[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SAINT LOUIS UNIVERSITY]

Reactions between Dry Inorganic Salts. IX. The Effect of Common Ions on the Transition Temperature of Cesium Chloride

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A study of the effect of cesium bromide on the transition temperature of cesium chloride has been carried out by the use of a multiple junction, differential thermocouple and by means of X-ray analysis. It has been established that cesium bromide raises the transition temperature of cesium chloride and that the rate of increase becomes greater with higher percentages of cesium bromide up to about 65 mole %. At this point the transition temperature is very close to the melting point. Above the transition temperature, X-ray patterns were obtained that indicated the formation of solid solutions of cesium chloride and cesium bromide having O_h^5 symmetry.

The reciprocal system $CsCl + KBr \rightleftarrows CsBr + KCl$ has been studied at below fusion temperatures by Wood and Vogt[2] as a part of a general study of the 60 reciprocal systems containing the common alkali halides.[3] Twelve of these 60 reciprocal systems contain cesium chloride but the system $CsCl + KBr \rightleftarrows CsBr + KCl$ has been studied the most because the two binary common ion solid solutions, potassium bromide–potassium chloride and cesium bromide–cesium chloride, which are miscible in all proportions at room temperature, readily form when crystal mixtures are heated at temperatures as much as 100 to 200° below the fusion temperature.

Cesium chloride is unique in that it is the only one of the alkali halides known to exhibit a crystalline transition between room temperature and the melting point at ordinary pressures. It might be expected that ion migration at temperatures near the transition point might be quite rapid and that a study of such ion migration rates might contribute much to the rapidly developing theories of solid state reactions having to do with crystal defects and diffusion as proposed by Schottky and Wagner[4] and others. It is the purpose of this investigation to study the effect of cesium bromide and potassium chloride on the transition temperature of cesium chloride. These two salts were selected because cesium bromide was known to form a solid solution with the low temperature form of cesium chloride and it was expected that potassium chloride would form a solid solution with the high temperature form.

Materials, Apparatus and Methods

The cesium salts, which were supplied by the McKay Chemical Company, were tested by means of the spectroscope and other alkali metals were found to be present in amounts not exceeding a few hundredths of a per cent. The potassium chloride was Mallinckrodt Analytical Grade. The method of differential thermal analysis (DTA) was used for observing the transition occurring in the various mixtures of cesium chloride. This method seems to have been first used by Le Chatelier[5] in 1887 and although it has since been used by many investigators, it nevertheless seems worthwhile to describe the experimental arrangement (Fig. 1) not only because it was very effective but also because it was easily constructed from inexpensive, easily available materials usually found in any laboratory. Of prime consideration is the elimination of temperature gradients between c, c′ and o. It is recommended that the furnace be constructed with several windings in such a way that a little more or a little less heat can be supplied to various zones as may be found necessary. Also it may be found necessary to vary the thickness of the outside vermiculite insulating layer to prevent temperature gradients during cooling. Provision should also be made for rapid cooling by raising the core and steel block out of the furnace or by lowering the furnace from around the block. An exhaustive bibliography of the literature to 1951 on the use of differential thermal analysis has been prepared by Smothers, Chiang and Wilson[6] and was found most helpful.

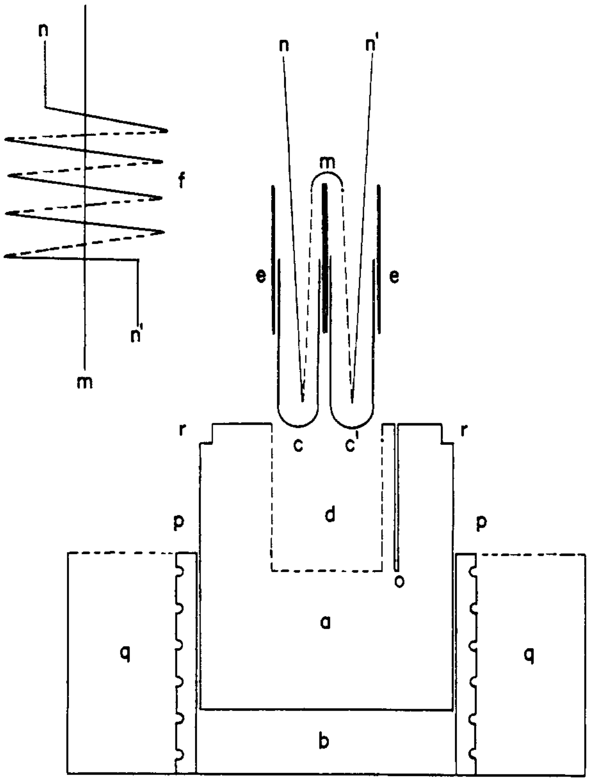

Fig. 1.

