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Structure of Sodium Diaquobis(benzene-1,2-dioxydiacetato)lanthanate(III) Tetrahydrate

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The crystal structure of sodium [diaquobis(benzene-1,2-dioxydiacetato)lanthanate(III)] tetrahydrate, $Na[La(H_2O)_2(C_{10}H_8O_6)_2]\cdot 4H_2O$, is reported. Crystals obtained from aqueous solution are triclinic, space group $P\bar{1}$, with $a = 12.350$ (4) Å, $b = 12.760$ (3) Å, $c = 8.783$ (3) Å, $\alpha = 101.54$ (2)°, $\beta = 95.28$ (2)°, $\gamma = 75.98$ (2)°, $Z = 2$, $d_{measd} = 1.86$ (2) g cm^{-3}, and $d_{calcd} = 1.81$ g cm^{-3}. Standard heavy-atom methods were employed in the structural solution. Full-matrix, least-squares refinement of the nonhydrogen atom parameters, based on 4337 counter-collected F_o's, led to a final R value of 0.041 and a final weighted R value of 0.054. The lanthanum ion is decacoordinate, with a primary coordination sphere comprised of two tetradentate benzene-1,2-dioxydiacetate ligands and two water molecules. The coordination polyhedron about the lanthanum ion approximates a s-bicapped square antiprism, with typical La–O separations. Individual sodium ions are hexacoordinate, and inversion-related sodium coordination polyhedra together form a distorted, edge-shared bioctahedron. The novel aspect of the structure is the multiple bridging between the lanthanum and sodium ion coordination spheres, primarily through the benzene-1,2-dioxydiacetate ligands. The molecular conformation of the lanthanum complex observed in this structure does not duplicate that found in solution by NMR techniques. These conformational differences are attributable to interactions involving the coordinating sodium ion and other crystal packing forces not expected to be present in solution.

Introduction

In lanthanide (Ln) complexes containing tightly bound and sterically restrictive polydentate ligands, it has been common practice to use solid-state structural information, when known, as a model for the conformational properties in solution. While Sinha[2] has recently pointed out some of the dangers associated with such a practice, the advent of lanthanide-shift NMR techniques (^1H, ^{13}C) has made the structure of lanthanide complexes in solution accessible[3] and the merits of this working hypothesis can be tested.

It has been shown that the tris(2,6-dicarboxypyridine) [dipicolonate] complexes of lanthanide cations have essentially the same structure in solution as in the solid state.[4,5] Dipicolonate is a rigid, tetradentate ligand, and thermodynamic studies have shown that dipicolonate complexes of lanthanides have free energies of formation which are higher than expected.[6,7] This unusual thermodynamic stability has been explained as a consequence of ligand rigidity which results in strong Ln–N interactions as well as the expected Ln–O bonds.[7] These Ln(dipicolonate)$_3$ complexes exhibit D_3 symmetry in solution as determined by ^1H NMR and display essentially the same symmetry in several X-ray structure analyses.[4] The solution and solid-state structure of Ln(dipicolonate)$_3$ complexes are so similar that X-ray crystallographic results have been employed directly in the analysis of ^{13}C NMR data.[5]

Benzene-1,2-dioxydiacetate (BDDA) forms 1:1 and 1:2 complexes with divalent ions and trivalent lanthanides.[7,8] Thermodynamic data indicate that the ligand is tetradentate, rigid, and approximately planar.[7,8] The crystal structure of the potassium salt of BDDA is also in accord with the tetradentate, planar nature of the BDDA ligand.[9] More recently, an NMR study of BDDA complexes of Yb^{3+}, Eu^{3+}, and Pr^{3+} supports these conclusions for Ln–BDDA complexes in solution.[10] In the $[Ln(BDDA)_2]^-$ anion in solution, the ligands have the same NMR shifts which could result from both ligands having the same structure relative to the Ln cation, from rapid ligand exchange, or from rapid conformational changes. In any case, the average Ln–O distances are increased, particularly for the ether oxygens. The lanthanide ions are in the plane of each of the two ligands, and it was suggested that these ligand planes are perpendicular in order to minimize electrostatic repulsion.

