Synthesis and Crystal Structre of Bipyridyl Comlexes of Praseodymium Nitrate and Chloride

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Abstract: Crystal structures of Pr $(NO_3)_3$ $(H_2O)_4$. $(C_{10}H_8N_2)_2H_2O$ and Pr Cl_3 $(H_2O)_4$. $(C_{10}H_{10}N_2)_{1.5}$ Cl_3 were solved using x-ray diffraction technique. The nitrate complex was orthorhombic with space group $P2_12_12_1$, whereas the chloride complex showed a monoclinic system with space group $p2_1/c$.

The Pr in the nitrate complex is 10-coordinate from three bidentate groups and four water molecules. The two independent bipyridyl molecules are lying on general positions and neither protonated nor coordinated to the central atom Pr. In the chloride complex, the Pr is 7-coordinate from three chlorides and four water molecules. The two bipyridyl molecules are uncoordinated to the central atom.

Keywords: Lanthanides, Crystal Structure, 4-Bipy, X-Ray Diffraction

1. Introduction

Lanthanide coordination is a challenging area due to both a variety of coordination geometries and potential applications. Adducts of hydrated lanthanide nitrates and chlorides with 4,4¯bipyridyl (4-bipy) of the type LnX.n H_2O.2(4-bipy) where Ln=La,Ce,Gd,Sm,Nd,Pr ;X=$(NO_3)_3$,Cl_3, ;and n=2-6 have been reported (Bukowska, 1978; Al-Rasoul, 1982; Bukowska, 1982; Weakley, 1982; Weakley, 1984; Al-Rasoul, 1987; Weakley, 1989; Ibrahim, 1993&1999; Ibrahim, 2005). These lanthanide complex compounds reveal interesting physical properties such as piezoelectricity, semi conductivity, and luminescency (Bukowska, 1978; Holler, 2010; Matthes, 2012; Matthes, 2016).

Single crystal x-ray structure analysis of the lanthanide nitrates and chlorides with (4-bipy) ligand complexes have proved that several structurally distinct series exist depending on the nature of the product and its sensitivity to the preparation conditions. However, the compounds of the type Pr (nitrate)-(4-bipy),Y(chloride)-(4-bipy), and Gd (chloride)-(4-bipy) so far subjected to single crystal x-ray structure analysis showed different coordination geometry and that the bidentate ligand(4-bipy) were uncoordinated to the central ion (Bukowska, 1982; Weakley, 1989).

In the present study, details of the preparation and crystal structures of $Pr(NO_3)_3(H_2O)_4.(C_{10}H_8N_2)_2H_2O$ and $PrCl_3(H_2O)_4.(C_{10}H_{10}N_2)_{1.5}Cl_3$ are reported using single crystal x-ray technique. The cell parameters

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and space groups are determined using weissenberg, de-jong, and oscillation photographs. Whereas the Fourier and Difference Fourier electron density maps are used for atoms positions in the crystals.

2. Experimental

2.1 Nitrate Compound

2 gm of Pr6 O11 (99.99% from Rare Earth Products-England) was dissolved in 15 ml of concentrated nitric acid. The mixture was heated up to dryness at 70°C thus forming white, green precipitate of praseodymium nitrate. 2 mmole of solid 4-bipy (99%, from BDH) was dissolved in 20 ml ethanol and gradually added to warm solution of 1 mmole praseodymium nitrate which was dissolved in 20 ml ethanol. The mixture was heated up to 80°C and kept at that temperature for 20 minutes with continuous stirring and then allowed to cool. After slow evaporation at room temperature for six days crystalline product was obtained and separated by filtration. Well-formed single crystal suitable for x-ray diffraction work were carefully selected among the crystalline product obtained.

2.2 Chloride Compound

2 mmole of solid 4-bipy (99% from BDH) was dissolved in 20 ml ethanol and was gradually added to a warm solution of 1 mmole of praseodymium chloride hexahydrate (99.9% from Rare Earth Products-England) dissolved in 20 ml ethanol. The mixture was heated up to 80°C for 20 minutes with continuous stirring and then allowed to cool. After slow evaporation at room temperature for 12 hours, well-formed single crystals were obtained and separated by filtration.