Results and Discussion

Before testing the effect of cesium bromide and potassium chloride on the transition temperature of cesium chloride, an effort was first made to determine the transition temperature for pure cesium

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[1] Taken in part from theses presented to the faculty of St. Louis University for the degree of Master of Science.

[2] L. J. Wood and J. Wm. Vogt, THIS JOURNAL, **66**, 1259 (1944).

[3] L. J. Wood and E. B. Thomas, *ibid.*, **56**, 92 (1934); **57**, 822 (1935); **58**, 1341 (1936); L. J. Wood and Harold Link, *ibid.*, **60**, 2320 (1938); **62**, 766 (1940).

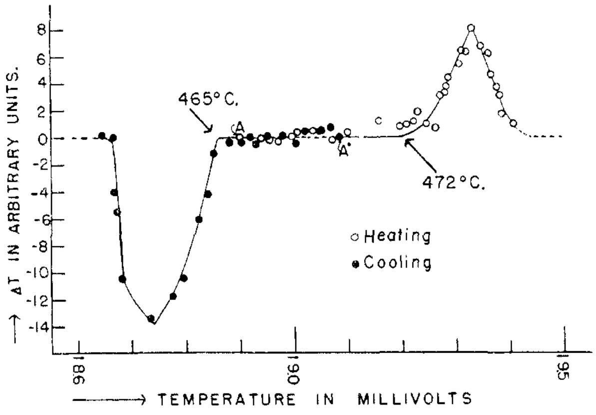
[4] C. Wagner and W. Schottky, *Z. physik. Chem.*, **B11**, 163 (1930); C. Wagner, *Z. physik. Chem., Bodenstein-Festband*, 177 (1931); **B22**, 181 (1933).

[5] H. Le Chatelier, *Bull. soc. franc. Mineral*, **10**, 204 (1887).

[6] W. J. Smothers, Y. Chiang and A. Wilson, *Univ. Arkansas Inst. Sci. Technol. Research Ser.*, **21**, 1 (1951).

chloride. This seemed quite appropriate because literature values for this transition temperature ranged from a low of 445° to a high of 479°. A value of 451°, obtained by the use of cooling curves, was reported by Zemezuzny and Rambach.[7] This same value was obtained by Sandonini and Scarpa[8] who also used cooling curves. A value of 479° was obtained in 1915 by Korrang[9] who used heating curves. In 1933 Wagner and Lippert[10] showed, by means of X-ray analysis, that the low temperature modification of cesium chloride (interpenetrating simple cubic) changed to face-centered cubic at the transition temperature which was reported to be 450 ± 5°. After further work, using X-ray analysis, these authors[11] reported that the transition of the low temperature form to the high temperature form occurred at 445 ± 5°. In 1934, West[12] using X-ray analysis, confirmed the high temperature modification to be face-centered cubic. In 1951 Menary, Ubbelohde and Woodward,[13] using X-ray analysis, reported the transition temperature to be 469°. In 1955 Johnson, Agron and Bredig[14] reported a transition temperature of 470°.

Using the differential thermocouple and other apparatus described above, cesium chloride was heated and cooled through the transition range and an effort was made to observe the temperature at which the beginning of transition occurred. A large number of preliminary observations were made, using different amounts of material and different heating rates. The most reliable results obtained are plotted in Fig. 2 in which the heating curve begins at A and the cooling curve at A′. As is to be seen from these curves, it is difficult or impossible to say precisely where the transition begins either when the temperature is increased or decreased. This may well be due to an appreciable change in the specific heat of the cesium chloride as the transition is approached and it is certainly true that by the time a difference in e.m.f. has been developed between the junctions of the differential thermocouple, the temperature of the beginning of transition already has been exceeded. In an effort to obviate these difficulties a static method was developed, by means of which the two transition temperatures 465 and 472° were determined.



TRANSITION OF CESIUM CHLORIDE

Fig. 2.

Using this static method for a determination of the upper transition temperature, the sample was heated to a predetermined temperature (near the transition range) and held at this temperature, as nearly as possible, for 30 minutes, after which it was cooled rapidly by removing the core from the furnace. A galvanometer deflection indicated that the selected 30 minute heating temperature was above the transition temperature and no deflection indicated that the selected heating temperature was below the transition temperature. A second heating temperature was then selected and the sample was heated and cooled as before. This very exacting and arduous process was repeated until the temperature corresponding to the transition CsCl O_h^1[15] → CsCl O_h^5[15] was approached as closely as permitted by the limits of observation (about ± 0.5°).

