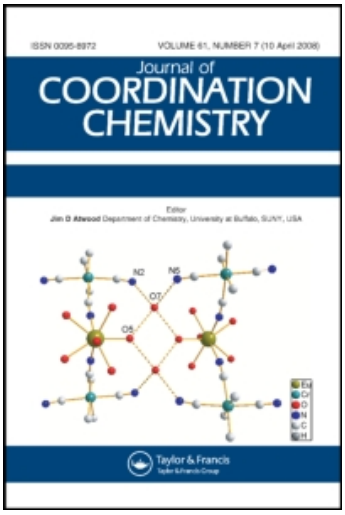

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Structure of a 1,8-Naphthyridine-N-Monoxide Complex with Neodymium Perchlorate

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To cite this Article Xinmin, Gan , Xin, Wang , Ning, Tang , Minyu, Tan , Kaibei, Yu and Zhongyuan, Zhou(1990) 'Synthesis and Structure of a 1,8-Naphthyridine-N-Monoxide Complex with Neodymium Perchlorate', Journal of Coordination Chemistry, 22: 4, 337 — 344
To link to this Article: DOI: 10.1080/00958979009408234
URL: http://dx.doi.org/10.1080/00958979009408234

J. Coord. Chem. 1991, Vol. 22. pp. 337-344
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NOTE

SYNTHESIS AND STRUCTURE OF A 1,8-NAPHTHYRIDINE-*N*-MONOXIDE COMPLEX WITH NEODYMIUM PERCHLORATE

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(Received February 21, 1990; in final form October 15, 1990)

The complex $Nd(napyo)_4(ClO_4)_3$ was formed by the reaction of neodymium perchlorate with 1,8-naphthyridine-*N*-monoxide (napyo) in methanol. The complex crystallizes in the monoclinic system, space group $C2/c$ with $Z = 12$. Lattice parameters are $a = 29.026(6)$, $b = 10.480(2)$, $c = 37.530(8)$ Å, $\beta = 100.97(1)°$, $V = 11208(4)$ Å^3, $Dc = 1.83\,gcm^{-3}$, $Do = 1.82\,gcm^{-3}$, $\mu = 11.48\,cm^{-1}$ (MoKα), $F(000) = 6516$. The structure was solved and refined to $R = 0.067$ for 6441 independent reflections with $I \geqslant 3\sigma(I)$. The compound contains two types of complex cation; $[Nd(napyo)_4]^{3+}$, with C_2 symmetry, and $[Nd(napyo)_4OClO_3]^{2+}$ with C_1 symmetry. The average Nd-N and Nd-O bond lengths are 2.610 Å and 2.383 Å for $[Nd(napyo)_4]^{3+}$ with an 8-coordinate Nd^{3+} ion and 2.638 Å and 2.464 Å for $[Nd(napyo)_4OClO_3]^{2+}$ with a 9-coordinate Nd^{3+} ion, respectively.

Keywords: Neodymium perchlorate, 1,8-naphthyridine-*N*-monoxide, complex X-ray structure

INTRODUCTION

Naphthyridine chemistry has long been an active research field.[1-4] Over the last twenty years, many metal complexes of 1,8-naphthyridine and its derivatives have been synthesized and characterized.[5-8] However, studies of metal complexes of 1,8-naphthyridine-*N*-monoxide (napyo) have only appeared recently.[9,10] As an extension to our previous work with napyo, we have now synthesized a series of complexes of napyo with lanthanide ions. Here we present results on the synthesis and structure of a complex of 1,8-naphthyridine-*N*-monoxide with neodymium perchlorate.

EXPERIMENTAL

Preparation

Neodymium perchlorate hexahydrate (0.110 g, 0.2 mmol) was added to a solution of napyo[2] (0.117 g, 0.8 mmol) in methanol (50 cm^3). The solution was placed in a

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TABLE I
Final Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^3$).

