Table I. Positional and Thermal Parameters[a] with Estimated Standard Deviations[b] for α-$2UO_2SO_4 \cdot 7H_2O$

atom	x	y	z	B, Å^2
U(1)	0	0.19112 (9)	0.07967 (3)	
U(2)	0.38767 (7)	0.70137 (9)	0.20043 (3)	
S(1)	0.1164 (3)	0.6890 (7)	0.1033 (2)	1.23 (6)
S(2)	0.2961 (4)	0.1933 (8)	0.1512 (2)	1.49 (6)
O(1)	−0.095 (1)	0.184 (2)	0.1451 (6)	3.6 (2)
O(2)	0.089 (1)	0.189 (2)	0.0113 (7)	3.6 (2)
O(3)	0.451 (1)	0.703 (2)	0.1239 (7)	3.6 (2)
O(4)	0.326 (1)	0.705 (2)	0.2758 (7)	3.3 (2)
O(5)	0.043 (1)	0.514 (2)	0.1194 (7)	3.0 (2)
O(6)	0.188 (1)	0.734 (2)	0.1604 (6)	3.0 (2)
O(7)	0.189 (1)	0.647 (3)	0.0492 (9)	4.6 (3)
O(8)	0.030 (1)	0.850 (2)	0.0940 (7)	3.8 (3)
O(9)	0.318 (1)	0.382 (2)	0.1826 (8)	4.0 (3)
O(10)	0.341 (1)	0.039 (2)	0.1947 (7)	3.3 (2)
O(11)	0.352 (1)	0.190 (3)	0.0904 (8)	4.5 (3)
O(12)	0.164 (1)	0.167 (2)	0.1467 (6)	3.2 (2)
O(13)	0.534 (1)	0.483 (2)	0.2460 (7)	3.3 (2)
O(14)	−0.126 (1)	0.439 (2)	0.0274 (7)	4.1 (3)
O(15)	0.656 (2)	0.204 (3)	0.1869 (9)	4.8 (3)
O(16)	−0.155 (1)	0.020 (2)	0.0223 (7)	3.4 (2)
O(17)	0.556 (1)	0.892 (2)	0.2368 (7)	3.4 (2)
O(18)	0.595 (2)	0.290 (4)	0.073 (1)	8.3 (6)
O(19)	0.248 (2)	0.725 (3)	0.4069 (9)	4.6 (3)
H(1)	0.5376	0.4933	0.291	*c*
H(2)	0.5749	0.3904	0.2263	
H(3)	−0.1889	0.4109	0.0021	
H(4)	−0.1691	0.5349	0.0496	
H(5)	0.7386	0.1982	0.1726	
H(6)	0.636	0.2337	0.1481	
H(7)	−0.1522	−0.0499	−0.0155	
H(8)	−0.1857	−0.0787	0.0458	
H(9)	0.6006	0.8398	0.271	
H(10)	0.5901	0.9967	0.2199	
H(11)	0.6272	0.3111	0.0313	
H(12)	0.5154	0.2564	0.0777	
H(13)	0.1952	0.7538	0.4414	
H(14)	0.2741	0.7182	0.3629	

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	1.05 (2)	0.98 (2)	1.54 (2)	0.01 (4)	−0.27 (2)	−0.01 (2)
U(2)	0.95 (2)	0.95 (2)	1.51 (2)	0.03 (4)	−0.18 (2)	−0.02 (2)

[a] The anisotropic temperature factor has the form $\exp(-0.25 \cdot (B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + ...))$. [b] Here and in the following tables the numbers in parentheses are the estimated standard deviations in the least significant digit. [c] Hydrogen positions were estimated and not refined. An arbitrary isotropic thermal parameter of 6.0 Å^2 was assigned to each of the hydrogen atoms.

Table II. Selected Interatomic Distances (Å)

U(1)-O(1)	1.75 (2)	U(2)-O(3)	1.77 (2)
-O(2)	1.76 (2)	-O(4)	1.74 (2)
-O(5)	2.40 (2)	-O(6)	2.41 (2)
-O(8)	2.36 (2)	-O(9)	2.34 (2)
-O(12)	2.33 (2)	-O(10)	2.36 (2)
-O(14)	2.47 (2)	-O(13)	2.41 (2)
-O(16)	2.42 (2)	-O(17)	2.41 (2)
S(1)-O(5)	1.49 (2)	S(2)-O(9)	1.46 (2)
-O(6)	1.48 (2)	-O(10)	1.48 (2)
-O(7)	1.44 (2)	-O(11)	1.44 (2)
-O(8)	1.47 (2)	-O(12)	1.50 (2)

up of very similar units of two bipyramids and two tetrahedra, as shown also in Figure 1 for comparison. The overall structures of these chains are different; in the chain in the α form the units are repeated according to the *b*-axis translation, while in the β form the replication is by a glide plane. As a result, alternate units in the latter case have reversed orientations. The interatomic distances and angles are comparable in the two forms.[2] The molecular volume is 2% smaller in the α form indicating a very slightly more efficient packing.