In order to compare the structure of $[Ln(BDDA)_2]^-$ complexes in the solid to that reported in solution, we undertook an X-ray structural investigation of the lanthanum complex $Na[La(BDDA)_2]\cdot 4H_2O$. The NMR study[10] used the paramagnetic ions Pr^{3+}, Eu^{3+}, and Yb^{3+}. However, neither the themodynamic parameters which covered La through Lu nor the NMR data indicated any significant structural changes across the lanthanide series. Hence, we assume that the structure of the crystalline La complex can be compared with the solution structures of the Pr, Eu, and Yb complexes.

Table I. Crystal Data

$a = 12.350$ (3) Å
$b = 12.760$ (2) Å
$c = 8.783$ (2) Å
$\alpha = 101.54$ (2)°
$\beta = 95.28$ (2)°
$\gamma = 75.98$ (2)°
$\lambda(Mo\ K\bar{\alpha}) = 0.710\,69$ Å
$V = 1314.3$ Å^3
$Na[La(H_2O)_2(C_{10}H_8O_6)_2]\cdot 4H_2O$
mol wt 552
space group $P\bar{1}$
$Z = 2$
$D_{measd} = 1.86$ (2) g cm^{-3}
$D_{calcd} = 1.81$ g cm^{-3}

Experimental Section

$Na[La(BDDA)_2]\cdot 4H_2O$ was prepared by the procedure of Kuhlberg and Choppin.[10] Colorless, transparent crystals in the form of irregular parallelepipeds were obtained by overnight evaporation of an aqueous solution. The crystals were unstable to air exposure and were coated with a thin layer of low-molecular weight petroleum grease and sealed in Lindemann capillary tubes for X-ray photographic work and intensity data collection.

Preliminary diffraction photographs showed the crystal to be triclinic. The space group was assumed to be $P\bar{1}$ and the successful solution and refinement of the structure in this space group indicate that the choice was the correct one (see below). Unit-cell dimensions and their associated standard deviations were obtained from a least-squares fit to the angular settings of 15 carefully centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer. The crystal density, measured by the method of neutral buoyancy in a mixture of carbon tetrachloride and bromoform, indicated the presence of one $Na[La(BDDA)_2]$ and approximately seven water molecules per asymmetric volume. However, the structural analysis shows the presence of only six water molecules. Complete crystal data are given in Table I.

The crystal chosen for data collection had the following faces and mean dimensions: (110)–($\bar{1}\bar{1}0$) 0.22 mm, (001)–(00$\bar{1}$) 0.19 mm, (1$\bar{1}$0)–($\bar{1}$10) 0.13 mm. The crystal was mounted on the diffractomer with the ($\bar{1}$10) face approximately perpendicular to the ϕ axis, and intensity data were collected at room temperature (23 °C) by the θ–2θ variable scan technique, using graphite-monochromatized Mo $K\bar{\alpha}$ radiation (λ 0.710 69 Å). Individual scan speeds were determined from a rapid scan at the calculated Bragg peak, and the scan rate varied from 2° min^{-1} (less than 100 counts in the rapid scan) to 24° min^{-1} (more than 1000 counts in the rapid scan). All 5082 reflections

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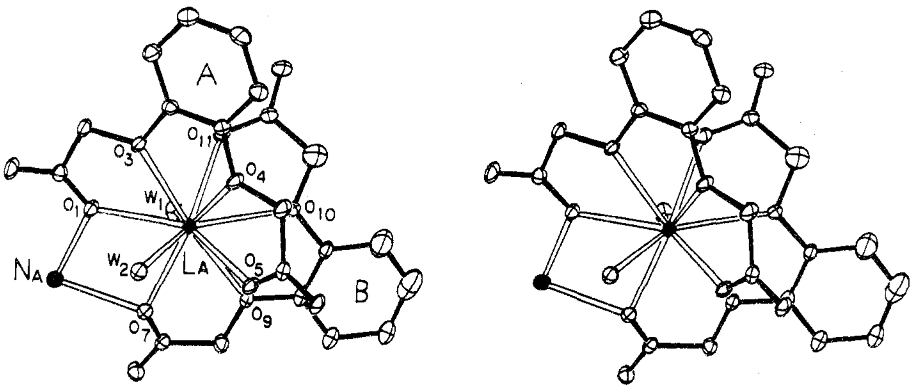

Figure 1. A stereoview of the $Na[La(H_2O)_2(BDDA)_2]$ complex showing part of the Na^+–O–La^{3+} bridging. The geometry of the La^{3+} coordination sphere is approximately a s-bicapped square antiprism with oxygen atoms O(3) and O(9) in the capping positions.

in the $+h$ hemisphere out to $2\theta = 50°$ were measured. Of these, the 745 reflections with $I < 2\sigma(I)$ (counting statistics) were considered unobserved and removed from the data set. Three standards ($21\bar{4}$, $\overline{222}$, and 321) were monitored after each 100 reflections during the course of the experiment, as a check on crystal stability and incident beam fluctuations.

