two bands undergo significant changes in both wave number and intensity on substitution of Y; *e.g.*, compare the spectra of $(M_6Cl_{12})Cl_6^{2-}$ with those of $(M_6Cl_{12})Br_6^{2-}$. These changes signify strong mixing of the normal modes arising from the $M_6X_{12}^{n+}$ unit and the M–Y bonds. However, the appearance of the strong bands at 172, 192, and 256 cm^{-1} in the spectra of $(Nb_6Cl_{12})I_6^{3-}$, $(Ta_6Cl_{12})Br_6^{2-}$, and $(Ta_6Br_{12})Cl_6^{2-}$, respectively, certainly indicates that the M-Y modes should be assigned higher wave numbers than those given by Mackay and Schneider or by Mattes.

It is notable that the spectra provided here by the $(Ta_6X_{12})Y_6^{2-}$ compounds each show six bands of sufficient intensity to merit designation as the six T_{1u} fundamentals. Only five of the fundamentals were recognized by Mackay and Schneider for the $(Nb_6Cl_{12})Y_n$ series and by Mattes for all of the compounds $(M_6X_{12})X_n$ (M = Nb, Ta; X = Cl, Br; n = 2, 3, 4). The data given here still do not permit identification of the sixth fundamental in the $(Nb_6Cl_{12})Y_6^{n-}$ complexes.[8] Mattes associated the unobserved fundamental with the metal-metal stretching modes (T_{1u}), whereas Mackay and Schneider associated it with the M–Y wagging modes (T_{1u}). This hitherto unidentified band can now be designated for the tantalum cluster anions; it is the fundamental of lowest wave number in the data given for each of these anions in Table II.

Data from the spectra of the DMSO adducts in the region below 600 cm^{-1} are given in Table III. All of these adducts have a strong band in the range 429–440 cm^{-1}, which may be assigned as the metal–oxygen stretching fundamental of coordinated DMSO. This is in accord with the assignment of the Nb–O stretch in compound II at 439 cm^{-1} by Mackay and Schneider.[3] Field and Kepert[9] also reported the Nb-O stretch at 417–449 cm^{-1} in the spectra of a series of oxygen donor–cluster complexes. It is significant that the M–O stretching modes for these cluster adducts are in the same wave number range of 410–500 cm^{-1} as reported for a large series of simple metal ion-DMSO complexes.[10]

TABLE III

INFRARED SPECTRA[a] OF DMSO–CLUSTER ADDUCTS IN THE REGION 40–500 CM^{-1}

I[b]	II[c]	III[d]	IV[e]	V[f]	VI[g]
435 vs	437 vs	440 vs	429 vs	440 s	433 s, br
338 s, br	340 vs	334 vs, br	337 w	330 vs, br	325 ms, br
290 s, br	. . .	. . .	312 w	262 m	. . .
252 s	270 ms	268 ms	262 vs	247 m, sh	. . .
240 m, sh	240 s	240 s	229 vs	227 m	224 s
198 mw	. . .	196 vw	. . .	192 w	199 w
118 vw	. . .	133 vw	165 w	140 w	145 w

[a] Band maxima and intensities same as in Table I. [b] I = $(Nb_6Cl_{12})Cl_3(DMSO)_3$. [c] II = $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$. [d] III = $(Nb_6Cl_{12})Br_2(DMSO)_4$. [e] IV = $[(Nb_6Br_{12})(DMSO)_6](ClO_4)_2$. [f] V = $(Ta_6Cl_{12})Cl_3(DMSO)_3$. [g] VI = $[(Ta_6Cl_{12})(DMSO)_6](ClO_4)_3$.

The strong cluster band at high wave number is present in the spectra of all of the DMSO adducts, and it is shifted only slightly from the value observed for the $(M_6X_{12})Y_6^{n-}$ ions of appropriate cluster oxidation state. In the spectrum of IV the two weak bands at 337 and 312 cm^{-1} evidently arise from a trace of free DMSO retained in the complex. The band in the region 224 to 240 cm^{-1} becomes more intense with increasing substitution of DMSO on the cluster (compare the spectra of I and V with those of II and VI). Consequently this latter band may arise from a ligand-dependent mode, possibly M–O–S or X–M–O bending. Finally, the bands at 290 cm^{-1} in I and 262 cm^{-1} in V apparently arise from the terminal Nb–Cl and Ta–Cl stretching vibrations, respectively, since they are absent in spectra of the ions completely substituted with DMSO.

