

Crystal Structure of Hexakis(1,8-naphthyridine)praseodymium(III) Perchlorate

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Crystals of hexakis(1,8-naphthyridine)praseodymium(III) perchlorate, $(C_8H_6N_2)_6Pr(ClO_4)_3$, are monoclinic, with space group $P2_1/c$. The cell dimensions are $a = 13.748$ (3) Å, $b = 16.979$ (6) Å, $c = 22.949$ (8) Å, and $\beta = 107.34$ (1)°, $V = 5113.14$ Å³. With $Z = 4$ the density is calculated to be 1.5850 g cm⁻³ which compares to a density measured by flotation in a KI solution of 1.583 g cm⁻³. A total of 2263 intensities above background were collected with a scintillation counter automated diffractometer by the θ - 2θ scan method. The structure was refined by block-diagonal least-squares methods to a conventional R_F factor of 0.049 and a weighted residual R_{wF} of 0.063. Anisotropic thermal parameters were obtained only for the metal atom and perchlorate groups. All six naphthyridine rings act as bidentate ligands forming a distorted icosahedron of nitrogen atoms about the metal. Pr-N bond distances range from 2.735 (12) to 2.768 (11) Å. Distortion of the icosahedron results principally from the unequal lengths of the nitrogen-nitrogen interatomic distances. Those which occur within individual naphthyridine ring systems are short averaging 2.257 (12) Å while those between adjacent nitrogen atoms in two different naphthyridine rings range from 2.890 (16) to 3.195 (16) Å. The rings are also arranged such that a polyhedron is not formed.

Introduction

Recently Foster and Hendricker prepared complexes of the type $M(napy)_6(ClO_4)_3$ and $M(napy)_5(ClO_4)_3$ where $M = La-Pr$ for the former compounds and $Nd-Eu$ for the latter and $napy$ is 1,8-naphthyridine.² Spectroscopic data indicated that the naphthyridine ligands are bidentate making the complexes respectively 12- and 10-coordinate. Bidentate ligands with small "bite" are known to form complexes with high coordination number; for example, nitrate ion can form 8-coordinate complexes of first-row transition elements^{3,4} and 12-coordinate complexes of rare earth metals.⁵ Similarly, 1,8-naphthyridine has been shown to form 8-coordinate first-row transition metal complexes when prepared as perchlorates.⁶⁻⁹ However, 1,8-naphthyridine metal complexes are known where the ligand is monodentate.^{10,11} In addition bidentate bridging of two nickel atoms in $[Ni(napy)_4X_2]B \cdot (C_6H_5)_4$ has been reported.¹² In this complex the nickel atoms have an average oxidation state of 1.5. Because of the variety of ways in which 1,8-naphthyridine bonds to metals and because spectral assignments are not always reliable,¹³ it was deemed worthwhile to determine the crystal structure of a rare earth $(napy)_6$ complex in order to establish the coordination with certainty.

Experimental Section

Crystals were kindly supplied by Dr. D. G. Hendricker, who had earlier determined them to be hexakis(1,8-naphthyridine)praseodymium(III) perchlorate, $(C_8H_6N_2)_6Pr(ClO_4)_3$.² The crystal chosen for study was a rectangular platelet of dimensions 0.05 mm \times 0.16 mm \times 0.27 mm and was mounted in a thin-walled Lindemann glass capillary. Preliminary Weissenberg and precession photographs revealed the crystal to be monoclinic with space group $P2_1/c$; systematic absences were $h0l$ with l odd and $0k0$ with k odd. Unit cell dimensions were determined from 25 reflections whose angles were accurately measured with a CAD-4 four-circle automated diffractometer. The data were then subjected to a least-squares analysis which yielded the constants $a = 13.748$ (3) Å, $b = 16.979$ (6) Å, $c = 22.949$ (8) Å, and $\beta = 107.34$ (1)°, so that $V = 5113.1$ Å³. Assuming $Z = 4$ we calculate the density to be 1.585 g/cm³ (mol wt 1220.16). This compares to a measured density, determined by flotation in KI solutions, of 1.583 g/cm³.

Intensities were measured by the θ - 2θ scan technique at a takeoff angle of 4° using Mo $K\alpha$ radiation (λ 0.7107 Å). Scan rates varied from 5.3°/min for the strongest reflections to 0.53°/min for the weakest. The scan widths were also varied according to the formula $3(0.7 + 0.2 \tan \theta)^\circ$. The left and right background counts were obtained simultaneously with the peak scan, being counted as the initial and final 25% of the scan. During data collection two standard reflections of high and medium intensities were recorded every time

a set of 32 reflections was recorded. These were used to place the data on a common scale. The changes in intensities of the standards were random with maximum fluctuation of 4%. Of the 4411 reflections scanned out to $2\theta_{max} = 60^\circ$ in $hk(\pm l)$ zones, 2263 had intensities greater than or equal to 3σ where $\sigma = (TOTAL\ CTS + BKGD\ CTS)^{1/2}$. The data were corrected for Lorentz and double polarization effects but not for absorption. The linear absorption coefficient is 11.87 cm⁻¹ so that μR lies between 0.03 and 0.09 in the plate cross section. Thus, variations about a mean intensity value would be of the order of 5% which is considered to be acceptable without correction.