Atom	*x/a*	*y/b*	*z/c*	*U*[a]
Nd(1)	5000	12927(1)	2500	44(1)
Nd(2)	3337(1)	9004(1)	5799(1)	49(1)
Cl(1)	3535(1)	12743(3)	5847(1)	69(1)
Cl(2)	2520(1)	2379(3)	2114(1)	57(1)
Cl(3)	973(1)	7595(3)	1242(1)	61(1)
Cl(4)	726(1)	2672(3)	520(1)	86(1)
Cl(5)	0	2548(5)	2500	82(2)
O(1)	4682(2)	14055(7)	1962(2)	54(2)
O(2)	4263(2)	11831(7)	2372(2)	54(2)
O(3)	2859(2)	9682(8)	5238(2)	61(3)
O(4)	3754(2)	9752(8)	6369(2)	58(3)
O(5)	2597(2)	7875(8)	5673(2)	60(3)
O(6)	4109(2)	8104(8)	5927(2)	61(3)
O(7)	3272(2)	11597(6)	5786(2)	71(3)
O(8)	3289(3)	13795(8)	5685(3)	212(6)
O(9)	3663(4)	12965(10)	6227(2)	193(6)
O(10)	3957(3)	12589(11)	5713(3)	309(6)
O(11)	2656(3)	3535(6)	2291(2)	112(4)
O(12)	2868(2)	1968(7)	1918(2)	78(3)
O(13)	2455(3)	1413(6)	2364(2)	92(4)
O(14)	2094(2)	2566(9)	1860(2)	114(4)
O(15)	614(2)	7853(8)	1443(2)	90(4)
O(16)	1036(3)	8675(6)	1031(2)	83(3)
O(17)	1392(2)	7315(9)	1488(3)	181(5)
O(18)	841(4)	6529(7)	1018(2)	153(5)
O(19)	1006(3)	3188(9)	284(2)	116(4)
O(20)	1036(4)	1991(14)	798(3)	313(6)
O(21)	396(4)	1833(11)	336(4)	272(6)
O(22)	511(4)	3656(8)	681(3)	174(5)
O(23)	−347(4)	1746(9)	2295(4)	247(7)
O(24)	203(7)	3307(9)	2265(4)	435(8)
O(23')	347(4)	1741(9)	2705(4)	500(8)
O(24')	−203(7)	3301(9)	2735(4)	358(8)
N(1)	4919(3)	14846(8)	1788(2)	47(3)
N(2)	5587(3)	14239(8)	2188(2)	48(3)
N(3)	4109(3)	11146(8)	2627(2)	45(3)
N(4)	4861(3)	11226(8)	2968(2)	48(3)
N(5)	3009(3)	10505(9)	5008(2)	55(3)
N(6)	3766(3)	10039(9)	5304(2)	56(3)
N(7)	3569(3)	10470(9)	6598(2)	55(3)
N(8)	2839(3)	9903(9)	6266(2)	54(3)
N(9)	2486(3)	6939(9)	5886(2)	52(3)
N(10)	3246(3)	6998(9)	6197(2)	52(3)
N(11)	4250(3)	7167(9)	5731(2)	53(3)
N(12)	3501(3)	7067(9)	5399(2)	55(3)
C(1)	4711(3)	15528(11)	1514(3)	64(4)
C(2)	4958(4)	16350(11)	1319(3)	77(4)
C(3)	5434(5)	16424(12)	1423(3)	70(4)
C(4)	5662(4)	15756(11)	1721(3)	58(4)
C(5)	6156(4)	15812(12)	1860(4)	72(4)

TABLE I (*cont.*)