Each reflection was assigned an observational variance based on the equation $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S, B_1, and B_2 are the scan and extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B = T_S/4$), and p (=0.04) represents the expected error in the diffracted beam intensity.[11] The data were adjusted to correct for changes in the intensities of the three standards owing to shutdown of the equipment during data collection and subsequent collection at a slightly reduced incident beam intensity. Intensities and their standard deviations were corrected for Lorentz and polarization effects; no correction for absorption was deemed necessary for our purposes [$\mu(\text{Mo K}\bar{\alpha}) = 19.69$ cm^{-1}, maximum and minimum transmission factors, on F^2, estimated to be 0.77 and 0.65]. The 4337 remaining squared-structure factors were placed on an approximate absolute scale by the method of Wilson.[12]

The position of the La^{3+} ion was determined from a three-dimensional Patterson synthesis and subsequent structure factor Fourier calculations allowed the positioning of the atoms in the BDDA ligands as well as three coordinated water molecules and three waters of hydration. Several cycles of isotropic and anisotropic refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, led to a final R value $[=\sum||F_o| - |F_c||/\sum|F_o|]$ of 0.041. The final weighted R value $[(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}]$ and goodness-of-fit value $[(\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV}))^{1/2}$, where NO = 4337 observations and NV = 361 variables] were 0.054 and 2.23, respectively. A final difference-Fourier map showed residual electron density with a maximum of 1.2 e/Å^3 near the La^{3+}. Some indications of probable hydrogen atom locations were also obtainable from this map, but we have made no attempt to quantitatively include the contributions of the hydrogen atoms in our calculations.

Scattering curves for all atoms were from a standard source.[13a] The scattering curve for the La ion was corrected for anomalous dispersion effects.[13b] Final atomic positional parameters are collected in Table II, while anisotropic thermal parameters and a list of observed and calculated structure factors have been deposited.[14] The crystallographic calculations were performed with a common set of computer programs.[15]

Results and Discussion

The sterochemistry of the $[La(H_2O)_2(BDDA)_2]^-$ anion is illustrated in Figure 1. The La^{3+} ion is decacoordinate with the primary coordination sphere made up of two independent tetradentate BDDA ligands and two water molecules. The overall geometry of the lanthanum coordination sphere approximates that of an s-bicapped square antiprism[16] with oxygen O(3) and O(9) in the axial positions and the capped "squares" defined by O(1), O(4), O(11), W(2) and O(5), O(7), O(10), W(1), Figure 1. The La–O bond lengths to the two independent tetradentate BDDA ligands are in the expected range (Figure 2), with the La–O(ether) distances being about 0.2 Å longer than the La–O(carboxylate) distances. The La–O(water) distances of 2.500 (4) Å to W(1) and 2.622 (4) Å to W(2) are also typical.[17]

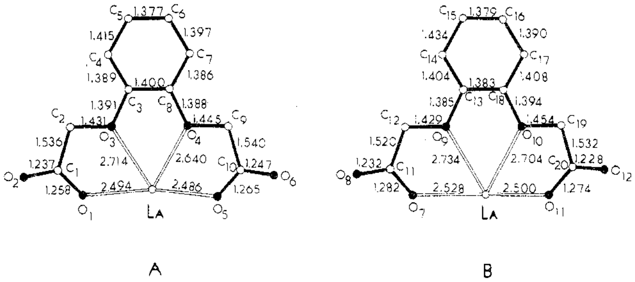

Figure 2. The two independent BDDA ligands. The esd's in the La–O distances are about 0.004 Å and the esd's in the C–O and C–C distances are about 0.01 Å.