Solution and Refinement of the Structure. A three-dimensional Patterson function was computed which gave a simple, straightforward solution for the position of the praseodymium atom. Successive Fourier and difference maps revealed the positions of all of the carbon, nitrogen, and chlorine atoms. All atoms were refined isotropically by block-diagonal methods to an R_F value of 0.084.¹³ A difference map prepared at this stage of the refinement showed that the oxygen atom electron densities were badly smeared out due to high thermal motion. The best results were obtained by placing oxygen atoms at the peak maxima and allowing them to refine with assignment of large anisotropic thermal parameters. This procedure duplicated the actual motion of the perchlorate groups to some extent but not completely. The motion is one of partial rotation or rocking about the chlorine atoms, a motion which our programs could not duplicate precisely. Most of the hydrogens were located in the difference map. However, their positions were idealized at distances of 0.95 Å from the carbon atoms and sp^2 geometry.¹⁴ Hydrogen atoms were assigned isotropic thermal parameters of 6 Å² in the refinement. Refinement was now continued with isotropic thermal parameters for all atoms except the metal and perchlorate groups which were assigned anisotropic temperature factors. After several more cycles the shifts in parameters were on the average about 0.1 their corresponding standard deviations and the refinement was considered to be complete. The final R_F was 0.049 and $R_{wF} = 0.063$, where $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights for each reflection given by $w = 1/|1 + [(|F_o| - P_1)/P_2]^2]$. The final values of P_1 and P_2 were 40 and 60, respectively.

A final difference map was featureless except for termination of series ripples about the metal atom and some residual density of less than 0.5 e/Å³ about the perchlorate groups. Neutral atom scattering factors for carbon, nitrogen, oxygen, and chlorine were taken from the compilation in ref 15 while that for Pr^{3+} was taken from the data of Cromer and Waber.¹⁶ Scattering factors for hydrogen were those of Stewart, Davidson, and Simpson.¹⁷ The final set of atomic coordinates and temperature parameters are given in Tables I and II for the heavy atoms and Table III for the hydrogen atoms. A table of final observed and calculated structure factors is available.¹⁸

Description of the Structure

Figure 1 provides a schematic of the praseodymium-naphthyridine complex ion and the numbering system used to identify the atoms. Each naphthyridine ring acts as a bidentate