Density measurements of the crystals by flotation method in a mixture of bromoform / benzene showed four molecule per unit cell for both compounds (dobs = 1.670, dcalc. =1.69 gm/cm3 for orthorhombic nitrate complex and dobs=1.855, dcalc=1.86 gm/cm3 for the monoclinic chloride complex). Oscillation, de-Jong, and precession photographs were taken for crystals of both compounds to establish the preliminary cell parameters and possible space groups. All the reflection conditions taken together implicate space group P212121 for the orthorhombic nitrate compound and P21/c for the monoclinic chloride compound. Crystals of both compounds were mounted on Stoe – STADI – 2 two circle diffractometers interfaced to (PDP 11/23+) computer. Accurate cell parameters were obtained from centered positions of sixteen well distributed general reflections in each compound.

Intensity data, for both crystals, were collected using the usual conditions. A total of 1446 reflections for the orthorhombic crystal and 4349 reflections for the monoclinic crystal with $I>2.8\ \delta\ (I)$ were observed and used in the structure determinations. All intensities were corrected for the Lorentz and polarization effects, whereas no absorption corrections were applied. Atomic scattering factors for Pr and other atoms were taken from International Tables for Crystallography (Ibers, 1974) and the mass absorption coefficients from Cromer and Liberman (Cromer, 1968). All the data processing and computation were carried out using SHELX-76 programs package (Sheldric, 1976). The molecular structures were projected using ORTEP program package (Johnson 1965) and the molecular geometry calculations were carried out using TAU program (Farid, 1988).

3. Results and Discussion

The structures are solved by the heavy-atom method. The heavy atoms were located from Patterson maps and difference Fourier maps were then calculated from the heavy atom position. After several repetitions of the process of adding new postulated atoms to the phasing calculations and of generating electron density maps all the non-hydrogen atoms in both compounds were located. The positions of the Pr atoms and all the non-hydrogen atoms were subjected to least-square refinement. The refinements were continued for both structures till the reliability factors R were reached value of (0.056) for the orthorhombic crystal and (0.052) for the monoclinic crystal. The crystallographic data for both crystals are given in table 1. Final positional and thermal parameters are presented in table 2. Bond lengths and angles are listed in table 3 and least-square planes and atom deviations are shown in table 4. Projections of the molecular structures and the coordination spheres around Pr atoms are presented as illustrated in Figures 1 to 5.

Table 1: Crystal data, intensity collection, and structure refinement for nitrate and chloride compounds

Chemical formula	$C_{20} H_{26} N_5 O_{14}$ Pr	$C_{15}H_{23}N_3O_4$Cl6Pr
M wt.	728.9	660.0
Cell Parameters:		
a (Å)	24.791(2)	11.882(2)
b (Å)	16.132(2)	14.039(5)
c (Å)	7.142(4)	17.129(3)
ß (°)	90	124.56(17)
Cell Volume $(Å)^3$	2857.29	2351.97
Z	4	4
Space group	$P2_12_12_1$	$P2_1/c$
$D_{obs.}$ (gm/cm^3)	1.67(15)	1.855(10)
D_{calc}. (gm/cm^3)	1.69	1.860
μ MO Kα (cm ^{1})	16.7	26.2
Crystal size (mm)	0.17*0.17*0.54	0.19*0.23*0.17
Scan width (°)	1.82+0.14(sin μ/tanθ)	1.95+0.12(sin μ/tanθ)
Scan speed (°/S)	0.1	0.1
Unique average data	1446 [$I>2\sigma(I)$]	4349 [$I>3\sigma(I)$]
$R=(\Sigma\Delta F/\Sigma F_o)$	0.056	0.052
$R_W=(\Sigma W\Delta F^2/\Sigma WF_o{}^2)^{1/2}$	0.061	0.061
Weighting scheme		
$W(hkl)=K/ [\sigma^2(F)+gF^2]$	K=3.3, g=0.004	K=0.9, g=0.0003

