The Crystal Structure of Lanthanoid Hexanitrite Complexes, $A_2A'Ln(NO_2)_6$

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Summary: A single crystal structure of $Cs_2NaLa(NO_2)_6$ and powder determination of $Cs_2NaNd(NO_2)_6$ and $Rb_2NaY(NO_2)_6$ show that these compounds have the lanthanoid ion oxygen coordinated and the soidum ion nitrogen coordinated in an inverse $A_2A'M(NO_2)_6$ structure. La-O = 2.82 A, Na = 2.50 A Cs-O = 3.33 A, Rb-O = 3.23 A. There is no evidence for the existence of strong complex ions in this structure.

The cubic compounds $A_2A'Ln(NO_2)_6$ where A is Cs^+ or Rb^+, A' is Na^+ and Ln is any lanthanoid La-Dy, including Y, have been known for many years.[1,2] Unit cell measurements[3,4] and simple calculations of the X-ray powder pattern of $Cs_2NaY(NO_2)_6$ associated these compounds with the vast array of hexanitrometallates where a transition metal ion is coordinated by six nitrogen atoms and A and A' are each coordinated by twelve oxygen atoms.[5,6,7,8]

Barnes and co-workers[4,9,10] have reported the spectra, semiconductivity and thermal decomposition of members of the series $Cs_2NaLn(NO_2)_6$. The results obtained were often surprisingly different from those for the transition metal analogues. The present study shows that the lanthanoid ions are, in fact, oxygen coordinated and the sodium ions nitrogen coordinated.

Experimental

Microcrystalline powders were prepared as described previously.[1,4] Single crystals were grown by the method used for the related cadmium complexes.[11]

$Cs_2NaLa(NO_2)_6$(I). After preliminary oscillation photographs intensity data were collected by Weissenberg photography. Layers hk(0-8) were collected for a crystal mounted with a cell edge parallel to the camera axis. In an F space group there are no reflexions common to odd and even layers in this setting. Accordingly a second crystal was mounted on a face diagonal and layers h'k'(0-2) collected to allow interlayer scaling. Intensities were measured by a computer controlled microdensitometer by the Science Research Council Microdensitometer Service, Darebury Laboratory, Daresbury, U.K. After merging symmetry equivalent reflexions, 126 unique planes had significant intensities.

The space group was assumed to be Fm^3 with the lanthanium and caesium atoms occupying special positions as in previous studies. The satisfactory thermal parameters obtained for these atoms confirm this assignment. Table 1. The sodium atom should also occupy a special position, but this atom refused to refine satisfactorily, giving an unacceptably large thermal parameter. A Fourier synthesis phased by the metal atoms showed the nitrite ion. Absorption corrections were applied but the refinement with isotropic thermal parameters terminated at R 0.115 using unit weights.

Considerable efforts were made to improve the refinement. The cell symmetry was reduced to orthorhombic, the sodium atom was allowed to move off the special position to give disorder, a secondary extinction parameter was introduced and the nitrite groups were disordered. None of these approaches gave any significant improvement in R. Since all the metal atoms occupy sites of cubic symmetry anisotropic thermal parameters are not appropriate. In view of the success obtained with compounds II and III (below) the difficulties with I are probably explained by some abnormality or twinning in the crystals used. The crystal quality was not high and the agreement of symmetrically related reflexions was not good.

$Cs_2NaNd(NO_2)_6$(II) and $Rb_2NaY(NO_2)_6$(III). Powder diffraction data were collected using a Phillips diffractometer with filtered copper radiation. Each peak position was scanned individually, integrating the K_{α_1} and K_{α_2} components and deducting stationary background counts. These intensities were corrected for the Lorentz-polarisation term, for multiplicity and for the coincidences of unrelated reflexions which occur in the cubic system.

Both structures refined to satisfactory R-factors (Table 1). In II the nitrogen z-coordinate seems unprobable. III, in which absorption is much less important, has no oddities. In both structures the sodium ion behaved normally.

All calculations, except for the reduction of the powder data, were performed using the SHELX 76

Table 1.