In a similar manner an effort was made to determine the transition temperature CsCl O_h^5 → CsCl O_h^1. In this case the cesium chloride was heated to a temperature well above the upper transition and cooled to a temperature near the lower transition range, at which temperature it was held, as nearly as possible, for 30 minutes. After numerous trials a temperature of 465° was approached for the transition CsCl O_h^5 → CsCl O_h^1 as shown by the data listed in Table I. In approaching the upper transition temperature corresponding to CsCl O_h^1 → CsCl O_h^5 it was found that after 30 minutes at 473° (very nearly) there was a galvanometer deflection upon cooling but that upon heating after the 30-minute period there was no definite deflection. Clearly the symmetry of all or nearly all of the cesium chloride was O_h^5 after 30 minutes at 473°. Upon dropping the temperature, continued observation indicated the CsCl O_h^1 → CsCl O_h^5 transition to be close to 472.5° which is shown in the graph rounded off to 472°.

In view of the results represented in Fig. 2, the wide divergence of the cesium chloride transition temperatures reported in the literature can be at least partly explained. Cooling curves would be expected to give low results (Zemezuzny and Rambach as well as Sandonini and Scarpa obtained 451°) and heating curves would be expected to give high results (Korrang obtained 479°). The X-ray method, while indispensable for a determination of crystal symmetry above and below the transition, is not well adapted to an accurate observation of the transition temperature (Wagner and Lippert reported 445° whereas Johnson, Agron and Bredig reported 470°). Obviously the thermocouple cannot be placed directly in the sample because this

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[7] S. Zemezuzny and F. Rambach, *Z. anorg. Chem.*, **65**, 418 (1910).

[8] C. Sandonini and G. Scarpa, *Mem. Accad. Lincei*, [5] **21**, 77 (1912).

[9] E. Korrang, *Z. anorg. Chem.*, **91**, 194 (1915).

[10] G. Wagner and L. Lippert, *Z. physik. Chem.*, **B21**, 471 (1933).

[11] G. Wagner and L. Lippert, *ibid.*, **B31**, 263 (1936).

[12] C. D. West, *Z. Krist.*, **88**, 94 (1934).

[13] J. W. Menary, A. R. Ubbelohde and I. Woodward, *Proc. Roy. Soc.* (*London*), **A208**, 158 (1951).

[14] J. W. Johnson, P. A. Agron and M. A. Bredig, THIS JOURNAL, **77**, 2734 (1955).

[15] The low temperature form of CsCl (interpenetrating simple cubic) has been commonly referred to as body-centered cubic. To avoid ambiguity, the low temperature form will be referred to as O_h^1 and the high temperature form as O_h^5.

would place it in the X-ray beam. The temperature then must be determined by some sort of calibration or comparison which unavoidably leads to some uncertainty. It is believed that a more fundamental difficulty is to be found in the likelihood that CsCl O_h^1 is still present untransposed for a brief temperature interval after the intensities of the X-ray diffraction lines have fallen below the limit of observation.

Preliminary results have been obtained in the authors' laboratory which appear to indicate that the actual beginning of transition may depend upon the previous history of the cesium chloride. In 1924 Cohen[16] submitted evidence to indicate that many, if not all, substances that exhibit a crystalline transition, show more or less retardation which opposes the change and leaves some untransposed material in the new crystals. The amount of such untransposed material would be expected to influence the reverse transition. More recently Thomas and Staveley[17] have studied the phenomenon of hysteresis. These authors attempted, without success, to eliminate hysteresis by inoculation, shock waves, holding the system at an appropriate temperature for long periods of time and by cooling in the presence of solvents. Because this paper is principally concerned with the effect of cesium bromide and potassium chloride on cesium chloride, the results obtained on the study of the hysteresis of cesium chloride will be reserved for another report.

