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The Sodium-Sulfur System. II. Polysulfides of Sodium[1]

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The polysulfides of potassium–K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6–are all known and well-characterized compounds. In the case of the analogous sodium compounds, only the disulfide, tetrasulfide, and pentasulfide are reported in the literature, whereas reports pertaining to the existence and isolation of the trisulfide, Na_2S_3, have been disputed. Past efforts to synthesize Na_2S_3 have always yielded the 1:1 eutectic Na_2S_2-Na_2S_4. A novel method to synthesize the sodium polysulfides in liquid ammonia, based on the reaction scheme $2NaCl + K_2S_x \rightarrow 2KCl\downarrow + Na_2S_x$ ($x = 3, 5, 6$), is described, yielding Na_2S_3 and Na_3S_5, but not Na_2S_6. The results of ESCA (electron spectroscopy for chemical analysis) applied to the polysulfides are discussed. The density and surface tension of molten Na_2S_4 and Na_2S_5 were determined at various temperatures.

Introduction

Several aspects of the sodium polysulfides Na_2S_2, Na_2S_4, and Na_2S_5 were discussed in a preceding article.[2] This report deals with the existence and stability of Na_2S_3 and Na_2S_6 and other properties of the individual sodium polysulfides. An examination of Table I, which is a tabulation of the presently known and well-characterized alkali metal polysulfides, reveals several interesting facts that may be helpful in understanding the previously mentioned problems concerning the trisulfide and the hexasulfide. Starting with potassium, polysulfides of the formulas M_2S_2 to M_2S_6 (M = K, Rb, Cs) are known and well characterized in the literature. In the case of Li, only the disulfide is known, whereas in the case of Na, contradictory results have been reported on the existence and isolation of Na_2S_3; and the highest polysulfide reported was Na_2S_5. Obviously ionic size is an important factor in determining the existence and stability of the polysulfides, and this explains the nonexistence of polysulfides of Li higher than the disulfide and the absence of Na_2S_6 from the table. However, the failure to synthesize or isolate Na_2S_3 is rather intriguing, as both Na_2S_4 and Na_2S_5 exist and are stable compounds even though the ions $S_4{}^{2-}$ and $S_5{}^{2-}$ are larger than the $S_3{}^{2-}$ ion.

Pearson and Robinson[3] questioned the existence of the trisulfide in the melt, although they reported the isolation of the hydrated solid $Na_2S_3 \cdot 8H_2O$. Earlier Thomas and Rule[4] assumed the existence of Na_2S_3 in their thermal study of Na_2S-S mixtures, whereas Bergstrom[5] observed that by allowing solutions of sodium and sulfur to react in liquid ammonia, the sequence of formation of the polysulfides was Na_2S, Na_2S_2, and Na_2S_4. Zintl and his coworkers[6] reported that they observed an inflection point corresponding to Na_2S_3 only once when they performed potentiometric titrations of solutions of sodium and sulfur in liquid ammonia. Similar work by Watt and Otto[7] seems to indicate that the previous observation must be attributed to some experimental error, since they obtained inflection points corresponding to Na_2S and Na_2S_4 only. More recent and exhaustive research by Feher and Berthold[8] showed that it was not possible to synthesize or isolate Na_2S_3 by (a) reacting solutions of the elements in liquid ammonia; (b) reacting the elements in boiling toluene, or (c) adding sodium to the toluene solution of the compounds or mixture with the formula $Na_2S_{3.5}$. The X-ray powder diffraction pattern showed that the product obtained from each of the reactions is a mixture of Na_2S_2 and Na_2S_4. Similar results were reported by Erametsa and Karlsson,[9] who tried to synthesize the trisulfide from the ethanolic solution of NaHS by adding the appropriate amount of sulfur and refluxing the solution for 1 hr.