Crystal data for $A_2NaLu(NO_2)_6$, in the cubic space group Em^3

	$Cs_2NaLa(NO_2)_6$ single crystal	$Cs_2NaNd(NO_2)_6$ powder	$Rb_2NaY(NO_2)_6$ powder
a/Å	11.38(1)	11.32(1)	10.90(1)
F(OOO) calc	1240	1252	1024
Z	4	4	4
μ(CuKα)/cm^{-1}	600	655	157
no. of parameters refined	9	9	9
no. of reflexions measured above background	126	43	45
R	0.115	0.053	0.084

crystallographic package[12] on the Dundee University DEC 10 computer. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[13] Observed and calculated structure factors are given in the appendix.

Results and Discussion

The structures of I, II and III, solved independently, each show the NO_2^- ions with the oxygen atoms directed towards lanthanoid and the nitrogen atom towards sodium. Fig. 1. This would appear to be the first example of an ordered inverse $A_2A'M(NO_2)_6$ structure. In $Cs_2CdCd(NO_2)_6$ where A' and M are identical the nitrite ions are disordered to an average structure.[11]

There is no reason to suppose that the nitrite ion in I, II or III departs singificantly from its usual dimensions. In $NaNO_2$[14] N-O 1.236 Å and O-N-O 115.4°. The values observed in the present work are typical of those published for $A_2A'M(NO_2)_6$ compounds except where diffractometry on single crystals with Mo radiation has expanded the data set towards 500 reflexions.[15]

Nitrite is a non-innocent ligand.[16] The distances between nitrite ion and its neighbours can only be interpreted with caution in any discussion of bonding. Transition metal complexes such as $K_3Co(NO_2)_6$ or $Co_2PbCu(NO_2)_6$ are usually discussed in terms of a strong complex ion $M(NO_2)_6^{n-}$ surrounded by counter ions in more or less close contact.[17] Most of these complexes are cubic Fm^3 at or above room temperature. At low temperatures Jahn-Teller distortion of particular d^n configurations may be frozen in, reducing the symmetry to orthorhombic Fmmm.[19] Taking mean M-N distances 1.98 Å (Co^{2+})[6] and 2.12 Å (Cu^{2+})[7,15] and using the ionic radii of Shannon and Prewitt[20] for Co^{2+}, Cu^{2+} and Na^+ the predicted Na-N distance in a hypothetical $Na(NO_2)_6^{5-}$ would be 2.38(3) Å compared with 2.50(2) Å for the mean of structures I and III. $NaNO_2$[14] has Na...N contacts of 2.59 Å. In $NaNH_2$[21] the Na-N distances are 2.36 and 2.50 Å.

The typical La-O distance with twelve coordinated oxygen atoms is 2.67 Å (e.g. 2.692 Å in perovskites[22] and 2.642 Å in $La_2Mg_3(NO_3)_{12}(H_2O)_{24}$[23]). The La-O distance in I (2.82 Å) is in good agreement with the Y-O distance in III (2.63 Å) allowing for the difference in radius of 0.17 Å. This suggests a radius for bidentate oxygen in NO_2^- as 1.35 Å, using Shannon and Prewitt's radius[20] for La^{3+} in 12-coordination (1.46 Å) or 1.46 Å using the older value of Geller[22] (1.346 Å). [The relative merits of various tabulations of ionic radii are not considered here]. The La site in I is identical to the A' site of T_h symmetry in $A_2A'M(NO_2)_6$. A-O distances are available for Ca (2.67 Å)[8], Ba (2.87 Å)[6] and Pb (2.79 Å).[6,15] Using the Shannon and Prewitt radii these give bidentate radii for oxygen in NO_2^- as 1.18, 1.13 and 1.19 Å. The only value resembling that from I and III occurs with Cd in the disordered $CsCd(NO_2)_3$, where the abnormally long Cd-O (2.795 Å) gives the bidentate radius as 1.35 Å.[11]

Joesten and co-workers[8,15,19] have made a detailed study of the A-O distances in $A_2A'Cu(NO_2)_6$. In their comparison they have used traditional Pauling ionic radii, introducing differences from the values quoted here , although the argument is not affected. The A site is twelve coordinate, differing from A' in having Td site symmetry. The oxygen atoms belong to twelve different NO_2 . The A-O distances in transition metal $A_2A'M(NO_2)_6$ complexes are largely independent of M. Typically we find (A-O) 3.22 Å (Cs) 3.15 Å (Rb), 3.14 Å