In summary it should be emphasized that definite assignments of all bands in these spectra cannot be made at this time. Indeed this must await a normal-coordinate analysis which takes account of mixing of the normal modes and which is based on more complete data, especially from Raman spectra. However the data reported here allow the following tentative conclusions.

(1) A band arising from the metal–metal stretching vibrations is not readily identified in $M_6X_{12}^{n+}$ clusters.

(2) Bands arising from the M–Y stretching vibrations are unambiguously identified only in those cases where they occur outside the immediate wave number range of the $M_6X_{12}^{n+}$ vibrational modes, *e.g.*, as in $(M_6X_{12})(DMSO)_6^{n+}$ or $(Ta_6Br_{12})Cl_6^{n-}$.

(3) Only one of the four bands arising from the $M_6X_{12}^{n+}$ vibrational modes (usually the one of highest frequency) undergoes little change in intensity or frequency with substitution of the Y atoms.

(4) The mixing of the normal modes appears to be less extensive in the $Ta_6X_{12}^{n+}$ compounds—hence the requisite fundamental bands can be identified with greater confidence.

Acknowledgment.—The authors are grateful to Miss Evelyn Conrad for her assistance in the measurement of the infrared spectra reported here.

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[8] The number of bands in the region 400–600 cm^{-1} for $(Nb_6Cl_{12})F_6^{4-}$ indicates a complicated structure where the terminal fluorine atoms probably occupy two or more nonequivalent positions in the compound $((C_2H_5)_4N)_4[(Nb_6Cl_{12})F_6]$.

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[10] B. F. G. Johnson and R. H. Walton, *Spectrochim. Acta*, **22**, 1853 (1966).

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Preparation of Cubic Chloro Complex Compounds of Trivalent Metals: Cs_2NaMCl_6[1a]

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Received September 5, 1969

The recent syntheses of $Cs_2NaAmCl_6$[2] and $Cs_2NaBkCl_6$[3] suggested that similar compounds might be

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

[2] K. W. Bagnall, J. B. Laidler, and M. A. A. Stewart, *J. Chem. Soc., A*, 133 (1968).

[3] L. R. Morss and J. Fuger, *Inorg. Chem.*, **8**, 1433 (1969).

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 hexachlorometalate(III) compounds are known,[4,5] the chloro complex 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.

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.

Experimental Section

The simplest technique for preparing Cs_2NaMCl_6 is to evaporate to dryness a hot aqueous HCl solution of the appropriate cations. This procedure was successful for the heavy lanthanides and for several other trivalent metals (Table I, preparation "E"). Some preparations obtained in this manner yielded a few X-ray powder diffraction lines of CsCl, NaCl, and/or unidentified phases; therefore, this technique is not suitable for the 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.

When a hot solution of 0.1 *M* Bi^{3+}, 0.2 *M* Cs^+, and 0.1 *M* Na^+ in 2 *M* HCl was cooled slowly, octahedral crystals of $Cs_2NaBiCl_6$ up to 2 mm thick were obtained (preparation "X," Table I). By contrast, similar solutions of Au^{3+} or Fe^{3+} formed acicular crystals which did not yield cubic powder patterns.

$Cs_2NaAmCl_6$ and $Cs_2NaBkCl_6$ were crystallized from aqueous solution by cooling and increasing HCl concentration (preparation "H," Table I). The only lanthanide compound which could be prepared in this fashion was $Cs_2NaLuCl_6$. A solution of 0.05 *M* Lu^{3+}, 0.1 *M* Cs^+, and 0.05 *M* Na^+ was cooled to −23° (CCl_4 slush) while bubbling in HCl gas. Although small crystals of $Cs_2NaLuCl_6$ were collected, powder patterns showed some coprecipitation of NaCl (which is quite insoluble in concentrated HCl) and the yield was low.