Table I. Alkali Metal Polysulfides

Li_2S	Li_2S_2				
Na_2S	α- and β-Na_2S_2		Na_2S_4	Na_2S_5	
K_2S	K_2S_2	K_2S_3	K_2S_4	K_2S_5	K_2S_6
Rb_2S	Rb_2S_2	Rb_2S_3	Rb_2S_4	Rb_2S_5	Rb_2S_6
Cs_2S	Cs_2S_2	Cs_2S_3	Cs_2S_5	Cs_2S_5	Cs_2S_6

The previous attempts to synthesize Na_2S_3 are characterized either by a somewhat high temperature, as in the case of using boiling toluene, or by the evolution of a high heat of reaction when elemental sodium and sulfur are reacting directly. Consequently, these two factors may affect the synthesis in an adverse manner if Na_2S_3 is unstable. Liquid ammonia has been used extensively as a reaction medium for the preparation of sodium and potassium polysulfides.[10] Its low boiling point (−33.3°) provides a conveniently low temperature, and in addition most of the polysulfides are readily soluble in this solvent. To avoid developing a high heat of reaction one could consider metathetical reactions similar to

$$2AgCl + Ba(NO_3)_2 \xrightarrow{NH_3(l)} 2AgNO_3 + BaCl_2\downarrow$$

instead of reacting the elements directly. The potassium polysulfides are known and well-characterized compounds and can be synthesized without difficulty.[10] They are also quite soluble in liquid ammonia and are therefore a natural choice for one of the reactants, leaving the choice of the second reactant to a multitude of sodium compounds. An examination of the solubility of sodium and potassium salts in liquid ammonia reveals that sodium chloride (3.02 g/100 g of solvent) is approximately 100 times more soluble than potassium chloride (0.04 g/100 g of solvent).[11] Based on the previous information, the following reaction scheme is proposed

$$2NaCl + K_2S_3 \rightarrow 2KCl\downarrow + Na_2S_3$$

[1] Presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

[2] D.-G. Oei, *Inorg. Chem.*, 12, 435 (1973).

[3] T. G. Pearson and P. L. Robinson, *J. Chem. Soc.*, 1492 (1930).

[4] J. S. Thomas and A. Rule, *J. Chem. Soc.*, 1079 (1917).

[5] F. W. Bergstrom, *J. Amer. Chem. Soc.*, 48, 146 (1926).

[6] E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. Phys. Chem., Abt. A*, 154, 27 (1931).

[7] G. W. Watt and J. B. Otto, *J. Electrochem. Soc.*, 98, 1 (1951).

[8] F. Feher and H. J. Berthold, *Z. Anorg. Allg. Chem.*, 273, 144 (1953).

[9] O. Erametsa and K. Karlsson, *Acta Polytech. Scand., Chem. Incl. Met. Ser.*, No. 15, 18 (1961).

[10] G. Brauer, "Handbuch der praparativen anorganischem Chemie," Ferdinand Enke Verlag, Stuttgart, 1960.

[11] L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," Wiley, New York, N. Y., 1956, p 120.

for the synthesis of the sodium trisulfide. Obviously the proposed reaction scheme does not have to be limited to the synthesis of the trisulfide and can be used for the general synthesis of any of the sodium polysulfides by using the corresponding potassium polysulfide

$$2NaCl + K_2S_x \rightarrow 2KCl\downarrow + Na_2S_x$$

Other aspects of the sodium polysulfides that were considered in this work include the determination of the density and surface tension of molten Na_2S_4 and Na_2S_5 at various temperatures. In addition, the result of ESCA (electron spectroscopy for chemical analysis) work on several polysulfides is discussed.

Experimental Section

Apparatus. X-Ray powder diffraction patterns were obtained with a Norelco X-ray diffractometer, Type 12045B/3, provided with a Type 42202 goniometer and Type 52250/1 Counter. The output of the diffractometer is connected to a revised GE Model 11GJ1 rate counter and strip chart recorder. The powdered specimens were mounted on glass slides and coated with Canada balsam. The X-ray source may be described by the following details: Cu tube, Ni filter, 45 kV, 28 mA. The scanning rates were $^1/_2$, 1, and 2°/minute, and the slide width was 1° 0.012″.

Densities were determined with precalibrated Vycor pycnometers. The pycnometers were inserted into a heating block with vertical slits to view the meniscus with a telescope.