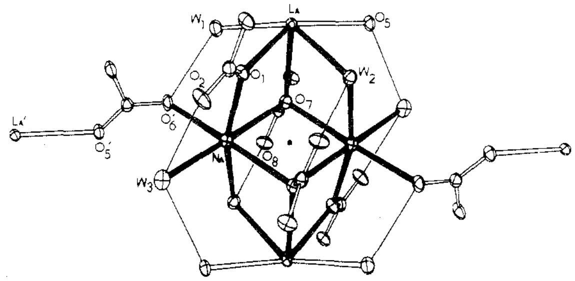

Figure 3. The edge-shared bioctahedral coordination of inversion-related Na^+ cations. Note also the trigonal capping of the edge-shared bioctahedron by the La^{3+} cations. Primed atoms are related to the unprimed atoms by the transformation $-x, -y, -1 - z$.

The Na^+ ion occupies a unique and functionally interesting site in the crystal. Individually, the sodium ions are six-coordinate, Figure 3, with two water molecules and four BDDA carboxylate oxygen atoms at typical Na–O distances (Table III). Furthermore, two Na^+ ions are linked across a crystallographic center of inversion, Figure 3, and together their coordination spheres form a distorted edge-shared bioctahedron trigonally capped by two inversion-related La^{3+} ions. One of the BDDA carboxylate oxygen atoms, O(7), is present in the coordination sphere of both symmetry-related Na^+ ions, Figure 3, and is also coordinated to the La^{3+} ion, Figures 1 and 3. Thus, the BDDA carboxylate oxygen atom O(7), in addition to its covalent bond to C(11), Figure 2, participates in coordination bonds to two Na^+ ions and one La^{3+} ion. The bond angles about O(7) are approximately tetrahedral. Moreover, the BDDA carboxylate oxygen atom O(1) and the water molecule W(2) also bridge the Na^+ and La^{3+} ions (Figures 1 and 3). Finally, one of the BDDA carboxylate groups, O(5)–C(10)–O(6), forms a bridging network of the type

Table II. Final Positional Parameters[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
La	2108.9 (2)	−2029.8 (2)	−1856.4 (3)	Na	405 (2)	−553 (2)	1819 (2)
O(1)	827 (3)	−2185 (3)	80 (4)	O(7)	1374 (3)	−136 (3)	−291 (4)
O(2)	−333 (4)	−2883 (4)	1169 (5)	O(8)	1649 (3)	1362 (3)	1376 (5)
O(3)	1073 (3)	−3724 (3)	−2332 (4)	O(9)	3327 (3)	−464 (3)	−1502 (4)
O(4)	1915 (3)	−3240 (3)	−4637 (4)	O(10)	4166 (3)	−2443 (3)	−2981 (5)
O(5)	1982 (3)	−1149 (3)	−4168 (4)	O(11)	3407 (3)	−3876 (3)	−1934 (4)
O(6)	2032 (3)	−1148 (3)	−6696 (4)	O(12)	4913 (3)	−5233 (4)	−2610 (7)
C(1)	305 (5)	−2906 (5)	150 (6)	C(11)	1919 (5)	602 (4)	272 (6)
C(2)	476 (5)	−3930 (5)	−1143 (6)	C(12)	2984 (5)	571 (5)	−491 (7)
C(3)	1329 (5)	−4570 (4)	−3607 (6)	C(13)	4264 (5)	−581 (5)	2331 (6)
C(4)	1158 (5)	−5617 (5)	−3687 (7)	C(14)	4767 (5)	287 (5)	2377 (7)
C(5)	1456 (5)	−6417 (5)	−5040 (7)	C(15)	5707 (6)	83 (6)	−3327 (8)
C(6)	1907 (5)	−6154 (5)	−6251 (7)	C(16)	6140 (5)	−979 (6)	−4064 (8)
C(7)	2066 (5)	−5097 (5)	−6173 (7)	C(17)	5638 (5)	−1840 (6)	−4041 (8)
C(8)	1777 (5)	−4308 (4)	−4852 (6)	C(18)	4701 (5)	−1627 (5)	−3132 (7)
C(9)	2106 (6)	−2863 (5)	−6013 (6)	C(19)	4863 (6)	−3351 (5)	−3297 (9)
C(10)	2034 (4)	−1618 (4)	−5880 (6)	C(20)	4351 (5)	−4289 (5)	−2538 (7)
W(1)	3201 (3)	−2020 (3)	686 (4)	W(4)	4700 (5)	−7010 (4)	−1453 (8)
W(2)	58 (3)	−1342 (3)	−2920 (4)	W(5)	3078 (5)	−4721 (4)	629 (6)
W(3)	−620 (4)	−1099 (4)	3830 (5)	W(6)	2620 (6)	−6763 (5)	−214 (9)

[a] $\times 10^4$ with esd values in parentheses.