Table 2: Atomic Coordinates and atomic displacement Parameters (all x 10^4) for:

a-$Pr(NO_3)_3(H_2O)_4.(C_{10}H_8N_2)_2$ H_2O

Atom	X	Y	Z	U_{eq}
Pr	4991(1)	6926(1)	-422(2)	334(5)
O1	4864(8)	6926(1)	-422(2)	334(5)
O2	5141(9)	5456(13)	1078(31)	853(78)
N1	4940(18)	5059(11)	-431(28)	412(11)
O3	4981(21)	4284(10)	-336(26)	773(12)
O4	5988((8)	6503(14)	548(43)	696(15)
O5	5482(8)	6696(16)	2928(30)	717(15)
N2	5942(9)	6584(14)	2245(42)	475(17)
O6	6331(8)	6526(14)	3240(35)	776(16)
O7	4494(9)	6634(16)	-3810(30)	756(16)
O8	3999(8)	6597(13)	-1366(38)	663(15)
N3	4035(10)	6604(14)	-3058(33)	494(16)
O9	3638(8)	6620(13)	-4077(29)	664(16)
OW1	4400(7)	7172(13)	-2272(23)	492(13)
OW2	5577(7)	7166(13)	-3188(27)	536(14)
OW3	4538(7)	8162(14)	-1683(35)	747(15)
OW4	5482(8)	8202(11)	462(39)	726(14)
OW5	4961(22)	4738(11)	4569(32)	969(15)
C1	2777(9)	4471(15)	8451(33)	335(59) *
C2	3313(12)	4740(18)	7820(41)	539(73) *
C3	3714(15)	4173(25)	7893(54)	747(99) *
N4	3619(9)	3318(13)	8422(32)	531(64) *
C4	3115(19)	3095(18)	8973(35)	458(60) *
C5	2680(11)	3657(17)	9038(36)	500(72) *
C6	2342(10)	5105(16)	8405(35)	432(68) *
C7	2448(10)	5949(17)	8772(40)	483(64) *
C8	2002(12)	6492(18)	8708(42)	532(71) *
N5	1482(9)	6240(14)	8321(31)	457(56) *
C9	1392(12)	5434(19)	8000(44)	579(79) *
C10	1807(10)	4813(15)	8024(37)	424(62) *
C11	2252(10)	652(18)	7316(36)	465(67) *
C12	2346(13)	1462(18)	6724(39)	534(73) *
C13	1908(12)	2027(21)	6806(44)	631(80) *
N6	1411(10)	1768(17)	7341(37)	701(75) *
C14	1306(13)	956(22)	7749(45)	632(85) *
C15	1723(12)	367(18)	7922(42)	573(76) *
C16	2720(11)	57(17)	7531(36)	449(67) *
C17	3244(13)	337(20)	7925(47)	667(87) *
C18	3645(12)	-275(19)	8028(45)	588(79) *
N7	3580(10)	-1080(15)	7609(32)	451(62) *
C19	3084(12)	-1375(17)	7320(38)	508(73) *
C20	2622(13)	830(21)	7159(43)	623(83) *

U is given as $U_{eq}= (U_{11} +U_{22} +U_{33})/ 3$

*Isotropic atomic displacement parameter.