The effect of cesium bromide on the transition temperature of cesium chloride was studied by making up mixtures of cesium chloride with 20, 40, 50 and 60 mole % of cesium bromide. The mixtures were first melted and then ground to a fine powder after cooling. Upon heating as described under experimental procedure above, the transition curves shown in Fig. 3 were obtained. Attempts to observe the transition temperature for higher percentages of cesium bromide failed because the transition temperature approached the melting point. To obtain Fig. 4, pure cesium chloride was substituted for the inert standard and a direct comparison of the 20% cesium bromide mixture with cesium chloride was obtained. Upon heating, the galvanometer began to deflect to the left at about 472° and returned to zero at about 486° but immediately began a deflection to the right as the transition in the mixture began. Upon cooling the transition in the mixture began at 480° which was followed almost immediately by the $O_h^5 \rightarrow O_h^1$ transition in the cesium chloride. The existence of a hysteresis is clearly seen for both the pure cesium chloride and the mixture. Cooling curves for 20, 40 and 60% cesium bromide were observed and the beginning of transition on heating and cooling has been plotted in Fig. 5. Because the static method described above for pure CsCl was not used for any of the mixtures, the absolute values for the beginning of transition have not been determined to the same degree of accuracy as was obtained in Fig. 2. Except for the mixture containing 60% or more cesium bromide the variation in the beginning of transition was about ±1.5°. It is certain that the transition temperatures increased with increasing percentages of cesium bromide. The temperature difference between the two curves of Fig. 5 is about 6°.

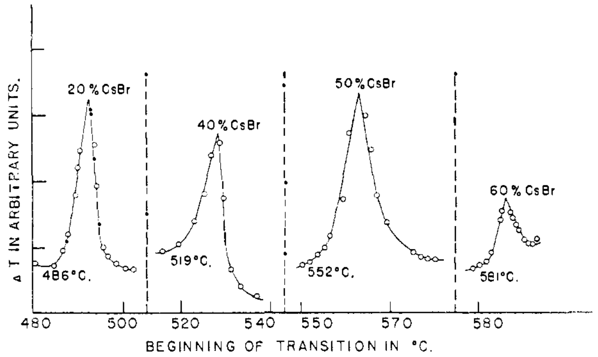

Fig. 3.

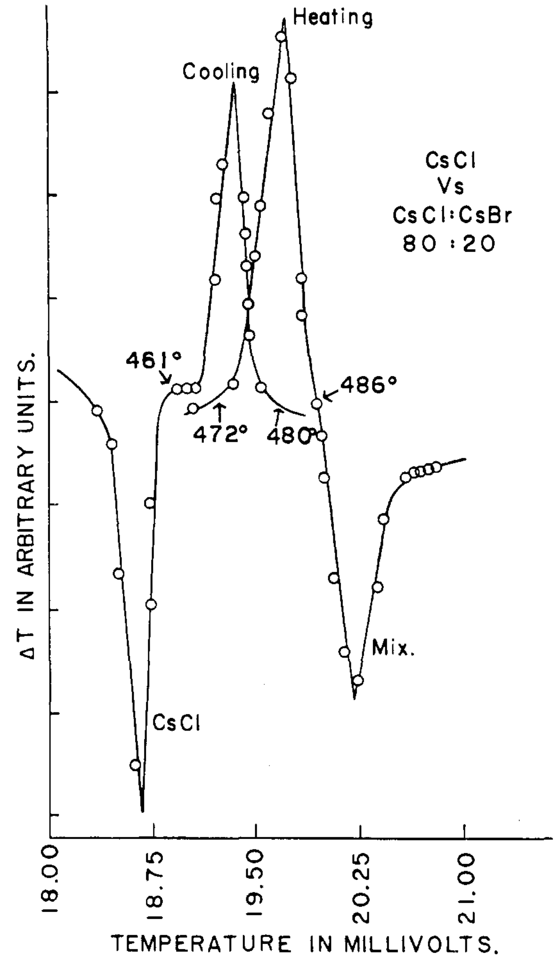

Fig. 4.

The almost equal amplitudes of the 20, 40 and 50% curves of Fig. 3, which are in turn almost equal to the amplitude observed for pure cesium chloride, are of interest. Because the grams of material heated and the heating rates were about the same in each case, the equal amplitudes can be taken to indicate that approximately the same amount of

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(16) E. Cohen and J. Kooy, *Z. physik. Chem.*, **109**, 81 (1924).

(17) D. G. Thomas and L. Staveley, *J. Chem. Soc.*, 2572 (1951).

