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The Crystal and Molecular Structure of 4,4'-Bipyridylium Tetranitratodiaquo-4,4'-Bipyridylceriate(III)

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The crystal structure of strong piezoelectric crystals $NC_5H_4 \cdot C_5H_4NH[Ce(NO_3)_4(H_2O)_2(NC_5H_4 \cdot C_5H_4N)]$ *has been determined from three-dimensional X-ray data. The compound crystallizes in the orthorhombic system, space group* $P2_12_12_1$, *with four molecules in a unit cell of dimensions* a = *18.586(2),* b = *19.955(2),* c = *7.306(1)* Å. *The structure was solved by the heavy atom method and refined by least-squares method to R = 0.031 (on* F_{obs}*) for 3458 diffractometric intensity data. The structure consists of 4,4'-bipyH$^+$ cations and complex* $[Ce(NO_3)_4(H_2O)_2 \cdot 4,4'\text{-bipy}]^-$ *anions*. The 4,4'-bipyH$^+$ cations are not planar. In the complex anion the cerium atom is eleven-coordinated by eight oxygen atoms of four bidentate* NO_3^- *ions, two oxygen atoms of two* H_2O *molecules and one N atom of monodentate 4,4'-bipy molecule. The anion coordination sphere is close to* C_s *symmetry and can be regarded as* C_8 *octadecahedron or* C_s*-square pyramid base–pentagonal pyramid cap. Average Ce–O(*NO_3*) and C–O(*H_2O*) distances are 2.666 and 2.551* Å *respectively. The Ce–N distances are 2.832* Å. *A complex three-dimensional network of hydrogen bonds is formed in the crystal structure.*

Introduction

Structural investigation of some 4,4'-bipyridyl complexes with lanthanides(III) was undertaken by us in order to elucidate the stereochemistry of these highly coordinated central ions and the co-ordination of bidentate 4,4'-bipy ligands [1]. A number of lanthanide complex compounds reveal interesting physical properties like piezoelectric or semi-conductive ones and can be applied in laser technique, in the technique of colour television and many others. The investigated compound is stable at room temperature, reveals strong piezoelectric properties and shows weak luminescence.

Up to the present day the co-ordination of 4,4'-bipy was structurally unknown. The investigation carried out by Czakis-Sulikowska and Radwańska-Doczekalska in solution indicated that the ligand is included into the co-ordination sphere of Ce(III) as bidentate bridge ligand. The compound obtained by Czakis-Sulikowska and Radwańska-Doczekalska was defined as $[Ce(NO_3)_3(H_2O)_4(4,4'\text{-bipy})_2]$ [2]. A sample of crystal was kindly provided by Professor M. Czakis-Sulikowska.

Experimental

Crystal data: $CeC_{20}H_{21}N_8O_{14}$; M = 738. Orthorhombic, a = 18.586(2), b = 19.995(2), c = 7.306(4). Space group $P2_12_12_1$. Density measurements by flotation (using CH_3I solution in benzene) showed four molecules per unit cell (d_{obs} = 1.80 g cm^{-3}, d_{calc} = 1.79 g cm^{-3}). F(000) = 1468; μ(MoKα radiation) = 18.42 cm^{-1}.

For intensity data collection a crystal was grinded to the form of a sphere with a radius of 0.015 cm and found to be of a good quality by photographic methods. Intensity data were collected on the CAD-4 single crystal automated diffractometer using MoKα radiation. Absorption corrections were not applied in view of the small size of the crystal.

Structure Determination and Refinement

The structure was solved by the heavy atom method using computer programs of X-ray System (1970) [3].

A cerium atom was located from Patterson's map and an electron density map was then calculated from the positions of Ce atoms. Since the scattering power of Ce atoms is only 15.8% of that of the whole structure, the first electron density map was very rough.

After several repetitions of the process of adding new postulated atoms to the phasing calculations and of generating new electron density maps, all the non-