All the water molecules are hydrogen bonded, and distances and angles for these bonds are listed in Table III.

Table III. Hydrogen Bond Distances and Angles

atoms	distances, Å		angle, deg
O(5)-O(13)-O(15)	2.86 (2)	2.65 (3)	120 (1)
O(7)-O(14)-O(19)	2.70 (3)	2.77 (2)	94 (1)
O(1)-O(15)-O(18)	2.94 (3)	2.58 (3)	89 (1)
O(11)-O(16)-O(19)	2.78 (3)	2.73 (3)	96 (1)
O(6)-O(17)-O(15)	2.84 (2)	2.62 (3)	113 (1)
O(7)-O(18)-O(11)	2.83 (4)	2.83 (4)	121 (1)
O(2)-O(19)-O(4)	2.90 (3)	2.92 (3)	157 (1)

Acknowledgment. We thank Dr. L. K. Templeton for assistance with the refinement of *f''*.

Registry No. α-$2UO_2SO_4 \cdot 7H_2O$, 39448-26-5.

Supplementary Material Available: Data processing formulas, table of angles, and the listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

References and Notes

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Crystal Structure of Tetrakis(2,2′-bipyridine dioxide)lanthanum Perchlorate: An Example of Cubic Eight-Coordination

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Received August 4, 1978

On the basis of ligand–ligand repulsions the cube is expected to be a much less favorable coordination geometry for discrete eight-coordinate complexes than the dodecahedron (D_{2d}) or the square antiprism (D_{4d}), for both of which structurally characterized examples abound in the literature.[1] However, of the comparatively few examples of ML_8 stoichiometry (L = unidentate ligand) whose structures have been determined, two of these in fact have cubic geometry, namely, PaF_8^{3-}[2] and $U(NCS)_8^{4-}$[3] in the form of its tetraethylammonium salt. The latter complex ion is of interest, for in the cesium salt it adopts the square-antiprismatic geometry[4] suggesting that the counterion and crystal-packing arrangement may dictate the geometry and that cubic eight-coordination may not be that unfavorable, at least for the heavier elements. Approximately cubic geometry is also apparently found in another complex of uranium, namely, tetrakis(bipyridyl)uranium,[5] and we have found for the octakis(pyridine *N*-oxide) complexes of the lighter lanthanides $Ln(pyO)_8^{3+}$ that while in one of the crystalline forms the complex ions have a square-antiprismatic geometry, in a second form the coordination polyhedron is distorted from the D_{4d} geometry toward that of a cube, rather

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0020-1669/78/1317-3702$01.00/0

than toward the dodecahedron or other eight-coordinate geometry.[6] As part of a continuing interest in the stereochemistries and electronic structures of complexes having *N*-oxide ligands we have determined the structure of the tetrakis complex of lanthanum perchlorate with the bidentate ligand 2,2′-bipyridine dioxide [$La(bpyO_2)_4^{3+}$] and find this to have nearly cubic coordination geometry. So far as we are aware this represents the first structurally characterized example of a complex containing this ligand, although many complexes containing it are known,[7] and the first example of cubic eight-coordination for a lanthanide.

Experimental Section

The complex $La(bpyO_2)_4(ClO_4)_3$ was prepared according to literature methods,[8] and crystals suitable for X-ray analysis were obtained from ethanolic solution. Anal. Calcd for $LaC_{40}H_{32}N_8O_{20}Cl_3$: C, 40.40; N, 9.42; H, 2.70; Cl, 8.95. Found: C, 40.48; N, 9.25; H, 2.51; Cl, 8.91. Preliminary Weissenberg and precession photography indicated *mmm* (D_{2h}) Laue symmetry, and the systematic absences, $hk0$ for $h + k \neq 2n$, $h0l$ for $l \neq 2n$, and $0kl$ for $k \neq 2n$, are in accord with the unambiguous choice of space group *Pbcn* (D_{2h}^{14}, No. 60).[9]

Data Collection. A wedge-shaped crystal having a maximum dimension of 0.30 mm was cut from a larger crystalline mass and mounted on the tip of a glass fiber. Intensity data were collected using an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle 3.1°, $\lambda(K\alpha_1)$ 0.709 26 Å, $\lambda(K\alpha_2)$ 0.713 54 Å). The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $11.0° \leq \theta(\text{Mo } K\bar{\alpha}) \leq 16.0°$ and measured at an ambient laboratory temperature of 22 ± 2 °C are $a = 12.990$ (4), $b = 25.884$ (7), and $c = 14.032$ (5) Å. A unit cell content of 4 formula units gives a calculated density of 1.695 g/cm^3, in good agreement with the observed value of 1.705 g/cm^3. This implies crystallographic C_2 or C_i symmetry for the complex ion and probable C_2 symmetry for one of the perchlorate ions, the others being in general positions.