Table I. Positional and Isotropic Thermal Parameters for the Nonhydrogen Atoms^a

Atom	x	y	z	B, Å ²	Atom	x	y	z	B, Å ²
Pr(1)	0.229 68 (7)	0.449 27 (5)	-0.242 73 (4)	3.39	N(32)	0.184 4 (9)	0.323 0 (7)	-0.180 7 (5)	4.9 (4)
Cl(11)	0.653 0 (3)	0.444 4 (3)	-0.399 4 (2)	5.92	C(32)	0.142 4 (12)	0.302 3 (9)	-0.138 9 (7)	5.4 (4)
O(11)	0.637 5 (22)	0.379 7 (9)	-0.435 5 (8)	14.4	C(33)	0.154 4 (13)	0.227 4 (10)	-0.110 0 (8)	5.8 (3)
O(12)	0.609 6 (15)	0.512 9 (10)	-0.430 0 (6)	11.3	C(34)	0.211 7 (15)	0.173 5 (11)	-0.126 6 (9)	7.1 (4)
O(13)	0.623 1 (15)	0.436 9 (9)	-0.348 6 (7)	10.8	C(35)	0.262 7 (11)	0.192 6 (9)	-0.170 7 (6)	4.5 (5)
O(14)	-0.245 0 (13)	0.458 5 (18)	-0.379 7 (13)	17.1	C(36)	0.327 8 (13)	0.142 7 (11)	-0.190 9 (8)	6.3 (4)
Cl(21)	0.729 4 (4)	0.612 2 (3)	-0.064 9 (2)	7.62	C(37)	0.370 8 (15)	0.167 1 (12)	-0.232 3 (8)	7.2 (3)
O(21)	0.667 2 (20)	0.551 8 (13)	-0.060 5 (10)	18.8	C(38)	0.349 8 (13)	0.244 3 (10)	-0.254 2 (7)	5.9 (4)
O(22)	0.701 2 (15)	0.644 8 (14)	-0.121 3 (8)	13.2	N(41)	0.303 7 (8)	0.536 4 (7)	-0.321 8 (5)	4.4 (3)
O(23)	0.706 7 (20)	0.664 9 (12)	-0.025 9 (9)	17.6	C(41)	0.307 2 (10)	0.479 7 (8)	-0.360 5 (6)	3.8 (3)
O(24)	-0.176 2 (14)	0.584 1 (16)	-0.043 4 (11)	17.2	N(42)	0.274 5 (10)	0.408 2 (8)	-0.347 5 (5)	5.3 (3)
Cl(31)	-0.109 9 (4)	0.273 5 (3)	-0.076 1 (2)	7.1	C(42)	0.271 0 (13)	0.347 2 (10)	-0.383 1 (8)	6.3 (3)
O(31)	-0.167 5 (19)	0.239 9 (16)	-0.128 5 (9)	16.4	C(43)	0.305 7 (14)	0.355 2 (11)	-0.436 3 (8)	6.5 (4)
O(32)	-0.073 1 (19)	0.336 6 (11)	-0.094 6 (15)	18.0	C(44)	0.343 7 (13)	0.425 4 (10)	-0.449 3 (8)	6.2 (4)
O(33)	-0.171 4 (13)	0.293 7 (11)	-0.043 2 (6)	9.8	C(45)	0.345 1 (12)	0.491 9 (10)	-0.412 8 (7)	5.5 (4)
O(34)	-0.037 9 (15)	0.218 8 (12)	-0.046 7 (9)	10.8	C(46)	0.376 5 (13)	0.566 1 (11)	-0.421 1 (7)	6.2 (4)
N(11)	0.043 1 (8)	0.469 4 (6)	-0.224 2 (5)	4.0 (3)	C(47)	0.370 4 (13)	0.621 8 (11)	-0.383 7 (8)	6.6 (4)
C(11)	0.073 5 (10)	0.492 6 (9)	-0.166 9 (6)	4.2 (3)	C(48)	0.332 4 (12)	0.606 9 (10)	-0.331 8 (7)	5.2 (4)
N(12)	0.177 2 (9)	0.498 3 (7)	-0.142 2 (5)	4.7 (3)	N(51)	0.340 1 (9)	0.577 9 (7)	-0.188 9 (5)	4.5 (3)
C(12)	0.215 0 (12)	0.525 6 (9)	-0.086 7 (7)	5.4 (3)	C(51)	0.268 0 (11)	0.634 9 (9)	-0.207 1 (7)	4.3 (3)
C(13)	0.150 8 (12)	0.549 7 (11)	-0.049 7 (7)	5.8 (4)	N(52)	0.176 1 (9)	0.604 6 (7)	-0.240 7 (5)	4.1 (2)
C(14)	0.049 1 (12)	0.546 9 (11)	-0.074 3 (7)	6.0 (3)	C(52)	0.100 9 (12)	0.655 7 (9)	-0.260 8 (7)	5.0 (4)
C(15)	0.004 4 (12)	0.521 3 (9)	-0.134 6 (7)	5.6 (3)	C(53)	0.111 2 (13)	0.736 6 (10)	-0.249 9 (7)	5.7 (4)
C(16)	-0.101 0 (14)	0.516 9 (10)	-0.167 9 (8)	6.8 (3)	C(54)	0.200 0 (13)	0.766 1 (11)	-0.215 1 (8)	6.3 (4)
C(17)	-0.129 8 (14)	0.493 2 (11)	-0.225 3 (8)	6.6 (3)	C(55)	0.283 1 (13)	0.715 4 (10)	-0.193 3 (8)	5.9 (4)
C(18)	-0.059 1 (12)	0.467 3 (9)	-0.254 5 (7)	5.1 (3)	C(56)	0.383 5 (14)	0.736 8 (11)	-0.159 7 (8)	6.7 (4)
N(21)	0.081 8 (9)	0.483 5 (7)	-0.349 5 (5)	4.7 (3)	C(57)	0.455 4 (13)	0.681 3 (10)	-0.139 9 (7)	5.9 (4)
N(22)	0.083 9 (9)	0.357 4 (7)	-0.321 4 (5)	5.0 (3)	C(58)	0.433 3 (13)	0.601 2 (10)	-0.155 0 (7)	5.5 (4)
C(21)	0.038 3 (12)	0.410 7 (9)	-0.362 0 (7)	4.8 (3)	N(61)	0.436 6 (9)	0.427 3 (6)	-0.219 9 (5)	4.2 (3)
C(22)	0.052 9 (14)	0.282 3 (10)	-0.332 3 (8)	6.4 (3)	C(61)	0.463 9 (11)	0.405 3 (9)	-0.161 9 (6)	3.9 (3)
C(23)	-0.030 9 (15)	0.263 6 (12)	-0.382 8 (9)	7.9 (5)	N(62)	0.381 3 (8)	0.407 3 (7)	-0.137 8 (5)	3.9 (2)
C(24)	-0.079 9 (14)	0.318 6 (11)	-0.422 6 (8)	7.1 (5)	C(62)	0.400 0 (12)	0.384 6 (9)	-0.080 4 (7)	5.1 (4)
C(25)	-0.044 9 (12)	0.397 5 (9)	-0.414 8 (7)	5.4 (4)	C(63)	0.495 7 (14)	0.359 3 (11)	-0.043 5 (8)	6.7 (4)
C(26)	-0.085 2 (14)	0.461 7 (11)	-0.450 5 (8)	6.7 (4)	C(64)	0.573 2 (14)	0.358 9 (11)	-0.066 0 (8)	6.8 (4)
C(27)	-0.044 0 (14)	0.532 8 (11)	-0.439 1 (8)	6.8 (4)	C(65)	0.562 3 (12)	0.383 3 (9)	-0.125 9 (8)	5.4 (4)
C(28)	0.041 1 (12)	0.541 0 (10)	-0.387 5 (7)	5.2 (3)	C(66)	0.635 1 (14)	0.383 6 (11)	-0.156 6 (8)	6.8 (4)
N(31)	0.290 4 (9)	0.294 7 (7)	-0.237 0 (5)	4.8 (3)	C(67)	0.610 6 (14)	0.407 3 (11)	-0.214 7 (8)	6.8 (4)
C(31)	0.244 2 (11)	0.267 8 (9)	-0.195 6 (6)	4.4 (3)	C(68)	0.507 8 (12)	0.427 6 (9)	-0.248 3 (7)	4.9 (4)