Atom	*x/a*	*y/b*	*z/c*	*U*[a]
C(6)	6342(4)	15103(12)	2156(4)	76(4)
C(7)	6061(3)	14294(11)	2319(3)	54(3)
C(8)	5411(3)	14934(9)	1913(3)	44(3)
C(9)	3652(3)	10821(12)	2572(3)	57(4)
C(10)	3487(4)	10082(12)	2828(3)	62(4)
C(11)	3772(4)	9671(11)	3124(3)	63(4)
C(12)	4257(4)	10021(10)	3190(3)	51(3)
C(13)	4591(4)	9687(12)	3495(3)	67(4)
C(14)	5047(3)	10107(12)	3526(2)	62(4)
C(15)	4416(3)	10789(9)	2933(3)	42(3)
C(16)	5162(4)	10874(10)	3260(3)	51(3)
C(17)	2708(4)	11124(13)	4766(3)	67(4)
C(18)	2846(5)	11982(14)	4521(3)	79(4)
C(19)	3314(5)	12129(12)	4530(3)	76(4)
C(20)	3646(4)	11493(12)	4785(3)	65(4)
C(21)	4142(4)	11603(13)	4829(4)	80(4)
C(22)	4419(4)	10983(14)	5087(4)	79(4)
C(23)	4228(4)	10184(13)	5332(3)	68(4)
C(24)	3494(4)	10668(11)	5038(3)	51(3)
C(25)	3828(4)	11126(12)	6853(3)	66(4)
C(26)	3644(5)	11849(13)	7107(3)	78(4)
C(27)	3161(5)	11896(12)	7075(3)	82(4)
C(28)	2881(4)	11257(11)	6803(3)	66(4)
C(29)	2377(5)	11235(13)	6733(4)	91(5)
C(30)	2137(5)	10583(14)	6449(4)	93(5)
C(31)	2366(4)	9913(14)	6218(4)	77(4)
C(32)	3075(4)	10513(11)	6545(3)	54(4)
C(33)	2042(4)	6506(12)	5827(3)	59(4)
C(34)	1913(4)	5532(12)	6039(3)	65(4)
C(35)	2225(5)	5017(12)	6305(4)	72(4)
C(36)	2700(4)	5475(11)	6378(3)	58(4)
C(37)	3061(5)	5028(12)	6649(3)	68(4)
C(38)	3499(4)	5533(13)	6691(3)	69(4)
C(39)	3574(4)	6525(12)	6467(3)	59(4)
C(40)	2820(3)	6457(10)	6160(3)	48(3)
C(41)	4703(4)	6754(12)	5814(3)	62(4)
C(42)	4863(4)	5766(13)	5622(3)	66(4)
C(43)	4571(4)	5199(11)	5353(3)	62(4)
C(44)	4094(3)	5592(10)	5252(3)	50(3)
C(45)	3755(4)	5100(11)	4968(3)	59(4)
C(46)	3314(4)	5568(11)	4903(3)	60(4)
C(47)	3196(3)	6543(12)	5122(3)	58(4)
C(48)	3940(3)	6587(10)	5454(3)	48(3)

[a] Equivalent isotropic U defined as one third of the orthogonalized U_{ij} tensor.

desiccator over $CaCl_2$ at room temperature. During about two weeks brown crystals of the title compound $Nd(napyo)_4(ClO_4)_3$ formed from the solution. The product was filtered, washed with ethanol and ether, and air dried. The yield was 52%. Calcd. for $Nd(napyo)_4(ClO_4)_3$: C, 37.42; H, 2.36; N, 10.91; Nd, 14.04%. Found: C, 37.52; H, 2.31; N, 10.77; Nd, 14.18%.

X-ray structure determination

Crystal data

$C_{32}H_{24}Cl_3N_8NdO_{16}$, $M = 1027.2$, monoclinic, space group $C2/c$, $a = 29.026(6)$, $b = 10.480(2)$, $c = 37.530(8)$ Å, $\beta = 100.97(1)°$, $V = 11208(4)$ Å^3, $Z = 12$, $Dc = 1.83\,gcm^{-3}$, Do (flotation in CCl_4/CH_2I_2) $= 1.82\,gcm^{-3}$, λ (MoKα) $= 0.7109$ Å, $\mu = 11.48\,cm^{-1}$, $F(000) = 6516$.

TABLE II
Selected bond lengths (Å).

