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Crystal and Molecular Structures of the Octakis(pyridine *N*-oxide) Lanthanide Complexes $M(PyO)_8(ClO_4)_3$, M = La and Nd

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The eight-coordinate complexes of lanthanum and neodymium with pyridine oxide as ligands both crystallize in two different monoclinic forms, space groups $P2_1/a$ and $C2/c$, the first modification giving only twinned crystals. The structures of the $C2/c$ modification of the lanthanum complex and the $P2_1/a$ form of the neodymium complex have been determined by conventional three-dimensional X-ray techniques, with diffraction data collected on a manual diffractometer, 1828 independent reflections being used for the former and 2114 reflections for the latter. The structures have been refined by full-matrix least-squares methods (in that of the neodymium complex, the ligands being treated as rigid groups) to residuals of $R = 0.081$ and 0.080 and $R_w = 0.095$ and 0.087 based on all reflections above background, for the lanthanum and neodymium complexes, respectively. The cell parameters are $a = 20.21$ (2) Å, $b = 17.67$ (2) Å, $c = 13.90$ (1) Å, and $\beta = 102.6$ (4)° for the lanthanum complex and $a = 22.50$ (2) Å, $b = 19.60$ (2) Å, $c = 13.24$ (2) Å, and $\beta = 58.9$ (3)° for the neodymium complex, while the observed and calculated densities are 1.60 and 1.641 g cm^{-3} and 1.59 and 1.596 g cm^{-3} for four molecules per unit cell for each complex. The eight-coordinate $La(PyO)_8^{3+}$ complex ion has crystallographically required C_2 symmetry and a coordination polyhedron of near-D_4 (422) symmetry, being intermediate between a cube and a square antiprism. The $Nd(PyO)_8^{3+}$ ion on the other hand has no required symmetry, but the complex as a whole has near-S_8 ($\bar{8}$) point symmetry with a coordination polyhedron closely approximating the square antiprism (D_{4d}, $\bar{8}2m$). The averaged La–O and Nd–O distances are 2.497 (12) and 2.407 (17) Å, respectively. In both structures, the complex cations are octahedrally surrounded by perchlorate ions, one in each structure being disordered.

Introduction

While detailed structural information has now been accumulated for a very large number of eight-coordinate complexes, that available for species containing equivalent unidentate ligands is still very limited, being confined principally to the octacyano complexes of molybdenum and tungsten,[1] various octafluoro species,[2] and the octathiocyanate complex of uranium, $U(NCS)_8^{4-}$. The latter is of especial interest in connection with discussions of the geometries of eight-coordination polyhedra and their relative stabilities, for in the cesium salt,[3] the square-antiprismatic (D_{4d}) geometry is found, while in the tetraethylammonium salt, the cubic configuration (O_h) is stabilized[4] and suggests that the two geometries are of comparable energy, the change of cation and crystalline environment being sufficient to stabilize the cubic form. This is in contrast to a consideration of ligand–ligand repulsion forces which indicate that the cubic geometry is energetically unfavorable relative to either the square antiprism or the triangulated dodecahedron (D_{2d}).[5] However, in addition to the uranium complex, the cube has also been characterized in another actinide complex, PaF_8^{3-},[6] and we have recently determined the structure of tetrakis(bipyridine *N*-oxide)lanthanum perchlorate,[7] which represents the first example of cubic coordination in lanthanide chemistry. The structures of the octakis(pyridine *N*-oxide) complexes reported here show that while the square-antiprismatic geometry is found in one crystalline form, in a second modification a geometry intermediate between a cube and a square antiprism is stabilized. It thus appears that, at least for the f-shell elements, the cube may not be an uncommon geometry, for in the examples characterized so far, there appear to be no constraints arising from the ligands which make the cube preferable to the square antiprism.

At the time that the present work was commenced, no complex of the lanthanides containing eight equivalent ligands had been characterized structurally,[8] and at the present time, only one, containing 2,6-dimethyl-4-pyrone as ligand, has been reported.[9] This has been described as having a distorted square-antiprismatic geometry. Preliminary results of the structure of the lanthanum complex have previously been reported.[10]

Experimental Section

The octakis(pyridine *N*-oxide) complexes of La, Nd, and Eu were prepared from either the metal carbonate or oxide, perchloric acid, and the purified ligand, with modifications of the procedure described by Melby and co-workers.[11] Crystals suitable for structure analyses were obtained from acetone/ethyl acetate solutions. Anal. Calcd for $LaC_{40}H_{40}N_8O_{20}Cl_3$: C, 40.10; N, 9.35; H, 3.34. Found: C, 40.31; N, 9.21; H, 3.64. Calcd for $NdC_{40}H_{40}N_8O_{20}Cl_3$: C, 39.96; N, 9.32; H, 3.33. Found: C, 40.42; N, 9.25; H, 3.50. Analytical results on the europium complex were unsatisfactory, and it is believed that a mixture of six- and eight-coordinate species was formed.

Optical examination of crystals of both the lanthanum and neodymium complexes suggested that two crystalline modifications existed for each, and this was confirmed by Weissenberg and precession photography with both Cu Kα and Mo Kα radiation. Both modifications of each complex were found to exhibit $2/m$ Laue symmetry and so to belong to the monoclinic system. One of the modifications (form II), however, was found to be composed of mirror-related twins, the twinning plane being normal to the a^* axis. The presence of this (100) twinning mirror plane operating on the monoclinic reciprocal lattice does not in this case result in a higher symmetry for the twinned

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Table I. Experimental Data for X-ray Diffraction Study of $M(PyO)_8(ClO_4)_3$ (M = La, Nd)

(A) Crystal Parameters at 19 °C

La complex (form I)	Nd complex (form II)
$a = 20.21$ (2) Å	$a = 22.50$ (2) Å
$b = 17.67$ (2) Å	$b = 19.60$ (2) Å
$c = 13.90$ (1) Å	$c = 13.24$ (2) Å
$\beta = 102.6$ (4)°	$\beta = 58.9$ (3)°
$V = 4844.3$ Å^3	$V = 4999.6$ Å^3
mol wt 1197.4	mol wt 1201.7
ρ(calcd) = 1.641 g cm^{-3}	ρ(calcd) = 1.596 g cm^{-3}
ρ(obsd) = 1.60 g cm^{-3}	ρ(obsd) = 1.59 g cm^{-3}
$Z = 4$	$Z = 4$
space group $C2/c$ (No. 15)	space group $P2_1/a$ (No. 14)

(B) Measurement of Intensity Data

radiation	La comp, Mo Kα (Zr filter) Nd comp, Cu Kα (Ni filter)
attenuator	one used–nickel foil
instrument takeoff angle	2°
cryst–detector dist	16.5 cm
source–cryst dist	14.6 cm
detector collimator	2 mm diameter
detector	scintillation counter (Mo Kα), proportional counter (Cu Kα)
scan type	coupled θ–2θ
scan speed	2°/min
scan range	$\Delta(2\theta) = (1.4 + 0.8 \tan \theta)$ centered about average peak position
bkgd measurement	stationary cryst–stationary counter, half scan time at beginning and end of scan
std rflctns	two measured every 30 rflctns, no significant deviation from average
cryst orientation	both complexes aligned with cryst c axis parallel to ϕ axis
max 2θ	38° for La comp, 78° for Nd comp
rflctns measured	La comp, 1828 independent measurements; Nd comp, 2114 independent measurements

(C) Treatment of Intensity Data

conversion to I and $\sigma(I)$	$I = (P - (B_1 + B_2))F$ (P = total count, B = bkgd) $\sigma(I) = ((P + B_1 + B_2)F^2 + (cI)^2)^{1/2}$, ignorance factor $c = 0.05$
abs coeff	La comp, $\mu = 10.8$ cm^{-1} (Mo); Nd comp, $\mu = 95.0$ cm^{-1} (Cu); no abs cor applied

composite; examination of *hkn* and *nkl* precession photographs indicated complete registry of reciprocal lattice points for the two individuals, only for levels with $l = 4n$ (i.e., 0, 4, 8, etc.). Since the reciprocal lattice points are separate for the remaining zones ($l \neq 4n$), the intensities for the two individuals can be measured directly. For the zones with $l = 4n$, the observed intensity of each reflection is the sum of the intensities for a pair of reflections, $hk4n$ and $h'k4n$ with $h + h' = -7n$ (n = 0, 1, 2, etc.). In the case of the zero level ($n = 0$) $h = -h'$, and since for monoclinic symmetry $|F(hk0)|^2 = |F(\bar{h}k0)|^2$, the intensities of $hk0$ reflections for one individual can be readily obtained if the relative proportion of the two components in the twin is known. In addition to the twinning, the $hk0$ zone showed nearly tetragonal symmetry (Laue group $4/mmm$) suggesting a structure possessing pseudosymmetry.