Pure single crystals of chloro complex compounds could be prepared from a melt; this technique ("A," Table I) is suitable if the partial pressure of MCl_3 in the melt is not dangerously high. The appropriate trichloride (commercially available or prepared by dehydrating hydrated trichloride[6]) is purified by sublimation in a quartz tube under high vacuum. The sublimate is melted into a side arm, which is then sealed off under vacuum and crystallized if possible by gradient solidification.[7] Under a dry atmosphere, a few grams of trichloride is added to the stoichiometric amounts of CsCl and NaCl (dried by heating) in a quartz tube of ~4-mm i.d. After evacuation, heating to 550° (any higher will sublime CsCl) to drive off residual water and adsorbed gases, and sealing off the quartz tube, the mixed chlorides are heated until molten (over 800°), mixed by inverting the tube, and lowered slowly through the temperature-gradient furnace used for the trichloride. Transparent crystals over 1 cm in length have been prepared.

TABLE I

COMPOUNDS Cs_2NaMCl_6

M^{3+}	Prepn[a]	Lattice parameter *a*, Å	Oxide ionic radius (CN 6), Å
Fe	E	10.3329 (6)	0.645
Ti	E	10.3940 (11)	0.67
Sc	E	10.4875 (10)	0.73
In	E	10.5313 (9)	0.79
Tl	E	10.6231 (3)	0.88
Lu	A, E, H	10.6550 (4)	0.848
Tm	E	10.6860 (8)	0.869
Er	A	10.7043 (5)	0.881
Y	A, E	10.7315 (15)	0.892
Dy	A	10.7426 (9)	0.908
Sb	E	10.7780 (20)	. . .
Gd	A, E	10.7918 (8)	0.938
Bk	H	10.8050 (10)	0.954
Eu	E	10.8095 (8)	0.950
Sm	E	10.8341 (9)	0.964
Bi	E, X	10.8386 (10)	1.02
Am	E, H	10.8548 (8)	0.985
Pu	A	10.8890 (6)	0.987
Nd	A, E	10.8894 (10)	0.995
Pr	A, E	10.9118 (13)	1.013
Ce	A	10.9458 (7)	1.034
La	A	10.9923 (9)	1.061

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

It may be possible to prepare other compounds of this type, since all trivalent cations and solvent systems have not been investigated. The only failures encountered were with Au(III) and Al(III).

X-Ray powder patterns were taken of all compounds and the cubic lattice parameters are given in Table I. X-Ray techniques and data treatment have been described.[3] A number of the preparations were analyzed, with the results shown in Table II.

TABLE II

ANALYSES OF Cs_2NaMCl_6 (%)

	Na		M		Cl	
M^{3+}	Calcd	Found	Calcd	Found	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

Since the appropriate cations were mixed in stoichiometric ratios when preparing the compounds, the analytical data reflect only

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(6) M. D. Taylor, *Chem. Rev.*, **62**, 503 (1962).

(7) D. M. Gruen, J. G. Conway, and R. McLaughlin, *J. Chem. Phys.*, **25**, 1102 (1956).

TABLE III

POWDER PATTERN LINE LISTS FOR $Cs_2Na(Fe, La, Pu)Cl_6$ (FACE-CENTERED CUBIC)

$\sum_i (h_i)^2$	$Cs_2NaFeCl_6$				$Cs_2NaLaCl_6$				$Cs_2NaPuCl_6$			
	d_{calc}	d_{obs}	I_{calc}	I_{obs}	d_{calc}	d_{obs}	I_{calc}	I_{obs}	d_{calc}	d_{obs}	I_{calc}	I_{obs}
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
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	0.8860	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	$0.81672\alpha_1$ $0.81666\alpha_2$	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	$0.79717\alpha_1$ $0.79728\alpha_2$	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	$0.81359\alpha_1$ $0.81358\alpha_2$	5.1	2
180					--	--	0.02	1	--	--	1.1	-
184					0.81037	$0.81031\alpha_1$ $0.81029\alpha_2$	5.6	3	0.80269	$0.80276\alpha_1$ $0.80252\alpha_2$	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	$0.78709\alpha_1$ $0.78701\alpha_2$	3.4	1	0.77976	0.77976	9.8	0

the gross uniformity of composition and anhydrous nature of each product.

