentration added to the system, X_t, which is a predetermined quantity in each solution, is related to the free ligand concentration by the expression

$$X_t = x + K_s\sum i\beta_i x^{i-1} + 2K_s^2\sum i\beta_{2i}x^{i-2} + 3K_s^3\sum i\beta_{3i}x^{i-3} + \dots \tag{4}$$

Since, by use of Newton's method, eq 4 can be solved for x if each stability constant is known, it was possible to write a computer program that allows the user to find the value of each β giving the best least-squares fit to the S vs X_t experimental data, proceeding from low ligand concentration where few terms are needed in the two expressions to higher concentrations where successively more terms must be introduced. The procedure is simplified by using the published values of K_s and β for the monomeric species, by ruling out certain chemically unlikely species such as $CuBr_5^{4-}$

(15) Blandamer, M. J.; Fox, M. F. *Chem. Rev.* **1970**, *70*, 59.
(16) Sharma, V. K.; Millero, F. J. *Inorg. Chem.* **1988**, *27*, 3256.

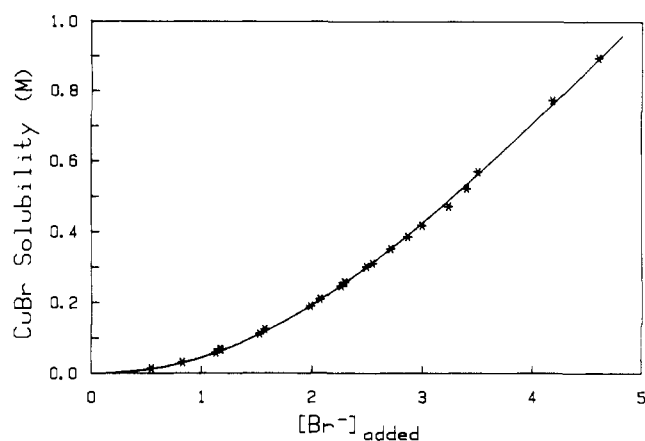**Figure 2.** Solubility at 25 °C of CuBr in solutions that contain 1 M H^+ at 5 M ionic strength versus total added concentration of Br^- (M).

Table II. Stability Constants Used for Fit to Solubility Data (Ionic Strength = 5.00 ± 0.05 M; $[H^+]$ = 1.00 M)

const	value	ref	method
K_s	1.3×10^{-9}	3	solubility
β_1	1412	16	kinetics
β_2	1.89×10^6	3	potentiometry
β_3	2.29×10^7	this work	monomer spectra, see above

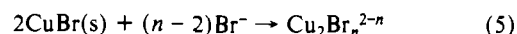**Table III.** Possible Di- and Trinuclear Complexes Giving Reasonable Fits to Solubility Data

complex	stability constant	$\sum(S - S_i)^2$
	Single Species	
$Cu_2Br_5^{3-}$	1.01×10^{16}	2.40×10^{-3}
$Cu_2Br_6^{4-}$	1.02×10^{16}	7.44×10^{-3}
$Cu_3Br_6^{3-}$	5.19×10^{24}	2.34×10^{-3}
$Cu_3Br_7^{4-}$	3.27×10^{24}	1.19×10^{-3}
	Mixture of Species	
$Cu_2Br_5^{3-}$	4.80×10^{15}	7.76×10^{-4}
$Cu_3Br_7^{4-}$	1.75×10^{24}	

or Cu_2Br^+, and by assuming that only dimers and trimers are the likely polynuclear species. Of course, it was necessary to perform several iterations of the calculation of stability constants followed by solubility measurements at the higher ligand concentrations in order to adjust the ionic strengths to a constant value.
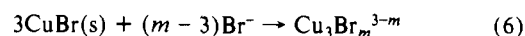
Figure 2 shows the final set of solubility vs total ligand concentration data for 1 M H^+, 5 M ionic strength. Table II lists the previously determined monomer stability constants used in calculating the polymer stability constants from the solubility data.

Several possibilities of a single di- or trinuclear species and one mixture thereof gave good fits to the solubility data. The optimum values for the stability constants of these likely complexes are shown in Table III along with the goodness of the fits as indicated by the total sum of the squares of the absolute residuals, $\sum(S - S_i)^2$, where S and S_i are the calculated and measured solubilities, respectively, at the gross bromide concentrations of the measurements.