b-PrCl3(H2O)4. (C10H10N2)1.5 Cl3

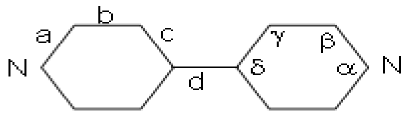
Atom	X	Y	Z	U_{eq}
Pr	2021(10)	5025((0)	5103(0)	182(2)
Cl1	3067(2)	4407(1)	4088(1)	301(2)
Cl2	2687(2)	6010(1)	6747(1)	313(8)
Cl3	-481(2)	6101(1)	4401(1)	246(6)
Cl4	77(2)	7988(1)	2932(1)	362(8)
Cl5	3487(2)	3007(1)	2236(1)	339(8)
Cl6	3853(2)	7063(1)	3586(1)	371(23)
OW1	149(5)	4288(4)	3600(4)	349(25)
OW2	3292(6)	3556(4)	5888(4)	394(23)
OW3	4458(5)	5571(4)	6028(4)	336(23)
OW4	2033(5)	6469(3)	4284(4)	313(21)
N1	2947(7)	1662(5)	3405(5)	405(31)
C1	3280(7)	355(5)	4704(5)	274(28)
C2	3722(12)	1277(8)	4968(8)	629(26)
C3	3574(14)	1939(9)	4310(9)	729(31)
C4	2557(12)	778(6)	3129(6)	584(47)
C5	2736(12)	99(6)	3780(6)	509(37)
C6	3442(7)	-363(5)	5420(5)	289(28)
C7	3948(13)	-57(6)	6328(6)	515(38)
C8	3985(11)	-691(6)	6960(6)	499(35)
C9	3241(12)	-1901(8)	5856(9)	665(28)
C10	3176(11)	-1299(8)	5202(8)	595(25)
N2	3622(7)	-1589(5)	6705(4)	365(29)
H1	3889(80)	-2082(55)	7192(55)	264(99) *
C11	84(7)	-343(5)	5344(5)	263(27)
C12	-330(13)	-1285(7)	5101(6)	572(38)
C13	-131(10)	-1882(6)	5797(7)	619(37)
C14	862(10)	-738(6)	6951(6)	426(4)
C15	706(11)	-79(5)	6302(6)	382(14)
N3	408(8)	-1623(5)	6677(5)	421(27)
H2	395(91)	-2050(65)	7040(65)	369(99) *

U_{eq}= (U_{11}+ U_{22}+ U_{33}+2U_{13} cos β) /3

*Isotropic atomic displacement parameter.

Table 3: Bond Length (Angstrom) and Angles (Deg.) with standard deviations in parenthesis for the Nitrate and Chloride complexes

(i)Coordination Polyhedron	
Pr—O_1 2.625(19)	Pr—Cl_1 2.787(2)
Pr---O_2 2.633(22)	Pr---Cl_2 2.819(2)
Pr---O_4 2.659(21)	Pr---Cl_3 2.916(1)
Pr---O_5 2.722(20)	Pr---OW_1 2.478(5)
Pr---O_7 2.744(21)	Pr---OW_2 2.457(5)
Pr---O_8 2.602(20)	Pr---OW_3 2.505(5)
Pr---OW_1 2.462(17)	Pr---OW_4 2.459(5)
Pr---OW_2 2.471(19)	
Pr---OW_3 2.455(21)	
Pr---OW_4 2.477(19)	

(ii)$4,4^{-}$ -bipyridyl molecules 				
Bond or Angle	Pyridine Rings		Pyridinium Rings	
	Range	Average(s.d.)	Range	Average(s.d.)
a	1.334-1.449	1.366(36)	1.311-1.340	1.325(12)
b	1.351-1.448	1.411(39)	1.363-1.393	1.379(14)
c	1.392-1.475	1.431(37)	1.354-1.414	1.381(12)
d	1.484-1.513	1.499(35)	1.444-1.512	1.478(12)
α	118.5-122.0	119.6(2.6)	120.0-122.7	120.9(1.1)
β	120.0-125.8	122.7(2.8)	118.3-124.3	120.6(0.9)
γ	114.9-117.6	116.5(2.6)	117.9-120.9	119.4(1.1)
δ	120.0-122.5	121.4(2.4)	117.3-119.8	118.3(0.8)

(iii)Hydrogen Bonds (Angstrom)	
Nitrate Complex	Chloride Complex
N_4—OW_2 2.730	N_1—Cl_4 3.503(II)
N_5---OW_4 2.777	N_3---Cl_4 3.068(III)
N_6---OW_1 2.640	OW1—Cl_4 3.081(II)
N_7---OW_3 2.717	OW_4—Cl_4 3.503