The systematic absences, $h0l$ for $h \neq 2n$ and $0k0$ for $k \neq 2n$, observed for the lattices of the individuals of form II indicated space group $P2_1/a$, a nonstandard setting of $P2_1/c$ (C_{2h}^5 No. 14). The systematic absences for form I, hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$, are consistent with space groups Cc (C_s^4 No. 9) or $C2/c$ (C_{2h}^6 No. 15), the latter requiring crystallographic symmetry for the cation and perchlorate ion.

Intensity data for both structures were collected on a G.E. manually operated XRD-6 diffractometer equipped with a quarter-circle goniostat. Diffractometer setting angles were calculated with the locally written program DIFSET. Unit cell dimensions were obtained from the 2θ values for the axial and some principal-zone reflections, centered by use of a fine detector slit. The values are listed in Table I(A), the standard deviations quoted being those obtained from the distribution of individual values. Details of the data collection parameters are listed in Table I(B).

The intensity data for one individual of the twinned crystal were measured with Cu Kα radiation, this being chosen rather than Mo Kα in order to enhance the angular separation of the reciprocal lattice points for the two individuals on levels with $l \neq 4n$. Only a few minor problems arising from overlap of reflections were encountered, and for the majority of low-order reflections with $l = 1$ and 3 where some overlap occurred, these were essentially eliminated by modification of the scan range. A crystal of dimensions 0.1 × 0.1 × 0.25 mm was used for data collection, no corrections being made for absorption. It was assumed that the contributions of the two individuals to the composite crystal were equivalent (vide supra) so that the intensities of the $hk0$ reflections were taken to be half of the measured values. The intensities of the reflections with l = 4, 8, and 12 were not measured. A total of 2114 independent reflections were measured, of which 360 had a net of intensity below background. Reflections with odd values of h as a class had much lower intensity than those for which h is even, suggesting pseudosymmetry in the structure.

The intensity data for the lanthanum complex (form I) were measured with Mo Kα radiation. A crystal of dimensions 0.1 × 0.2 × 0.2 mm was used, and no corrections were made for absorption. Of the 1828 independent reflections measured, 245 had a net intensity of zero or lower. As in the case of the neodymium complex, pseudosymmetry in the structure was suggested, reflections having $k + l$ odd being generally weaker than those with $k + l$ even. Together with the C-centering requirement, this suggested a pseudo-F-centered arrangement.

Structure Solution and Refinement

While both structures were solved by standard heavy-atom procedures, the process was complicated by the extensive pseudosymmetry present in both forms I and II. Examination of three-dimensional Patterson functions indicated that the metal atoms (lanthanum in I, neodymium in II) lay in or very close to the glide planes (the n glide in $C2/c$ for I and the a glide in II). In the case of the lanthanum complex, the vectors were consistent with the special positions 4(c) or 4(d) having inversion symmetry or 4(e) with $y \approx {}^1/_4$, having twofold symmetry. Since an eight-coordinate geometry with a center of symmetry seemed unlikely, the latter was chosen as the site for the lanthanum atom. The vector map was also consistent with the location of one set of four chlorine atoms in the 4(e) positions with again the atoms lying on or very close to the n glide plane. An initial electron density map phased on the lanthanum and this chlorine atom slightly displaced from the glide plane exhibited a pseudomirror plane and gave two alternative positions for the chlorine in the eightfold general position. Structure factor and least-squares calculations led to an unambiguous choice for the coordinates of this atom, the agreement factors based on the three heavy atoms being $R_F = 0.35$ and $R_w = 0.39$.[12] Subsequent Fourier syntheses and structure factor calculations served to locate all nonhydrogen atoms except the oxygen atoms of the perchlorate ion located on the twofold axis. After least-squares refinement of the remainder of the structure, it was clear from a difference Fourier synthesis that this perchlorate ion exhibits a static disorder, two half ions being related by the twofold axis. The four oxygen atoms of one half ion were accordingly refined as a rigid body constrained to lie on the twofold axis. The chlorine atom was not included as part of the rigid body, but it was clear from the results of the refinement that there was no significant displacement of this atom from the center of gravity of the tetrahedron of oxygen atoms.

In the final cycles of refinement, all atoms were refined with isotropic temperature factors, apart from the lanthanum and the atoms of the perchlorate ion in the general position, which were treated anisotropically. The oxygen atoms of the disordered perchlorate ion were assigned a group temperature factor, while the chlorine atom of this ion was also treated isotropically. Four cycles of the mixed refinement with weights calculated according to $w^{1/2} = 2LpF_o/\sigma(I)$ where $\sigma(I)$ is defined in Table I(C) (a total of 170 variables) led to final residuals of 0.081 and 0.095 for approximately 1600 reflections with a net intensity above zero.[13] The residual for all reflections was 0.102, and the "goodness of fit" parameter for the refinement, defined as $\sum w(|F_o| - |F_c|)^2/(n_o - n_c)$, was 2.42, suggesting that the weights had been overestimated. In the final cycle, the largest shift in a parameter was 0.26 of its standard deviation.

Examination of the Patterson map for the neodymium complex (form II) showed a specialized arrangement of Nd–Nd and Nd–Cl vectors suggestive of extensive pseudosymmetry. While the Nd–Nd vectors (${}^1/_2$, ${}^1/_2$, 0; ${}^1/_2$, 0, 0; 0, ${}^1/_2$, 0) are in accord with the occurrence of two pairs of nonequivalent centrosymmetric complexes, this possibility was excluded, and, as noted above, it was concluded that the neodymium atom lies in or very close to the glide plane, i.e., $y \approx {}^1/_4$. Of the two possible coordinates consistent with the above set of vectors, namely, $\sim{}^1/_4, \sim{}^1/_4, \sim 0$ and $\sim 0, \sim{}^1/_4, \sim 0$, the former was selected on the basis of the approximate fourfold symmetry exhibited by the *hk*0 precession photograph. It appeared that the structure would be pseudotetragonal viewed along *c*, and such pseudosymmetry is consistent with the symmetry-related set of coordinates on the basis of the first position. (In $P2_1/a$ the set of general equivalent positions is $\pm(x, y, z)$ and $\pm({}^1/_2 + x, {}^1/_2 - y, z)$.) In addition, on the assumption of a similar ligand configuration around neodymium as that found in the lanthanum complex, the second possible coordinate was thought unlikely since it would lead to conflict with the centrosymmetrically related molecules.