^a Esd's for the Pr, Cl, and O atoms are not given in this table since their anisotropic thermal parameters are given in Table II.

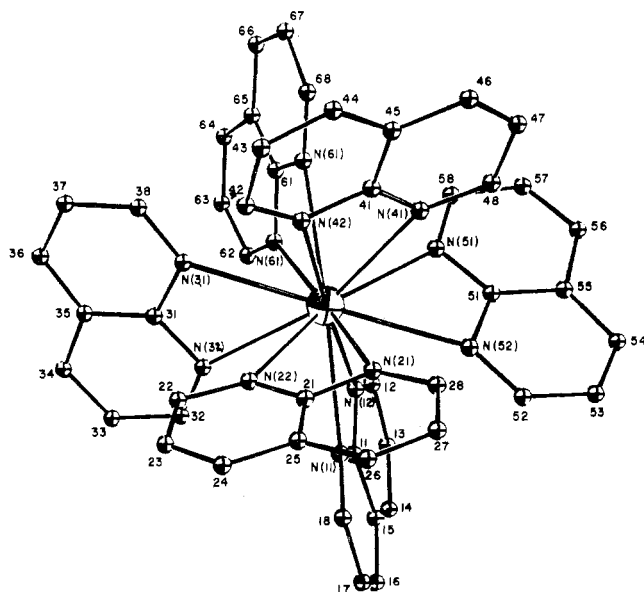


Figure 1. ORTEP drawing²² of the complex hexakis(1,8-naphthyridine)praseodymium(III) ion showing the numbering scheme used in the tables.

ligand making the praseodymium atom 12-coordinate. The coordination geometry is shown in Figures 2 and 3 while the bond distances and angles are given in Table IV. Metal-nitrogen distances range from 2.735 (12) to 2.768 (11) Å with an average of 2.748 (9) Å.¹⁹ The coordination polyhedron is that of a distorted icosahedron as seen in Figures 2 and 3.

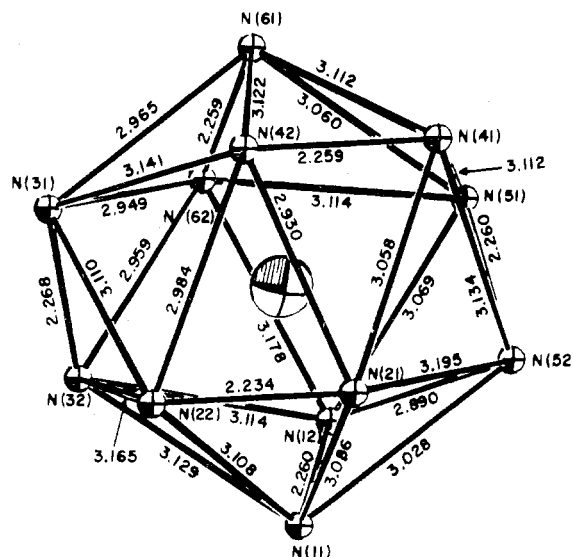


Figure 2. ORTEP drawing of icosahedral coordination sphere formed by the nitrogen atoms bonded to praseodymium in the hexakis(1,8-naphthyridine)praseodymium(III) ion.

However the arrangement of the rings is not that of a patchohedron.⁵ An ideal patchohedron would have T_h symmetry and four 3 axes. That this is not the case is seen in Figure 3.