Although the best fit is obtained with the mixture of $Cu_2Br_5^{3-}$ and $Cu_3Br_7^{4-}$, a verifying experiment was performed in which changes in colligative properties were measured upon adding CuBr to equilibrated solutions. The stoichiometry for such an addition may be written, for dimer formation, as

$$2CuBr(s) + (n - 2)Br^- \rightarrow Cu_2Br_n^{2-n} \tag{5}$$

or, for trimer

$$3CuBr(s) + (m - 3)Br^- \rightarrow Cu_3Br_m^{3-m} \tag{6}$$

where n and m are integers. It follows that the ratio of change
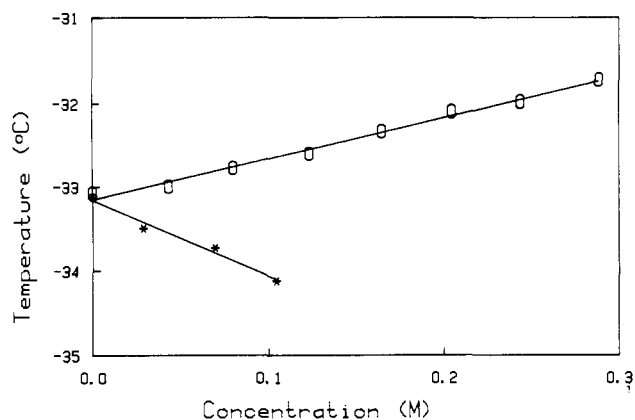
Figure 3. Freezing point (°C) versus added concentration of (O) CuBr or (✕) NaBr (M) for a 5 M solution of NaBr.

in ionic concentration, ΔM_I, to the concentration of CuBr added, ΔM_C, is given by

$$\Delta M_I / \Delta M_C = (n - 3)/2 \tag{7}$$

for dimer formation, or

$$\Delta M_I / \Delta M_C = (m - 4)/3 \tag{8}$$

for trimer formation.

The colligative property measured was the freezing point, and the system chosen for study was a 5 M NaBr solution since it would give the highest solubility of CuBr and the least chance for precipitation of solute prior to reaching the freezing point. Figure 3 shows the freezing point of such a solution as a function of added CuBr concentration, along with the calibration of freezing point depression of the 5 M NaBr solution by the addition of NaBr(s). The ratio of slopes of the two plots is −2.18, but since the van't Hoff factor for the calibration run should be 2, we can assume that the value for $\Delta M_I / \Delta M_C$ is 1.09, confirming that the polynuclear complex must be either $Cu_2Br_5^{3-}$ or $Cu_3Br_7^{4-}$, or a mixture of both. The curve through the solubility data of Figure 2 is thus the best-fitting plot to eq 3 using the stability constants for the di- and trinuclear species of the mixture.

The identification of the polynuclear species as a mixture of $Cu_2Br_5^{3-}$ and $Cu_3Br_7^{4-}$ is reasonable on structural grounds. The likely structures for these complexes are
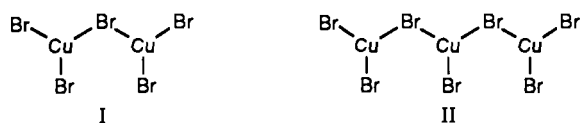
both of which retain the coordination number of 3 of the monomer, $CuBr_3^{2-}$, from which they are formed. This is consistent with the finding that in the solid state the coordination number of the copper in such halocuprate(I) complexes is essentially dependent on the ligand/copper ratio and not on copper concentration.[17,18]

Spectra of Polynuclear Complexes. The presence of polynuclear complexes is also confirmed spectroscopically. Seven spectra were taken at a constant free ligand concentration of 1.5 M (prepared from stock solutions by taking the concentrations of the equilibrated bromocuprates into account) and varying CuBr concentration, and four of these are shown in Figure 4. The isosbestic points at 255 and 291 nm suggest that at least one of the polynuclear species must have a red-shifted absorption band compared to those of the monomers. The measured extinction coefficient, ϵ, can be written in terms of the individual extinction coefficients of the equilibrated monomer and two polynuclear complexes, ϵ_m, ϵ_{25}, and ϵ_{37}, the concentrations of complexes, c_2, c_3, c_{25}, and c_{37}, and total copper concentration, c_0, as follows:

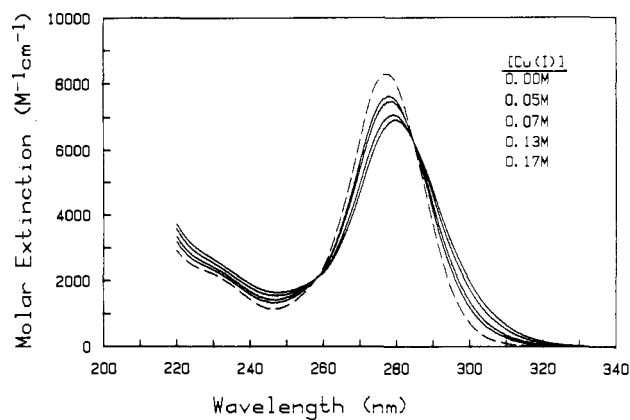$$\epsilon = [(c_2 + c_3)\epsilon_m + c_{25}\epsilon_{25} + c_{37}\epsilon_{37}]/c_0 \tag{9}$$

Figure 4. Molar extinction spectra at 25 °C of solutions containing CuBr at the concentrations given, at 1 M H⁺, 5 M ionic strength, and 1.5 M free bromide ion concentration. Extrapolated monomer spectrum (--) is also shown.
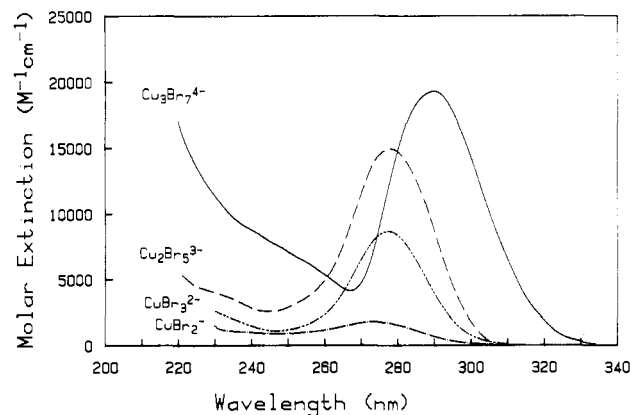

Figure 5. Resolved spectra at 25 °C of (−·−) $CuBr_2^-$, (−···−) $CuBr_3^{2-}$, (--) $Cu_2Br_5^{3-}$, and (—) $Cu_3Br_7^{4-}$ at 1 M H⁺ and 5 M ionic strength.

The concentrations of all species were calculated for each solution from the values of β, and the spectrum of the monomer (ϵ_m vs λ, also shown in Figure 4 as the dashed curve) was obtained by extrapolations of ϵ vs [CuBr] at all wavelengths back to the ordinate by using a least-squares quadratic curve-fitting program. The individual spectra of $Cu_2Br_5^{3-}$ and $Cu_3Br_7^{4-}$ were then computed four times, by using eq 9 and four of the possible five pairs of spectra from Figure 4,[19] and the results were averaged and smoothed, yielding the spectra shown in Figure 5, which also shows the spectra of the monomers.

The values of the extinction coefficients of the dimer are almost double those of $CuBr_3^{2-}$ with no significant differences in the values of λ_{max}, suggesting that the spectral behavior of each trigonal-planar copper moiety in the dimer structure, I, is nearly identical with that of the copper in $CuBr_3^{2-}$. This is not the situation in the trimer, $Cu_3Br_7^{4-}$, which has an extinction coefficient almost 3 times that of the monomer and shows a considerable red-shift (1500 cm⁻¹) in the CTTS band, suggesting that although all three copper chromophores are involved in the absorption, there is some kind of energy-lowering perturbation arising, perhaps, from a conformational distortion of structure II.

Supplementary Material Available: Tables of spectral data for resolution of monomer spectra at [H⁺] = 10⁻⁷ M, μ = 1 M, at [H⁺] = 1 M, μ = 1 M, at [H⁺] = 10⁻⁷ M, μ = 5 M, and at [H⁺] = 1 M, μ = 5 M, calculated equilibrium constants in each solvent, and calculated monomer spectral data in each solvent, matrix rank plots in each solvent, and plots of monomer spectra in each solvent (35 pages). Ordering information is given on any current masthead page.

(17) Andersson, S.; Jagner, S. *Acta Chem. Scand.* **1987**, *A41*, 230.
(18) Andersson, S.; Jagner, S. *Acta Chem. Scand.* **1989**, *A42*, 691.

(19) The pair excluded was that consisting of the spectra at 0.17 and 0.13 M CuBr, since these did not differ enough to give a reliable result.