The initial electron density map phased on the neodymium atom at ${}^1/_4, {}^1/_4, 0$ ($R_F = 0.49$ and $R_w = 0.52$) was very difficult to interpret but enabled the tentative choice of positions for two of the three independent chlorine atoms selected from the Patterson map to be confirmed. The coordinates of these three atoms were refined in one cycle of full-matrix least-squares refinement, and a second electron density map based on the new coordinates gave plausible positions for the eight ligand oxygen atoms situated around neodymium in a square-antiprismatic array and suggested that the third perchlorate ion was statically disordered between two sites. While in subsequent electron density maps the extent of the pseudomirror symmetry was considerably reduced, interpretation was complicated, presumably by the absence of the reflections with $l = 4n$ from the Fourier summations. Coordinates for all the atoms of the eight pyridine rings and the oxygen atoms of two of the perchlorate ions were eventually obtained from a sequence of three electron density syntheses, each preceded by one cycle of least-squares refinement of the positional parameters of the atoms determined in the previous map.

In view of the large number of atoms in the asymmetric unit (77, allowing for the disorder of one perchlorate), it was decided to refine the eight pyridine ring fragments of the ligands as rigid groups, each having the geometry of free pyridine. The perchlorate oxygen atoms were treated similarly, a Cl–O bond distance of 1.43 Å being assumed in deriving the dimensions of the tetrahedron. After two cycles of such refinement, in which the rigid groups were each assigned a group isotropic temperature factor and the remaining atoms were also treated isotropically, the residuals R_F and R_w stood at 0.137 and 0.151, respectively. Examination of electron density and difference density maps at this stage revealed the oxygen atoms of the disordered perchlorate ion as two sets of weak overlapping peaks, the two sets being approximately related by a pseudocenter of inversion. While one set did appear to be somewhat more intense than the other, equal occupation of the two sites was assumed, no attempt being made to refine a population parameter.

Further refinement, treating the oxygen atoms of the two "half ions" as rigid groups and the associated "half" chlorines as independent atoms and assigning individual isotropic thermal parameters to the atoms in the pyridine rings, led after three cycles of full-matrix refinement to residuals of $R_F = 0.082$ and $R_w = 0.088$. For a further two cycles, the neodymium atom was refined anisotropically, and the scale factor for the *hk*0 reflections was permitted to vary relative to that for the remainder of the reflections (vide supra). However, the ratio of the scale factors did not differ significantly from unity, indicating that the assumption that the two individuals contribute equally to the twinned composite is valid for the structural model used. The final residuals were 0.080 and 0.087, respectively, for the 1734 reflections, with a net nonzero intensity, all of which were used in the refinement, while the residual for all reflections was 0.091. The number of variables refined was 182, and the "goodness of fit" parameter at the end of the final cycle was 1.04. The largest shift to error ratio for any parameter was 0.38. The weights used in the least-squares refinements were calculated with the formula noted above.

Scattering factors for all neutral atoms used in the structure factor and least-squares calculations were taken from the tabulation of Cromer and Waber,[14] the anomalous dispersion corrections being included for the lanthanum and neodymium atoms.[15] Computations were carried out initially on the ATLAS computer at Harwell, England, with the X-RAY 63 package of programs of Stewart et al.[16] and later on a CDC 6600 computer at the University of Massachusetts with local modifications of Zalkin's FORDAP Fourier program and Prewitt's SFLSR full-matrix least-squares program incorporating rigid-body refinement routines. Tables of observed and calculated structure factors are available for both complexes,[17] while Tables II–V list the final atomic coordinates, thermal parameters, and rigid-body

Table II. Fractional Atomic Coordinates and Thermal Parameters for $La(PyO)_8(ClO_4)_3$ [a,b]

atom	*x*	*y*	*z*	*B*, Å²
La	0.0	0.2523 (1)	0.250	2.19
O(1)	−0.0250 (6)	0.1384 (7)	0.3427 (9)	4.06 (34)
N(1)	0.0196 (7)	0.0989 (8)	0.4105 (11)	3.48 (32)
C(11)	0.0178 (9)	0.1060 (10)	0.5070 (14)	3.74 (41)
C(12)	0.0652 (9)	0.0670 (11)	0.5772 (14)	4.34 (44)
C(13)	0.1138 (10)	0.0207 (11)	0.5473 (14)	4.67 (44)
C(14)	0.1132 (9)	0.0146 (11)	0.4482 (14)	4.48 (44)
C(15)	0.0652 (9)	0.0557 (11)	0.3782 (14)	4.12 (42)
O(2)	0.1037 (6)	0.2217 (7)	0.3782 (9)	3.52 (32)
N(2)	0.1419 (6)	0.2671 (7)	0.4453 (10)	3.04 (30)
C(21)	0.1364 (9)	0.2613 (10)	0.5393 (14)	4.15 (41)
C(22)	0.1769 (10)	0.3094 (11)	0.6092 (14)	4.94 (46)
C(23)	0.2204 (9)	0.3608 (11)	0.5807 (14)	4.18 (43)
C(24)	0.2239 (9)	0.3634 (11)	0.4835 (15)	4.66 (46)
C(25)	0.1826 (9)	0.3154 (10)	0.4131 (13)	4.05 (42)
O(3)	−0.0924 (6)	0.2815 (8)	0.3362 (9)	4.33 (35)
N(3)	−0.1329 (7)	0.2392 (8)	0.3764 (10)	3.45 (31)
C(31)	−0.1284 (9)	0.2456 (11)	0.4741 (14)	4.65 (43)
C(32)	−0.1713 (11)	0.1988 (12)	0.5173 (15)	5.44 (49)
C(33)	−0.2154 (10)	0.1516 (11)	0.4605 (15)	5.16 (47)
C(34)	−0.2175 (10)	0.1442 (11)	0.3608 (15)	5.16 (47)
C(35)	−0.1749 (9)	0.1915 (11)	0.3197 (14)	4.40 (43)
O(4)	0.0427 (6)	0.3644 (8)	0.3548 (9)	4.29 (36)
N(4)	0.0219 (7)	0.4362 (8)	0.3628 (10)	3.55 (32)
C(41)	0.0711 (9)	0.4893 (10)	0.3650 (14)	4.28 (42)
C(42)	0.0524 (10)	0.5649 (12)	0.3781 (15)	5.32 (49)
C(43)	−0.0116 (10)	0.5822 (11)	0.3876 (14)	4.63 (45)
C(44)	−0.0592 (9)	0.5254 (10)	0.3842 (13)	3.70 (40)
C(45)	−0.0417 (9)	0.4510 (10)	0.3714 (12)	3.36 (38)
Cl(1)	0.0	0.2226 (6)	0.750	6.81 (52)
Cl(2)	0.2442 (3)	0.4370 (4)	0.2094 (5)	4.31 (29)
O(11)[c]	0.0618	0.2677	0.7773	15.0 (12)[d]
O(12)[c]	0.0152	0.1477	0.7414	
O(13)[c]	−0.0380	0.2533	0.6576	
O(14)[c]	−0.0386	0.2355	0.8239	
O(21)	0.2072 (9)	0.4390 (12)	0.1127 (13)	8.29 (91)
O(22)	0.2075 (10)	0.4682 (11)	0.2724 (14)	7.71 (80)
O(23)	0.2584 (12)	0.3630 (13)	0.2329 (16)	10.16 (120)
O(24)	0.3039 (10)	0.4852 (14)	0.2134 (15)	8.41 (89)

[a] Standard deviations in parentheses. [b] Atoms La, Cl(2), O(21), . . ., O(24) refined anisotropically. Only equivalent *B* is reported for the general perchlorate group. For La: $B_{11} = 2.47$ (6), $B_{22} = 1.70$ (6), $B_{33} = 2.32$ (7), and $B_{13} = 0.38$ (5) where the form of the thermal ellipsoid is $\exp[-(\Sigma_i \Sigma_j h_i h_j r_i^* r_j^* B_{ij})/4]$, with $i, j = 1, 2, 3$. [c] These atoms refined as a rigid group constrained to lie on the twofold axis: center of gravity 0.0, 0.2260 (16), 0.25. [d] Group temperature factor.