Data were collected using the θ–2θ scan mode, with a θ scan range of $(0.55 + 0.35 \tan \theta)°$ centered about the calculated Mo $K\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on both sides of the aforementioned limits for the measurements of background radiation. The scan rates varied from 0.6 to 4.0° θ/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $I = ((\text{FF})/S)(P - 2(B_1 + B_2))$, where P is the counts accumulated during the peak scan, B_1 and B_2 are the left and right background counts, S is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities were computed as $\sigma_I^2 = ((\text{FF})^2/S^2)(P + 4(B_1 + B_2)) + 0.002I^2$. A total of 2719 independent reflections having $2° \leq 2\theta(\text{Mo}/K\bar{\alpha}) \leq 43°$ were measured in the region $+h$, $+k$, $+l$, and, of these, five standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu(\text{Mo } K\bar{\alpha}) = 1.15$ mm^{-1}), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization factors including the corrections for the monochromator. The 352 reflections having $I \leq 0.2\sigma_I$ were treated as unobserved and were assigned $F_o = [c\sigma_I/Lp]^{1/2}$ and $\sigma_{F_o} = 0.5F_o/c$, where $c = 0.2$ and Lp is the Lorentz–polarization factor.

Solution and Refinement of Structure. All computations were carried out on a CDC Cyber 74 computer using local modifications of Zalkin's FORDAP Fourier program, Germain, Main, and Woolfon's direct-methods program MULTAN, Prewitt's SFLS and SFLSR full-matrix least-squares routines, and various locally written programs. Neutral-atom scattering factors were taken from the tabulation by Cromer and Waber,[10] and an anomalous dispersion correction was included for the lanthanum atom.[11] The agreement factors are defined in the usual manner,[12] and in all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ the weights being evaluated as $w^{1/2} = 2LpF_o/\sigma_I$. The solution of the structure was relatively straightforward, although extensive pseudosymmetry was evident in an initial Fourier map based on the lanthanum atom coordinates derived from a Patterson synthesis. Initial coordinates for 18 independent atoms, including the lanthanum, were in fact obtainable by direct methods despite the pseudosymmetry. Coordinates for the remaining non-hydrogen atoms apart from the oxygen atoms of the perchlorate group situated on the twofold axis were obtained by standard Fourier difference techniques, and three cycles of isotropic unit weight refinement of these atoms led to residuals $R = 0.129$ and $R_w = 0.143$. Examination of a difference electron density map suggested the presence of static disorder in the perchlorate ion on the twofold axis, but it had very poor definition of the oxygen peaks around the chlorine. This group of oxygen atoms was accordingly included in the structure, refined as a rigid body defined by a Cl–O bond distance of 1.43 Å, and constrained to lie on the twofold axis. Initially each oxygen atom of the tetrahedron was permitted to have a separate isotropic thermal parameter but this treatment was unsatisfactory, and so the model adopted had one group thermal parameter and did not include the chlorine as a part of the group. In further refinement all the remaining atoms were treated anisotropically, and a total of four full cycles (each cycle being treated as two "half" cycles because of program size limitations) led to convergence (all $\Delta/\sigma < 0.35$) with $R = 0.066$ and $R_w = 0.086$ based on all 2719 independent reflections. The total number of variables refined was 305. While the thermal parameters for the oxygen atoms of the general perchlorate ion converged to rather high values, suggesting thermal disorder, the geometry of this ion appeared reasonable (Table III), and no extra peaks indicating any static disorder were evident in difference maps.

Table I. Positional Parameters for $La(bpyO_2)_4(ClO_4)_3$[a,b]

atom	x	y	z
La	0.0	0.23372 (2)	0.25
O1	0.0086 (4)	0.2354 (2)	0.0713 (4)
N1	0.0666 (5)	0.2681 (2)	0.0238 (4)
C11	0.0243 (7)	0.3137 (3)	−0.0049 (6)
C12	0.0871 (8)	0.3489 (3)	−0.0577 (6)
C13	0.1893 (7)	0.3372 (3)	−0.0783 (6)
C14	0.2295 (6)	0.2895 (3)	−0.0484 (6)
C15	0.1671 (7)	0.2558 (3)	0.0020 (5)
O2	0.1810 (4)	0.2292 (2)	0.1910 (4)
N2	0.2154 (4)	0.1943 (2)	0.1271 (4)
C21	0.2572 (6)	0.1497 (4)	0.1582 (7)
C22	0.2950 (7)	0.1133 (3)	0.0945 (7)
C23	0.2860 (7)	0.1216 (3)	−0.0002 (8)
C24	0.2404 (6)	0.1690 (3)	−0.0319 (6)
C25	0.2061 (6)	0.2042 (3)	0.0332 (6)
O3	0.0827 (4)	0.1536 (2)	0.3142 (3)
N3	0.0282 (5)	0.1160 (2)	0.3551 (5)
C31	0.0135 (6)	0.1182 (3)	0.4540 (6)
C32	−0.0411 (7)	0.0795 (4)	0.5003 (7)
C33	−0.0806 (7)	0.0386 (4)	0.4468 (8)
C34	−0.0655 (6)	0.0360 (3)	0.3461 (8)
C35	−0.0121 (6)	0.0770 (3)	0.3013 (6)
O4	0.0903 (4)	0.3144 (2)	0.3042 (3)
N4	0.1177 (5)	0.3152 (2)	0.2428 (4)
C41	0.2123 (6)	0.3507 (3)	0.2035 (6)
C42	0.2417 (7)	0.3900 (4)	0.1447 (6)
C43	0.1761 (8)	0.4311 (4)	0.1238 (6)
C44	0.0776 (7)	0.4317 (3)	0.1641 (6)
C45	0.0507 (6)	0.3909 (3)	0.2251 (5)
Cl1	0.2766 (2)	0.0141 (1)	0.3575 (2)
O11	0.2118 (5)	0.0465 (2)	0.4143 (5)
O12	0.3119 (10)	0.0421 (4)	0.2828 (7)
O13	0.3575 (6)	−0.0015 (3)	0.4141 (7)
O14	0.2202 (8)	−0.0305 (3)	0.3272 (5)
Cl2	0.50	0.2997 (2)	0.25

