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PREPARATION OF CUBIC CHLOROCOMPLEX COMPOUNDS OF TRIVALENT METALS: Cs_2NaMCl_6 [1a]

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DISCLAIMER

PREPARATION OF CUBIC CHLOROCOMPLEX COMPOUNDS OF TRIVALENT METALS: Cs_2NaMCl_6[1a]

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ABSTRACT

Compounds of stoichiometry Cs_2NaMCl_6, where M represents many tri-valent d- and f-transition metal cations, have been prepared by a variety of techniques as powders and as single crystals. X-Ray powder patterns show that these compounds are all face-centered cubic. The variation in lattice parameter of these compounds is discussed as a function of trivalent cation radius.

INTRODUCTION

The recent syntheses of $Cs_2NaAmCl_6$[2] and $Cs_2NaBkCl_6$[3] suggested that similar compounds might be stable for other trivalent cations of comparable ionic size. We have prepared and characterized such a set of compounds, of empirical formula Cs_2NaMCl_6, for a large number of trivalent cations M(III). In each compound the trivalent ion is surrounded octahedrally (site symmetry O_h) by six chloride ions.

Although a number of other hexachlorometallate(III) compounds are known,[4,5] the chlorocomplex compounds Cs_2NaMCl_6 possess a unique set of desirable properties which suggest their use in a variety of experimental situations: they are isostructural; they are soluble in water or in dilute acids; they have considerable thermal and chemical stability, particularly in comparison with the anhydrous trichlorides; they can be prepared by a variety of straightforward techniques; and they can usually be grown as single crystals.

EXPERIMENTAL SECTION

The original preparation of $Cs_2NaAmCl_6$[2] involved simply evaporating a solution of $2Cs^+ - Na^+ - Am^{3+}$ in HCl to dryness. $Cs_2NaBkCl_6$ may be precipitated from dilute HCl solution by blowing HCl gas over the solution and cooling.[3] Similar precipitation of $Cs_2NaAmCl_6$ from HCl solution in this laboratory required higher HCl concentration and lower temperature, while no such compound of Pu(III) could be precipitated under any conditions. We interpreted this precipitation behavior to mean that the solubility of Cs_2NaMCl_6

decreases with decreasing ionic size of actinide ion M(III). This hypothesis has been tested with several other trivalent cations of decreasing ionic radius.

The simplest technique for producing Cs_2NaMCl_6 is to dissolve the cations in their stoichiometric ratios in hot aqueous HCl and to evaporate the solution to dryness on a hot plate. This procedure is successful for the heavy lanthanides and for several other trivalent metals. Some preparations obtained by this approach yielded a few X-ray powder diffraction lines of CsCl, NaCl, and/or unidentified phases. Undoubtedly some hydrated trichloride or oxychloride precipitates along with the binary (uncomplexed) chlorides; therefore, the evaporation-to-dryness technique is not suitable for preparation of reproducibly pure complex chlorides. For two of the compounds special conditions were required to ensure the presence of trivalent cations: $Cs_2NaTlCl_6$ was prepared in the presence of H_2O_2, and $Cs_2NaTiCl_6$ was synthesized by dissolving Ti metal in 2CsCl - NaCl - aqueous HCl and evaporating to dryness under argon.

Crystals of Cs_2NaMCl_6 may be grown directly from aqueous solutions of those cations which complex readily with chloride. For example, $Cs_2NaBiCl_6$ was obtained as octahedral crystals up to 2 mm thick by slowly cooling a hot solution of 0.1 $\underline{M}$ Bi^{3+}, 0.2 $\underline{M}$ Cs^+, and 0.1 $\underline{M}$ Na^+ in 2 $\underline{M}$ HCl. By contrast, similar solutions of Au^{3+} or Fe^{3+} formed needle-like crystals which did not yield cubic powder patterns. These precipitates may have been tetrachloro complex compounds, since Au(III), for example, forms mostly 4-coordinate complexes.