Table 2

Atomic coordinates (x10^4) and isotropic thermal parameters (Å^{2}x10^3) with estimated standard deviations in parenthesis.

a) Symmetry constrained coordinates common to I, II and III

	x/a	y/b	z/e
La	0	0	0
Na	0	0	5000
Cs	2500	2500	2500
N	0	0	z_N
0	0	y_O	z_O

b) Refined parameters

	I	II	III
z_N	2800(12)	2500(10)	2700(9)
U_N	98(26)	50(19)	79(20)
y_O	1000(12)	900(10)	940(10)
z_O	2270(13)	2200(9)	2220(10)
U_O	94(15)	55(15)	97(17)
U_{La}	12(2)	13(3)	31(5)
U_{Na}	441(270)	70(40)	99(36)
U_{Cs}	20(2)	29(3)	58(5)

Table 3

Interatomic distances (Å) and angles (^{o}), with estimated standard deviations in parentheses

	I	II	III
Ln-O	2.82(2)	2.69(2)	2.63(2)
Cs-O	3.33(2)	3.38(2)	3.23(2)*
Na-N	2.50(2)	2.83(2)	2.51(2)
N-O	1.29(4)	1.07(4)	1.15(4)
O-N-O	124.2(2)	143.2(3)	115.4(2)

*Rb-O

(Tl), 3.12 Å (K). Deducting the cation radii the remainder increases as A decreases 1.20 Å (Cs) 1.28 Å (Rb), 1.26 Å (Tl), 1.38 Å. This leads to the proposition that smaller cations become progressively looser in the A site. Joesten[15] has correlated this with the change in temperature of the Fmmm → Fm^3 phase transition in $A_2PbCu(NO_2)_6$. In I the Cs-O distance (3.33 Å) gives a remainder 1.31 Å. In III Rb-O (3.23) gives 1.36 Å. These show the same trend as the previous values but from a larger starting point.

Thus it appears that the nitrite ion in I is relatively remote from La^{3+}, Na^+ and Cs^+. There is no reason to consider discrete complex ions such as $La(NO_2)_6^{3-}$ or $Na(NO_2)_6^{5-}$ This is consistent with the failure of attempts to correlate the lattice vibrational modes of these compounds with a model involving a rigid complex.[4] Lattice energy calculations[10] have suggested that I is only meta-stable. It forms from solution very rapidly but cannot be recrystallised or grown slowly from saturated solution, unlike at least some of the transition metal analogues.[15] An efficient mechanism for crystal growth appears to override the thermodynamic stability of the system to give crystals which can be removed from the mother liquor. If the crystals are not removed they would eventually be replaced by other products as equilibrium is established.