The surface tension was determined by Wilhelmy's plate method.[12] The corrosive nature of sulfur and the sulfides necessitated the use of a quartz plate instead of the platinum plate. A Rossano surface tension balance (Roller Smith torsion balance) was used to determine the magnitude of the counteracting force.

ESCA work was done by Dr. Royal Albridge, Department of Chemistry, Vanderbilt University, as part of a contract with Ford Motor Co. during an evaluation period of ESCA equipment.

Materials. K_2S_3, K_2S_5, and K_2S_6 were prepared according to Brauer.[10] K_2S_3 was prepared from the ethanolic solution of potassium ethanolate which was converted into the monosulfide by H_2S. Addition of the required amount of sulfur yields the trisulfide: $K_2S + 2S \rightarrow K_2S_3$.

K_2S_5 was prepared similarly from the ethanolic solution of the hydrosulfide and the proper amount of sulfur: $2KHS + 4S \rightarrow K_2S_5 + H_2S(g)$.

K_2S_6 was synthesized from K_2S_3 or K_2S_5 and the corresponding amount of sulfur. The mixture was heated in a sealed evacuated tube for several hours at 550°. Identifications of the compounds and their purities were ascertained by dta and the X-ray powder diffraction pattern.

Synthesis in liquid ammonia was carried out in a wide-mouthed erlenmeyer provided with three ground-joint outlets. Liquid NH_3 was delivered through one of the joints from a lecture bottle while hydrogen gas was passed through the system. The third outlet was connected to a separatory funnel containing the potassium polysulfide solution. Proper outlets with drying agents were provided for relief of excess pressure. A magnetic stirrer was used during the synthesis. Approximately 0.1 mol of NaCl/250 ml of liquid NH_3 and 0.05 mol of polysulfide/150 ml of liquid NH_3 was used for the preparation. The precipitate was separated from the filtrate with a coarse-frit filter. All operations were performed in a H_2 or Ar atmosphere. The precipitate and the residue from the filtrate were analyzed by dta and X-ray diffraction. Na_2S_4 and Na_2S_5 used in this work were synthesized according to Brauer.[2,10]

Results and Discussion

The results of the experiments to synthesize sodium polysulfides according to the newly proposed reaction scheme

$$2NaCl + K_2S_x \rightarrow 2KCl\downarrow + Na_2S_x$$

in liquid ammonia, for $x = 3$, 5, and 6, are deduced from X-ray diffraction pattern of the precipitate obtained from the reaction mixture (see Figure 1B and C)

$$2NaCl + K_2S_3 \rightarrow 2KCl\downarrow + Na_2S_3$$

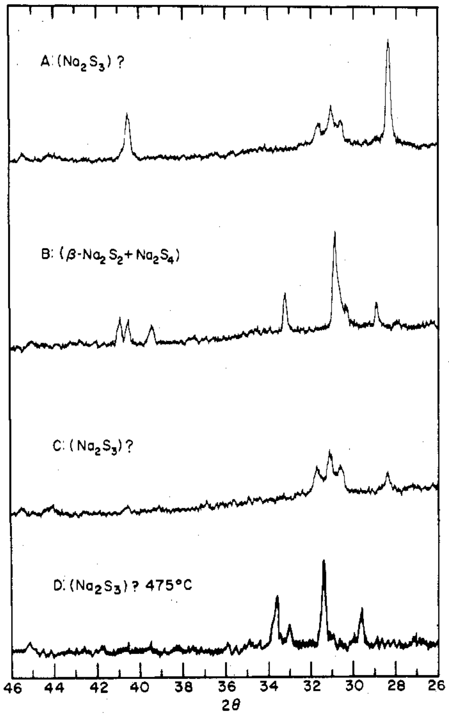

Figure 1. X-Ray diffraction patterns for (A) the product of the reaction $K_2S_3 + 2NaCl$ in liquid NH_3, (B) the 1:1 eutectic mixture Na_2S_2-Na_2S_4, (C) the purified product from (A), and (D) the product of (C) after heating to 475°.