[a] Esd's in parentheses. [b] The oxygen atoms of perchlorate ion 2 (O21. . .O24) were refined as a rigid group constrained to the twofold axis. The group parameters are as follows (angles in radians): x_c, 0.50; y_c, 0.3003 (5); z_c, 0.25; ϕ, −2.832 (1); θ, −2.384 (1); ρ, 0.477 (1).

The residuals for all reflections (2053) with $I > 3\sigma_I$ were $R = 0.054$ and $R_w = 0.084$, and the "goodness of fit" parameter $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ had the value 2.24 at the end of the refinement, suggesting that the weights were overestimated. The final positional and thermal parameters are listed in Tables I and II, and a table of observed and calculated structure factor amplitudes is available.[13]

Discussion of Structure

Tables III and IV summarize the pertinent structural information for the eight-coordinate complex formed by lan-

Table II. Thermal Parameters for $La(bpyO_2)_4(ClO_4)_3$[a,b]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
La	2.27 (3)	3.87 (3)	2.32 (3)		0.11 (2)	
O1	2.98 (24)	5.00 (27)	2.77 (24)	−0.91 (20)	0.31 (18)	0.18 (19)
N1	3.78 (33)	4.74 (32)	2.45 (25)	−0.59 (25)	0.03 (24)	0.27 (23)
C11	5.26 (48)	6.28 (48)	3.98 (41)	−0.21 (36)	−0.07 (34)	1.13 (38)
C12	8.03 (58)	5.69 (43)	4.27 (39)	−0.32 (43)	0.13 (40)	2.10 (35)
C13	6.23 (52)	5.63 (48)	3.59 (38)	−0.10 (40)	1.14 (36)	0.36 (36)
C14	5.56 (44)	5.41 (43)	3.16 (36)	−1.29 (36)	1.40 (33)	−0.73 (35)
C15	4.12 (43)	4.78 (36)	2.40 (32)	−0.38 (35)	0.68 (31)	−0.63 (30)
O2	2.68 (22)	5.67 (30)	3.81 (27)	0.15 (19)	0.59 (19)	−0.47 (22)
N2	3.10 (30)	5.25 (35)	3.42 (31)	−0.01 (26)	0.92 (24)	−0.40 (29)
C21	3.56 (39)	5.98 (48)	7.17 (59)	0.30 (36)	0.87 (39)	2.03 (45)
C22	4.82 (47)	5.02 (43)	5.98 (41)	−0.17 (35)	2.62 (43)	−0.41 (41)
C23	3.85 (43)	5.66 (49)	7.62 (66)	−1.08 (35)	1.64 (43)	−1.61 (47)
C24	4.82 (41)	4.65 (41)	4.78 (40)	−0.89 (17)	2.05 (35)	−1.31 (37)
C25	3.56 (40)	5.27 (43)	3.92 (40)	−0.41 (32)	1.28 (32)	0.09 (37)
O3	3.08 (22)	4.35 (24)	4.30 (25)	0.30 (20)	0.30 (19)	0.52 (20)
N3	3.06 (32)	4.71 (32)	4.00 (33)	0.45 (25)	−0.33 (22)	0.78 (26)
C31	3.65 (39)	6.12 (43)	4.78 (47)	2.25 (31)	0.99 (31)	1.38 (36)
C32	5.27 (45)	5.67 (46)	7.18 (55)	1.61 (39)	1.23 (42)	2.51 (49)
C33	5.18 (48)	4.86 (57)	7.44 (60)	2.61 (42)	1.67 (45)	3.45 (48)
C34	2.74 (39)	3.62 (43)	9.37 (62)	0.63 (31)	0.07 (39)	1.63 (43)
C35	4.23 (41)	3.62 (35)	5.12 (40)	0.46 (32)	0.22 (35)	0.24 (34)
O4	3.32 (22)	4.57 (26)	3.06 (22)	−0.16 (18)	−0.47 (19)	−0.16 (19)
N4	4.00 (33)	4.51 (30)	3.10 (29)	−0.26 (27)	0.22 (25)	−0.61 (25)
C41	3.62 (42)	5.86 (43)	4.53 (41)	−1.42 (34)	1.25 (35)	−1.12 (35)
C42	5.50 (48)	7.88 (60)	4.91 (45)	−2.17 (32)	1.31 (39)	−2.17 (45)
C43	8.05 (60)	5.42 (49)	5.62 (51)	−1.94 (46)	1.19 (46)	−0.83 (41)
C44	6.18 (51)	5.13 (43)	5.32 (45)	−1.59 (40)	1.28 (40)	−0.01 (38)
C45	3.74 (37)	4.41 (41)	3.80 (38)	−0.42 (33)	0.18 (30)	−0.61 (31)
Cl 1	6.86 (13)	4.18 (11)	4.71 (11)	0.06 (9)	0.76 (10)	0.13 (9)
O11	6.39 (34)	7.00 (36)	9.66 (46)	1.20 (28)	1.25 (34)	−2.25 (35)
O12	18.20 (115)	9.43 (53)	10.04 (54)	−2.40 (58)	7.97 (69)	1.63 (48)
O13	7.59 (45)	11.34 (54)	15.00 (76)	2.90 (42)	−3.25 (50)	0.20 (51)
O14	17.13 (77)	7.20 (41)	7.71 (42)	−2.91 (42)	0.10 (47)	−1.90 (57)
Cl 2	11.23 (15)[c]					