The only lanthanide element which can be successfully precipitated from aqueous HCl as Cs_2NaMCl_6 appears to be lutetium. A solution of 0.05 $\underline{M}$ Lu^{3+}, 0.05 $\underline{M}$ Na^+, and 0.1 $\underline{M}$ Cs^+ in HCl was cooled to $-23°$ (CCl_4 slush) while bubbling HCl gas into the solution. Although $Cs_2NaLuCl_6$ did precipitate, it was contaminated with some NaCl (which is quite insoluble in concentrated HCl) and the yield was low. Solvent systems other than water may prove more suitable for preparations by this technique.

When pure single crystals of chlorocomplex compounds are desired, they may be prepared from a melt of mixtures of the anhydrous chlorides; this technique is appropriate as long as the partial pressure of MCl_3 in the melt is not dangerously high. First the appropriate trichloride is prepared in pure form by subliming impure trichloride (commerically available or prepared by dehydrating the hydrated trichloride in a stream of HCl gas at elevated temperature[6]) in a quartz tube under high vacuum. The sublimed trichloride is then melted into a sidearm of ~3 mm i.d., which is sealed off under vacuum and recrystallized by gradient solidification from the melt.[7] (Trichlorides exhibiting the hexagonal UCl_3 structure may be obtained as single crystals by gradient solidification. In all cases, impurities will "zone-refine" to the top or bottom of the quartz tube.) The sidearm is cracked open in a dry-box, and a few grams of trichloride is weighed out under a dry atmosphere. The sublimed trichloride is added to the stoichiometric amounts of NaCl and CsCl (dried by heating nearly to their melting points) in a quartz tube of ~4 mm i.d. in a dry box. The quartz tube is evacuated, heated to 550° C (any higher will sublime CsCl) to drive off residual water and adsorbed gases, and sealed off under vacuum. The mixed chlorides are heated until molten (over 800° C),

mixed by inverting the tube a few times, and lowered slowly through the temperature-gradient furnace used for the trichloride. Transparent single crystals over a centimeter in length have been prepared by this technique.

Table I presents a list of all compounds of the Cs_2NaMCl_6 type which have been prepared to date. With the exceptions of the Ti compound (which appears to oxidize slowly to Ti(IV)) and the Y compound (which is rapidly attacked by water vapor), all appear to be stable in room air. When prepared as powders by evaporation of solutions to dryness, many become noticeably hygroscopic after a few weeks.

It may be possible to prepare other compounds of this type, since all possibilities have not been investigated. The only failures encountered thus far have been with Au(III) and Al(III).

X-Ray powder patterns have been taken of all compounds prepared and the cubic lattice parameters are given in Table I. The X-ray technique and data treatment have been described by Morss and Fuger.[3] Error limits represent standard deviations calculated from least-squares treatment of diffraction lines of selected films; experience has shown that _four_ such standard deviations correspond roughly to 95% confidence, taking into account systematic errors such as sample eccentricity, non-uniform film shrinkage, sample impurities and film readers' habits. When preparations were available both as single crystals and as evaporation residues, lattice parameters of both preparations were measured and were found to be within each other's error limits. For most samples, the Nelson-Riley extrapolation for sample absorption was applied.

A number of the preparations were analyzed, with the results shown in Table II. In general, since the appropriate ions were mixed in stoichiometric

Table I

Compounds Cs_2NaMCl_6

M^{3+}	Preparation[a]	Lattice parameter, a	Oxide Ionic Radius (CN6)	Chloride Ionic Radius (CN6)
Fe	E	10.3329 (6)	0.645	0.61
Ti	E	10.3940 (11)	0.67	0.64
Sc	E	10.4875 (10)	0.73	0.68
In	E	10.5313 (9)	0.79	0.71
Tl	E	10.6231 (3)	0.88	0.75
Lu	A, E, H	10.6550 (4)	0.848	0.768
Tm	E	10.6860 (8)	0.869	0.783
Er	A	10.7043 (5)	0.881	0.792
Y	A, E	10.7315 (15)	0.892	0.806
Dy	A	10.7426 (9)	0.908	0.811
Sb	E	10.7780 (20)	----	0.829
Gd	A, E	10.7918 (8)	0.938	0.836
Bk	H	10.8050 (10)	0.954	0.842
Eu	E	10.8095 (8)	0.950	0.845
Sm	E	10.8341 (9)	0.964	0.857
Bi	E, X	10.8386 (10)	1.02	0.86
Am	E, H	10.8548 (8)	0.985	0.867
Pu	A	10.8890 (6)	0.987	0.884
Nd	A, E	10.8894 (10)	0.995	0.885
Pr	A, E	10.9118 (13)	1.013	0.896
Ce	A	10.9458 (7)	1.034	0.913
La	A	10.9923 (9)	1.061	0.936