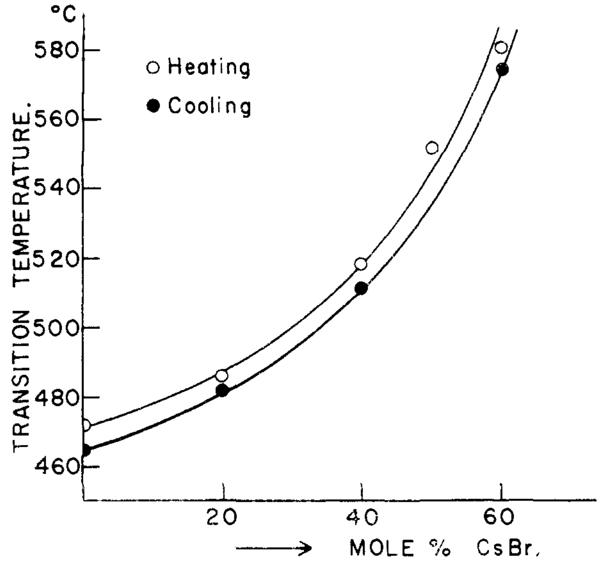

Fig. 5.

TABLE I

THE TRANSITION OF CsCl O_h^5 CsCl O_h^1 (STATIC METHOD)

Sample cooled from 20 mv. and held in the indicated range for 30 min.

Case 1—19.000–19.040 mv. range		Case 2—18.820–18.850 mv. range	
Mv.	Min. in the range	Mv.	Min. in the range
19.000(465.33°)	0	18.840	0
19.020	3	18.830	3
19.035	6	18.850(464.77°)	6
19.000	10	18.855	7
19.040	15	18.820(464.06°)	12
19.020	18	18.825	15
19.000	21	18.840	18
19.020(465.42°)	24	18.830	21
19.040	26	18.830	24
19.015	30	18.830	27
		18.830	30
After 30 min. the sample was cooled rapidly. Beginning at about 18.60 mv. there was a galvanometer deflection of 15 units corresponding to CsCl O_h^5 CsCl O_h^1.		After 30 min. the sample was cooled rapidly. There was no galvanometer deflection, which indicated that the CsCl transition had occurred already.	

TABLE II

THE X-RAY PATTERN[a] FOR A 60:40 MOLAR MIXTURE OF CsCl- CsBr AT 500 AND 580°

500°				580°			
Line no. and I	*d*, obsd.	*hkl*	*d*, calcd. *a* = 4.284	Line no. and I	*d*, obsd.	*hkl*	*d*, calcd. *a* = 7.227
1–M	4.28	100	4.28	1–M	4.16	111	4.17
2–S	3.03	110	3.03	2–S	3.62	200	3.61
3–W	2.48	111	2.47	3–M	2.56	220	2.56
4–M	2.138	200	2.142	4-W	2.181	311	2.180
5–W	1.913	210	1.916	5–W	2.082	222	2.086
6–M	1.747	211	1.749	6–VW	1.802	400	1.807
7–VW	1.521	220	1.515	7–VW	1.617	420	1.616
8–VW	1.355	310	1.355	8–VW	1.476	422	1.475
9-VVW	1.142	321	1.145				

[a] The pattern at 500° is body-centered. This solid solution with unit cell edge = 4.284 is between *a* for CsBr O_h^1 = 4.369 and *a* for CsCl, O_h^1 = 4.224 (Table III). The pattern at 580° is face-centered. This solid solution with unit cell edge = 7.227 is between CsCl O_h^5 = 7.098 and CsBr O_h^5 = 7.349 (calcd.) (Table III).

heat was observed in each transition.[18] If upon heating a solid solution of cesium chloride and cesium bromide from room temperature through the transition range, the solid solution (having O_h^1 symmetry) unmixes into pure cesium bromide O_h^1 and pure cesium chloride O_h^5, the amplitudes of the curves of Figure 3 would be expected to decrease with decreasing percentage of cesium chloride. This unmixing of the solid solution might perhaps be expected since it has been shown by Wagner and Lippert[11] and also by Johnson and co-workers[14] that cesium bromide does not exhibit a CsBr $O_h^1 \rightarrow$ CsBr O_h^5 transition analogous to that of cesium chloride at any temperature below its melting point. If, on the other hand, cesium bromide should undergo the $O_h^1 \rightarrow O_h^5$ transition in the presence of cesium chloride, the amplitudes of the transition curves (Fig. 3) might be expected to be approximately as found.

This latter hypothesis was tested by means of X-ray analysis of a 60:40 molar mixture of cesium chloride and cesium bromide held at 500, 525, 550 and 580°. At 500° the mixture was below the beginning of transition as shown in Fig. 3. At 525° the mixture was in the transition range, at 550° slightly above and at 580° well above the transition range. At 500° all of the interference lines belonged to an O_h^1 pattern (Table II) with a unit cell edge of about 4.284 Å. This value of 4.284 is definitely larger than 4.224 shown in column 3 of Table III for pure CsCl O_h^1 at 500° and is definitely smaller than 4.369 shown in column 7 of Table III for pure CsBr O_h^1 at 500° and is in excellent agreement with the value of 4.282 calculated for the 60:40 mixture based on the assumption that no transition takes place at 500°.