*4,4'-bipy = 4,4'-bipyridyl with molecular formula $C_{10}H_8N_2$.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Anisotropic Thermal Parameters ($\times 10^4$) of the Non-hydrogen Atoms. The estimated standard deviations ($\times 10^4$) are in parentheses. The anisotropic temperature factor is of the form $\exp[-2\pi^2/a^{*2}h^2U_{11} + ... + 2b^*c^*klU_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce(1)	5259(0)	4734(0)	9285(0)	257(0)	283(0)	272(0)	2(1)	4(1)	−4(1)
O(11)	3775(1)	4738(2)	8976(7)	366(19)	535(19)	464(22)	−3(19)	−58(17)	−45(22)
O(12)	4252(2)	4900(1)	11655(5)	348(21)	673(23)	421(23)	19(18)	57(20)	−29(19)
O(13)	3106(2)	5062(2)	11244(7)	303(30)	994(31)	822(32)	114(24)	115(27)	−178(26)
O(21)	5435(2)	3651(2)	11360(6)	424(23)	502(21)	509(22)	20(18)	73(19)	106(19)
O(22)	4640(2)	3561(1)	9226(6)	382(19)	367(17)	504(18)	−43(15)	−90(22)	50(19)
O(23)	4900(2)	2699(2)	10940(7)	797(27)	349(26)	722(29)	−39(20)	18(26)	156(24)
O(31)	5628(2)	4915(1)	12877(5)	305(18)	540(19)	352(19)	45(15)	2(17)	−54(16)
O(32)	6500(1)	4826(1)	10962(5)	341(17)	524(18)	322(20)	29(15)	−1(17)	85(18)
O(33)	6728(1)	5047(2)	13847(6)	380(22)	720(22)	370(26)	−7(18)	−61(2)	105(19)
O(41)	4617(2)	5899(2)	8557(6)	522(25)	472(23)	614(23)	22(20)	140(21)	30(20)
O(42)	5508(2)	5989(1)	10435(5)	448(19)	409(19)	43(23)	−37(15)	−111(18)	83(18)
O(43)	4882(2)	6860(2)	9698(6)	640(20)	317(26)	389(30)	−109(22)	−67(24)	96(23)
O(W1)	6054(1)	5343(1)	7081(5)	485(18)	344(20)	388(19)	125(17)	83(17)	40(19)
O(W2)	4783(1)	4562(1)	5969(4)	274(13)	327(14)	286(16)	−42(16)	37(16)	−11(12)
N(1)	8783(1)	1342(2)	4987(6)	419(23)	355(23)	419(23)	−89(19)	−42(20)	18(20)
N(2)	6239(2)	3835(2)	7626(6)	283(20)	362(20)	366(22)	−23(17)	−13(18)	−44(19)
N(3)	1718(2)	8458(2)	3024(7)	514(25)	334(25)	477(27)	92(21)	53(23)	−10(23)
N(4)	3973(2)	5749(7)	4991(7)	520(27)	424(26)	491(27)	127(22)	138(23)	82(24)
N(11)	3699(2)	4904(2)	10656(7)	290(22)	454(23)	521(23)	62(17)	62(24)	−86(23)
N(21)	5009(2)	3294(2)	10520(6)	409(20)	347(21)	439(24)	−14(17)	−45(20)	54(21)
N(31)	6302(2)	4899(2)	12423(6)	395(19)	277(20)	462(25)	−29(16)	−1(19)	45(19)
N(41)	5001(2)	6262(2)	9444(6)	267(19)	436(21)	307(22)	−8(16)	9(18)	−16(17)
C(1)	8999(2)	1946(2)	5553(9)	390(27)	447(27)	482(32)	−84(22)	−18(28)	−16(28)
C(2)	8518(2)	2456(2)	6061(7)	381(25)	373(25)	435(31)	2(21)	10(23)	−41(23)
C(3)	7787(2)	2336(2)	6034(6)	289(20)	317(20)	229(25)	−22(16)	−17(18)	16(18)
C(4)	7566(2)	1701(2)	5441(8)	404(26)	299(26)	577(32)	4(22)	−17(25)	−8(25)
C(5)	8074(3)	1229(2)	4956(8)	505(30)	314(30)	537(30)	−47(25)	−23(27)	−48(26)
C(6)	6032(2)	3224(2)	7087(7)	290(25)	355(26)	467(26)	−15(21)	−35(23)	−93(23)
C(7)	6514(2)	2731(2)	6572(7)	273(25)	414(25)	435(27)	21(21)	−34(23)	−69(23)
C(8)	7250(2)	2860(2)	6573(6)	253(20)	298(20)	266(22)	−11(18)	−13(19)	−24(29)
C(9)	7462(2)	3499(2)	7091(7)	339(24)	269(24)	439(26)	41(20)	59(20)	−31(23)
C(10)	6948(2)	3966(2)	7591(7)	324(23)	278(23)	425(26)	−3(20)	−11(22)	−58(21)
C(11)	1429(3)	7863(2)	3479(8)	387(28)	398(27)	461(29)	71(23)	34(25)	6(25)
C(12)	1861(2)	7314(2)	3859(7)	324(25)	357(24)	448(29)	2(20)	2(20)	−25(21)
C(13)	2607(2)	7366(2)	3753(7)	331(22)	327(22)	285(25)	17(18)	18(19)	−2(19)
C(14)	2902(2)	7989(2)	3251(8)	419(28)	371(28)	445(31)	−56(23)	60(24)	−16(25)
C(15)	2423(3)	8517(2)	2914(8)	524(28)	310(28)	478(31)	−46(24)	84(27)	−7(27)
C(16)	4219(3)	6234(3)	3999(9)	408(32)	611(33)	564(40)	166(28)	23(32)	62(30)
C(17)	3795(3)	6768(3)	3511(9)	450(33)	523(33)	502(34)	51(27)	8(29)	−37(29)
C(18)	3081(2)	6788(2)	4144(7)	332(20)	272(20)	313(23)	22(17)	28(23)	5(22)
C(19)	2834(3)	6259(2)	5222(8)	474(29)	381(29)	487(34)	41(24)	35(25)	−71(26)
C(20)	3297(3)	5734(3)	5643(7)	593(31)	378(31)	556(33)	85(26)	130(35)	10(36)