[a] A = heating anhydrous chlorides in quartz tube; E = evaporating HCl solution to dryness; H = precipitating from cold conc. HCl; and X = growing crystals from dilute HCl by cooling/evaporation.

Table II

Analyses of Cs_2NaMCl_6

M^{3+}	Na, Calcd.	Found	M, Calcd.	Found	Cl, Calcd.	Found
Fe	4.12	4.25	10.02	10.15	38.16	37.87
La					33.22	33.1
Ce			21.84	21.8	33.16	33.1
Nd			22.35	22.4	32.45	32.8
Gd			23.88	23.6	32.10	32.0
Dy			24.48	24.6	32.04	31.9
Er			25.02	24.7	31.82	31.8
Lu	3.40	3.40	25.86	26.0	31.45	31.36

ratios when preparing the compounds, the analytical data reflect only the

gross uniformity of composition and anhydrous nature of each product.

RESULTS AND DISCUSSION

The X-ray powder patterns of all compounds Cs_2NaMCl_6 can be indexed

on the basis of a face-centered-cubic lattice. When powders were prepared

from single crystals, all lines were indexable. When the compounds had been

prepared as a powder (by evaporation), a few extraneous low-angle lines were

often present; most of these could be identified as CsCl or NaCl. X-Ray

powder pattern line lists for three representative compounds are displayed in

Table III. Observed intensities represent visual estimates (10 = very strong,

0 = trace). As is the case for $Cs_2NaBkCl_6$,[3] the observed intensities are

consistent with the atomic positions of space group Fm3m (O_h^5). The proposed

structure is the "ideal cryolite" arrangement,[8] typified by $(NH_4)_3AlF_6$,[9]

which is one of many complex compounds of the general formula $A_xB'B''X_{3x}$ in

which the ionic radii of A and X are comparable. To a good approximation the

crystals of Cs_2NaMCl_6 contain "planes" of $(Cs^+ + 3Cl^-)$ which stack in cubic

closest packing, ABCABCABC, with Na^+ and M^{3+} each filling half the octahedral

holes formed by $6Cl^-$. Diagrams of the unit cell, which is similar to that of

the "anti-fluorite" structure, are presented by Wells[8] and by Cotton and

Wilkinson.[10]

Figure 1 displays the lattice parameters of the lanthanide compounds

$Cs_2NaLnCl_6$ as a function of atomic number (equivalently as a function of the

number of f electrons) of Ln(III). The double-concave shape of the curve

(compared to the dashed curve, a second-order polynomial fitted to the ions with spherical f-electron configurations) may be compared with similar curves obtained for the lattice parameters of the iron garnets[11] or the heats of formation of aqueous lanthanide complexes.[12] The effect is similar to but smaller than the more pronounced effects in the $3d$ series:[13] superimposed upon the overall contraction of the lanthanide ions (as the effective nuclear charge on the outer electrons increases) is the additional contraction due to lanthanide ions with non-spherical f electron configurations. The non-spherical electron distribution enables ligand ions to be drawn closer to Ln(III), yielding a small shrinkage in the lattice parameter. The shrinkage in a appears to be greatest at about f^2 (Pr^{3+}) and f^9 (Dy^{3+}).