[a] Esd's in parentheses. [b] The form of the anisotropic thermal ellipsoid is given by $\exp[-\Sigma_i\Sigma_j h_i h_j r_i^* r_j B_{ij}/4]$ with $i, j = 1,2,3$, and r_i^* is the ith reciprocal axis. [c] This atom was refined isotropically. The group isotropic temperature factor for oxygens O21. . .O24 was 17.90 (57).

thanum perchlorate with 2,2′-bipyridine dioxide. Although the complex ion is crystallographically only required to possess C_2 symmetry—the twofold axis bisecting a pair of bidentate dioxide ligands—it approximates very closely to D_4 symmetry, and the view down the pseudo-fourfold axis given in Figure 1 illustrates this point very clearly. The coordination polyhedron also has nearly perfect D_4 symmetry and is in fact only slightly deformed from that of a cube (O_h). The departures from cubic geometry take the form of a slight compression along the pseudo-C_4 axis, which alone would produce a square prism (D_{4h}), and a slight rotation of one set of fourfold related oxygen atoms relative to the twofold related set of four such that all planes of symmetry in the polyhedron are destroyed. This rotation carried to its limit (45°) would produce the square antiprism (D_{4d}). Using the Hoard and Silverton nomenclature,[14] the bidentate ligands span the *l* edges of the polyhedron, and the angles of inclination, θ, of the La–O bonds to the pseudo-C_4 axis average 56.1° compared to 57.3° for the square antiprism and 54.73° for the cube. From the dihedral angle data in Table IV, the angle of rotation away from the D_{4h} geometry is seen to be 4.6°, and the average oxygen–oxygen distances are 2.801 (7) Å for the *l* edges spanned by the ligands and 2.940 (7) Å for the *s* edges. The four oxygen atoms constituting one of the square faces of the polyhedron are coplanar, and the two square faces are parallel to within the esd's, the dihedral angle being 0.2°. The average lanthanum–oxygen distance of 2.506 (5) Å is identical with that found in $La(pyO)_8^{3+}$[6] and in other eight-coordinate complexes.[15]

The mode of coordination of the ligands is similar to that for pyridine *N*-oxide in most of its complexes, the coordination planes M–O–N being almost orthogonal to the planes through the corresponding pyridine rings. The average dihedral angle is 88.4°. As is evident from Figure 1, the seven-membered chelate ring is markedly puckered, and while examination of a structural model indicates that the bpyO$_2$ ligand must be markedly nonplanar, there is no structural evidence for its conformation in uncoordinated form. The dihedral angles between the pyridine rings average 61.4°, and this is close to the value estimated from NMR contact shift measurements on $Co(bpyO_2)_3^{2+}$.[16] It would seem from the structural results reported here and an examination of molecular models of both tetrakis and tris complexes that bpyO$_2$ is a quite rigid ligand

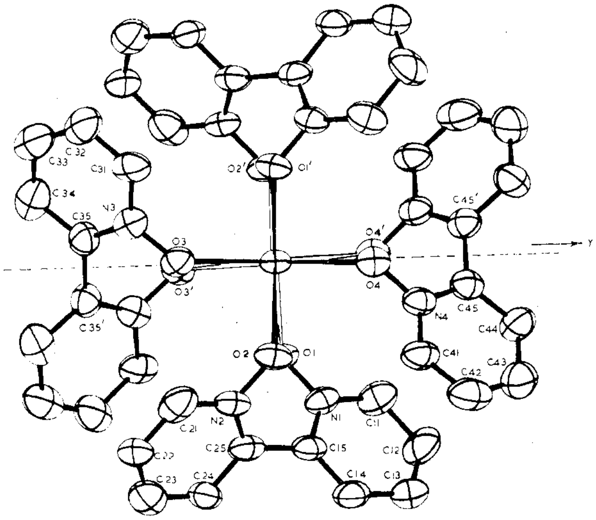

Figure 1. ORTEP plot of the structure of the $La(bpyO_2)_4^{3+}$ complex ion viewed along the pseudo-fourfold axis. Thermal ellipsoids are at the 50% probability level.