Each ring makes an angle of about 48° with the metal atom, the average value for the six rings being 48.5 (3)°. This value is considerably smaller than the same angle in the iron(II)-naphthyridine complex,⁶ 56.6 (1.2)°, and undoubtedly derives

Table II. Anisotropic Thermal Parameters ($\times 10^4$) for Praseodymium and Perchlorate Group Atoms^a

Atom	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Pr(1)	52.6 (5)	34.9 (3)	20.6 (2)	1.9 (12)	30.0 (5)	-0.3 (7)
Cl(11)	97 (3)	48 (2)	21 (1)	-15 (5)	42 (3)	7 (3)
O(11)	567 (44)	63 (8)	50 (5)	-166 (31)	208 (26)	-52 (11)
O(12)	287 (24)	106 (10)	38 (4)	35 (25)	89 (17)	60 (11)
O(13)	305 (24)	72 (8)	53 (5)	18 (23)	189 (19)	17 (12)
O(14)	91 (13)	259 (25)	135 (12)	-6 (33)	96 (21)	-78 (20)
Cl(21)	101 (4)	68 (3)	36 (1)	43 (6)	44 (4)	10 (3)
O(21)	326 (31)	123 (14)	82 (8)	-133 (37)	-114 (27)	55 (9)
O(22)	219 (21)	188 (18)	56 (6)	113 (33)	112 (18)	83 (17)
O(23)	441 (39)	112 (12)	88 (8)	-23 (35)	318 (33)	-24 (17)
O(24)	126 (15)	271 (25)	98 (9)	194 (32)	98 (20)	181 (25)
Cl(31)	107 (4)	59 (2)	35 (1)	28 (5)	57 (4)	-7 (3)
O(31)	340 (31)	190 (19)	58 (7)	44 (41)	115 (24)	-67 (19)
O(32)	264 (28)	68 (19)	195 (17)	-11 (26)	246 (37)	76 (21)
O(33)	200 (16)	146 (13)	42 (4)	228 (26)	97 (15)	29 (12)
O(34)	222 (21)	140 (13)	84 (7)	210 (28)	174 (21)	91 (16)

^a The anisotropic thermal motion factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Hydrogen Atom Positional Parameters

Atom	x	y	z
H(12)	0.2980	0.5318	-0.0683
H(13)	0.1851	0.5690	-0.0022
H(14)	-0.0007	0.5663	-0.0468
H(16)	-0.1592	0.5340	-0.1453
H(17)	-0.2114	0.4935	-0.2518
H(18)	-0.0848	0.4456	-0.3013
H(22)	0.0923	0.2348	-0.3017
H(23)	-0.0595	0.2034	-0.3894
H(24)	-0.1458	0.3028	-0.4610
H(26)	-0.1552	0.4540	-0.4896
H(27)	-0.0751	0.5831	-0.4691
H(28)	0.0762	0.6008	-0.3768
H(32)	0.0950	0.3473	-0.1249
H(33)	0.1172	0.2145	-0.0747
H(34)	0.2211	0.1126	-0.1066
H(36)	0.3340	0.0832	-0.1766
H(37)	0.4187	0.1275	-0.2499
H(38)	0.3874	0.2653	-0.2880
H(42)	0.2415	0.2898	-0.3719
H(43)	0.3037	0.3045	-0.4666
H(44)	0.3727	0.4305	-0.4890
H(46)	0.4089	0.5782	-0.4588
H(47)	0.3956	0.6824	-0.3915
H(48)	0.3292	0.6558	-0.3006
H(52)	0.0250	0.6348	-0.2887
H(53)	0.0459	0.7757	-0.2693
H(54)	0.2080	0.8301	-0.2039
H(56)	0.4036	0.7998	-0.1484
H(57)	0.5323	0.6985	-0.1119
H(58)	0.4935	0.5567	-0.1386
H(62)	0.3364	0.3850	-0.0607
H(63)	0.5054	0.3411	0.0040
H(64)	0.6490	0.3394	-0.0364
H(66)	0.7150	0.3647	-0.1325
H(67)	0.6709	0.4128	-0.2375
H(68)	0.4871	0.4414	-0.2974

from the much longer Pr-N bond distance. Both metal-nitrogen bonds, formed by each bidentate ligand, are equal within two standard deviations. As a result the angles subtended at the nitrogen atoms are also nearly equal. This differs from the situation in the iron(II)-naphthyridine complex where three of the ligands formed one short and one long metal-nitrogen bond.