hydrogen atoms were located. Full matrix least squares refinement was then carried out. At the beginning of the refinement R was 0.40. After 3 cycles of refining of scale, positional parameters and individual Us for each atom, R was reduced to 0.074. A difference electron density map was calculated in order to locate the hydrogen atoms. Two very high maxima were located and the postulated formula $[Ce(NO_3)_3(H_2O)_4(4,4'\text{-bipy})_2]$ was replaced by 4,4'-bipy $H[Ce(NO_3)_4(H_2O)_2(4,4'\text{-bipy})]$. After 3 cycles of refinement with anisotropic thermal parameters and locating of 17 hydrogen atoms, R was reduced to 0.031. All the observed reflections were given unit weights and unobserved ones were not included into the summations. Atomic scattering factors used are those given in International Tables [4] for Ce and by P. A. Doyle and P. S. Tumer for N, C, O and H atoms [5].

Fractional atomic co-ordinates and anisotropic thermal parameters of the non-hydrogen atoms are presented in Table I. The co-ordinates of hydrogen atoms given in Table II represent the unrefined posi-

TABLE II. Fractional Coordinates (× 10^3) of the Hydrogen Atoms from the Difference Map.

	x	y	z
H(1)	951	203	561
H(2)	867	284	650
H(4)	713	160	497
H(6)	545	314	714
H(7)	634	232	604
H(9)	799	365	661
H(10)	709	429	797
H(14)	339	801	300
H(15)	265	897	287
H(16)	455	618	350
H(17)	394	715	250
H(19)	234	620	564
H(20)	318	533	390
$H_w(1)$	617	573	700
$H_w(2)$	450	428	550
$H_N(4)$	435	527	550

tions as read directly from the difference map. The refinement of the H co-ordinates by least-squares method deteriorated the H–C and H–O distances.

Description and Discussion of the Structure

Molecular Packing

The relative arrangement of anions and cations in the structure is determined by a complex three-dimensional network of hydrogen bonds. This is illustrated in Fig. 1 which presents the contents of the unit cell viewed from the direction of the crystal z axis.

Big complex anions occupy the positions close to the corners and centers of the walls of a unit cell. The anion columns extend along the z axis. In the columns $[Ce(NO_3)_4(H_2O)_2$ 4,4'-bipy$]^-$ ions are linked together by means of hydrogen bond O(W2)–H–O(31). The 4,4'-bipy molecules and 4,4'-bipyH$^+$ cations occupy bridge positions between the complex anions. The uncomplexed 4,4'-bipyridylium ion is hydrogen bonded to the co-ordinated water molecules O(W1), O(W2) and oxygen atom O(41) of nitrate ion. The monodentate 4,4'-bipy molecule is hydrogen bonded to the co-ordinated water molecule O(W2). The ion 4,4'-bipyH$^+$ and 4,4'-bipy molecule stack along the z axis and the rings $N(1)C_5$, $N(3)C_5$ and $N(2)C_5$ are almost ideally parallel (see Table VIII). The shortest distance between the carbon atoms of