O_1---OW_5 2.828	N_1---Cl_5 3.074
O_2---OW_5 2.786	OW_2—Cl_5 3.098(III)
OW_4—OW_5 2.710	OW_3---Cl_5 3.246(I)
	N_2---Cl_6 3.157(III)
	N_3---Cl_6 3.541(III)
	OW_2—Cl_6 3.118(I)
	Symmetry(I)= -X, -Y, -Z
	(II)=-X,0.5+Y,0.5-Z
	(III)=X,0.5-Y,0.5+Z

The equations of the planes are expressed in direct space as:

PX+QY+RZ=S

Table 4: Least square planes and atomic deviations (Angstrom)
a-Nitrate complex

Plane (1):0.2251X+0.2471Y+0.9425Z=9.0221					
N_4	-0.0108	C_1	-0.0015	C_2	-0.0200
C_3	0.0269	C_4	-0.0100	C_5	0.0151
Plane (2): -0.1571X-0.1491Y+0.9763Z=3.7290					
N_5	-0.0440	C_6	-0.0077	C7	0.0039
C_8	0.0024	C_9	0.0006	C_{10}	0.0052
Plane (3):0.2043X+0.2395Y+0.9492Z=6.3454					
N_6	0.0291	C_{11}	0.0069	C_{12}	-0.0339
C_{13}	0.0181	C_{14}	-0.0611	C_{15}	0.0398
Plane (4): -0.1689X-0.1440Y+0.9751Z=4.0936					
N_7	0.0428	C_{16}	0.0015	C_{17}	-0.0111
C_{18}	0.0349	C_{19}	0.0322	C_{20}	-0.0131
Dihedral angles: Plane (1) – Plane (2) = 32.5^0 Plane (3) –Plane (4) = 31.1^0					

b-Chloride complex

Plane (1):0.9515X-0.2372Y-0.3618Z=0.6820					
N1	0.0281	C1	0.0230	C2	0.0039
C3	0.0246	C4	0.0017	C5	0.0225
Plane (2):0.9477X-0.2120Y-0.2387Z=1.6901					
N2	-0.0185	C6	0.0539	C7	0.0342
C8	0.0047	C9	0.0070	C10	0.0245
Plane (3): -0.8989X+0.2506Y+0.3593Z=3.0629					
N3	0.0182	C11	0.0115	C12	-0.0052
C13	-0.0100	C14	-0.0110	C15	-0.0182
Dihedral angles: Plane (1) – Plane (2) = 7.70 Plane (3) – Plane (4) =0.00 (inversion center)					

A perspective view of the coordination polyhedron of the nitrate compound, Figure 1, shows that the coordination number of Pr is ten comprising six oxygen atoms of three bidentate nitrate ligands with average bond length Pr-O(NO3) of 2.664Å, and four oxygen atoms of four water molecules with average bond length Pr-O (H2O) of 2.446Å.