At 580° all of the interference lines belonged to an O_h^5 pattern (Table II) and there was no indication of an O_h^1 pattern. Furthermore the unit cell edge of 7.227 Å. for this O_h^1 pattern is definitely larger than 7.098 shown in column 5 of Table III for CsCl O_h^5 at 580° and definitely smaller than 7.349 shown in column 9 of Table III for CsBr O_h^5 at 580° and is not too far from a calculated unit cell edge value 7.198 for the 60:40 mixture obtained by taking 60% of 7.098 and 40% of 7.349. It is clear that the solid solution, stable below the transition temperature, does not unmix (as might be expected) to pure cesium chloride O_h^5 and cesium bromide O_h^1 upon being heated to 580°. In view of the O_h^5 pattern, with its intermediate unit cell edge of 7.227 Å., it seems necessary to conclude that the cesium bromide in the mixture, in the presence of the cesium chloride, also undergoes the $O_h^1 \rightarrow O_h^5$ transition. The X-ray results obtained at 525° showed a well developed O_h^1 pattern with the beginning of an O_h^5 pattern. At 550 there was an O_h^1 pattern and an O_h^5, the lines of each being of about equal intensity.

Obviously it is not possible to observe experimentally, either the unit cell edge of CsCl O_h^1 above the transition temperature or the unit cell edge of CsCl O_h^5 below the transition temperature. These

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[18] The transition temperature of the 60% mixture was approaching the melting temperature and it was difficult to maintain a comparable heating rate.

TABLE III

UNIT CELL EDGES AT VARIOUS TEMPERATURES AS CALCULATED BY MEANS OF THE LINEAR COEFFICIENT OF EXPANSION AND AN OBSERVED VALUE AT A NEARBY TEMPERATURE

	CsCl(O_h^1) $a_t = 4.199 + 2.5 \times 10^{-4}$ ($t - 400$) Wagner and Lippert a in Å.		CsCl(O_h^5) $a_t = 7.075 + 4.2 \times 10^{-4}$ ($t - 525$) Wagner and Lippert a in Å.		CsBr(O_h^1) $a_t = 4.377 + 3.2 \times 10^{-4}$ ($t - 525$) Johnson, Agron and Bredig a in Å.		CsBr(O_h^5) (see Table IV) a in Å.	
T, °C.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
400	4.199	[a]						
500		4.224		7.064		4.369		
525		4.231	7.075	[a]	4.377	[a]		
550		4.237		7.086		4.385		
580		4.244		7.098		4.395		7.349

[a] Indicates observed value was used as the basis for the computation.

TABLE IV

CALCULATION OF UNIT CELL EDGE FOR CsBr O_h^5

		Unit cell edge in Å.		Ratio of cell edges
Salt	°C.	O_h^1	O_h^5	O_h^1/O_h^5
CsCl	580	4.244[a]	7.098[a]	0.5979
RbCl	25	3.88	6.49	.5982[b]
RbBr	25	4.07	6.79	.5998[b]
CsBr	580	4.395	7.349[c]	

[a] From Table III. [b] These ratios calculated from high pressure data by Bridgman [P. W. Bridgman, *Phys. Rev.*, 67, 363 (1927)]. [c] The cesium chloride O_h^1 to O_h^5 cell edge ratio was rounded off to 0.598 and this ratio divided into 4.395 to get a unit cell edge for CsBrO_h^5 at 580°.

were gotten (Table III) by extrapolating from an observed value in the stable temperature range by the use of coefficients of expansion as indicated in the table. The unit cell edges for CsBr O_h^1 listed in column 7 of Table III were calculated by the use of a coefficient of expansion based on the work of Johnson, Agron and Bredig.[14] Wagner and Lippert[11] and also Krishnan and Srinivasan[19] have studied the expansion of cesium bromide. The results of Johnson, Agron and Bredig appear to be more consistent than the results of Wagner and Lippert and less accurate than the results of Krishnan and Srinivasan but the measurements of Johnson and coworkers extended up to 600° whereas those of Krishnan and Srinivasan extended only to 297°. Although apparently reliable unit cell edge values for cesium chloride and cesium bromide at room temperature are available (4.123 and 4.294 Å. according to Wood and Vogt[2] and more recently 4.123 and 4.295 Å. according to Swanson and Fuyat[20]) it seems best, for purposes of direct comparison, to apply the coefficients of expansion for cesium chloride and cesium bromide respectively to the unit cell edges observed at the elevated temperatures.