Nd(1)-O(1)	2.371(7)	Nd(2)-O(6)	2.393(7)
Nd(1)-O(2)	2.394(7)	Nd(2)-O(7)	2.725(7)
Nd(1)-N(2)	2.631(9)	Nd(2)-N(6)	2.655(9)
Nd(1)-N(4)	2.588(9)	Nd(2)-N(8)	2.652(9)
Nd(2)-O(3)	2.397(7)	Nd(2)-N(10)	2.621(9)
Nd(2)-O(4)	2.384(6)	Nd(2)-N(12)	2.622(9)
Nd(2)-O(5)	2.421(7)		

TABLE III
Selected bond angles (°).

O(1)-Nd(1)-O(1')	120.2(3)	O(4)-Nd(2)-O(7)	73.1(2)
O(1)-Nd(1)-O(2)	83.1(2)	O(4)-Nd(2)-N(6)	105.6(2)
O(1)-Nd(1)-O(2')	126.7(2)	O(4)-Nd(2)-N(8)	62.3(2)
O(1)-Nd(1)-N(2)	62.6(2)	O(4)-Nd(2)-N(10)	80.8(3)
O(1)-Nd(1)-N(2')	86.5(2)	O(4)-Nd(2)-N(12)	130.8(2)
O(1)-Nd(1)-N(4)	146.8(2)	O(5)-Nd(2)-O(6)	127.5(3)
O(1)-Nd(1)-N(4')	81.4(2)	O(5)-Nd(2)-O(7)	115.3(2)
O(2)-Nd(1)-O(2')	122.6(4)	O(5)-Nd(2)-N(6)	125.5(2)
O(2)-Nd(1)-N(2)	142.3(2)	O(5)-Nd(2)-N(8)	74.1(3)
O(2)-Nd(1)-N(2')	73.2(2)	O(5)-Nd(2)-N(10)	62.4(2)
O(2)-Nd(1)-N(4)	63.7(2)	O(5)-Nd(2)-N(12)	76.2(3)
O(2)-Nd(1)-N(4')	77.4(2)	O(6)-Nd(2)-O(7)	117.1(2)
N(2)-Nd(1)-N(2')	117.0(4)	O(6)-Nd(2)-N(6)	75.9(3)
N(2)-Nd(1)-N(4)	149.3(2)	O(6)-Nd(2)-N(8)	127.9(2)
N(2)-Nd(1)-N(4')	82.0(3)	O(6)-Nd(2)-N(10)	76.2(3)
N(4)-Nd(1)-N(4')	93.0(4)	O(6)-Nd(2)-N(12)	75.9(3)
O(3)-Nd(2)-O(4)	143.3(3)	O(7)-Nd(2)-N(6)	67.7(3)
O(3)-Nd(2)-O(5)	68.2(2)	O(7)-Nd(2)-N(8)	67.2(3)
O(3)-Nd(2)-O(6)	131.1(2)	O(7)-Nd(2)-N(10)	142.7(2)
O(3)-Nd(2)-O(7)	70.3(2)	O(7)-Nd(2)-N(12)	141.5(2)
O(3)-Nd(2)-N(6)	62.3(2)	N(6)-Nd(2)-N(8)	134.8(3)
O(3)-Nd(2)-N(8)	100.3(2)	N(6)-Nd(2)-N(10)	146.9(3)
O(3)-Nd(2)-N(10)	129.3(2)	N(6)-Nd(2)-N(12)	75.9(3)
O(3)-Nd(2)-N(12)	82.2(3)	N(8)-Nd(2)-N(10)	77.3(3)
O(4)-Nd(2)-O(5)	128.1(2)	N(8)-Nd(2)-N(12)	146.7(3)
O(4)-Nd(2)-O(6)	69.7(2)	N(10)-Nd(2)-N(12)	75.8(3)

A single crystal of dimension of $0.4 \times 0.6 \times 0.7$ mm was selected for data collection on an R3M/E diffractometer with graphite-monochromated MoKα radiation, using the $\theta/2\theta$ scan technique. Some 25 reflections were used for measuring