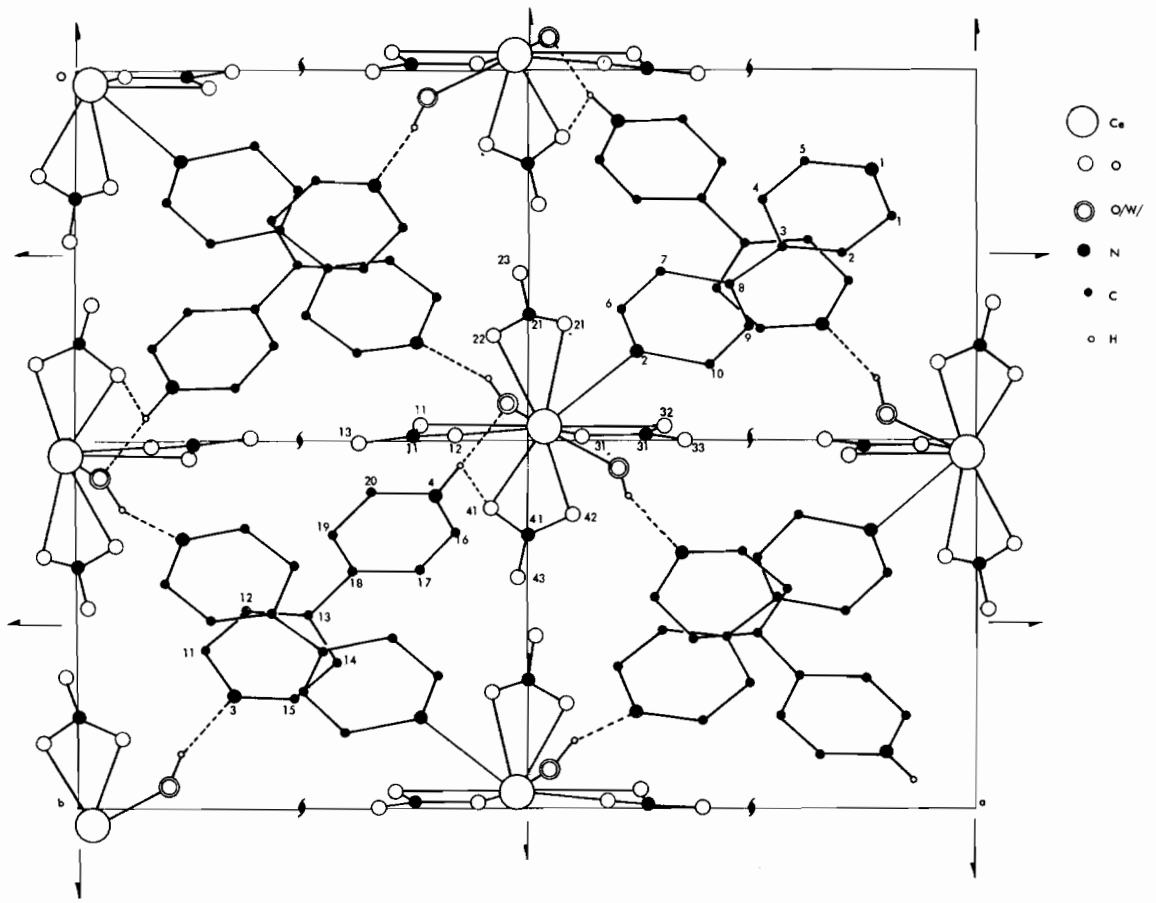

Figure 1. A projection of the structure along the z axis.

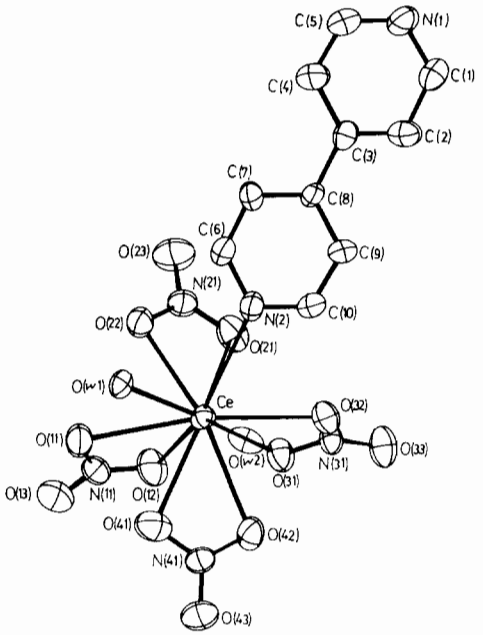

Figure 2. Ortep projection of the anion $[Ce(NO_3)_4(H_2O)_2$ 4,4′-bipy$]^-$.

the parallel pyridine rings is 3.417 Å. This value corresponds to the sum of Van der Waals radii of C atoms [6]. Each anion column is surrounded by 4 columns built of the 4,4′-bipy molecule and 4,4′-bipyH$^+$ ions stacking along the z axis. Fig. 2 shows the Ortep projection along the z axis of the anion $[(Ce(NO_3)_4)H_2O)_2$ 4,4′-bipy$]^-$.

Complex Anion $[Ce(NO_3)_4(H_2O)_2(4,4'\text{-bipy})]^-$

The co-ordination sphere of atoms forming an undecaco-ordination polyhedron around the central Ce atom is presented in Fig. 3 which shows the numbering of atoms and interligand distances in the complex anion.

The Ce atom is eleven co-ordinated by eight oxygen atoms O(11), O(12), O(21), O(22), O(31), O(32), O(41), O(42) of four bidentate nitrate ions, two oxygen atoms O(W1) and O(W2) of two water molecules and one nitrogen atom N(2) of a monodentate 4,4′-bipy molecule. Undecaco-ordination polyhedra are not common in inorganic chemistry. More favourable for high coordination numbers are deca and dodecaco-ordination polyhedra [7]. The