The rapid and continuous rise in the transition curve shown in Fig. 5 is of interest. When a foreign component (cesium bromide O_h^1 in this case) is more soluble in the low temperature form (cesium chloride O_h^1) than in the high temperature form (cesium chloride O_h^5), it is to be expected that the transition temperature will be raised[21] and if at some higher temperature, the foreign constituent becomes more soluble in the high temperature form than in the low, the transition temperature should pass through a maximum.[22] As is to be seen in Fig. 5, the transition curve does not pass through a maximum, as far as it is possible to observe it below the melting temperature.[23] This absence of a maximum in the transition curve might tentatively be explained if it were assumed that pure cesium bromide does in reality undergo the $O_h^1 \rightarrow O_h^5$ transition at an immeasurably small temperature interval below the melting point. The cesium chloride O_h^5 resulting from its own transition would then be soluble in the high temperature form of cesium bromide and the transition temperature of the cesium bromide would be lowered below the melting point. Johnson, Agron and Bredig[14] have pointed out that cesium bromide undergoes an increase of about 27% in its molecular volume upon melting whereas cesium chloride O_h^5, which is stable just under the melting point, expands only about 10 per cent. These authors conclude that the change from 8- to 6-fold coördination ($O_h^1 \rightarrow O_h^5$) which takes place for cesium chloride at 472°, far below the melting point, takes place in cesium bromide as part of the fusion process.

The 60:40 solid solution of cesium chloride and cesium bromide was found to melt at about 615° at which temperature the molecular volume of this mixture, just before melting, would be expected to be a little more than 56 cc. as extrapolated from the unit cell edge at 580°. On the assumption that the CsBr in the solid solution has O_h^5 symmetry at the time of melting, the molecular volume of the liquid would be calculated to be 110% of that of the solid or about 62 cc. If the molecular volumes of liquid cesium chloride and cesium bromide listed by Johnson and co-workers at the melting points be used for calculating a molecular volume for the 60:40 mixture (assuming additivity), a value of about 63 cc. is obtained which is certainly somewhat too high because the mixture melts at about 25° below the average melting points of the pure salts.

These calculations appear to lend support to the hypothesis that the transposed cesium chloride O_h^5 lowers the transition of the cesium bromide below the melting point. In this work the common ion cesium was added as cesium bromide and the raising of the transition temperature of the cesium chloride has been observed. This study is being continued by adding the common ion chloride as either potassium chloride or rubidium chloride.

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(19) R. S. Krishnan and R. Srinivasan, *Proc. Phys. Soc.* (*London*), **B69**, 679 (1956).

(20) H. E. Swanson and R. K. Fuyat, Natl. Bur. Standards (U. S). Circ. 539, Vol. II, p. 44 (1953); Vol. III, p. 49 (1954).

(21) A. Findley, "Phase Rule," 9th edition, Dover, 1951, p. 170.

(22) W. Grahmann, *Jahrb. Min.*, 1, 1 (1920)

(23) It would be difficult to observe a transition if it occurred only a few degrees below the melting temperature, *e.g.*, 2 or 3° below.

In 1910 Zemezuzny and Rambach,[7] using thermal analysis, reported that both potassium chloride and rubidium chloride form a solid solution with cesium chloride and that each of these salts lowers the transition temperature of cesium chloride but that this lowering could no longer be detected when the amount of the potassium chloride or rubidium chloride exceeded a few per cent. Preliminary results of the X-ray analysis indicate that these salts do indeed produce lowering of the transition temperature of cesium chloride. The extent of this lowering and its correlation with composition will be reported shortly in another publication.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XVII. Reaction of Complexes of Cobalt(II) and Quadridentate Amines with Hydroxide Ions

BY HANS B. JONASSEN AND GAYLE T. STRICKLAND[1]

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When hydroxide ions are added to solutions containing the triethylenetetramine-cobalt(II) ion (abbrev. $[\text{Cotrien}]^{2+}$), the existence of the complexes $[\text{CotrienOH}]^+$ and the oxolated polymer (–O–Cotrien–O–) are indicated. Under similar conditions the tris-(2-aminoethyl)-amine-cobalt(II) (abbrev. $[\text{Cotren}]^{2+}$) ion forms $[\text{CotrenOH}]^+$ and the dimer $[\text{Co}_2\text{tren}_2(\text{OH})_{3/2}]^+$. Studies have shown that of these tetramine complexes only the $[\text{Co}_2\text{tren}_2(\text{OH})_{3/2}]^+$ can decompose H_2O_2. The stereochemical reasons for this are discussed.