Figure 2 shows the fairly linear relationship between the lattice parameter of Cs_2NaMCl_6 and ionic radius of M(III). The ionic radii are the "oxide" radii of Table I, taken from the compilation of Shannon and Prewitt[14] with the exception of the actinide ions, which are those tabulated by Peterson and Cunningham.[15] Although these radii have been determined for sixfold coordination, they have been derived principally from internuclear distances in oxides. It was considered worthwhile to derive ionic radii for trivalent cations from the compounds Cs_2NaMCl_6 for the following reasons.

1. Sesquioxide lattice parameters are often very sensitive to the presence of excess oxygen.[16]

2. There is no unique crystal structure from which the ionic radii may be derived in oxide or fluoride coordination.

3. It is often assumed that ionic radii calculated from chlorides will differ from those derived from oxides only by a constant (the "covalency" correction).[17]

Table III. Powder pattern line lists for $Cs_2Na(Fe,La,Pu)Cl_6$ (Face-centered cubic).

$\Sigma_i (h_i)^2$	Cs₂NaFeCl₆				Cs₂NaLaCl₆				Cs₂NaPuCl₆			
	d_{calc}	d_{obs}	I_{calc}	I_{obs}	d_{calc}	d_{obs}	I_{calc}	I_{obs}	d_{calc}	d_{obs}	I_{calc}	I_{obs}
3	--	--	0.5	-	6.339	6.250	1.6	4	--	--	4	-
4	5.154	5.161	2	4	--	--	0.02	-	--	--	0.3	-
8	3.647	3.639	10	10	3.884	3.872	10	10	3.831	3.834	10	10
11	3.111	3.109	0.2	1	3.312	3.306	1.6	6	3.269	3.258	3.5	4
12	2.979	2.974	11	9	3.171	3.168	5	8	3.131	3.129	1.4	2
16	2.580	2.582	10	9	2.747	2.757	10	10	2.713	2.714	8	9
19	--	--	0.1	-	2.521	2.530	1.0	3	2.491	2.493	2.2	3
20	2.308	2.309	1	4	--	--	0.04	-	2.428	2.429	0.3	1
24	2.107	2.104	5	7	2.243	2.245	8	10	2.217	2.211	8	8
27	1.987	1.986	0.1	4	2.115	2.116	1.0	3	2.091	2.091	2.1	4
32	1.825	1.825	5	8	1.943	1.942	10	9	1.9203	1.9175	7	7
35	1.745	1.745	0.1	2	1.857	1.858	1.2	4	1.8369	1.8386	2.4	4
36	1.7210	1.7223	0.4	3	--	--	0.03	-	1.8113	1.8136	0.2	1
40	1.6328	1.6321	2	5	1.7376	1.7380	5	6	1.7186	1.7181	4	5
43	--	--	0.03	-	1.6759	1.6763	0.5	2	1.6577	1.6559	1.0	2
44	1.5569	1.5566	3	6	1.6568	1.6562	3	4	1.6388	1.6388	0.5	1
48	1.4907	1.4901	2	5	1.5863	1.5859	4.0	5	1.5692	1.5682	2.9	4
51	1.4462	1.4445	4.0	1	1.5389	1.5383	0.8	2	1.5225	1.5214	1.7	2
52	1.4322	1.4316	0.2	1	--	--	0.01	-	--	--	0.1	-
56	1.3802	1.3804	2	5	1.4686	1.4702	6.5	7	1.4531	1.4523	6.0	7
59	1.3447	1.3457	0.05	0	1.4308	1.4304	1.0	3	1.4158	1.4147	2.2	3
64	1.2911	1.2907	1	3	1.3738	1.3720	2.1	2	1.3595	1.3586	1.6	2
67	1.2619	1.2622	0.01	0	1.3427	1.3415	0.3	1	1.3288	1.3287	0.6	1
68	1.2526	1.2530	0.3	1	--	--	0.01	-	1.3190	1.3174	0.2	1
72	1.2173	1.2172	1.2	4	1.2953	1.2957	3.6	4	1.2819	1.2814	3.4	5
75	--	--	0.03	-	1.2691	1.2671	0.7	2	1.2561	1.2556	1.4	3
76	1.1849	1.1854	1.5	3	1.2607	1.2599	1.4	1	--	--	0.2	-
80	1.1549	1.1548	2.7	5	1.2288	1.2271	6.6	5	1.2163	1.2161	4.8	4
83	--	--	0.03	-	1.2064	1.2063	0.8	1	1.1942	1.1942	1.6	2
84	1.1271	1.1277	0.2	2	--	--	0.01	-	--	--	0.2	-
88	1.1012	1.1013	0.6	3	1.1717	1.1687	1.9	3	1.1598	1.1587	1.8	2
91	--	--	0.02	-	1.1522	1.1528	0.5	1	1.1406	1.1408	1.0	2
96	1.0544	1.0554	2.2	5	1.1218	1.1205	5.5	4	1.1105	1.1104	4.1	3