Table III. Bond Distances (A) and Angles (deg) in $La(bpyO_2)_4(ClO_4)_3$

(a) Coordination Polyhedron			
La–O1	2.511 (6)	La–O2	2.495 (5)
La–O3	2.504 (5)	La–O4	2.512 (5)
O2–O3	2.907 (7)	O2–O4	2.961 (7)
O1′–O4	2.979 (7)	O1′–O3	2.912 (7)
O1–O2	2.804 (7)	O3–O3′	2.803 (7)
		O4–O4′	2.797 (6)
O2–La–O3	71.2 (2)	O2–La–O4	72.5 (2)
O4–La–O1′	72.8 (2)	O3–La–O1′	71.0 (2)
O1–La–O2	68.1 (2)	O3–La–O3′	68.1 (2)
O3–La–O4	112.3 (2)	O4–La–O4′	67.7 (2)
		O2–La–O1′	112.0 (2)
(b) Bipyridine Dioxide Ligands			
O1–N1	1.314 (8)	O2–N2	1.348 (8)
N1–C11	1.365 (10)	N2–C21	1.350 (11)
C11–C12	1.430 (12)	C21–C22	1.389 (13)
C12–C13	1.392 (13)	C22–C23	1.352 (14)
C13–C14	1.405 (12)	C23–C24	1.431 (13)
C14–C15	1.384 (12)	C24–C25	1.365 (11)
C15–N1	1.378 (11)	C25–N2	1.347 (10)
C15–C25	1.495 (11)		
O1–N1–C11	118.4 (6)	O2–N2–C21	119.5 (7)
N1–C11–C12	118.3 (8)	N2–C21–C22	121.0 (9)
C11–C12–C13	120.8 (8)	C21–C22–C23	119.6 (8)
C12–C13–C14	119.0 (8)	C22–C23–C24	118.5 (8)
C13–C14–C15	119.2 (8)	C23–C24–C25	120.0 (8)
C14–C15–N1	121.6 (7)	C24–C25–N2	119.9 (7)
O1–N1–C15	120.6 (6)	O2–N2–C25	119.6 (6)
C11–N1–C15	121.1 (6)	C21–N2–C25	120.9 (7)
N1–C15–C25	117.5 (6)	N2–C25–C15	119.1 (7)
C14–C15–C25	121.0 (7)	C24–C25–O15	120.7 (7)
O3–N3	1.333 (8)	O4–N4	1.334 (8)
N3–C31	1.402 (11)	N4–C41	1.347 (11)
C31–C32	1.388 (13)	C41–C42	1.363 (13)
C32–C33	1.395 (14)	C42–C43	1.395 (14)
C33–C34	1.428 (15)	C43–C44	1.399 (12)
C34–C35	1.415 (12)	C44–C45	1.403 (11)
C35–N3	1.364 (10)	C45–N4	1.369 (10)
C35–C35′	1.475 (12)	C45–C45′	1.492 (11)
O3–N3–C31	118.0 (6)	O4–N4–C41	120.0 (6)
N3–C31–C32	120.2 (8)	N4–C41–C42	119.7 (8)
C31–C32–C33	118.9 (9)	C41–C42–C43	121.6 (9)
C32–C33–C34	121.2 (10)	C42–C43–C44	118.9 (9)
C33–C34–C35	118.1 (10)	C43–C44–C45	117.7 (8)
C34–C35–N3	119.8 (8)	C44–C45–N4	121.1 (7)
O3–N3–C35	120.3 (6)	O4–N4–C45	119.0 (6)
C31–N3–C35	121.7 (7)	C41–N4–C45	120.9 (7)
N3–C35–C35′	117.3 (7)	N4–C45–C45′	118.4 (7)
C34–C35–C35′	122.5 (8)	C44–C45–C45′	120.4 (7)
La–O1–N2	122.9 (4)	La–O2–N2	124.3 (4)
La–O3–N3	122.2 (4)	La–O4–N4	121.7 (4)
(c) General Perchlorate Ion			
Cl1–O11	1.430 (7)	Cl1–O12	1.356 (10)
Cl1–O13	1.378 (9)	Cl1–O14	1.432 (8)
O11–Cl1–O12	108.5 (6)	O11–Cl1–O13	107.5 (6)
O11–Cl1–O14	109.6 (5)	O12–Cl1–O13	110.2 (6)
O12–Cl1–O14	112.0 (6)	O13–Cl1–O14	108.9 (6)

despite possible variations in the dihedral angle of the two rings.