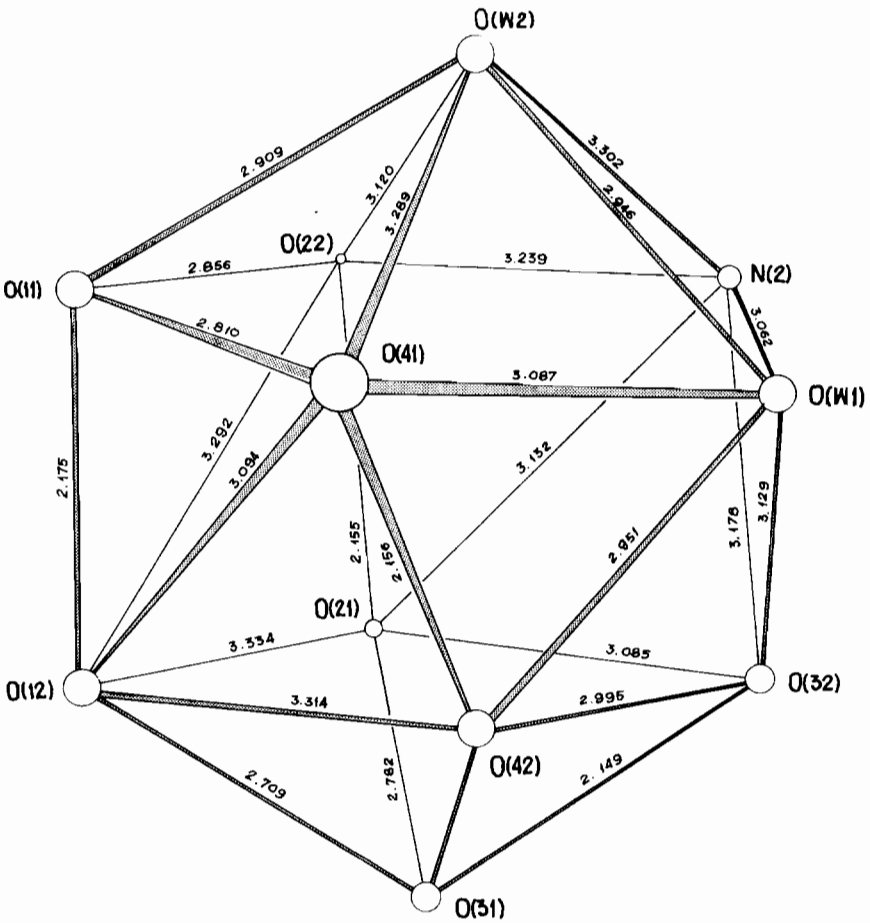

Figure 3. The co-ordination polyhedron of Ce(III) as C_s-octadecahedron.

TABLE III. Bond Lengths (Å) and Angles (°) in Ce(III) Co-ordination Polyhedron with Standard Deviations in Brackets.

Ce(III) Polyhedron as Undeca-co-ordination C_s-octadecahedron $Ce(O_{NO_3})_8(O_W)_2N$			
Ce–O(11)	2.769(4)	O(11)–Ce–O(22)	64.02(11)
Ce–O(12)	2.572(4)	O(22)–Ce–N(2)	72.88(12)
Ce–O(21)	2.664(4)	N(2)–Ce–O(W1)	69.77(12)
Ce–O(22)	2.614(3)	O(W1)–Ce–O(41)	73.23(13)
Ce–O(31)	2.737(4)	O(41)–Ce–O(11)	62.38(13)
Ce–O(32)	2.618(3)	O(12)–Ce–O(21)	79.08(11)
Ce–O(41)	2.670(4)	O(21)–Ce–O(32)	71.48(13)
Ce–O(42)	2.686(4)	O(32)–Ce–O(42)	68.75(12)
Ce–O(W1)	2.501(4)	O(42)–Ce–O(12)	78.10(12)
Ce–O(W2)	2.601(4)		
Ce–N(2)	2.832(4)		
O(W2)–Ce–O(11)	65.51(11)	O(12)–Ce–O(22)	78.81(12)
O(W2)–Ce–O(22)	73.51(13)	O(21)–Ce–O(22)	48.19(11)
O(W2)–Ce–O(41)	77.19(12)	O(22)–Ce–O(W2)	73.51(13)
O(W2)–Ce–O(W1)	70.51(13)	O(W2)–Ce–O(11)	65.51(11)
O(W2)–Ce–N(2)	74.71(11)	O(W2)–Ce–O(41)	77.19(12)
O(31)–Ce–O(12)	61.28(12)	O(W1)–Ce–O(32)	75.33(11)
O(31)–Ce–O(21)	62.00(11)	O(W1)–Ce–O(42)	69.23(12)
O(31)–Ce–O(32)	47.26(11)	O(41)–Ce–O(12)	72.33(13)
O(31)–Ce–O(42)	62.22(12)	O(32)–Ce–N(2)	71.23(12)
Ce(III) Polyhedron as $CeL_4(O_W)_2N$ where L is the Centre of Gravity for the Two Co-ordinated Oxygen Atoms of Bidentate NO_3^-			
Pentagonal bipyramid base			
Ce–L(1)	2.441(4)	L(1)–Ce–L(2)	78.90(12)
Ce–L(2)	2.409(4)	L(2)–Ce–N(2)	69.30(12)
Ce–L(4)	2.452(4)	N(2)–Ce–O(W1)	69.80(12)
Ce–O(W1)	2.501(4)	O(W1)–Ce–L(4)	69.42(12)
Ce–N(2)	2.832(4)	L(4)–Ce–L(1)	76.76(13)
Ce–two vertices line			
Ce–L(3)	2.454(4)	L(3)–Ce–O(W2)	162.31(13)
Ce–O(W2)	2.601(3)		