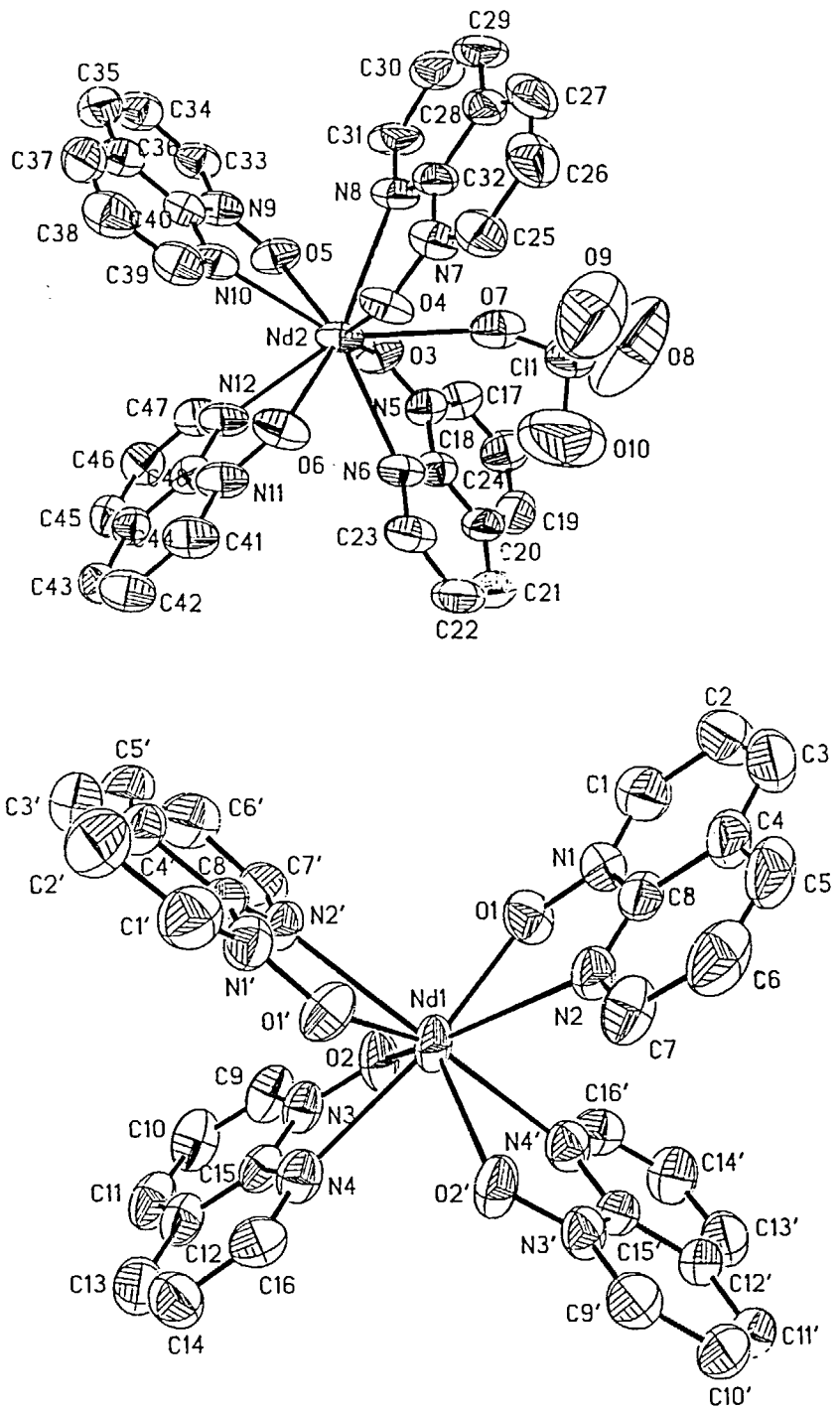

FIGURE 1. Structure and numbering scheme for the complex cations.