The original precipitate is still contaminated with NaCl. However, when the first filtrate is reduced to approximately half of its original volume, the precipitate is KCl. The precipitate obtained from $2NaCl + K_2S_5$ and $2NaCl + K_2S_6$ is similarly identified as KCl by X-ray diffraction. It is quite obvious from these patterns that the proposed reaction scheme proceeds as predicted, namely, with the formation of a precipitate of KCl. The final test of the success of the reaction scheme is, of course, the identification of the sodium polysulfide from the filtrate. The patterns for trisulfide and the hexasulfide, however, have not been reported in the literature.

Therefore, we have used the pentasulfide as a test case. Indeed the X-ray diffraction pattern and dta of the product obtained by evaporating the solvent from the filtrate correspond unequivocally to that of Na_2S_5. Thus, we conclude that the proposed reaction scheme provides a new avenue for the synthesis of sodium polysulfides.

In the case of the trisulfide, the X-ray diffraction pattern shows without doubt that the precipitate is KCl. Previous work has indicated that the melt or mixture with the same ratio (Na:S = 2:3) is a eutectic with the 1:1 composition Na_2S_2-Na_2S_4. Thus it is logical to compare the X-ray diffraction pattern of the product from the filtrate with the pattern of the eutectic (Figure 1B). Patterns A and C show the X-ray diffraction pattern of the product from the filtrate; in pattern A the product is obviously still contaminated with KCl. This comparison proves that the product is not the eutectic found in previous preparations.

When the product was subjected to dta, several interesting events occurred as manifested by the presence of the exotherm. In curve A of Figure 2 the exotherm indicates that a reaction is taking place around 100°. Evidently this dta curve does not resemble the dta curves of the reactants, namely, NaCl, which shows a smooth curve without transitions within the temperature range considered, and K_2S_3,

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(12) R. Ruyssen, *Bull. Cl. Sci., Acad. Roy. Belg.*, 4, No. 1 (1942); 7, No. 1 (1945).

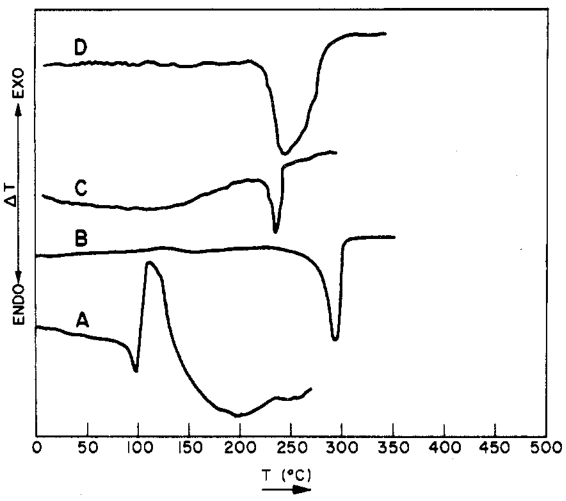

Figure 2. Dta curves for (A) the product of the reaction K_2S_3 + 2NaCl in liquid HN_3, (B) K_2S_3, (C) the 1:1 eutectic mixture Na_2S_2-Na_2S_4, and (D) the product of (A) after heating to 475°.

shown in Figure 2B. However, when this product is heated to 475° and then subjected to dta again, a curve (Figure 2D) is obtained identical with that of the eutectic (Figure 2C). Similar evidence is obtained from the X-ray diffraction patterns shown in Figure 1. The original pattern of the product (C), which does not resemble any of the previously obtained patterns (α- and β-Na_2S_2, Na_2S_4, Na_2S_5, α-S_8, K_2S_3), is transformed into a pattern (D) that is the same as that of the eutectic (B) after heating the product. These results indicate that Na_2S_3 can be synthesized *via* the new reaction scheme

$$2NaCl + K_2S_3 \rightarrow 2KCl\downarrow + Na_2S_3$$

and that it disproportionates around 100° into the 1:1 eutectic Na_2S_2-Na_2S_4. This explains, also, why all the previous efforts to prepare the trisulfide from boiling toluene or ethanol have always yielded a mixture of di- and tetrasulfides.