Table III. Continued.

$\sum\limits_i (h_i)^2$	Cs$_2$NaFeCl$_6$				Cs$_2$NaLaCl$_6$				Cs$_2$NaPuCl$_6$			
	d_{calc}	d_{obs}	I_{calc}	I_{obs}	d_{calc}	d_{obs}	I_{calc}	I_{obs}	d_{calc}	d_{obs}	I_{calc}	I_{obs}
99	--	--	0.02	-	1.1047	1.1064	0.7	1	1.0936	1.0927	1.4	2
100	--	--	0.1	-	--	--	0.00	-	--	--	0.1	-
104	1.0130	1.0133	1.4	4	1.0778	1.0777	5.0	5	1.0671	1.0659	4.8	5
107	0.9987	0.9996	0.03	1	1.0626	1.0633	0.7	1	1.0520	1.0529	1.5	2
108	0.9941	0.9940	1.4	3	--	--	1.4	-	--	--	0.2	-
115	--	--	0.02	-	1.0250	1.0242	0.5	1	1.0149	1.0149	1.0	1
116	0.9592	0.9620	0.2	1	--	--	0.00	-	--	--	0.4	-
120	0.9431	0.9438	0.7	4	1.0034	1.0039	3.1	2	0.9935	0.9932	3.0	3
123	--	--	0.01	-	--	--	0.4	-	0.9814	0.9832	0.9	1
128	0.9132	0.9136	0.9	2	0.9716	0.9708	2.5	2	0.9621	0.9623	1.9	2
131	0.9027	0.9010	0.04	1	0.9604	0.9607	1.2	2	0.9510	0.9512	2.5	3
132	--	--	0.2	-	--	--	0.00	-	--	--	0.3	-
136	0.8360	0.8859	0.9	3	0.9426	0.9426	3.1	2	0.9334	0.9332	3.1	3
139	--	--	0.02	-	--	--	0.7	-	0.9233	0.9228	1.6	1
140	0.87322	0.87326	2.2	3	--	--	2.0	-	--	--	0.2	-
144	0.86101	0.86095	2.6	4	0.9160	0.9162	6.6	2	0.9071	0.9075	5.1	4
147	--	--	0.02	-	0.9066	0.9074	0.6	1	0.8979	0.8979	1.3	1
148	--	--	0.07	-	--	--	0.00	-	--	--	0.2	-
152	0.83806	0.83812	1.3	3	0.8916	0.8918	5.1	3	0.8830	0.8830	5.3	4
155	--	--	0.04	-	0.8829	0.8831	1.2	1	0.87442	0.87477	2.6	2
160	0.81686	0.81672α_1 0.81666α_2	2.4	3	0.8690	0.8692	6.1	2	0.86067	0.86083	4.8	3
163	--	--	0.02	-	--	--	0.4	-	--	--	0.8	-
164	0.80684	0.80708	0.3	1	--	--	0.01	-	0.85013	0.85033	1.0	1
168	0.79718	0.79717α_1 0.79728α_2	1.2	2	0.8481	0.8481	4.1	2	0.83997	0.84017	4.4	3
171	0.79016	0.79001	0.07	0	0.84060	0.84065	1.9	1	0.83258	0.83276	4.1	3
172	0.78787	0.78770	1.9	1	--	--	1.4	-	--	--	0.1	-
176	--	--	5.1	-	0.82858	0.82880	7.8	2	0.82069	0.82082	6.3	2
179					0.82161	0.82174	2.2	1	0.81380	0.81359α_1 0.81358α_2	5.1	2
180					--	--	0.02	1	--	--	1.1	-
184					0.81037	0.81031α_1 0.81029α_2	5.6	3	0.80269	0.80276α_1 0.80252α_2	6.5	3
187					--	--	1.2	-	0.79624	0.79636	2.9	1
192					--	--	4.2	-	0.78582	0.78577	3.9	0
195					0.78719	0.78709α_1 0.78701α_2	3.4	1	0.77976	0.77976	9.8	0