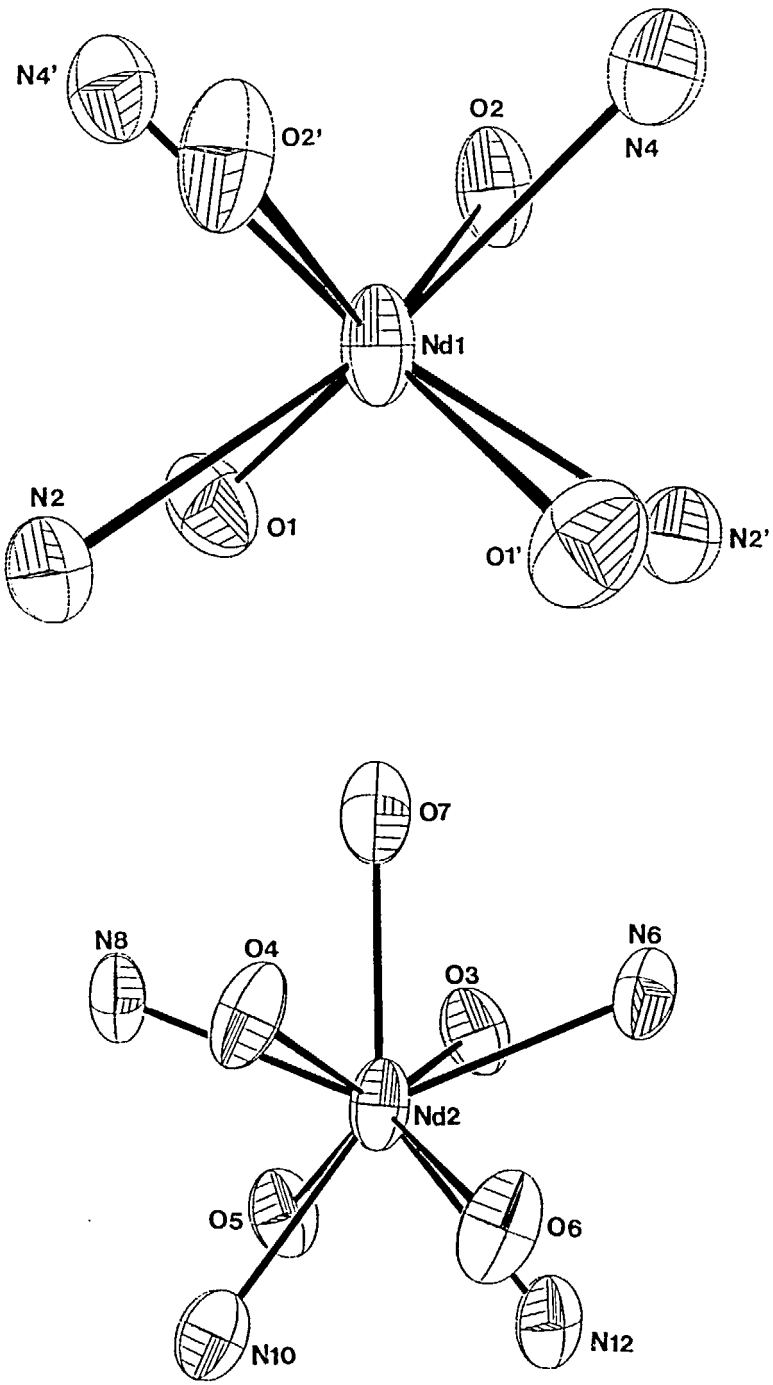

FIGURE 2. Coordination geometries of the central Nd(1) and Nd(2) atoms.

lattice parameters and 16476 independent reflections were collected in the range $3° \leqslant 2\theta \leqslant 45°$. Of these, 6411 reflections with $I \geqslant 3\sigma(I)$ were used in the structure determination and refinement. The structure was solved by the Patterson method and Fourier techniques and refined, with unit weights, by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms and isotropic thermal parameters for H atoms. The final values $R = 0.067$, $Rw = 0.067$ were obtained. Lists of H atom coordinates, anisotropic thermal parameters and observed and calculated structure factors have been deposited with the Editor-in-Chief

RESULTS AND DISCUSSION

Final atomic coordinates and equivalent thermal parameters are given in Table I, and selected bond lengths and bond angles in Tables II and III. Figure 1 shows the structure and the numbering scheme for the complex cations. Figure 2 shows the coordination spheres of the Nd(1) and Nd(2) atoms. Figure 3 illustrates the molecular packing arrangement in the unit cell.