Table III. *Selected Distances (Å) and Angles (deg)*

(a) Na Coordination Sphere

Distances

Na–O(1)	2.300 (4)	Na–O(7)	2.502 (4)
Na–O(6)	2.343 (4)	Na–O(7′)[a]	2.529 (4)
Na–W(2)	2.368 (4)	Na–W(3)	2.557 (5)

Angles

O(1)–Na–O(6)	89.4 (1)	O(6)–Na–O(7′)	178.2 (1)
O(1)–Na–W(2)	162.8 (1)	O(6)–Na–W(3)	85.6 (1)
O(1)–Na–O(7)	75.3 (1)	W(2)–Na–O(7)	89.7 (1)
O(1)–Na–O(7′)	92.4 (1)	W(2)–Na–O(7′)	77.7 (1)
O(1)–Na–W(3)	100.7 (1)	O(7)–Na–O(7′)	85.1 (1)
O(6)–Na–W(2)	100.8 (1)	W(2)–Na–W(3)	93.9 (1)
O(6)–Na–O(7)	95.9 (1)	O(7)–Na–W(3)	175.7 (1)
		O(7′)–Na–W(3)	93.5 (1)

(b) Intraligand Bond Angles

ligand A		ligand B	
O(2)–C(1)–O(1)	126.6 (6)	O(8)–C(11)–C(12)	125.9 (5)
O(1)–C(1)–C(2)	117.5 (5)	O(7)–C(11)–C(12)	118.3 (5)
C(1)–C(2)–O(3)	107.5 (5)	C(11)–C(12)–O(9)	109.6 (5)
C(2)–O(3)–C(3)	116.4 (4)	C(12)–O(9)–C(13)	115.5 (4)
O(3)–C(3)–C(4)	123.7 (5)	O(9)–C(13)–C(14)	123.6 (5)
C(4)–C(3)–C(8)	120.5 (5)	C(14)–C(13)–C(18)	120.4 (6)
C(3)–C(4)–C(5)	118.9 (5)	C(13)–C(14)–C(15)	118.9 (6)
C(4)–C(5)–C(6)	120.1 (6)	C(14)–C(15)–C(16)	118.7 (6)
C(5)–C(6)–C(7)	120.8 (6)	C(15)–C(16)–C(17)	122.5 (7)
C(6)–C(7)–C(8)	119.5 (6)	C(16)–C(17)–C(18)	118.2 (6)
C(7)–C(8)–C(3)	120.2 (5)	C(17)–C(18)–C(13)	121.0 (6)
C(7)–C(8)–O(4)	124.4 (5)	C(17)–C(18)–O(10)	122.6 (6)
C(8)–O(4)–C(9)	116.4 (4)	C(18)–O(10)–C(19)	114.1 (5)
O(4)–C(9)–C(10)	108.2 (5)	O(10)–C(19)–C(20)	108.0 (5)
C(9)–C(10)–O(5)	119.6 (5)	C(19)–C(20)–O(11)	117.8 (5)
O(6)–C(10)–O(5)	125.0 (5)	O(12)–C(20)–O(11)	127.6 (6)

[a] Primed atoms are related to unprimed atoms by the transformation −*x*, −*y*, −*z*.

La^{3+}–O–C–O–Na^+ (Figure 3). This multiplicity of bridging interactions between the coordination spheres of the lanthanum and sodium ions is clearly a dominant feature of this crystal structure and must play a major role in prescribing the molecular conformation adopted by the $[La(H_2O)_2(BDDA)_2]^-$ anion. Such a multiplicity of interactions is unlikely to carry over to the solution structure of $Na[La(BDDA)_2]$ in high-dielectric solvents due to the solvation shielding.

In this regard, the crystalline molecular structure of the $[La(H_2O)_2(BDDA)_2]^-$ anion does not seem to duplicate closely the structure of several $[Ln(BDDA)_2]^-$ complexes in solution as determined by NMR techniques. The BDDA ligands in the solid show some puckering of the oxyacetate arms of the ligands, in contrast to the near planarity of the ligands in solution. Other small deviations from the solution parameters are observed in the La–O distances and certain ligand bond angles; however, we draw no detailed conclusions based on these small variations. The dihedral angle between the two phenyl rings of the BDDA ligands is 30° in the crystalline structure while this angle was suggested to be approximately 90° in the solution structure, as such a disposition of the ligands provides the most symmetric structure and, in the absence of perturbing influences, is the most likely for these ionic complexes.