The distortion of the icosahedral symmetry arises from the extreme shortness of the N-C-N bite and the particular mode of bidentate bonding. The average N-C-N bond angle is $113(1)^\circ$ and the average N-N distance $2.257(12) \text{ \AA}$. This angle is smaller than the corresponding angle in the uncoordinated ligand.²⁰ Contraction of the angle upon formation of a four-membered ring seems to be a common occurrence.^{6,21} Nitrogen-nitrogen distances between adjacent nitrogen atoms

Table IV. Interatomic Distances (Å) and Angles (deg) for the Praseodymium-Naphthyridine Complex Ion

Distances			
Pr-N(11)	2.743 (12)	Pr-N(41)	2.758 (12)
Pr-N(12)	2.743 (12)	Pr-N(42)	2.744 (12)
Pr-N(21)	2.739 (12)	Pr-N(51)	2.735 (12)
Pr-N(22)	2.748 (12)	Pr-N(52)	2.743 (12)
Pr-N(31)	2.748 (12)	Pr-N(61)	2.760 (12)
Pr-N(32)	2.746 (12)	Pr-N(62)	2.768 (11)
Angles			
N(11)-Pr-N(12) ^a	48.7 (3)	N(12)-Pr-N(21)	112.1 (4)
N(11)-Pr-N(21)	68.5 (3)	N(12)-Pr-N(22)	113.7 (4)
N(11)-Pr-N(22)	68.9 (3)	N(12)-Pr-N(31)	113.7 (4)
N(11)-Pr-N(31)	113.4 (3)	N(12)-Pr-N(32)	69.1 (4)
N(11)-Pr-N(32)	69.5 (3)	N(12)-Pr-N(41)	129.1 (4)
N(11)-Pr-N(41)	125.5 (3)	N(12)-Pr-N(42)	176.2 (4)
N(11)-Pr-N(42)	129.2 (4)	N(12)-Pr-N(51)	68.2 (4)
N(11)-Pr-N(51)	104.4 (3)	N(12)-Pr-N(52)	63.6 (3)
N(11)-Pr-N(52)	67.0 (3)	N(12)-Pr-N(61)	113.3 (3)
N(11)-Pr-N(61)	161.0 (3)	N(12)-Pr-N(62)	70.4 (4)
N(11)-Pr-N(62)	113.2 (3)		
		Range ^b	Average
Pr-N(11)-C(11)	99.2 (9)	98.5 (8)-101.3 (9)	99.5 (1.0)
Pr-N(12)-C(11)	97.7 (9)	97.7 (9)-100.0 (9)	98.9 (8)
Naphthyridine Ring Distances			
	Ring 1	Range	Average
N(11)-C(11)	1.315 (17)	1.315-1.370	1.343 (25)
N(12)-C(11)	1.372 (19)	1.315-1.404	1.362 (29)
N(11)-C(18)	1.371 (19)	1.303-1.371	1.331 (24)
N(12)-C(12)	1.309 (19)	1.306-1.344	1.319 (14)
C(12)-C(13)	1.455 (24)	1.396-1.455	1.421 (21)
C(13)-C(14)	1.343 (24)	1.315-1.370	1.340 (18)
C(14)-C(15)	1.405 (23)	1.398-1.430	1.408 (12)
C(15)-C(16)	1.424 (26)	1.364-1.424	1.395 (23)
C(16)-C(17)	1.321 (25)	1.296-1.343	1.325 (16)
C(17)-C(18)	1.404 (25)	1.401-1.458	1.419 (23)
C(11)-C(15)	1.452 (23)	1.391-1.458	1.422 (26)

^a N-Pr-N angles are given for N(11) and N(12) only. However, each naphthyridine ring forms a similar set of corresponding angles to within 1° of those listed. ^b The entries listed under "range" are the high and low values for these angles in all six naphthyridine rings.

not in the same fused-ring system are considerably larger than those fixed by the fused-ring system, ranging from $2.890(16) \text{ \AA}$ for N(12)-N(52) to $3.195(16) \text{ \AA}$ for N(21)-N(52). This produces two kinds of triangles in the icosahedron, those containing two long sides and one short side (almost isosceles) and those with three almost equal sides (equilateral). There are a total of twelve isosceles triangles and eight equilateral. The groupings of five each at the top and bottom contain three isosceles and two equilateral while the central group of 10

Table V. Mean Plane Equations for the Naphthyrindine Rings and Deviations (Å) of Atoms from the Plane

Ring	Equation	χ^2
I [N(11)-N(12)]	$0.1356x + 0.9319y - 0.3364z = 9.3847$	44.0
II [N(21)-N(22)]	$0.8189x - 0.1877y - 0.5424z = 5.4775$	32.7
III [N(31)-N(32)]	$-0.5962x - 0.3375y - 0.7285z = 1.2373$	12.0
IV [N(41)-N(42)]	$-0.7953x + 0.2327y - 0.5597z = 1.0041$	13.5
V [N(51)-N(52)]	$0.5321x + 0.1304y - 0.8366z = 7.9144$	8.2
VI [N(61)-N(62)]	$-0.1329x - 0.9470y - 0.2924z = -6.4682$	14.5