Returning to the case of the hexasulfide, we observed earlier that KCl is precipitated from the reaction mixture 2NaCl + K_2S_6. The X-ray powder diffraction pattern of the product from the filtrate is compared with the patterns for Na_2S_4 and Na_2S_5. It resembles the pattern for Na_2S_5 except for the presence of several extra peaks. A comparison with the patterns for K_2S_5 and K_2S_6 shows that the product is certainly not potassium penta- or hexasulfide. A cursory look at the dta curve of this product (Figure 3A) provides some clues as to the origin of the extra lines in the X-ray pattern. The dta curve indicates that the product is contaminated with sulfur, and indeed the extra lines in the diagram can be matched with lines in the α-S_8 pattern. When this sulfur is removed by washing with toluene, the result is a product with a dta curve (Figure 3B) matching that of Na_2S_5. The X-ray diffraction pattern of this purified product also shows that it is sodium pentasulfide. From the previous results we conclude that Na_2S_6 does not exist and that we have the following reaction in liquid ammonia

$$2NaCl + K_2S_6 \rightarrow 2KCl\downarrow + Na_2S_5 + S$$

Experiments with molten salt systems occasionally require a knowledge of the density and surface tension of the molten salt. Values of the density and surface tension of molten Na_2S_4 and Na_2S_5 do not exist in the literature and have therefore been determined in this work. The values determined by methods described in the Experimental Section are as follows. Na_2S_4: density (g cm^{-3}): 1.678 at 450°, 1.776 at 400°, 1.827 at 350°; surface tension (dyn cm^{-2}): 130 at 440°, 134 at 400°, 136 at 350°. Na_2S_5: density (g cm^{-3}): 1.669 at 450°, 1.728 at 400°, 1.754 at 350°; surface tension (dyn cm^{-2}): 114 at 430°, 116 at 400°, 121 at 360°.

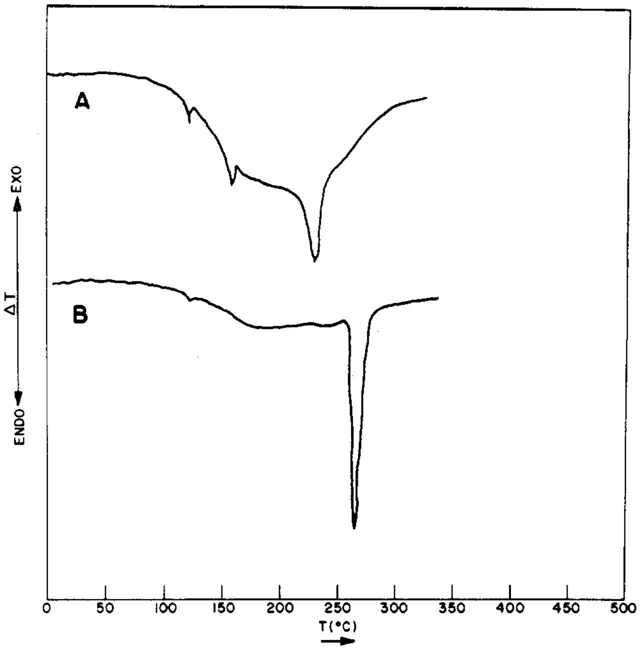

Figure 3. Dta curves for (A) the product of the reaction K_2S_6 + 2NaCl in liquid NH_3 and (B) the purified product of (A).