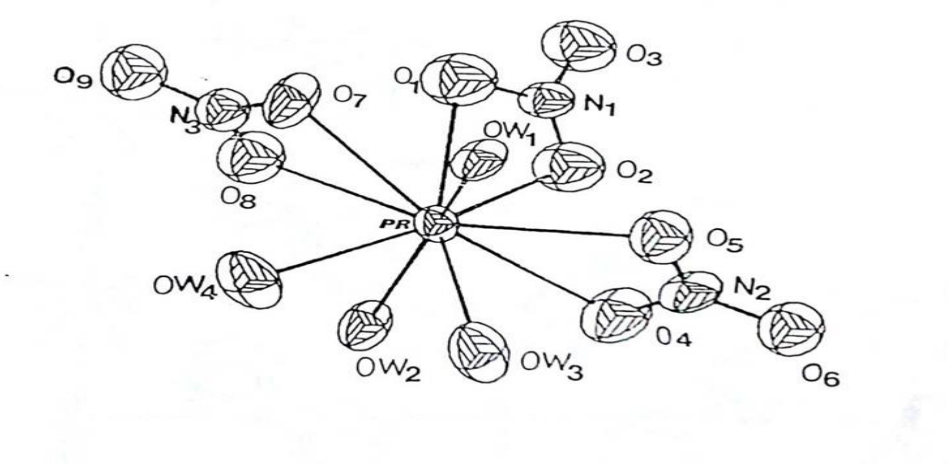


Figure 1: Perspective view of coordination sphere of Pr $(NO_3)_{3.}$ $(H_2O)_4$

A projection along the a-axis to the coordination polyhedron shows that the Pr (NO3)3 (H2O)4 molecule has an approximately C2 symmetry, Figure 2; in agreement with its Nd isomorph (Al-Rasoul, 1987) and with the crystal structure of the same molecular formula but ambiguous space group (Weakley 1989). However, in his work, Weakley used the Weissenberg photographs data for space group determination and suggested Pb21m, Pbm2, and Pbmm as possible space groups but all the attempts to solve the crystal structure in the above space groups were unsuccessful. Therefore, these unsuccessful attempts prompted Weakley to solve the structure using the space group reported previously (Al-Rasoul, 1987). The present investigation gives much clearer picture of the space group determination due to the oscillation, de-jong, and precession photographs data which was unambiguously showed the space group to be P212121 in similarity to the Nd-compound isomorph (Al-Rasoul, 1987).

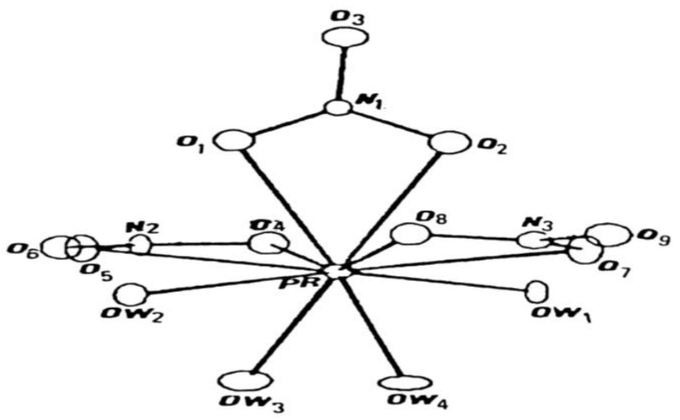


Figure 2: Coordination sphere of Pr(NO3)3(H2O)4 viewed a long a- axis

The nitrate groups in the coordination sphere around Pr seems to preserve planarity with an average N-O bond length 1.244Å (bond of chelating oxygen atoms), average terminal N-O bond length 1.224Å and an average interbond angles O –N – O 119.7°. These values are consistent with

The corresponding values were reported in the previous investigations. In Figure 3 which shows packing of unit cell contents viewed down C-axis, two independent 4-bipy molecules occupy general positions in the unit cell. The water molecule (OW5) and the nitrogen atoms of the 4-bipy molecules are involved in short interatomic contacts with ligand water molecules indicating a network of hydrogen bonds, able (3iii).