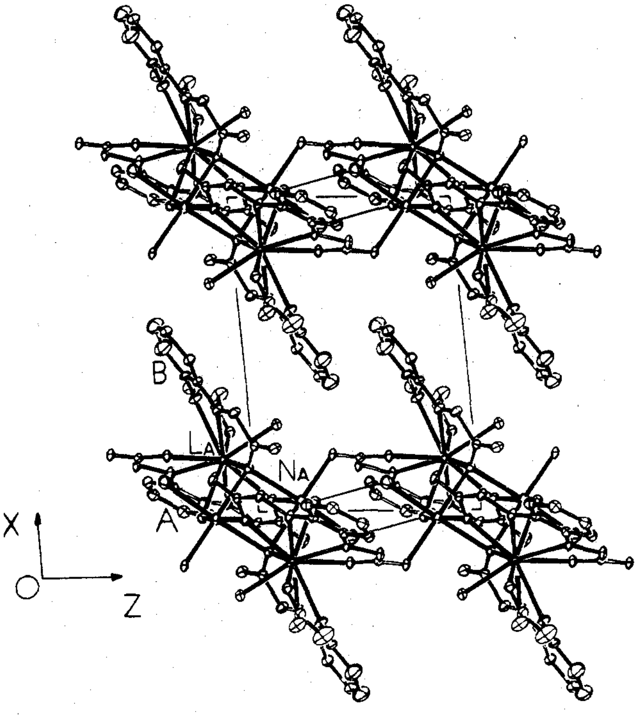

Figure 4. Projection of the structure onto the *ac* plane. Note in particular the polymerization of the complexes along the *c* axis (see the text) as well as the stacking of the phenyl rings of the BDDA ligand B.

Clearly, a major obstacle to the duplication of the probable solution conformation is the presence of the coordinating sodium ion in the crystalline structure. The coupling of the La^{3+} and the Na^+ coordination spheres via the BDDA ligands obviates the ligand conformations which can approximate a

Table IV. Possible Hydrogen Bonding Scheme

donor (D)	acceptor (A)	D···A, Å	∠A···D···A, deg
W(4)	W(4)(1 − *x*, −*y*, −*z*)	2.676 (6)	109.9 (5)
	O(6)(*x*, *y*, 1 + *z*)	2.724 (7)	
W(2)	O(8)(−*x*, −*y*, −*z*)	2.617 (6)	111.3 (6)
	W(3)(*x*, *y*, −1 + *z*)	2.955 (7)	
W(3)	O(2)(*x*, *y*, *z*)	2.899 (7)	130.8 (7)
	O(5)(1 − *x*, −*y*, −*z*)	2.926 (6)	
W(4)	O(12)(*x*, *y*, *z*)	2.739 (7)	114.2 (5)
	W(6)(*x*, *y*, *z*)	2.805 (8)	
W(5)	O(11)(*x*, *y*, *z*)	2.783 (7)	106.5 (6)
	O(12)(1 − *x*, −1 − *y*, −*z*)	2.892 (8)	
W(6)	W(5)(*x*, *y*, *z*)	2.743 (6)	123.3 (4)
	O(2)(−*x*, −1 − *y*, −*z*)	2.986 (6)	

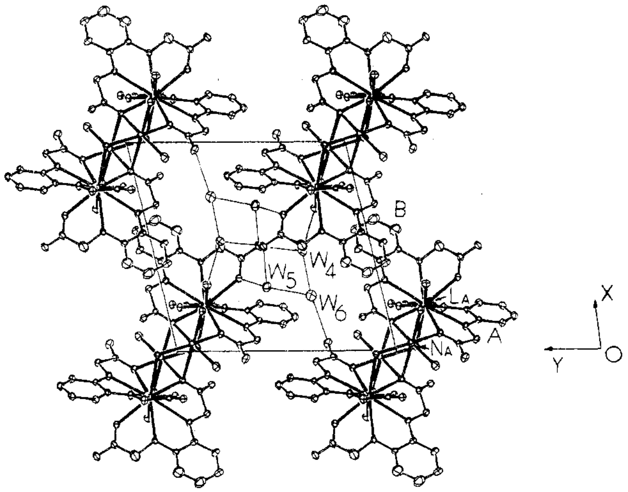

Figure 5. Projection of the structure onto the *ab* plane. Note the large number of hydrogen bonds, denoted by thin lines, between the waters of hydration and the complexes and among the waters of hydration.