Table II. Relative Intensity of S 2p Electron from S^0 and S^-

		Rel intens S^0 (162.5 eV): S^- (159.7 eV)
$S_2{}^{2-}$	$\vert\overline{\underline{S}}-\overline{\underline{S}}\vert$	0:1
$S_3{}^{2-}$	$\vert\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}\vert$	1:2
$S_4{}^{2-}$	$\vert\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}\vert$	1:1
$S_5{}^{2-}$	$\vert\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}\vert$	3:2

Samples of α-Na_2S_2, K_2S_3, Na_2S_4, and Na_2S_5 have been studied by ESCA. (K_2S_3 was used instead of the less stable Na_2S_3, and the ESCA study is focused on the $S_2{}^{2-}$, $S_3{}^{2-}$, and $S_4{}^{2-}$ species.) The results are given in Table II. The binding energies for the S 2p electron in the polysulfides were found to be 162.5 eV for the S^0 state and 159.7 eV for the S^- state. This agrees quite well with other values obtained by Siegbahn and his coworkers.[13] More interesting than this agreement is the ratio of intensities of the S 2p electrons for the S^0 and S^- state in the molecule. This provides direct and unequivocal evidence that the polysulfide chain has the unbranched structure as illustrated in the table employing the conventional bar notation for the lone pair and bonding electron pair.

Conclusions

The results of this study of the sodium polysulfides can be summarized as follows.

1. The proposed metathetical reaction in liquid ammonia, 2NaCl + $K_2S_x \rightarrow 2KCl\downarrow + Na_2S_x$, provides another avenue for the synthesis of sodium polysulfides.

2. Sodium trisulfide can be synthesized according to the previous method, but it decomposes around 100° into a mixture corresponding to the 1:1 eutectic Na_2S_2-Na_2S_4.

3. Sodium hexasulfide does not exist, and efforts to synthesize this hexasulfide from the potassium salt according to the previous scheme resulted in sodium pentasulfide and sulfur.

4. The density and surface tension of molten Na_2S_4 and

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(13) K. Siegbahn, *et al.*, "ESCA," Almquest and Weksells, Uppsala, 1967, p 132.

Na_2S_5 were determined at various temperatures.

5. ESCA work on the polysulfides provides conclusive evidence of the unbranched chain structure of the polysulfide linkage.

Registry No. K_2S_3, 37488-75-8; Na_2S_3, 37488-76-9; Na_2S_6, 37188-08-2; K_2S_6, 37188-07-1; Na_2S_5, 37488-74-0; Na_2S_4, 37488-78-1; Na_2S_2, 22868-13-9.

Acknowledgments. I wish to thank Ford Motor Co. for their permission to publish this and the previous work.[2] I also wish to thank Drs. S. Gratch, J. V. Petrocelli, R. P. Tischer, and M. A. Dzieciuch for their valuable advice and comments. For the ESCA work we are indebted to Dr. Royal Albridge, Department of Chemistry, Vanderbilt University.

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Exchange Interactions in Polynuclear Transition Metal Complexes. Structural Properties of Cesium Tribromocuprate(II), $CsCuBr_3$, a Strongly Coupled Copper(II) System

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The crystal structure of the antiferromagnetic (μ_{eff} 0.11 BM at 23°) compound cesium tribromocuprate(II), $CsCuBr_3$, has been determined from three dimensional X-ray (Mo Kα) counter data. The compound crystallizes in the orthorhombic system, space group $C222_1$ ($D_2{}^5$), with $a = 12.776$ (2) Å, $b = 7.666$ (2) Å, $c = 12.653$ (4) Å (23°), $\rho_c = 4.67$, $\rho_o = 4.52$ (4) g/cm³, $V = 1239.2$ Å³, $Z = 8$. Full-matrix-least-squares refinement based on 842 unique reflections gave final discrepancy factors of $R_1 = 0.069$ and $R_2 = 0.074$ on F. The structure contains facial-bridged $[Cu_2Br_9]^{5-}$ dimers, which share corners with six other dimers in a three-dimensional network. A comparison of the structures of $CsCuBr_3$ and $CsCuCl_3$ and a consideration of the Goodenough–Kanamori rules strongly suggests that spin coupling through one of the linear Cu–Br–Cu bridge groups is responsible for the low magnetic susceptibility observed for the compound at room temperature. A reexamination of the structure of Cs_2CuBr_4, cesium tetrabromocuprate(II), using three-dimensional counter data, is also reported. The details of the structure are in substantial agreement with those reported previously (B. Morosin and E. C. Lingafelter, *Acta Crystallogr.*, **13**, 807 (1960)), although there are some differences in the copper–bromine bond lengths. Least-squares refinement based on 634 unique reflections gave final discrepancy factors of $R_1 = 0.079$ and $R_2 = 0.069$. The space group is *Pnma* ($D_{2h}{}^{16}$) with $a = 10.168$ (4), $b = 7.954$ (3), $c = 12.914$ (5) Å, $\rho_c = 4.12$, $\rho_o = 4.02$ (6) g/cm³, $V = 1044.4$ Å³.