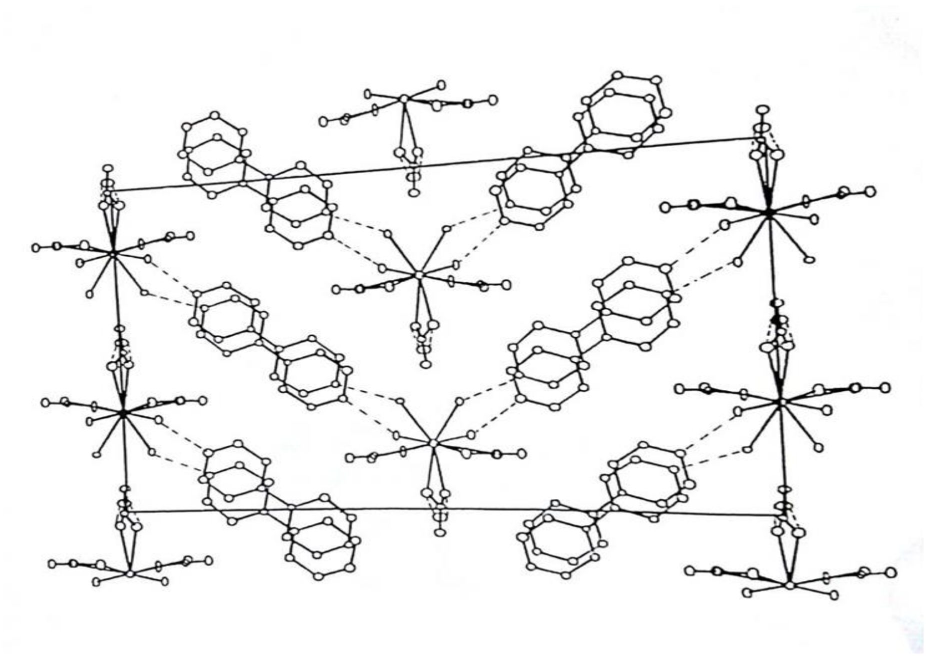


Figure 3 : Unit cell content of nitrate complex molecules viewed down c- axis. Dashed lines indicate hydrogen bonds

On the other hand, the coordination polyhedron of the chloride compound shown in Figure 4 imply that the coordination number of Pr is seven comprising three Cl atoms with an average bond length Pr – Cl of 2.841Å and four water molecules with an average Pr – O (H2O) bond length of 2.578Å. These values were consistent with 2.909Å and 2.518Å, respectively, obtained for the structure [PrCl3(EO4)]2 (Rogers 1992). In Figure 5 which shows the packing of the unit cell contents viewed down C-axis, two independent 4-bipy molecules were observed, one laying on a general position and the other on crystal inversion center. Three uncoordinated Cl ions were found in the structure laying in general positions in the unit cell. The high resolution of the intensity data allowed a successful location of hydrogen atoms which strongly imply the protonation of the 4 – bipy molecule. The (Cl3)3- which acts as a counter ion of the (4 – bipy H3)3+ enter into hydrogen bonds with N1, N2 of the 4 – bipyridinum and N3 and N'3 of the 4 – bipyridinum (Table 3 iii).

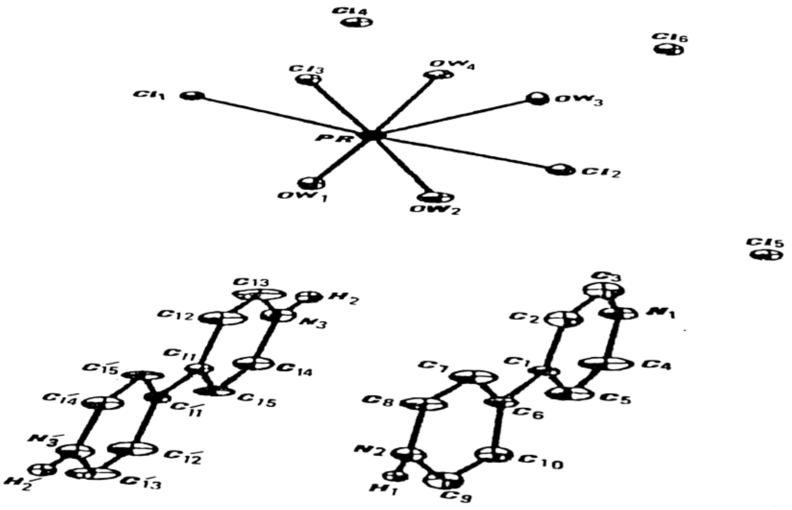


Figure 4: Perspective view of chloride complex molecules primed atoms related to unprimed atoms by inversion center