Table III. Atomic Positional and Thermal Parameters for Nongroup Atoms in $Nd(PyO)_8(ClO_4)_3$ [a]

atom	*x*	*y*	*z*	*B*, Å²
Nd	0.25838 (7)	0.25536 (7)	−0.00572 (13)	*b*
O(1)	0.1612 (8)	0.2852 (9)	0.1837 (17)	9.14 (51)
O(2)	0.2344 (8)	0.1545 (8)	0.1186 (15)	6.34 (52)
O(3)	0.3580 (8)	0.2349 (9)	0.0091 (15)	5.19 (47)
O(4)	0.2877 (8)	0.3541 (8)	0.0655 (16)	6.14 (48)
O(5)	0.1655 (8)	0.2028 (9)	−0.0198 (16)	4.87 (44)
O(6)	0.3074 (9)	0.1702 (8)	−0.1521 (17)	5.36 (46)
O(7)	0.3494 (8)	0.3066 (9)	−0.1876 (17)	6.45 (50)
O(8)	0.2045 (9)	0.3428 (8)	−0.0617 (17)	6.59 (53)
Cl(1)	0.4634 (4)	0.0096 (4)	0.3037 (9)	6.90 (26)
Cl(2)	0.0346 (4)	0.0191 (4)	0.6841 (9)	6.30 (23)
Cl(3)[c]	0.2542 (8)	0.2468 (8)	0.4825 (13)	6.62 (30)
Cl(4)[c]	0.2444 (8)	0.2512 (9)	0.5362 (15)	9.14 (50)

[a] Standard deviations in parentheses. [b] Refined anisotropically: $B_{11} = 3.41$ (8), $B_{22} = 3.04$ (8), $B_{33} = 2.24$ (8), $B_{12} = 0.00$ (8), $B_{13} = -0.62$ (5), and $B_{23} = 0.03$ (7) where the form of the thermal ellipsoid is $\exp[-(\Sigma_i \Sigma_j h_i h_j r_i^* r_j^* B_{ij})/4]$ with $i, j = 1, 2, 3$. [c] Occupancy factors for these atoms = 0.50.

Table IV. Rigid-Body Parameters for $Nd(PyO)_8(ClO_4)_3$

	x_c	y_c	z_c	ϕ	θ	ρ
			(a) Pyridine Rings[c]			
1	0.0783 (6)	0.2088 (6)	0.3750 (11)	1.527 (1)	2.944 (1)	−0.979 (1)
2	0.3156 (5)	0.0748 (5)	0.1564 (10)	2.798 (2)	2.157 (1)	−0.348 (2)
3	0.4328 (5)	0.3191 (6)	0.0576 (11)	3.111 (2)	−1.871 (1)	−0.734 (2)
4	0.2065 (5)	0.4332 (5)	0.2558 (12)	0.846 (1)	2.580 (1)	−1.886 (1)
5	0.1576 (4)	0.0883 (6)	−0.1219 (11)	0.427 (1)	2.167 (1)	0.876 (1)
6	0.4231 (7)	0.1715 (5)	−0.3698 (12)	−1.748 (1)	−2.755 (1)	1.494 (1)
7	0.3496 (5)	0.4220 (7)	−0.3084 (11)	−0.789 (1)	−2.519 (1)	0.669 (1)
8	0.0854 (6)	0.3446 (4)	−0.0575 (11)	2.982 (2)	1.740 (1)	−2.988 (4)
			(b) Oxygen Tetrahedra[a,c]			
1	0.4639 (6)	0.0082 (5)	0.3025 (11)	−2.790 (1)	3.075 (1)	0.527 (1)
2	0.0334 (6)	0.0211 (5)	0.6916 (12)	1.413 (1)	−2.838 (1)	0.108 (1)
3[b]	0.2563 (10)	0.2507 (12)	0.4726 (21)	−2.084 (2)	2.726 (2)	−1.503 (2)
4[b]	0.2470 (12)	0.2502 (12)	0.5312 (22)	2.954 (2)	−2.936 (3)	2.146 (2)

[a] Group temperature factors: 11.59 (38), 11.13 (37), 14.56 (75), and 16.55 (81), respectively. [b] Occupancy factors for these groups = 0.50. [c] The numbers in the left hand column are the ring numbers for the pyridine rings and the group numbers for the oxygen tetrahedra.

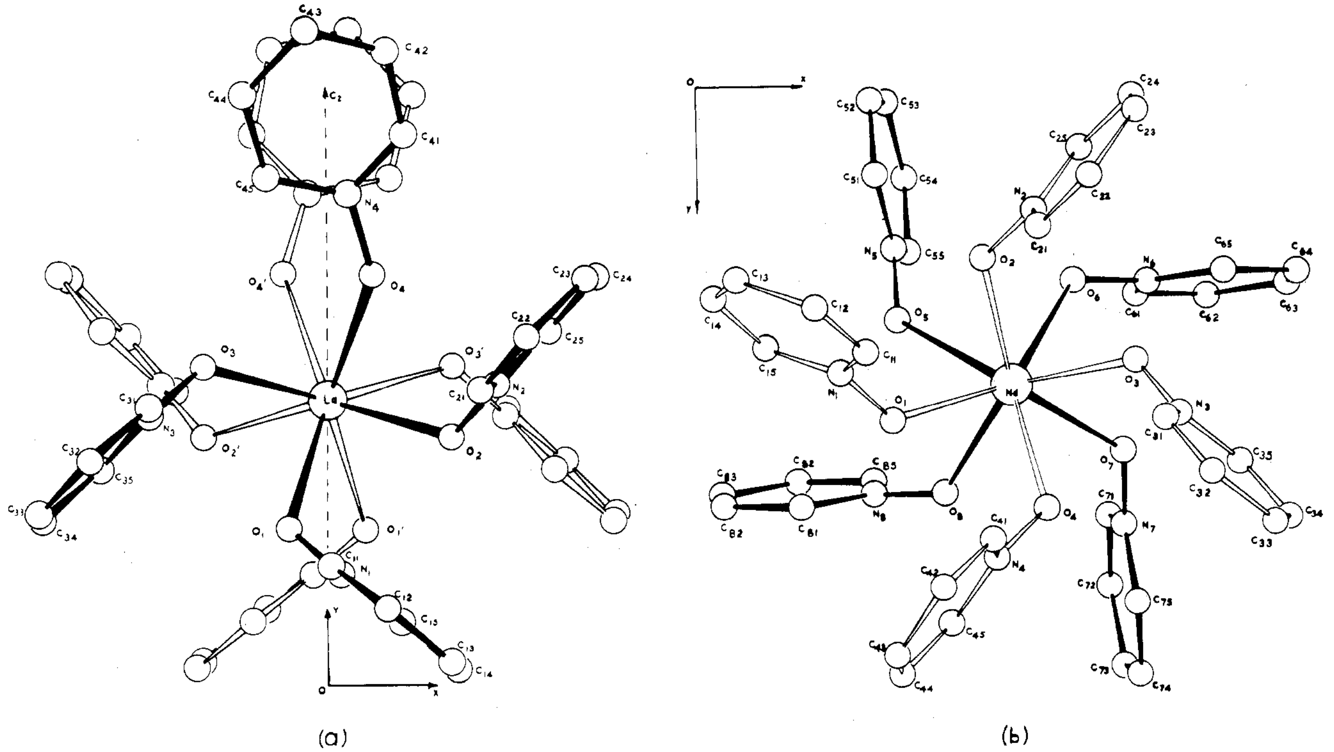

Figure 1. Structures of the $La(PyO)_8^{3+}$ (a) and $Nd(PyO)_8^{3+}$ (b) ions viewed along the respective crystal *c* axes.

parameters for the two complexes.