Results

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

Lattice-parameter error limits represent standard deviations calculated from least-squares treatment of all diffraction lines of selected films; experience has shown that *four* such standard deviations correspond roughly to 95% confidence limits, taking into account systematic errors such as sample eccentricity, nonuniform 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 found to be within each other's error limits; the weighted average lattice parameters are listed in Table I. For most samples, the Nelson–Riley extrapolation for sample absorption was applied.

The X-ray powder patterns of all compounds Cs_2NaMCl_6 could 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 in 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 "antifluorite" structure, are presented by Wells[8] and by Cotton and Wilkinson.[10]

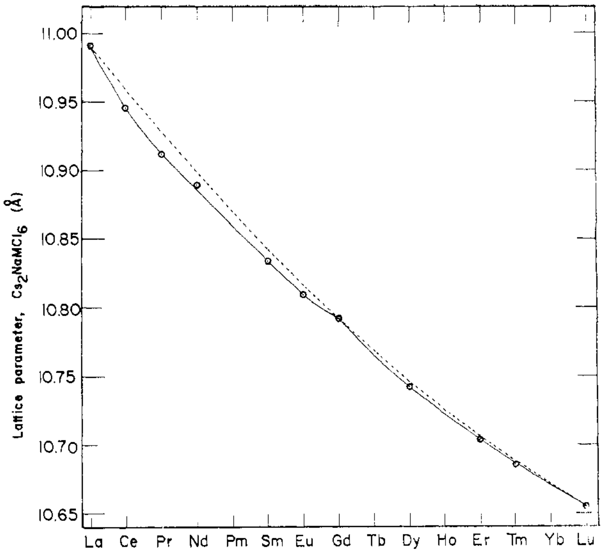

Figure 1.—Lattice parameters of $Cs_2NaLnCl_6$.

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 nonspherical f electron configurations. The nonspherical 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

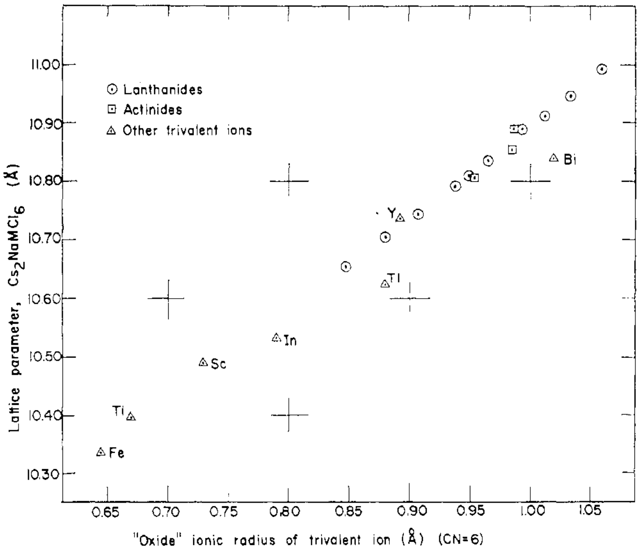

Figure 2.—Lattice parameter of Cs_2NaMCl_6 *vs.* M(III) "oxide" radius.

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of M(III). The ionic radii are sixfold-coordination "oxide" radii (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]

Acknowledgments.—We wish to thank Professor B. B. Cunningham for many helpful discussions.

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The Preparation and Infrared Spectra of *cis*-Dihalodiamminepalladium(II) Complexes

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Received September 11, 1969

We report here a new method for the preparation of the three complexes *cis*-Pd$(NH_3)_2X_2$ (X = Cl, Br, I). The preparation of the iodo complex has not previously been fully described.[1] According to Layton, *et al.*,[2] the method of preparation given by Grinberg and Shulman[3] for the *cis*-dichloro and *cis*-dibromo complexes yields impure products that isomerize in the solid state (the bromide more rapidly than the chloride) to the corresponding *trans* complexes. This has also been the experience in our laboratory.[4,5]