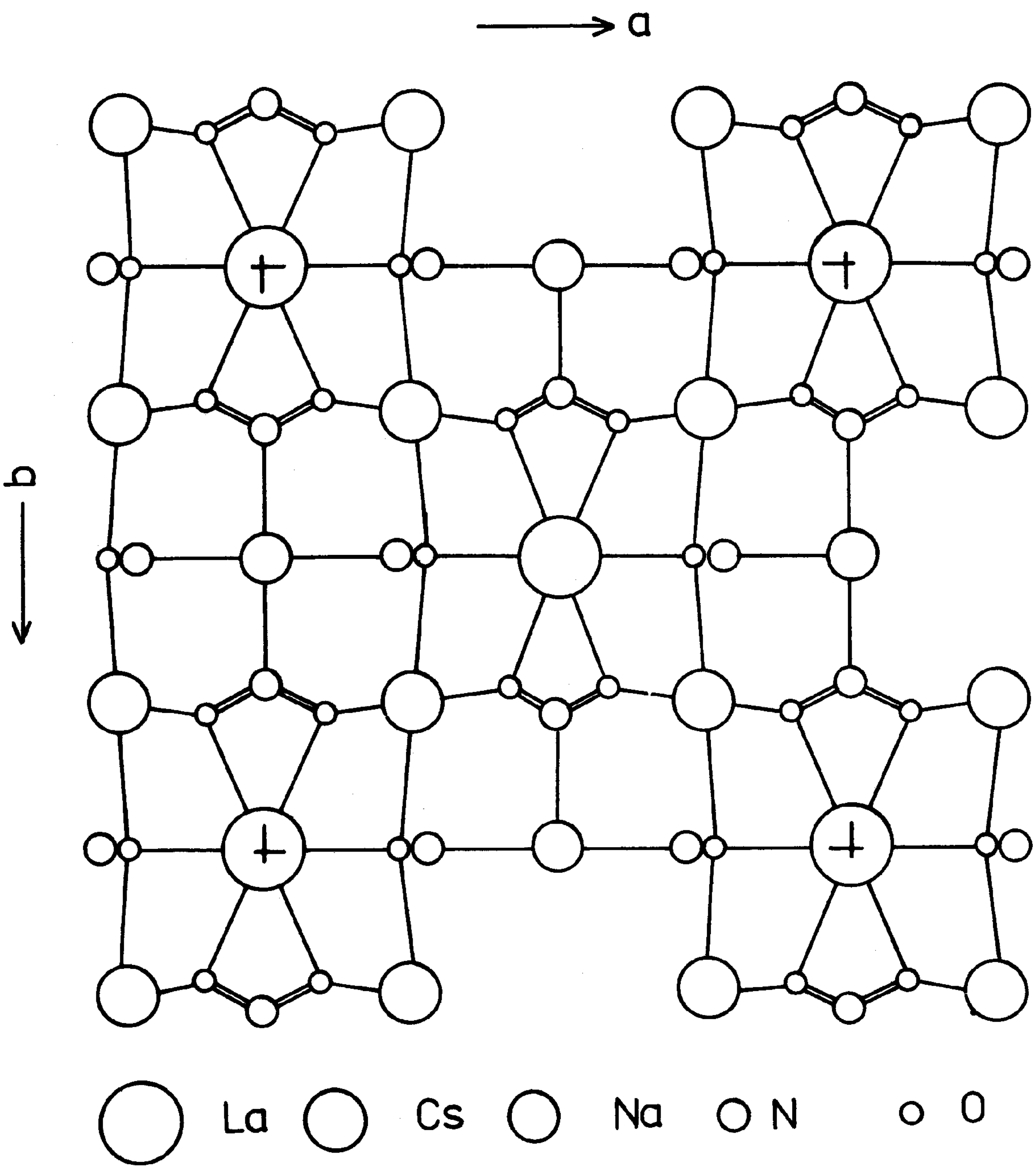

Fig. 1. $Cs_2NaLa(NO_2)_6$ structure, viewed down the c axis. Section from C = 0 to C = 0.25.