Results and Discussion of Structures

Tables VI–IX summarize the pertinent structural information for the lanthanum and neodymium pyridine oxide complexes, $M(PyO)_8(ClO_4)_3$, Table VI giving a comparison of the dimensions of the eight coordination polyhedra in the two complex ions. Figure 1 illustrates the two ions as viewed down their respective crystal *c* axes and shows clearly the differing configurations of pyridine oxide ligands in the two forms. The complex ions in I possess crystallographically required C_2 point symmetry, but apart from the orientation of one ligand, the complex ions approximate to D_4 symmetry. While there are no crystallographic symmetry requirements for the complex ions in II, they approximate the uncommon S_8 ($\bar{8}$) point symmetry. In the first-row transition-element hexakis complexes, the corresponding S_6 ($\bar{3}$) point group symmetry is crystallographically required for the $M(PyO)_6^{2+}$ ions.[18,19]

The coordination polyhedra in both complexes may be termed square antiprismatic although in the case of the lanthanum complex there is an appreciable deviation from this geometry, apparently toward that of the square prism (cube). The distortion is well illustrated in the view of the complex given in Figure 1(a), and it takes the form of a rotation of one square face of the polyhedron (defined by O(1) to O(4)) away from the 45° projected angle characterizing the D_{4d} geometry by ca. 14°, to give a coordination polyhedron of D_4 symmetry. While the observed deviations from this point group as indicated by the O···O distances in Table VI appear significant, the esd's are relatively large, so that a description in terms of D_4 symmetry appears appropriate. The projected O(*m*)–La–O(*n*)′ (*m* and *n* = 1–4) angles average 31.3 and 58.6°, and the two sets of *l* edges (using D_{4d} polyhedron nomenclature[20]) average 3.045 and 3.418 Å. The two sets of atoms comprising the twofold related square faces approach coplanarity with a small dihedral angle of approximately 1° between them.

The departure from the square-antiprismatic geometry can be rationalized in terms of the steric interactions between one set of PyO ligands and the twofold related set. On the assumption of "edge-on" orientation for the ligands, in which the M–O–N plane is roughly orthogonal to the ligand plane,

Table V. Positional and Thermal Parameters for Rigid-Group Atoms in $Nd(PyO)_8(ClO_4)_3$

atom	*x*	*y*	*z*	*B*, Å^2
N(1)	0.1189	0.2467	0.2781	6.06 (56)
C(11)	0.1438	0.2255	0.3461	7.00 (83)
C(12)	0.1035	0.1867	0.4457	10.33 (98)
C(13)	0.0363	0.1698	0.4749	8.67 (84)
C(14)	0.0112	0.1920	0.4039	9.82 (96)
C(15)	0.0540	0.2306	0.3054	10.46 (106)
N(2)	0.2751	0.1150	0.1340	5.55 (60)
C(21)	0.2786	0.1264	0.2312	5.71 (73)
C(22)	0.3196	0.0861	0.2565	6.36 (69)
C(23)	0.3575	0.0333	0.1796	6.07 (76)
C(24)	0.3534	0.0221	0.0794	6.95 (85)
C(25)	0.3115	0.0640	0.0588	7.95 (88)
N(3)	0.3943	0.2766	0.0340	6.11 (62)
C(31)	0.4437	0.3152	−0.0532	6.30 (78)
C(32)	0.4839	0.3591	−0.0318	7.41 (87)
C(33)	0.4725	0.3629	0.0819	7.56 (86)
C(34)	0.4213	0.3227	0.1712	8.31 (96)
C(35)	0.3828	0.2798	0.1444	6.27 (79)
N(4)	0.2460	0.3941	0.1600	5.02 (55)
C(41)	0.2429	0.3797	0.2622	5.61 (77)
C(42)	0.2030	0.4188	0.3617	7.90 (88)
C(43)	0.1658	0.4735	0.3546	6.34 (78)
C(44)	0.1694	0.4878	0.2485	8.60 (98)
C(45)	0.2102	0.4469	0.1521	5.52 (74)
N(5)	0.1611	0.1464	−0.0705	5.50 (59)
C(51)	0.1455	0.0873	−0.0102	6.78 (82)
C(52)	0.1414	0.0271	−0.0603	7.63 (87)
C(53)	0.1539	0.0284	−0.1748	6.88 (84)
C(54)	0.1700	0.0894	−0.2362	5.93 (76)
C(55)	0.1733	0.1484	−0.1814	6.46 (80)
N(6)	0.3667	0.1709	−0.2598	6.53 (64)
C(61)	0.3587	0.1810	−0.3529	7.34 (88)
C(62)	0.4154	0.1819	−0.4663	8.03 (91)
C(63)	0.4812	0.1722	−0.4831	7.22 (86)
C(64)	0.4887	0.1618	−0.3862	7.39 (87)
C(65)	0.4301	0.1614	−0.2749	6.59 (80)
N(7)	0.3492	0.3662	−0.2484	11.60 (84)
C(71)	0.3377	0.3594	−0.3383	12.20 (113)
C(72)	0.3378	0.4156	−0.4012	9.45 (98)
C(73)	0.3500	0.4797	−0.3703	9.59 (105)
C(74)	0.3619	0.4859	−0.2772	10.20 (111)
C(75)	0.3611	0.4279	−0.2176	7.65 (89)
N(8)	0.1463	0.3440	−0.0605	6.59 (66)
C(81)	0.0868	0.3543	0.0429	7.11 (85)
C(82)	0.0238	0.3551	0.0489	6.58 (80)
C(83)	0.0226	0.3451	−0.0543	6.87 (84)
C(84)	0.0845	0.3346	−0.1606	5.70 (76)
C(85)	0.1459	0.3343	−0.1610	6.59 (81)
O(11)	0.3938	−0.0158	0.3658	
O(12)	0.4641	0.0805	0.2895	
O(13)	0.5000	−0.0232	0.1888	
O(14)	0.4971	−0.0090	0.3664	
O(21)	0.0414	0.0923	0.7046	
O(22)	0.0979	−0.0128	0.6518	
O(23)	0.0124	0.0118	0.6075	
O(24)	−0.0182	−0.0065	0.8028	
O(31)	0.2668	0.2608	0.3575	
O(32)	0.1905	0.2782	0.5587	
O(33)	0.3101	0.2845	0.4803	
O(34)	0.2579	0.1793	0.4931	
O(41)	0.2516	0.2551	0.6348	
O(42)	0.2638	0.3148	0.4727	
O(43)	0.1780	0.2314	0.5639	
O(44)	0.2947	0.1997	0.4542	

Table VI. Dimensions of the Coordination Polyhedra in the $La(PyO)_8{}^{3+}$ and $Nd(PyO)_8{}^{3+}$ Ions: Distances (Å) and Angles (deg)