While a square-antiprismatic coordination geometry with the ligands chelating the *l* edges is very unlikely for this complex, owing to the bite distance, a configuration with the ligands chelating the *s* edges is stereochemically very reasonable and would lead to a geometry having overall D_2 point symmetry. Such a geometry is well established for other tetrakis chelate eight-coordinate complexes. Clockwise rotation of the upper portion of the complex, indicated by ligands 1 and 2, through an angle of 45° relative to the lower portion (ligands 3 and 4) would produce a square-antiprismatic structure with no interference between the $bpyO_2$ ligands.

Table IV

Least-Squares Planes[a] in $La(bpyO_2)_4{}^{3+}$

plane	*l*	*m*	*n*	*d*
1 (O2, O3, O4, O1′)	0.8046	0.0007	0.5938	3.486
2 (ring 1)[b]	−0.2950	−0.4242	−0.8562	3.478
3 (ring 2)	−0.8985	−0.4386	−0.0171	4.735
4 (ring 3)	−0.8502	0.5096	−0.1321	−0.571
5 (ring 4)	−0.3595	−0.5047	−0.7849	7.815
6 (La, O1′, O2)	0.0442	0.9989	−0.0156	−5.988
7 (La, O3, O4)	0.5941	−0.0411	−0.8033	3.067

Distances of Atoms from Planes (A × 10^3)

plane	atoms and distances
1	O2, 1.0; O3, 1.0; O4, 1.0; O1′, 1.0
2	N1, 6; C11, 0; C12, −7; C13, 8; C14, −2; C15, −5; O1, −4
3	N2, 16; C21, 5; C22, 17; C23, −16; C24, −18; C25, −3; O2, 25
4	N3, 11; C31, 3; C32, −5; C33, −1; C34, 13; C35, −20; O3, 41
5	N4, −4; C41, −1; C42, 2; C43, 2; C44, −6; C45, 7; O4, 64

Dihedral Angles (deg)

planes	angle	planes	angle
2 and 3	62.3	3 and 5′	7.6
4 and 4′[c]	61.3	6 and 7	90.1
5 and 5′	60.7	6 and 7′	85.4
2 and 4	7.2		

[a] The form of the plane is $lX + mY + nZ + d = 0$ where X, Y, and Z are orthogonal coordinates in A. The weights for the ith atom were calculated according to $w_i = (a\sigma_x b\sigma_y c\sigma_z)^{-2/3}$. [b] The atoms used in calculating the planes 2–5 are those comprising the pyridine rings. [c] The primes refer to twofold-related rings.

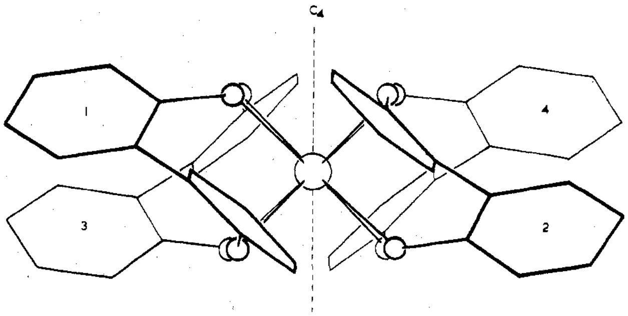

Figure 2. Framework diagram of the structure of $La(bpyO_2)_4{}^{3+}$ viewed normal to the pseudo-fourfold axis (idealized representation).

The configuration of the ligands in the cubic geometry leads to almost parallel orientations for the four pairs of neighboring pyridine rings, i.e., 1 with 4 and 2 with 3′ in Figure 1, the average dihedral angle being 7.4°. The ring to ring contact distances range from 3.42 (1) to 3.71 (1) Å and so indicate a rather efficient packing arrangement of ligands around the lanthanum atom. Since this stacking arrangement is more efficient in the cube than in the square antiprism, it is possible that this factor contributes to the stabilization of the former geometry.

Registry No. $La(bpyO_2)_4(ClO_4)_3$, 12407-31-7.

Supplementary Material Available: Observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Tautomerism in Monocarbahexaborane(7)

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Received July 8, 1978

Microwave studies[1] of monocarbahexaborane(7) indicate a structure which is best described as a distorted octahedron with C_s symmetry (Figure 1A). The molecule possesses a bridge hydrogen which, at normal temperatures, is known[2] to tautomerize rapidly, equating borons 2, 3, 4, and 5 on the NMR time scale. Speculation on the location of this bridge hydrogen in the static structure has tended to favor a four-center face bond, where the hydrogen is linked to borons 2, 3, and 6. Calculations by the CNDO method support this theory.[1]

Our calculations, using the partial retention of diatomic differential overlap (PRDDO) method,[3] indicate that the unique hydrogen is best described as participating in a slightly delocalized equatorial–equatorial bridge bond, which interacts only weakly with boron 6. Thus our results do not favor a four-center face bond. Calculations of the barrier, using an assumed intermediate (Figure 1B) with an equatorial–apical (B_6) bridge, produced values in reasonable agreement with the experimental barrier and showed that the transition from an equatorial–equatorial to an equatorial–apical bridge proceeds smoothly, without a metastable intermediate.