undecaco-ordination polyhedron observed in the investigated structure can be treated as a slightly corrugated C_s-octadecapolyhedron. Such type of co-ordination polyhedron has not been described in any known structure of high co-ordination numbers. The approximate plane of symmetry for this polyhedron is assigned by atoms Ce, O(W2), O(11), O(12), O(31), O(32). Table IV shows the least-squares plane of the 5 atoms and the distances of individual ligands from the plane. Both the distances and the lengths of the edges in the co-ordination polyhedron point to its approximate C_s symmetry. The observed polyhedron can also be described as a C_s tetragonal pyramid base–pentagonal pyramid cap. Bond lengths and the angles between them in a co-ordination polyhedron are given in Table III.

The average Ce–O(nitrate) distance = 2.666 Å is longer than average the Ce–O (water) one = 2.551 Å. The Ce–N distance = 2.832 Å is the longest one in the co-ordination polyhedron. The co-ordination of nitrate group can be considered as symmetrical, but it is less symmetrical than in twelve co-ordinated ion $[Ce(NO_3)_6]^{-3}$ in $Ce_2Mg_3(NO_3)_{12}\cdot 12H_2O$ [8] where the Ce–O bonds from one NO_3^- ion range from 2.612 to 2.675 Å. In the investigated structure the differences in the Ce–O bond lengths for the individual NO_3^- groups are 0.197, 0.050, 0.115, 0.016 Å.

If the nitrate groups are considered as single L groups bonded to cerium atom [9], then the co-ordination polyhedron resembles the pentagonal bipyramid. Tables III and IV present bond lengths, angles and least-squares planes and lines of the bipyramid. The data point to the fact that the description of the co-ordination polyhedron as the one of D_{5h} symmetry is not very precise. The Ce–ligand bond lengths vary considerably (Ce–N(2) = 2.832, Ce–L(1) = 2.441 Å). The angles between the bonds also differ from the theoretical values 72° and 180°.

TABLE IV. Least-squares Planes in Ce(III) Co-ordination Polyhedron. The planes are of the form AX + BY + CZ = D, where X, Y, Z are in Å units.

The C_s Plane of C_s-octadecahedron $Ce(O_{NO_3})_8(O_W)_2N$.

	Deviations	
Ce	−0.0091	
O(W2)	−0.0013	Defining plane:
O(11)	−0.0101	
O(12)	0.0318	Plane equation:
O(31)	−0.0342	
O(32)	0.0229	0.015X + 0.989Y − 0.149Z = 8.502
O(21)	−2.3717	
O(42)	2.3532	
N(2)	−1.5767	
O(W1)	1.4568	
O(22)	−2.3396	
O(41)	2.3551	

The Base Plane and Ce–O(W1)–L(3) Line of Pentagonal Bipyramid Ce $L_4(O_W)_2N$

Base Plane	Deviation	
N(2)	−0.0636	
O(W1)	−0.2205	Plane equation:
L(1)	−0.4199	
L(2)	0.3043	0.539X + 0.119Y + 0.834 = 11.870
L(4)	0.3998	
Line		
Ce	0.2587	Line equation:
O(W2)	0.1255	$\frac{X - 9.978}{0.475} = \frac{Y - 9.442}{0.123} = \frac{Z - 6.616}{0.871}$
L(3)	0.1332	
		Plane–Line Angle = 85.77°

TABLE V. The Bond Lengths (Å) and Angles (°) in Four Nitrate Groups with Standard Deviations in Brackets.

	Group 1	Group 2	Group 3	Group 4
[a]N(X1)–O(X1)	1.279(7)	1.253(6)	1.272(5)	1.252(6)
N(X1)–O(X2)	1.261(6)	1.267(6)	1.244(6)	1.263(6)
[b]N(X1)–O(X3)	1.224(7)	1.239(6)	1.225(6)	1.221(6)
	Group 1	Group 2	Group 3	Group 4
O(X1)–N(X1)–O(X2)	117.65(41)	117.62(45)	117.28(39)	117.99(42)
O(X2)–N(X1)–O(X3)	122.14(49)	121.32(44)	122.47(40)	121.05(44)
O(X1)–N(X1)–O(X3)	120.21(45)	121.05(45)	120.25(40)	120.95(45)

[a]X is the number of nitrate group. [b]O(X3) are the terminal (uncoordinated) atoms of NO_3^- ions.