	(a) $La(PyO)_8{}^{3+}$		
La–O(1)	2.500 (11)	La–O(3)	2.497 (12)
La–O(2)	2.493 (12)	La–O(4)	2.498 (12)
		av La–O	2.497
O(1)–O(2)	2.935 (17)	O(1)–O(3)	2.864 (17)
O(2)–O(4)	2.794 (18)	O(3)–O(4)	3.059 (17)
		av O–O	2.913
O(1)–O(1)′	2.965 (17)	O(4)–O(4)′	3.046 (17)
O(2)–O(3)′	3.124 (16)	av	3.045
O(1)–O(2)′	3.464 (17)	O(3)–O(4)′	3.371 (16)
		av	3.418
O(1)–La–O(2)	71.9 (5)	O(1)–La–O(3)	70.1 (5)
O(2)–La–O(4)	68.0 (5)	O(3)–La–O(4)	75.6 (5)
O(1)–La–O(1)′	73.6 (6)	O(2)–La–O(3)	78.4 (5)
O(1)–La–O(2)′	89.1 (6)	O(4)–La–O(4)′	76.2 (5)
		O(3)–La–O(4)′	86.2 (6)
	(b) $Nd(PyO)_8{}^{3+}$		
Nd–O(1)	2.399 (19)	Nd–O(5)	2.421 (18)
Nd–O(2)	2.447 (18)	Nd–O(6)	2.356 (19)
Nd–O(3)	2.383 (17)	Nd–O(7)	2.431 (19)
Nd–O(4)	2.390 (17)	Nd–O(8)	2.426 (18)
		av Nd–O	2.407
O(1)–O(2)	2.925 (26)	O(2)–O(3)	2.857 (25)
O(3)–O(4)	2.703 (27)	O(4)–O(1)	2.789 (28)
O(5)–O(6)	2.810 (25)	O(6)–O(7)	2.793 (28)
O(7)–O(8)	2.883 (29)	O(8)–O(5)	2.846 (26)
		av O–O	2.826
O(1)–Nd–O(2)	74.3 (6)	O(2)–Nd–O(3)	72.5 (6)
O(3)–Nd–O(4)	69.0 (6)	O(4)–Nd–O(1)	71.3 (7)
O(5)–Nd–O(6)	72.1 (7)	O(6)–Nd–O(7)	71.4 (7)
O(7)–Nd–O(8)	72.8 (7)	O(8)–Nd–O(5)	71.9 (6)
		av O–Nd–O	71.9
O(1)–O(5)	3.099 (27)	O(1)–O(8)	3.084 (27)
O(2)–O(5)	3.095 (26)	O(2)–O(6)	3.091 (26)
O(3)–O(6)	3.156 (26)	O(3)–O(7)	3.051 (28)
O(4)–O(7)	3.036 (28)	O(4)–O(8)	3.105 (28)
		av O–O	3.090
O(1)–Nd–O(5)	80.0 (7)	O(1)–Nd–O(8)	79.5 (7)
O(2)–Nd–O(5)	78.9 (6)	O(2)–Nd–O(6)	80.1 (6)
O(3)–Nd–O(6)	83.5 (7)	O(3)–Nd–O(7)	78.7 (7)
O(4)–Nd–O(7)	78.0 (7)	O(4)–Nd–O(8)	80.3 (7)
		av O–Nd–O	79.9

Table VII. Selected Distances (Å) and Angles (deg) in $La(PyO)_8(ClO_4)_3$

	(a) Cation[a]		
La–O(1)–N(1)	127.7 (10)	La–O(2)–N(2)	129.0 (9)
La–O(3)–N(3)	130.1 (10)	La–O(4)–N(4)	136.3 (10)
N(1)–O(1)	1.348 (19)	N(3)–O(3)	1.319 (18)
N(2)–O(2)	1.339 (17)	N(4)–O(4)	1.349 (19)
N(1)–C(11)	1.356 (24)	N(1)–C(15)	1.347 (23)
C(11)–C(12)	1.392 (26)	C(12)–C(13)	1.409 (27)
C(13)–C(14)	1.379 (27)	C(14)–C(15)	1.415 (26)
N(2)–C(21)	1.339 (23)	N(2)–C(25)	1.329 (22)
C(21)–C(22)	1.410 (27)	C(22)–C(23)	1.381 (26)
C(23)–C(24)	1.369 (28)	C(24)–C(25)	1.420 (26)
N(3)–C(31)	1.346 (23)	N(3)–C(35)	1.333 (23)
C(31)–C(32)	1.422 (28)	C(32)–C(33)	1.344 (29)
C(33)–C(34)	1.383 (29)	C(34)–C(35)	1.415 (27)
N(4)–C(41)	1.363 (23)	N(4)–C(45)	1.342 (22)
C(41)–C(42)	1.411 (29)	C(42)–C(43)	1.363 (28)
C(43)–C(44)	1.384 (26)	C(44)–C(45)	1.383 (25)
	(b) Anions		
Cl(1)–O(11)	1.460 (29)	Cl(1)–O(12)	1.370 (39)
Cl(1)–O(13)	1.450 (30)	Cl(1)–O(14)	1.437 (31)
Cl(2)–O(21)	1.389 (22)	Cl(2)–O(22)	1.381 (20)
Cl(2)–O(23)	1.363 (22)	Cl(2)–O(24)	1.467 (21)

[a] Average angles (deg): C–N–C = 124.1 (6), N–C–C = 118.1 (10), C–C–C = 119.9 (8).

the D_{4d} polyhedron would produce contact distances of ca. 2.1 Å between the hydrogens bonded to carbons C(*m*5) and C(*n*5)′, while the observed distances (based on a C–H distance of 1.0 Å) average 2.64 Å. In a similar way, a cubic polyhedron would also produce short H–H distances of ca. 2.0 Å, so that the observed intermediate geometry appears to maximize ligand–ligand contact distances for the particular ligand arrangement in which the "rotation direction" of one set of ligands is opposite to that of the other set. As noted, the ligand planes are roughly normal to the M–O–N coordination planes, apart from ligand 4. The dihedral angles for the two com-

Table VIII. Selected Distances (Å) and Angles (deg) in $Nd(PyO)_8(ClO_4)_3$

(a) Cation			
O(1)-N(1)	1.345 (23)	O(2)-N(2)	1.294 (22)
O(3)-N(3)	1.312 (22)	O(4)-N(4)	1.359 (21)
O(5)-N(5)	1.323 (21)	O(6)-N(6)	1.360 (24)
O(7)-N(7)	1.420 (21)	O(8)-N(8)	1.300 (23)
Nd-O(1)-N(1)	131.1 (8)	Nd-O(2)-N(2)	130.9 (8)
Nd-O(3)-N(3)	129.1 (8)	Nd-O(4)-N(4)	129.0 (8)
Nd-O(5)-N(5)	133.1 (8)	Nd-O(6)-N(6)	130.3 (9)
Nd-O(7)-N(7)	132.1 (7)	Nd-O(8)-N(8)	133.3 (9)
		av	131.2
(b) Anions			
Cl(1)-O(11)	1.430 (17)	Cl(1)-O(12)	1.402 (17)
Cl(1)-O(13)	1.454 (17)	Cl(1)-O(14)	1.431 (17)
Cl(2)-O(21)	1.484 (18)	Cl(2)-O(22)	1.406 (18)
Cl(2)-O(23)	1.351 (18)	Cl(2)-O(24)	1.484 (18)
Cl(3)-O(31)	1.553 (34)	Cl(3)-O(32)	1.399 (34)
Cl(3)-O(33)	1.446 (34)	Cl(3)-O(34)	1.337 (34)
Cl(4)-O(41)	1.397 (35)	Cl(4)-O(42)	1.441 (35)
Cl(4)-O(43)	1.396 (35)	Cl(4)-O(44)	1.485 (35)

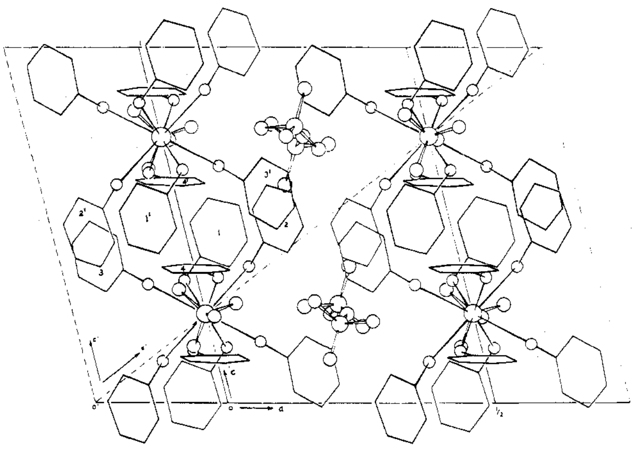

Figure 2. [010] projection of $La(PyO)_8(ClO_4)_3$ (crystal form I) showing the contents of one-half unit cell. The alternative axes a' and c' are indicated by the broken lines (see text). Interplanar distances between pyridine ligands: $1-1^I$, 3.65 Å; $4-4^I$, 3.47 Å; $2-3^I$, 3.69 Å.

plexes average 69°, and this mode of "out-of-plane" coordination seems to be the normal one for pyridine *N*-oxide, the angle in $Co(PyO)_6^{2+}$, for example, being 72.2°.