Durig and Mitchell[6] developed a method for obtaining more stable specimens of the *cis*-dichloro and *cis*-dibromo complexes that involved carrying out at low temperature the reaction used by Grinberg and Shulman. However, attempts to prepare *cis*-Pd$(NH_3)_2I_2$ by these methods always yielded the *trans* isomer. The main evidence for the identity of the products in the above experiments comes from infrared spectra, as we have not been able to find any solvent that would allow dipole moment measurements to be made. The results given by Perry, *et al.*,[7] which are representative of several reports in the literature, show that, for the chlorides and bromides, there are marked differences between the infrared spectra of the *cis* and *trans* isomers. Other tests that have been used for distinguishing the *cis* from the *trans* isomers are not so conclusive. The *cis*- and *trans*-chloro complexes have both been investigated using X-ray techniques[2,8] but their structures have not been fully established in this way. The uv spectra of *cis*- and *trans*-Pd$(NH_3)_2Cl_2$ in aqueous solution (containing about 10% ethanol) show only small differences.[9] The *cis*-dichloro- and *cis*-dibromodiammines also differ from the respective *trans* isomers in their reactions with potassium iodide solution.[3]

Experimental Section

Tetraamminepalladium(II) perchlorate (I) was prepared as described previously.[1]

cis-**Dihalodiamminepalladium(II) Complexes.**—A 2.3-g sample of I was dissolved in 75 ml of 0.2 *M* perchloric acid and allowed to stand overnight at room temperature. To the yellow solution was added a concentrated solution of sodium halide whereupon a solid precipitated immediately and was filtered rapidly, washed with water, alcohol, and ether, and dried *in vacuo* over silica gel. The chloro and bromo complexes were dull yellow microcrystalline solids and the iodo complex was brown.

Anal. Calcd for $Pd(NH_3)_2Cl_2$: N, 13.25; H, 2.84; Cl, 33.55. Found: N, 12.9; H, 2.9; Cl, 33.0. Calcd for $Pd(NH_3)_2Br_2$: N, 9.33; H, 2.00; Br, 53.23. Found: N, 9.3, H, 2.0; Br, 52.6. Calcd for $Pd(NH_3)_2I_2$: N, 7.10; H, 1.52; I, 64.39. Found: N, 6.5; H, 1.4; I, 64.4.

On adding NaSCN to the yellow solution, a pink precipitate was deposited. *Anal.* Calcd for $[Pd(NH_3)_4][Pd(SCN)_4]$: C, 9.36; H, 2.34; N, 21.84. Found: C, 9.4; H, 2.3; N, 21.7. No precipitate was formed on adding either $NaNO_2$ or NaOCN.

Infrared measurements (in the range 4000–250 cm^{-1}) were made on Nujol mulls with a Perkin-Elmer 457 spectrophotometer. The uncertainty in the infrared measurements was ±3 cm^{-1}.

Results and Discussion

When an aqueous solution of tetraamminepalladium(II) perchlorate is treated with excess perchloric acid, the aquation of the Pd(II) ion proceeds only as far as the replacement of two ammonia molecules.[1] The addition of chloride ion to a dilute solution of the diaquodiammine results in a rapid change in the uv spectrum, presumably owing to a fast anation reaction and the formation of chloro complexes. Solutions containing different concentrations of acid and chloride differ in their uv spectra and the spectra also change with time. However, in the spectra of several such solutions a shoulder at 290 nm was observed and, as this had been reported[9] to be a feature of aqueous *cis*-Pd$(NH_3)_2Cl_2$, it was suspected that the original diaquodiammine solution probably contained at least some *cis* isomer. Rasmussen and Jørgensen,[10] on the basis of much less slender evidence, have concluded that the diaquodiamminepalladium(II) ion exists mainly in the *cis* form. The present results support this conclusion. As anation reactions of Pd(II) complexes are expected to be fast and as all the known palladium(II) dihalodiammines are only slightly soluble in water, the addition of halide ions to a concentrated aqueous solution of the diaquodiammine would be expected to result in precipitation of the dihalodiammine of the same configuration as the aquo ion. The distinctive infrared absorptions (in the region 1200–300

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