Ring I	Ring II	Ring III
N(11) -0.017 (10)	N(21) 0.013 (12)	N(31) -0.017 (12)
N(12) 0.009 (12)	N(22) -0.052 (13)	N(32) 0.022 (12)
C(11) -0.070 (15)	C(21) -0.027 (16)	C(31) 0.024 (15)
C(12) 0.051 (16)	C(22) 0.029 (19)	C(32) -0.012 (16)
C(13) 0.006 (18)	C(23) 0.027 (21)	C(33) -0.025 (17)
C(14) -0.023 (19)	C(24) -0.003 (19)	C(34) 0.012 (19)
C(15) -0.012 (16)	C(25) 0.003 (17)	C(35) 0.008 (15)
C(16) -0.001 (19)	C(26) -0.031 (19)	C(36) 0.000 (17)
C(17) 0.046 (19)	C(27) 0.005 (19)	C(37) -0.001 (19)
C(18) 0.010 (15)	C(28) 0.036 (16)	C(38) -0.011 (17)

Ring IV	Ring V	Ring VI
N(41) -0.011 (12)	N(51) 0.002 (12)	N(61) 0.009 (11)
N(42) -0.023 (13)	N(52) -0.000 (11)	N(62) -0.020 (11)
C(42) -0.009 (14)	C(51) 0.001 (15)	C(62) -0.006 (14)
C(42) 0.017 (19)	C(52) 0.005 (15)	C(62) -0.005 (16)
C(43) 0.032 (19)	C(53) 0.018 (17)	C(63) 0.024 (19)
C(44) -0.018 (17)	C(54) -0.031 (17)	C(64) -0.013 (19)
C(45) -0.018 (18)	C(55) -0.013 (17)	C(65) -0.030 (17)
C(46) -0.012 (18)	C(56) 0.030 (18)	C(66) 0.001 (19)
C(47) 0.020 (19)	C(57) -0.001 (17)	C(67) -0.017 (19)
C(48) 0.022 (17)	C(58) -0.010 (17)	C(68) 0.030 (15)

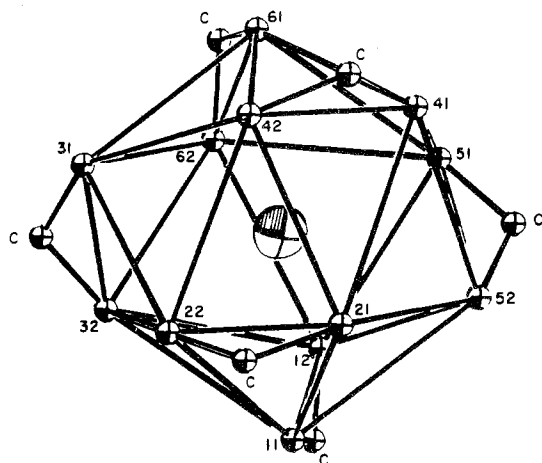
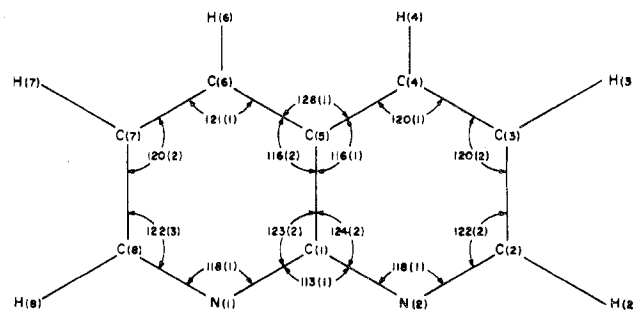


Figure 3. Same drawing as Figure 2 but including the N-N bridging carbon atoms.

contain six isosceles and four equilateral. In the central grouping the arrangement is i, i, e, i, i, e, i, i, e, e (i = isosceles, e = equilateral). This unsymmetrical arrangement of ligands destroys the $\bar{3}$ axis as well as the $\bar{5}$ symmetry of the icosahedron. In particular, the rings containing N(31), N(32), and N(51)-N(52) bridge the pentagons formed by N(31), N(42), N(41), N(51), N(62) and by N(32), N(22), N(21), N(52), N(12) whereas in the polyhedron these fused-ring nitrogens would belong to only one of these pentagons. Since each of the pentagons contains only one side formed by the nitrogens of a fused-ring system, the other four sides are considerably longer again causing severe distortion. This is evident in Figures 2 and 3 where the pentagons show up as neither planar nor regular. The only symmetry ascribable to the polyhedron is a pseudo-twofold axis which bisects the edges defined by N(42)-N(21) and N(12)-N(62). In this respect it is a unique 12-coordinate complex.