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CS2NALA(NO2)6 PAGE 1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	1	1	242	186	0	6	6	355	329	0	4	8	359	353	3	7	9	101	91	3	3	11	98	96
2	2	2	292	−336	2	6	6	65	−88	2	4	8	60	−96	5	7	9	68	89	5	3	11	112	92
1	1	3	145	153	4	6	6	298	320	4	4	8	295	301	7	7	9	78	79	7	3	11	86	81
1	3	3	165	172	6	6	6	44	−66	6	4	8	65	−79	1	9	9	84	87	1	5	11	116	96
3	3	3	187	215	1	1	7	102	126	0	6	8	99	−84	3	9	9	69	81	3	5	11	105	89
0	2	4	215	−230	3	1	7	176	129	2	6	8	295	278	5	9	9	56	76	5	5	11	88	83
2	2	4	493	508	5	1	7	63	104	4	6	8	83	−67	0	0	10	57	−52	3	7	11	96	82
0	4	4	454	470	1	3	7	163	141	6	6	8	252	247	2	0	10	322	284	5	7	11	92	79
2	4	4	84	−105	3	3	7	175	153	0	8	8	224	265	6	0	10	214	242	0	0	12	209	246
4	4	4	323	364	5	3	7	134	127	2	8	8	50	−66	0	2	10	328	291	2	0	12	63	−58
1	1	5	159	160	1	5	7	146	144	4	8	8	231	241	2	2	10	121	−92	4	0	12	186	221
3	1	5	220	183	3	5	7	147	132	6	8	8	41	−52	4	2	10	300	279	6	0	12	56	−48
1	3	5	181	113	5	5	7	89	106	8	8	8	181	194	8	2	10	236	214	0	2	12	82	−61
3	3	5	156	160	1	7	7	108	111	1	1	9	136	124	2	4	10	276	264	2	2	12	192	224
1	5	5	79	109	3	7	7	137	119	3	1	9	129	114	6	4	10	234	227	4	2	12	45	−49
3	5	5	80	111	5	7	7	138	107	5	1	9	106	108	0	6	10	226	252	6	2	12	209	200
5	5	5	49	73	7	7	7	133	97	1	3	9	128	103	2	6	10	86	−67	0	4	12	207	208
0	0	6	114	−123	0	0	8	384	417	3	3	9	101	104	4	6	10	242	237	4	4	12	207	207
2	0	6	469	438	2	0	8	142	−92	5	3	9	95	103	6	6	10	43	−49	2	6	12	200	198
4	0	6	176	−162	4	0	8	343	338	7	3	9	86	89	2	8	10	228	211	4	6	12	37	−39
0	2	6	383	344	6	0	8	71	−84	1	5	9	70	96	4	8	10	44	−43	1	1	13	85	83
2	2	6	166	−143	0	2	8	124	−111	3	5	9	101	87	1	1	11	100	96	3	1	13	71	81
4	2	6	352	372	2	2	8	363	324	5	5	9	37	84	3	1	11	128	91	5	1	13	55	75
0	4	6	125	−84	4	2	8	78	−74	7	5	9	65	79	5	1	11	80	87	1	3	13	80	78
2	4	6	392	415	6	2	8	316	292	1	7	9	118	90	1	3	11	104	98	3	3	13	62	78
4	4	6	103	−110																				
1	1	1	140	152	0	4	4	282	303	4	6	6	128	128	6	2	8	111	113	7	5	9	33	26
0	2	2	285	273	4	4	4	198	205	5	1	7	49	33	4	4	8	119	127	2	0	10	104	105
2	2	2	274	−278	1	1	5	97	111	3	3	7	70	62	6	6	8	78	78	6	0	10	78	73
1	1	3	58	60	3	1	5	84	116	5	7	7	42	42	0	8	8	99	93	4	2	10	87	98
1	3	3	68	53	3	3	5	89	79	7	7	7	36	35	1	1	9	54	64	6	2	10	81	57
3	3	3	97	84	3	5	5	49	52	0	0	8	235	221	3	1	9	41	53	6	4	10	75	62
0	0	4	544	516	2	0	6	230	252	2	0	8	48	−13	5	1	9	41	51	0	0	12	84	81
2	0	4	111	71	2	2	6	68	−75	4	0	8	154	155	7	1	9	34	37	4	0	12	73	64
2	2	4	305	315	4	2	6	180	179	2	2	8	134	147	7	3	9	36	32	2	2	12	70	62
1	1	1	206	229	2	2	4	510	510	4	0	6	148	−132	0	0	8	421	421	2	0	10	264	261
0	0	2	43	−50	0	4	4	504	513	2	2	6	133	−126	4	0	8	330	329	6	0	10	212	205
0	2	2	511	475	4	4	4	387	394	4	2	6	346	351	2	2	8	312	317	4	2	10	264	255
2	2	2	383	−359	1	1	5	162	187	4	4	6	88	−81	4	4	8	274	296	8	2	10	183	184
1	1	3	121	133	3	1	5	154	201	0	6	6	312	295	6	6	8	212	221	6	4	10	183	186
1	3	3	127	122	3	3	5	161	153	4	6	6	300	289	4	8	8	226	224	5	3	11	107	95
3	3	3	158	158	3	5	5	114	109	3	1	7	114	106	1	1	9	121	134	0	0	12	238	238
0	0	4	752	746	0	0	6	106	−92	3	3	7	133	133	7	5	9	107	67	2	2	12	183	184
2	0	4	123	55	2	0	6	414	454	5	3	7	111	111										

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