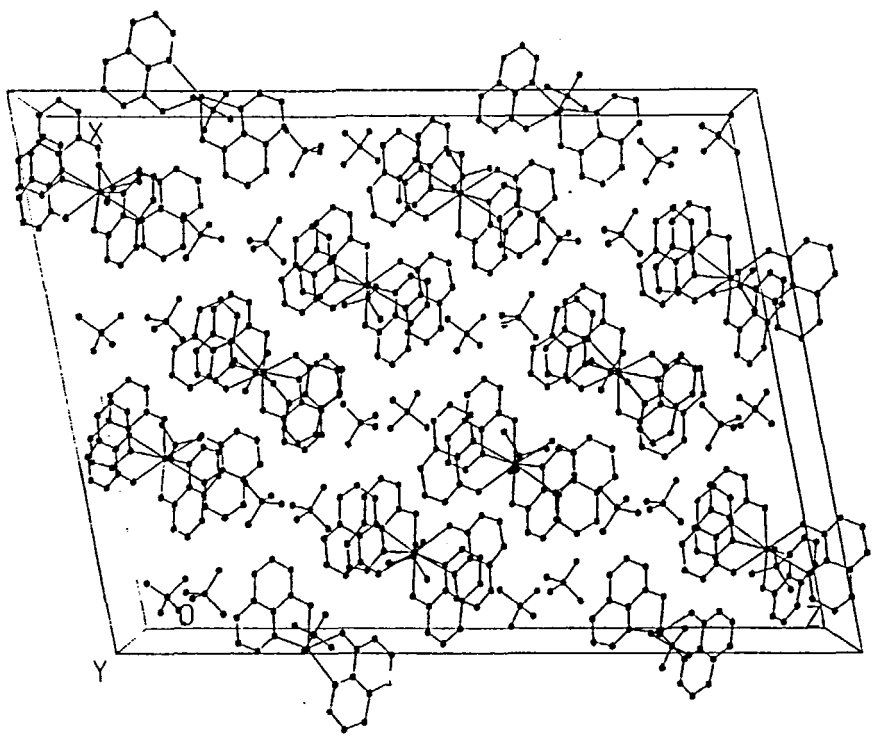

FIGURE 3. Molecular packing in the unit cell.

The cell consists of discrete complex cations $[Nd(napyo)_4]^{3+}$ lying on a C_2 axis, $[Nd(napyo)_4OClO_3]^{2+}$ ions with no crystallographic symmetry, and separate perchlorate ions. In $[Nd(napyo)_4]^{3+}$, the central atom is bonded to four nitrogen atoms and four oxygen atoms from four napyo ligands with the coordination geometry of

Nd(1) corresponding to a distorted square antiprism. The bond lengths lie in the range: Nd(1)–N, 2.588–2.631 Å; Nd(1)–O, 2.371–2.394 Å. In $[Nd(napyo)_4OClO_3]^{2+}$, the central atom is bonded to nine atoms; eight donors are derived from four napyo ligands and one oxygen atom from a coordinated perchlorate group. The coordination geometry is a distorted, monocapped, square antiprism. The bond lengths lie in the ranges: Nd(2)–N, 2.621–2.655 Å; Nd(2)–O, 2.384–2.725 Å. The mean Nd–N bond length (2.638 Å) and mean Nd–O bond length (2.464 Å) in $[Nd(napyo)_4OClO_3]^{2+}$ is about 0.03 Å and 0.08 Å longer (2.610 Å and 2.383 Å) than in $[Nd(napyo)_4]^{3+}$, respectively. The increase in bond length is to be expected in going from 8- to 9-coordination. It is interesting to note that coordination numbers of the metal ion in the same compound are different. A similar situation has also been found in another other neodymium complex.[11]

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