In Table IV we have listed the observed bond distances for naphthyrindine ring 1 which is the one containing N(11) and N(12). In the column next to these values are listed the ranges

Figure 4. Averaged bond angles for the six naphthyrindine rings.¹⁹ N(1), N(2) correspond to the N(11), N(21) etc. positions in the six rings and similarly for the other atoms.

of the corresponding bond distances for all six rings, and in the last column the averages. These averages conform to the bond lengths expected for such systems.^{6,20} The bond angles are shown in Figure 4 as averages for all six ring systems. The esd's for individual values lie between 1 and 2°. Comparison of these angles with those of the uncoordinated ligand²⁰ show a slight decrease in the N-C-N bond angle with concomitant increase in the opposite exterior angle C(4)-C(5)-C(6) over the corresponding angles in the free ligand. The adjacent interior angles increase and decrease, respectively, to compensate for these changes. A similar distortion of the rings was observed with the iron-naphthyrindine complex. Thus, while the errors in the bond angles of the individual coordinated ligands are large enough to negate such a conclusion, the persistent observance of this effect makes it appear that this decrease in the N-C-N angle on coordination is real.

The ligands are relatively planar as shown by the mean plane equations and deviations therefrom in Table V. Almost all of the deviations are within 1-3 σ from the plane. The uncoordinated ligand was shown to be nonplanar whereas coordination of the ligand in the iron(II) complex forced the rings to become planar. The same effect appears to hold for the praseodymium complex.

The packing within the unit cell is shown in Figure 5. Praseodymium-naphthyrindine complex ions are positioned on

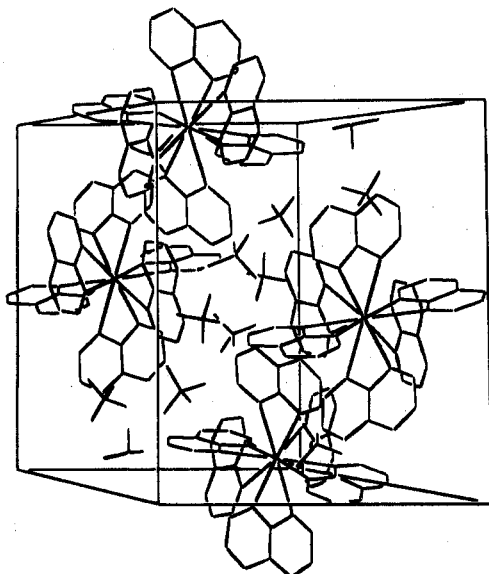


Figure 5. Packing diagram for hexakis(1,8-naphthyridine)praseodymium(III) perchlorate.

Table VI. Bond Lengths (Å) and Angles (deg) of the Perchlorate Groups

Distances			
Cl(11)–O(11)	1.353 (17)	Cl(21)–O(23)	1.366 (23)
Cl(11)–O(12)	1.397 (18)	Cl(21)–O(24)	1.331 (22)
Cl(11)–O(13)	1.354 (17)	Cl(31)–O(31)	1.353 (23)
Cl(11)–O(14)	1.360 (22)	Cl(31)–O(32)	1.309 (23)
Cl(21)–O(21)	1.358 (26)	Cl(31)–O(33)	1.335 (18)
Cl(21)–O(22)	1.354 (19)	Cl(31)–O(34)	1.377 (21)
Angles			
O(11)–Cl(11)–O(12)	114 (1)	O(22)–Cl(21)–O(23)	108 (1)
O(11)–Cl(11)–O(13)	115 (1)	O(22)–Cl(21)–O(24)	118 (1)
O(11)–Cl(11)–O(14)	108 (1)	O(23)–Cl(21)–O(24)	112 (1)
O(12)–Cl(11)–O(13)	109 (1)	O(31)–Cl(31)–O(32)	104 (1)
O(12)–Cl(11)–O(14)	106 (1)	O(31)–Cl(31)–O(33)	108 (1)
O(13)–Cl(11)–O(14)	106 (1)	O(31)–Cl(31)–O(34)	107 (1)
O(21)–Cl(21)–O(22)	112 (1)	O(32)–Cl(31)–O(33)	110 (1)
O(21)–Cl(21)–O(23)	100 (1)	O(32)–Cl(31)–O(34)	115 (1)
O(21)–Cl(21)–O(24)		O(33)–Cl(31)–O(34)	112 (1)

either side of the 110 planes in groups of two. Each grouping is surrounded on four sides by perchlorate ions. On the other two sides complex ions are near neighbors but there are no short contacts between them. The perchlorate groups are far from the centers of charge. As a result they undergo high

thermal motion similar to that observed in the iron(II) complex.⁶ Bond distances and angles for the perchlorate groups are listed in Table VI. It was shown previously that the observed bond lengths are considerably shortened as a result of the thermal motion.⁶

The praseodymium–nitrogen bond lengths reported here are about 0.1 Å longer than those in the chloropentaquaterpyridylpraseodymium(III) ion [2.625 (3) and 2.635 (4) Å].²³ However, an increase of about this magnitude is to be expected in going from an 8- to a 12-coordinate bonding situation.

Registry No. $(C_8H_6N_2)_6Pr(ClO_4)_3$, 39334-34-4.

Supplementary Material Available: Listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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