The high deviation of that polyhedron from the D_{5h} symmetry is a result of various sizes of individual ligands, various ways of their co-ordination and is also influenced by the formation of numerous hydrogen bonds by the co-ordinated water molecules and some oxygen atoms from NO_3 groups. It seems more justified to consider the investigated co-ordination polyhedron as the C_s octadecahedron than as a pentagonal bipyramid.

Ligand Geometries

The nitrate groups are nearly planar. Table VI shows the least-squares planes of the nitrate groups and deviations of atoms from the planes. Bond distan-

Table VI. Least-squares Planes of four Nitrate Groups.

Plane 1	Deviations	Plane 2	Deviations	Plane 3	Deviations	Plane 4	Deviation
N(11)	−0.0011	N(21)	0.0173	N(31)	−0.0475	N(41)	0.1402
O(11)	0.0006	O(21)	−0.0057	O(31)	0.0153	O(41)	−0.0579
O(12)	0.0000	O(22)	−0.0056	O(32)	0.0162	O(42)	−0.0389
O(13)	0.0004	O(23)	−0.0060	O(33)	0.0159	O(43)	−0.0434

Plane 1: 0.1792X + 0.9541Y − 0.2397Z = 8.724
Plane 2: 0.7146X − 0.2687Y − 0.6459Z = −0.0983
Plane 3: −0.0595X + 0.9792Y − 0.1941Z = 7.1587
Plane 4: 0.5505X + 0.4427Y − 0.7078Z = 5.5798

TABLE VII. Bond Lengths (Å) and Angles (°) in 4,4'-Bipy Molecule and 4,4'-BipyH$^+$ ion.

4,4'-Bipy Molecule				4,4'-BipyH$^+$ Ion			
N(1)–C(1)	1.340(7)	C(1)–N(1)–C(5)	116.89(47)	N(3)–C(11)	1.347(7)	C(11)–N(3)–C(15)	119.39(48)
N(1)–C(5)	1.335(7)	N(1)–C(1)–C(2)	123.04(48)	N(3)–C(15)	1.317(7)	N(3)–C(11)–C(12)	121.17(49)
C(1)–C(2)	1.405(8)	C(1)–C(2)–C(3)	119.77(47)	C(11)–C(12)	1.388(8)	C(11)–C(12)–C(13)	120.37(46)
C(2)–C(3)	1.379(7)	C(2)–C(3)–C(4)	116.78(44)	C(12)–C(13)	1.393(7)	C(12)–C(13)–C(14)	117.89(44)
C(3)–C(4)	1.403(7)	C(3)–C(4)–C(5)	119.74(49)	C(13)–C(14)	1.411(7)	C(13)–C(14)–C(15)	117.57(48)
C(4)–C(5)	1.381(8)	C(4)–C(5)–N(1)	123.74(53)	C(14)–C(15)	1.404(8)	C(14)–C(15)–N(3)	123.58(51)
N(2)–C(6)	1.339(7)	C(6)–N(2)–C(10)	117.03(42)	N(4)–C(16)	1.320(8)	C(16)–N(4)–C(20)	123.25(58)
N(2)–C(10)	1.344(6)	N(2)–C(6)–C(7)	122.93(46)	N(4)–C(20)	1.342(7)	N(4)–C(16)–C(17)	120.47(59)
C(6)–C(7)	1.384(7)	C(6)–C(7)–C(8)	120.25(46)	C(16)–C(17)	1.364(7)	C(16)–C(17)–C(18)	119.53(57)
C(7)–C(8)	1.392(7)	C(7)–C(8)–C(9)	116.65(43)	C(17)–C(18)	1.407(6)	C(17)–C(18)–C(19)	118.30(47)
C(8)–C(9)	1.390(7)	C(8)–C(9)–C(10)	119.82(44)	C(18)–C(19)	1.396(7)	C(18)–C(19)–C(20)	119.49(52)
C(9)–C(10)	1.385(7)	C(9)–C(10)–N(2)	123.28(45)	C(19)–C(20)	1.392(6)	C(19)–C(20)–N(4)	118.92(58)
C(3)–C(8)	1.500(6)			C(13)–C(18)	1.480(6)		

TABLE VIII. Least-squares Planes of NC_5 Rings in 4,4'-Bipy Molecule and 4,4'-BipyH$^+$ Ion.