There appears to be no readily apparent explanation for the orientation of ligand 4. Examination of intermolecular contacts suggests that crystal packing is not a major influence in determining its configuration. The angle La–O(4)–N(4) is significantly larger than the remainder, presumably reflecting the short O(3)···H(45) distance of 2.24 Å.

For the coordination polyhedron in $Nd(PyO)_8^{3+}$, the projected angles giving the relative orientations of the two square faces of the square antiprism range from 42.1 to 47.8°. To within the large standard deviations, however, the polyhedron can be taken to have D_{4d} symmetry with an l/s ratio of 1.093. The average inclination of the Nd–O bonds to the normals to the square faces is 55.5°, while the comparable angles for the $La(PyO)_8^{3+}$ complex average 55.8°. The shape parameters for the idealized square antiprism are l/s = 1.057 and θ = 57.3°.[20] The atoms constituting the two square faces approach coplanarity more closely in this complex than those in the lanthanum complex, and the dihedral angle between the crystallographically unrelated planes is very small.

While the preceding discussion deals with the polyhedron in $La(PyO)_8^{3+}$ as lying along the reaction path interconnecting the square antiprism and the cube, it is pertinent to examine the dihedral angles (δ) between the shape-determining edges, as defined by Muetterties and Guggenberger,[21] to assess the suitability of this description. These angles, together with the ϕ angles, are summarized for both complex ions in Table IX, part 3(B). It can readily be seen that the deviations from the idealized values for the square antiprism are appreciably larger in the case of the lanthanum complex than those for the neodymium complex and that the polyhedron in the former may be described as lying on the path connecting the square antiprism and the dodecahedron, rather than the cube, since for this latter geometry, all δ angles are zero.

Table IX. Least-Squares Planes Parameters for $M(PyO)_8{}^{3+}$ Ions

(1) Equations of Planes[a]

atoms	plane no.	l	m	n	d
(i) M = La					
O(1), O(2), O(3), O(4)	1	−0.1435	0.0075	0.9896	4.904
N(1), C(11), . . ., C(15)	2	0.6241	0.7772	0.0803	1.277
N(2), C(21), . . ., C(25)	3	0.7076	−0.6873	0.1637	−1.182
N(3), C(31), . . ., C(35)	4	−0.6828	0.7099	−0.1728	4.628
N(4), C(41), . . ., C(45)	5	0.0695	−0.1091	0.9916	3.992
(ii) M = Nd					
O(1), O(2), O(3), O(4)	6	0.5261	0.0178	0.8503	4.418
O(5), O(6), O(7), O(8)	7	0.5314	0.0105	0.8471	1.728

(2) Distances of Atoms from Plane[b]

1 O(1), −64; O(2), 66; O(3), −60; O(4), −63; La, 1402
2 N(1), −1; C(11), −4; C(12), 2; C(13), 3; C(14), −8; C(15), 7
3 N(2), 1; C(21), 0; C(22), 1; C(23), −4; C(24), 7; C(25), −6
4 N(3), 5; C(31), −4; C(32), 11; C(33), 21; C(34), −15; C(35), 2
5 N(4), 2; C(41), −2; C(42), 0; C(43), 2; C(44), 0; C(45), −2
6 O(1), 21; O(2), −20; O(3), 21; O(4), −22; Nd, 1372
7 O(5), 30; O(6), −31; O(7), 29; O(8), −29; Nd, 1352

(3) Dihedral Angles (deg)

(A) Plane 1 with plane 1′: 0.88
Plane 6 with plane 7: 0.60

(B) Polyhedron Shape Angles[c]

	δ		ϕ
(i) $La(PyO)_8{}^{3+}$ [d]	6.9	43.0	17.8
	7.2	38.7	17.9
(ii) $Nd(PyO)_8{}^{3+}$	2.6 (1.9)	49.3 (2.4)	21.7 (3.1)
(iii) square antiprism	0.0	52.4	24.5
	0.0	52.4	
(iv) dodecahedron	29.5	29.5	0.0
	29.5	29.5	
(v) cube	0.0	0.0	0.0

[a] Of form $lX + mY + nZ - d = 0$ where X, Y, and Z are coordinates referred to orthogonal axes with X and Y parallel to the crystallographic x and y axes. [b] In Å × 10^3. Numbers in the left column are the plane numbers. [c] For the definition of these dihedral angles, see ref 21. [d] For the lanthanum complex, the two trapezoidal planes in the dodecahedral description are defined by O(1)O(2)′O(2) and O(4)′ and by O(3)′O(4)O(3)O(1)′. In the case of the neodymium complex, since no obvious choice for this pair of planes is evident, an average over all possible sets is given, with the standard deviation based on the spread of values.

The La–O and Nd–O distances in the two complexes average 2.497 (12) and 2.407 (18) Å, respectively, the difference reflecting the expected contraction in radius for the heavier lanthanide. The lanthanum–oxygen distance is close to the values observed in other eight-coordinate complexes of this element with oxygen ligands, e.g., those in the dimethylpyrone complex, averaging 2.48 Å.[9]

The mode of packing of the complex cations and the perchlorate ions in the two monoclinic unit cells is illustrated