These M(III) ionic radii for sixfold chloride coordination were derived as follows:

1. Using radii of Shannon and Prewitt, preliminary M(III) radii were calculated by assuming that all ions along the unit-cell edge of Cs_2NaMCl_6 are in contact. Thus,

$$r(Y^{3+}) = 1/2 \, [10.736 - 2r(Na^+) - 4r(Cl^-)]$$
$$= 1/2 \, [10.736 - 2(1.01) - 4(1.81)]$$
$$= 0.738 \, \text{Å.}$$

2. The radii for the monoclinic trichlorides (which have sixfold coordination) were calculated from the internuclear distances derived from the structural data of Templeton and Carter.[18] For example, in YCl_3, each Y(III) has two Cl^- each at 2.58, 2.63, and 2.69 Å. Thus, $r(Y^{3+}) = 2.63 - 1.81 = 0.82$ Å.

3. Shannon and Prewitt note that compounds with highly symmetric structures (NaCl, CaF_2, etc.) have shorter internuclear distances than the sum of ionic radii. Since this effect is also noted for Cs_2NaMCl_6, the M – Cl distances in the monoclinic trichlorides have been considered more appropriate. For the rare earths whose trichlorides have the YCl_3 structure, the radii calculated by step (2) above average 0.07 Å greater than those calculated by (1). Therefore, 0.07 Å has been added to the radii for sixfold chloride coordination, $r(^{VI}M^{3+})$. These ionic radii are tabulated as "chloride" radii in Table I.

4. For comparison, internuclear distances have been calculated from

the accurate structural data for the hexagonal trichlorides $(La-Gd)Cl_3$ with

nine-fold coordination.[19] The ionic radii $r(^{IX}M^{3+})$ in these chlorides average

0.206 Å greater than the "chloride" radii so that 0.21 Å is the six- to nine-

fold coordination correction for other such ions. Applying Morosin's

positional parameters[19] to the hexagonal actinide trichlorides (for which only

the lattice parameters have been published to high accuracy) gives the same

value for the six- to nine-fold coordination correction for the M(III) ionic

radii.

Comparison of the two sets of ionic radii of Table I shows that they

do not differ merely by a constant. Even where the "oxide" radii were derived

from a series of isostructural oxides,[20] the "chloride" radii change more

slowly than do the "oxide" radii. As might be expected, therefore, the

correction from oxide to chloride crystal radii is not a constant.

Since the "chloride" radii have been derived from a set of isostruc-

tural compounds, the primary advantage of this set of radii is its self-

consistency. However, since the assignment of precise values to individual

ionic radii is always somewhat arbitrary, differences of radii are much more

significant than their absolute values.

FOOTNOTES AND REFERENCES

(1) (a) This work was performed under the auspices of the U. S. Atomic
     Energy Commission. (b) Participant in the summer Undergraduate Train-
     ing Program in Nuclear Chemistry.

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FIGURE CAPTIONS

Fig. 1.   Lattice parameters of $Cs_2NaLuCl_6$.

Fig. 2.   Lattice parameter of Cs_2NaMCl_6 vs. M(III) "oxide" radius.

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Fig. 1

Fig. 2