Plane 1	Deviations	Plane 2	Deviations	Plane 3	Deviations	Plane 4	Deviations
N(1)	0.0037	N(2)	−0.0126	N(3)	0.0033	N(4)	−0.0078
C(1)	−0.0060	C(6)	−0.0073	C(11)	−0.0058	C(16)	0.0122
C(2)	0.0069	C(7)	0.0019	C(12)	0.0023	C(17)	−0.0075
C(3)	−0.0055	C(8)	0.0080	C(13)	0.0029	C(18)	−0.0009
C(4)	0.0034	C(9)	0.0071	C(14)	−0.0052	C(19)	0.0052
C(5)	−0.0025	C(10)	0.0028	C(15)	0.0024	C(20)	−0.0011

Plane equations

Plane 1: −0.0348X − 0.3265Y + 0.9446Z = 0.8225
Plane 2: −0.0651X − 0.3090Y + 0.9483Z = 0.7882
Plane 3: −0.0348X − 0.2616Y + 0.9645Z = 4.6314
Plane 4: 0.3050X + 0.4841Y − 0.8201Z = −1.2805

Angles: Plane 1–Plane 2 = 2.02°
Plane 3–Plane 4 = 21.82°
Plane 1–Plane 3 = 3.89°
Plane 2–Plane 3 = 3.35°

ces and angles in the four nitrate groups are shown in Table V. The unco-ordinated nitrate ion is known to be planar with all the ONO interbond distances equal to 1.245 ± 0.001 Å [10]. In the co-ordinated nitrate groups their planarity is preserved but the N–O bond lengths and ONO interbond angles are different. In

TABLE IX. Hydrogen Bonds (Å) and Angles (°).

X–H···Y	X···Y	X–H	H···Y	X–H···Y
O(W1)–H(W1)····N(3)	2.696	0.81	1.91	163.5
O(W2)–H(W2)····N(1)	2.686	0.84	1.86	153.8
N(4)–H(N4)·····O(W2)	2.901	1.23	1.68	171.9
N(4)–H(N4)·····O(41)	2.883	1.23	2.61	89.9
O(W2)–·····O(31)	2.840			

the investigated structure one can observe the same regularities of the change of bond lengths and angles as in most structurally known, symmetrically co-ordinated NO_3^- groups [10]. As can be seen from Table V, in all the four NO_3^- groups the terminal N–O bond (av. 1.227 Å) is shorter and the N–O bonds involving the co-ordinated oxygen atoms (av. 1.261 Å) are longer than the N–O bonds in unco-ordinated nitrate ion. The O–N–O interbond angles involving both the co-ordinated oxygen atoms are smaller than 120° (av. 117.6°) and the other two angles are correspondingly greater (av. 121.2°).

Bond distances, angles and least-squares planes in 4,4′-bipy molecule and 4,4′-bipyH$^+$ ion are shown in Tables VII and VIII. The 4,4′-bipy molecule is planar (the angle between N(1)C_5–N(2)C_5 planes is only 2.01°) while the 4,4′-bipyH$^+$ ion is not planar (the angle between N(3)C_5–N(4)C_5 planes is 21.82°). C(3)–C(8) (C_{sp^2}–C_{sp^2}) single bond in planar molecule is 1.500(6) Å. Twisting of the two pyridyne rings round the C–C bond does not result in its lengthening in 4,4′-bipyH$^+$ ion. The obtained length of C(13)–C(18) bond is 1.480(6) Å. The lengths of analogous bonds in all the four, structurally independent rings NC_5 agree, with the differences not higher than 3σ. The mean length of C–N bonds in the rings is 1.336 Å. No regular differentiation of C–C bond length in the rings can be observed. The mean lengths of the four C–C bonds are 1.392, 1.387, 1.399, 1.389 Å. The mean length of C–C bond in the rings equals 1.391 Å.

As follows from the data of Table VII, in all the NC_5 rings a regular differentiation of the values of interbond angles takes place.

All the C–N–C angles are smaller than 120° in three pyridyne rings and their mean value is 117.8°. For the four rings the C–C–N angles are greater than 120° with the mean value of 122.1°; interbond C–C–C angles on the bridge carbon atoms are smaller than 120° with the mean value of 117.4°; the mean value of C–C–C angles on the carbon atoms adjacent to the bridge carbon is 119.6°.

Hydrogen Bonds

Figure 1 presents the scheme of hydrogen bonds between $[Ce(NO_3)_4(H_2O)_2$ 4,4′-bipy$]^-$ and 4,4′-bipyH$^+$ ions. It can be suggested that beside N–H···O and O–H···N bonds marked in the figure, there exists a hydrogen bond O–H···O between the complex anions adjacent along the z axis. In spite of the fact that we did not manage to locate the hydrogen atom of this bond on a difference map, its existence is indicated by a considerable shortening of the distances between oxygen atoms O(W2)–O(31) = 2.840 Å. Table IX presents lengths and angles for the observed hydrogen bonds. These are not linear bonds but clearly angular as in the case of most known examples [11]. We noticed a very interesting weak bifurcated hydrogen bond between the N(4) atom of 4,4′-bipyH$^+$ ion and O(W2) and O(41) atoms.

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