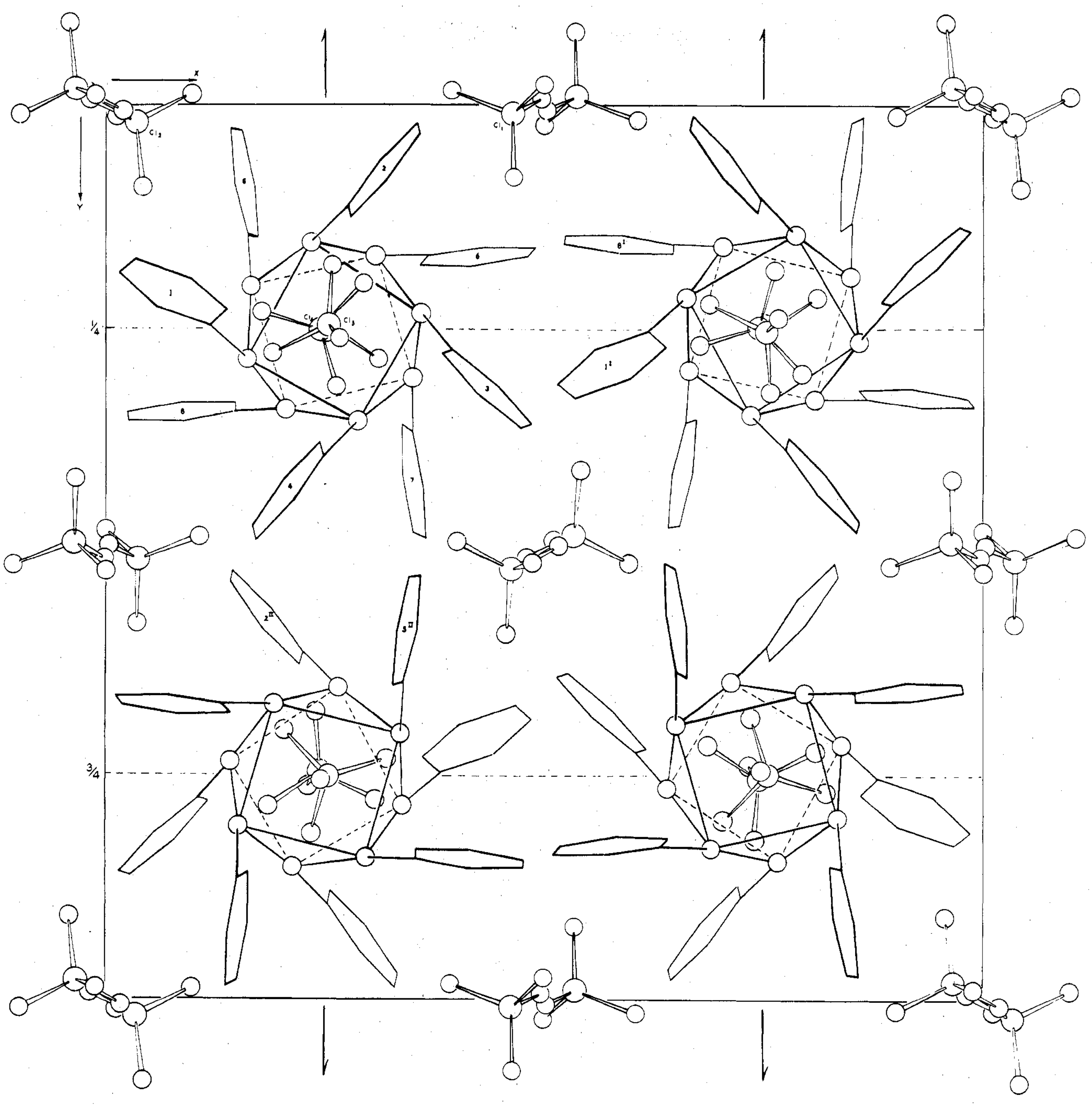

Figure 3. Projection of the contents of one unit cell of $Nd(PyO)_8(ClO_4)_3$ (crystal form II) along the crystal *c* axis, showing the pseudo-fourfold arrangement of complex cations and perchlorate ions. The shortest intermolecular distances between the ligand rings indicated: 4–2^{II}, 3.85 Å; 7–5^{II}, 4.13 Å; 3–1^{I}, 3.97 Å; 6–8^{I}, 4.06 Å.

in Figures 2 and 3, the latter clearly showing the pseudotetragonal arrangement of ions found in crystalline form II when viewed along the *c* axis. Since the two forms for both lanthanum and neodymium cocrystallize from the same solution, the ion packing arrangement in the two unit cells might be expected to be similar. With the choice of alternative axes as indicated in Figure 2, the size and shape of the unit cell for I are indeed very similar to those obtained for II, with pairs of $La(PyO)_8{}^{3+}$ ions being related by the *a* glide plane as for II. The principal difference between the two arrangements is that the two pairs are related by a *c* glide in I and by the twofold screw axis in II.

In both structures, the complex ions are surrounded roughly octahedrally by the perchlorate ions at distances of approximately 7 Å, the ions lying on the pseudo-fourfold axes of the complexes being those exhibiting the static disorder. The packing appears to be governed mainly by the complex ions, all ligand ring contacts, including those involving ring 4 in I, between neighboring ions appearing to be acceptable and to be in the range 3.4–3.8 Å. Finally, on the basis of the observed arrangement of ions in II, it is difficult to see any underlying structural origin for the occurrence of the twinning in this crystalline form, despite the presence of the pseudosymmetry exhibited by the structure.

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Registry No. $La(PyO)_8(ClO_4)_3$, 18041-61-7; $Nd(PyO)_8(ClO_4)_3$, 18347-48-3.

Supplementary Material Available: Observed and calculated structure factor amplitudes for $La(PyO)_8(ClO_4)_3$ and $Nd(PyO)_8(ClO_4)_3$ (23 pages). Ordering information is given on any current masthead page.

References and Notes

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Crystal and Molecular Structure, Spectroscopy, and Magnetism of Diaquobis(imidazole)-*catena*-μ-(squarato-1,3)-nickel(II). A One-Dimensional Polymer

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The crystal and molecular structure of diaquobis(imidazole)-*catena*-μ-(squarato-1,3)-nickel(II), $NiC_4O_4(C_3N_2H_4)_2(H_2O)_2$, has been determined by a single-crystal X-ray analysis using three-dimensional diffractometer data. The compound crystallizes in the monoclinic system, with two formula units in a centrosymmetric unit cell, with space group $P2_1/c$ and lattice parameters a = 7.478 (1) Å, b = 11.539 (2) Å, c = 8.101 (2) Å, and β = 109.27 (2)°. The structure was solved with a direct method. A refinement by full-matrix least-squares procedures converged to $R_F = 0.023$ and $R_{wF} = 0.032$ for 1576 independent observed reflections. The Ni(II) ions are octahedrally surrounded by four oxygens of two water molecules and two squarato anions and two nitrogens of the imidazole ligands. The crystal structure contains chains of (squarato-1,3)-bridged Ni(II) ions. These chains are held together by strong hydrogen bonds between the noncoordinating oxygens of the squarato anions and the water molecules, forming a two-dimensional sheet of Ni(II) ions. These sheets are held together by weaker hydrogen bonds between the imidazole hydrogens and coordinating squarato oxygens. The Ni–N bond length (2.076 (1) Å) and Ni–O_w bond length (2.069 (1) Å) are normal. The Ni–O_s bond length (2.121 (1) Å) is rather long compared with that of similar compounds. Infrared, far-infrared, Raman, and ligand-field spectroscopies all agree with the observed crystal structure. The magnetic susceptibility data in the temperature region 1.2–100 K could best be described by neglecting the influence of the exchange coupling, yielding a zero-field splitting parameter D and $\bar{g}$ value of +5.8 (2) cm^{-1} and 2.28 (3), respectively. Fitting of the data with the available theory for Heisenberg one-dimensional coupled $S = 1$ ions, with both D and $J \neq 0$, yielded poor results.

Introduction

In magnetochemistry there is a still increasing interest for new types of bridging ligands, in order to obtain further insights into the mechanisms of the phenomenon of superexchange interactions between paramagnetic ions. A recent review on magnetically investigated transition-metal chain compounds was published by Carlin and van Duyneveldt.[1]

Recently, the magnetism and spectroscopy of a series of oxalato-bridged coordination compounds built up by chemical chains were studied.[2] Very recently, an X-ray structure investigation of one compound within this series evidenced an earlier proposed chain structure.[3] The magnetic superexchange interactions via the oxalato anions appeared to be quite large, i.e., in the order of about -10 cm^{-1}. Dimeric oxalato-bridged compounds have been investigated thoroughly and interactions of similar magnitude were found.[4] Within the dimeric compounds it is known that the magnetic superexchange interactions are strongly reduced by substitution of the oxalato ions by squarato ions.[4] One of the aims of the present investigation is to obtain a squarato-bridged chain compound and find out what happens with the superexchange interactions. To explain the value of the exchange constant, J value, in terms of the structure, we have undertaken a structural and spectroscopic study of $NiSq(IzH)_2(H_2O)_2$ (NISIA), where Sq is the squarato dianion and IzH is imidazole.

Experimental Section

IR, far-IR, Raman, and ligand-field spectra were recorded and magnetic susceptibility measurements (4.2–100 K) were performed as described elsewhere.[2] Ac susceptibility measurements in the temperature region 1.2–4.2 K were performed at a frequency of 663 Hz with a mutual inductance detector described in detail elsewhere.[5] Transparent blue-green crystals of NISIA were slowly grown from a mixture of a solution of $NiCl_2$ in water (0.01 mol/L), a solution of $H_2C_4O_4$ in water (0.01 mol/L), and a solution of $C_3N_2H_4$ (imidazole) in water (0.02 mol/L).

A specimen showing sharp optical extinctions under crossed polarizers was mounted along the c axis. On the basis of the observed extinctions ($0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$) on the spectrometer, the crystal was found to belong to the monoclinic system, space group $P2_1/c$.

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