symmetric stereochemistry related to the 90° angle between the ligand planes. However, this can be overcome since the presence of three sodium ions in the $[\mathrm{Ln(dipicolonate)_3}]^{3-}$ crystal structures noted earlier does not preclude the approximate duplication of the solution conformation. However, in this case, the coordination sphere of the lanthanide ion is completely occupied by the ligand donor atoms.

As indicated previously, the packing forces operative in this crystal are highly important and structurally varied. The basic dimeric unit formed about inversion-related Na^+ ions (Figure 3) is polymerized along the crystallographic *c* axis via the La^{3+}–O(5)–C(10)–O(6)–Na^+ linkage described above and as illustrated in the *ac* projection of Figure 4. The cohesive forces along the *c* axis are further enhanced by the formation of an intercomplex hydrogen bond involving water molecules W(2) and W(3), Table IV, and stacking of the phenyl rings of BDDA ligand B (Figure 4). Within the stacks of phenyl rings, the following contacts are worthy of mention: C(15)···C(15′; 1 − *x*, −*y*, −1 − *z*) 3.28 Å, C(15)···C(16′) 3.26 Å, and C(16)···C(14′) 3.43 Å.

In contrast, the packing forces in the *ab* plane, Figure 5, are mainly composed of hydrogen-bonding interactions involving the three waters of hydration W(4), W(5), and W(6). In Table IV, we propose what we believe is a reasonable hydrogen bonding scheme, although in the absence of definitive information on the positions of the hydrogen atoms, this scheme can only be considered probable. The waters of hydration form a channel along the *c* axis parallel to the polymerization of the complexes; it is possible that this water channel could accommodate the seventh water molecule indicated by the density measurement.

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Registry No. $\mathrm{Na[La(H_2O)_2(BDDA)_2]\text{-}4H_2O}$, 68438-46-0.

Supplementary Material Available: Anisotropic thermal parameters and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Florida State University. (b) The Johns Hopkins University.
(2) S. P. Sinha, *Struct. Bonding (Berlin)*, **30**, 1 (1976).
(3) W. D. Horrocks, Jr., in "NMR of Paramagnetic Molecules", G. N. Lamar, W. D. Horrocks, Jr., and R. H. Holm, Eds., Academic Press, New York, 1973, Chapter 12; A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
(4) H. Donato, Jr., and R. Martin, *J. Am. Chem. Soc.*, **94**, 4129 (1972); J. Albertsson, *Acta Chem. Scand.*, **24**, 1213 (1970); **26**, 985, 1005, 1023 (1972).
(5) J. F. Desreux and C. N. Reilly, *J. Am. Chem. Soc.*, **98**, 2105 (1976).
(6) I. Grenthe and I. Tobiasson, *Acta Chem. Scand.*, **17**, 2101 (1963); I. Grenthe, *J. Am. Chem. Soc.*, **83**, 360 (1961).
(7) G. R. Choppin and Y. Hasegawa, *Inorg. Chem.*, **16**, 2931 (1977).
(8) K. Suzuki, T. Haltori, and K. Yamasaki, *J. Inorg. Nucl. Chem.*, **30**, 161 (1968).
(9) E. A. Green, W. L. Duax, G. M. Smith, and F. Wudl, *J. Am. Chem. Soc.*, **97**, 6689 (1975).
(10) L. Kullberg and G. R. Choppin, *Inorg. Chem.*, **16**, 2926 (1977).
(11) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(12) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).
(13) (a) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); (b) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(14) Supplemental material.
(15) Zalkin's FORDAP for Fourier series, Ibers' NUCLS for least squares and structure factors, and Johnson's ORTEP for distances, angles, and illustrations. All other programs used were locally written.
(16) W. J. Rohrbaugh and R. A. Jacobson, *Inorg. Chem.*, **13**, 2535 (1974).
(17) S. P. Sinha, *Struct. Bonding (Berlin)*, **25**, 69 (1976).