Both the ground state and the transition state were fully optimized by the PRDDO method, using the orbital exponents listed in Table I, with the exception of the terminal C–H and B–H distances, which were fixed at 1.09 and 1.19 Å, respectively. Energies of the two structures were also determined using ab initio 4-31G calculations[4] on the PRDDO-optimized coordinates.

Optimized (PRDDO) framework distances and overlap populations for the ground state are given in Tables IIa and IIIa. The unique hydrogen is 0.33 Å farther from boron 6 than from borons 2 and 3, and the H_b–B_6 overlap population is 0.09, compared with the H_b–B_2 overlap population of 0.34. These data indicate that the unique hydrogen interacts primarily with the equatorial borons and has only a very limited bonding interaction with the apical boron. The H_b–B_6 overlap, while too small to be considered part of a four-centered bond, may be a factor in the lowering of the barrier for tautomerism. Even more striking is the difference in the electron density plot. In marked contrast to the B_2–H_b–B_3 plot (Figure 2A), the B_2–H_b–B_6 plot (Figure 2B) shows an area of low electron density separating the hydrogen from the apical boron.

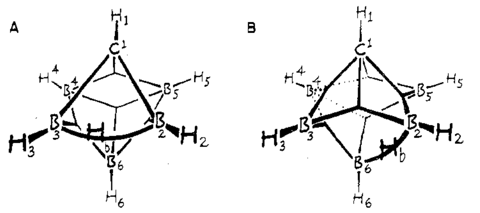

Figure 1. Localized valence structures using the Boys' criterion:[7-9] (A) for the ground state; (B) for the transition state. Dotted lines to B_4 represent electron populations from 0.45 to 0.52 e.

Table I. Orbital Exponents Used for All Calculations

	1s	2s	2p
C	5.67	1.6725	1.6725
B	4.68	1.375	1.375
H	1.24		

Table II. Framework Bond Lengths

atoms	*a*	*b*	*c*
C_1–B_2 (C_1–B_3)	1.59	1.60	1.60
C_1–B_4 (C_1–B_5)	1.65	1.63	1.63
B_2–B_3	1.865	1.87	1.87
B_2–B_5 (B_3–B_4)	1.68	1.70	1.70
B_4–B_5	1.71	1.72	1.72
B_2–B_6 (B_3–B_6)	1.90	1.89	1.89
B_4–B_6 (B_5–B_6)	1.68	1.70	1.70
H–B_2 (H–B_3)	1.41		
H–B_6	1.74		

atoms	*d*	atoms	*d*
C_1–B_2	1.61	B_3–B_6 (B_5–B_6)	1.81
C_1–B_3 (C_1–B_5)	1.58	B_4–B_6	1.69
C_1–B_4	1.63	H–B_2	1.37
B_2–B_3 (B_2–B_5)	1.79	H–B_3 (H–B_5)	2.30
B_2–B_6	1.85	H–B_6	1.35
B_3–B_4 (B_4–B_5)	1.68		

[a] Fully optimized geometry for ground state. [b] Geometry used to calculate potential surface in Figure 3. [c] Microwave geometry from ref 1. [d] Fully optimized transition state.

Table III. Overlap Populations

atoms	*a*	atoms	*a*
C_1–B_2	0.584 19	B_2–B_6	0.288 43
C_1–B_4	0.482 53	B_4–B_6	0.601 95
B_2–B_3	0.204 31	H_b–B_2	0.339 30
B_2–B_5	0.508 99	H_b–B_6	0.088 31
B_4–B_5	0.447 40		

atoms	*b*	atoms	*b*
C_1–B_2	0.518 07	B_3–B_6	0.432 81
C_1–B_3	0.584 81	B_4–B_6	0.552 15
C_1–B_4	0.418 18	H_b–B_2	0.375 93
B_2–B_3	0.378 01	H_b–B_3	−0.011 63
B_2–B_6	0.306 37	H_b–B_6	0.374 44
B_2–B_4	0.513 89		

[a] Overlap populations over atoms for optimized ground-state structure. [b] Overlap populations over atoms for optimized transition-state structure.

A quadratic synchronous transit[5] using the ground state, the transition state, and an orthogonally optimized structure at path coordinate 0.5 produced a smooth energy profile which shows no sign of any intermediate between the ground state and the transition state. The calculated barriers (19.6 kcal mol^{-1} using PRDDO and 22.4 kcal mol^{-1} using 4-31G) are in reasonable agreement with the experimental value of 14 ± 0.5 kcal mol^{-1}.

In order to rule out the possibility that the unique hydrogen might flip onto the C_1–B_2–B_3 face, we calculated, using PRDDO, a potential surface for the movement of the unique hydrogen in the plane of symmetry. For this calculation we

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