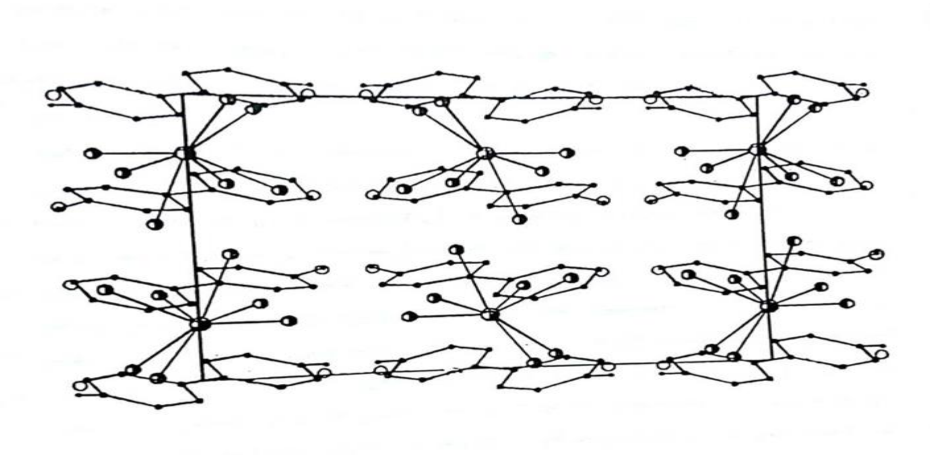


Figure 5: Unit cell content of chloride complex molecules viewed down c-axis. Hydrogen bonds omitted for clarity

However, Bukowska and Tosik (Bukowska, 1982) investigated the crystal structure of gadolinium and Yettrium chloride-4bipy complexes and reported that the Gd and Y cations are eight coordinated with eight water molecules. Moreover,they reported the structures to be tetragonal(space group P4-c2) and orthorhombic(space group Pcca) respectively. In addition, very recently many reports appeared in the literature investigating the complexes of Praseodymium chloride with 4-bipy (Matthes, 2013; Matthes 2015). The authors used the anhydrous solvothermal reaction as preparation method (Matthes, 2013) and found that all the structures to be binuclear or higher, and the crystal structure systems are orthorhombic with space group Cmcm and the cation is eight coordinates by the chlorides and the ligands (Matthes, 2015).

The dimensions of the 4 – bipyridyl molecules in the nitrate and chloride compounds are summarized in Table (3ii). The bond length and angles were, generally, in agreement with the previous reported values (Al-Rasoul, 1987, Weakley, 1989, Ibrahim, 1993&1999). At the levels of the resolution achieved in the present study, there was no significant difference in the dimension of the protonated and unprotonated bipyridyl rings. In the nitrate compounds the bipyridyl rings were planar and rotated with respect to each other about the central bonds C1 – C6 and C11 – C16 by 32.5° and 31.1° respectively; whereas in the chloride compound the rings were rotated by 7.7° and 0.0°. The different dihedral angles between the pyridyl rings are appreciable and appear merely to reflect the requirements of crystal packing and are not correlated with the central C-C bond length. In the chloride compound, the dihedral angle is constrained to be zero for the 4-bipy molecules on inversion centers.

4. Conclusion

From the inspection of the previous studies and the results of the present work, it seems that several structural systems exhibited by hydrated adducts of 4-bipy and lanthanide nitrate and chloride. Although the preparation procedure is simply via slow evaporation method, the products are highly sensitive to the solvent composition.

The present investigation indicated unambiguously the space group of the Pr-nitrate-(4-bipy) complex to be P212121 by analyzing the data obtained from oscillation, de-jong, and precession x-ray cameras. This was in disagreement with the space group of the same molecular formula reported by Weakley using data from weissenberg x-ray photographs (Weakley 1989).

Moreover, the present study showed that the Pr-chloride-(4-bipy) complex is monoclinic with space group P21/c and the Pr ion is seven coordinates via three chlorides and four water molecules. The 4-bipy ligand in both crystals are shown to be uncoordinated to the central ion Pr but positioned in the unit cell through a net of hydrogen bonds.

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