Introduction

Kato, Jonassen, and Fanning[1] have noted that, in many cases, copper(II) complexes containing the bromide ion have magnetic moments lower than those of the corresponding chloride complexes. Inoue, Kishita, and Kubo[2] recently investigated the magnetic susceptibilities of $KCuBr_3$ and $CsCuBr_3$ and found that $KCuBr_3$ is isostructural with $KCuCl_3$[3] with μ_{eff} equal to 1.52 and 0.83 BM at room and liquid nitrogen temperatures, respectively. $CsCuBr_3$ was reported to have only a very slight paramagnetism and it was concluded that the unpaired electrons of the copper atoms are almost completely coupled. The unusual magnetic behavior of this copper(II) complex suggested that a complete structural study of $CsCuBr_3$ would be of considerable interest. In this paper, we present the results of a single-crystal analysis of $CsCuBr_3$ and a reexamination of the crystal structure of Cs_2CuBr_4.

Experimental Section

Crystal Preparation. Both $CsCuBr_3$ and Cs_2CuBr_4 are obtained as products when aqueous solutions 2 *M* in $CuBr_2$ and 1 *M* in $CsBr_3$ are mixed together. Since both $CsCuBr_3$ and Cs_2CuBr_4 are dark red and since recrystallization of $CsCuBr_3$ from water results in disproportionation according to the reaction

$$3CsCuBr_3 \xrightarrow{H_2O} Cs_2CuBr_4 + CsCuBr_3 + CuBr_2$$

the separation and identification of $CsCuBr_3$ is difficult. The composition and crystal habit (see below) of Cs_2CuBr_4 were first identified by single-crystal X-ray photographs. $CsCuBr_3$ was then separated mechanically from Cs_2CuBr_4 under a microscope. Both $CsCuBr_3$ and Cs_2CuBr_4 appear to be air stable.

Anal. Calcd for $CsCuBr_3$: Cu, 14.54; Br, 54.98. Found: Cu, 13.94; Br, 54.56.

Magnetic Susceptibility Measurements. The room-temperature magnetic susceptibility measurements were made on a standard Gouy apparatus with a Sartorius Model 2604 balance and an Alpha Al-7500 electromagnet with 4-in. diameter pole faces. A 1.9-cm pole gap was used for all measurements. A glass sample tube having a diameter of 8 mm and a sample length of 14.25 cm was suspended below the balance in a Plexiglas chamber to eliminate air-currents. Temperatures were read from a thermometer placed in this chamber; $HgCo(NCS)_4$ was used as a standard to "calibrate" the balance.[4]

Data Collection and Solution of the Structures. Intensity data were measured on an automated Picker four-circle X-ray diffractometer which utilized monochromatic Mo Kα radiation (oriented graphite crystal monochromator) for data collection. A symmetrical 2θ scan was taken about the position calculated for Kα_1 with stationary-crystal, stationary-counter background counts of 10 sec being made at the beginning and the end of the scan range. The scan range was 1.5° plus an increment determined by the wavelength dispersion. Copper foil attenuators of various thicknesses were automatically inserted in front of the counter aperture whenever the counting rate exceeded 10,000 counts/sec. Observed reflections were defined by the criterion $I_{\text{obsd}} > 3\sigma_c(I)$ where $\sigma_c = [I_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$, I_c is the total integrated counts, t_c/t_b is the ratio of the time spent counting the peak intensity to the time spent counting the background intensities, and B_1 and B_2 are back-

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[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[2] M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **6**, 900 (1967).

[3] R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).

[4] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).