Introduction

The complex compounds formed between polyamines and cobalt(II) have been investigated in various laboratories.[2-4] Jonassen and Frey[5] reported that the complex formed by the cobalt(II) ion and tetraethylenepentamine (abbrev. tetren) was able to be oxygenated in basic methanol solution.

The purpose of this study was to determine the types of complexes formed between cobalt(II) ion and the tetramines, triethylenetetramine and tris-(2-aminoethyl)-amine (abbrev. trien and tren, respectively) in the presence of hydroxide ions and to attempt to elucidate the stereochemical structure of the possible hydroxy complexes.

Experimental

A. **Reagents.** (1) **Separation and Purification of Trien and Tren.**—The amine mixture containing approximately 62% trien and 38% tren, which was obtained from Carbide and Carbon Chemical Corporation, was separated and purified as follows.

Two hundred grams of the mixture was dissolved in ethanol and cooled to approximately 5° in an ice-bath. Concentrated hydrochloric acid was added dropwise from a buret at such a rate that the temperature was kept below 10°. A white crystalline precipitate formed after a time and this was removed in several fractions.

The addition of hydrochloric acid was eventually continued until a thick creamy white precipitate formed. Again fractions were taken until precipitation ceased. The dark reddish mother liquor was discarded.

The middle fractions of the white crystalline precipitate were combined and the first and last fractions were discarded. This was also done with the creamy white precipitate. Each salt was recrystallized several times by dissolving it in a minimum of hot water and precipitating it with an excess of cold ethanol. The salts were washed with acetone, then ether and then dried in a vacuum desiccator.

The salts were analyzed mercurimetrically[6] for chloride. The crystalline salt which precipitated first was found to be 99.5% tren·3HCl. The slightly cream-colored salt with a satiny luster was found to be 99.8% pure trien·4HCl.

(2) **Other Reagents.**—Carbonate-free solutions of sodium hydroxide were prepared and standardized against potassium acid phthalate. The solution of cobalt(II) ion was standardized electrolytically. All other reagents used were of C.P. quality. All aqueous solutions were prepared with oxygen-free water.

Oxygen-free nitrogen was prepared by leading the gas through an acid solution of chromous ion in a continuous cycle so that the oxidized chromic ion immediately was reduced by zinc amalgam.

B. **Apparatus.**—The conductometric titrations were performed with a standard potentiometer in a Wheatstone Bridge arrangement using vertical platinized electrodes.

Potentiometric measurements were obtained with a Beckman Model G *p*H meter. Spectrophotometric measurements were made with a Model B spectrophotometer. Standard one cm. matched Pyrex cells were used. Much difficulty was encountered because of oxidation of the solution during transfer to the absorption cell. The oxidation product was intense reddish-brown and absorbed strongly at 360 mμ. Even slight oxidation obscured all measurements up to about 550 mμ. A number of techniques were tried to prevent oxidation; the one which gave the most reproducible results is given in detail below.

A Pyrex cell, hypodermic syringe, two hypodermic needles and a 50-ml. flask with a nitrogen inlet tube near the bottom and a nitrogen exit tube near the top were thoroughly cleaned and dried at 120°. Pure nitrogen was bubbled through the component solutions for a period of 30 minutes to remove dissolved oxygen. The nitrogen was introduced into each solution through a pipet of the proper size to transfer a portion of the solution into the sample flask. This also served to flush the air out of the pipet. The Pyrex cell was fitted with a rubber cap made from the upper portion of a medicine dropper bulb. A trace of glycerol was used to form a seal between the cell and cap. Also, a strip of Scotch Tape was placed around the cap and cell in such a manner that the cap was securely held in place. Two hypodermic needles were inserted into the cap, one of which served as a nitrogen inlet and the other as a nitrogen outlet. In this manner the atmospheric oxygen was flushed out of the cell. The outlet needle was then coupled to the hypodermic syringe. The nitrogen was allowed to force the plunger back and thus fill the syringe. The syringe was then disconnected from the needle and the nitrogen was forced out with the plunger. This was repeated several times in order to flush all atmospheric oxygen out of the syringe.

The 50-ml. flask was flushed out with nitrogen. Then the proper amount of each component was transferred into this flask, using the pipets which were serving as nitrogen

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[1] Abstracted in part from the M.S. Thesis of Gayle T. Strickland, June, 1956.

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