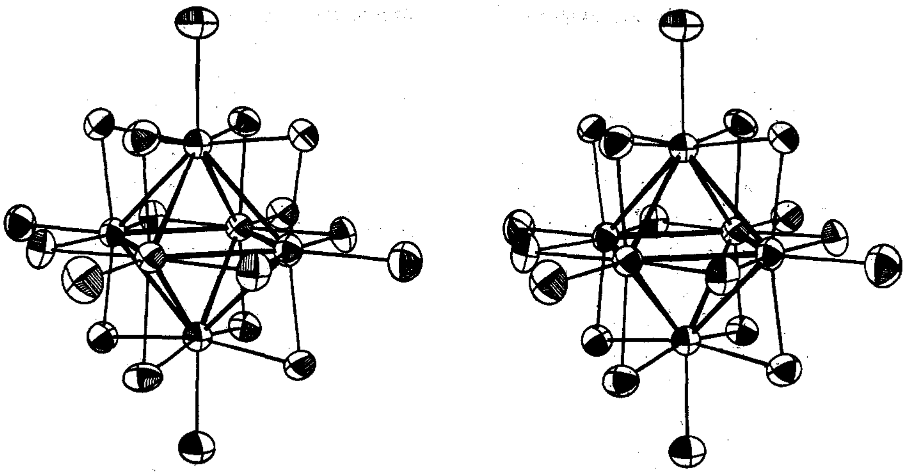

Figure 2.—A stereoscopic view of the $Ta_6Cl_{18}{}^{2-}$ anion cluster.

TABLE VI
COMPILATION OF SOME DISTANCES[a] IN $(M_6X_{12})Y_mL_{6-m}{}^{(n-m)+}$-CONTAINING COMPOUNDS

Compd	d(M–M), Å		d(M–X), Å	d(M–Y), Å	d(X–X), Å
Ta_6I_{14}[2]	2.805 3.080	2.90[b]	2.754		3.785
$Ta_6Cl_{14}\cdot 7H_2O$[3]	2.96				
Ta_6Cl_{15}[4]	2.925		2.434	2.564	3.408
$H_2[Ta_6Cl_{18}]\cdot 6H_2O$	2.962		2.414	2.507	3.384
Nb_6Cl_{15}[5]	2.895 2.955	2.915[b]	2.407	2.58	3.385
$K_4(Nb_6Cl_{18})$[6]	2.915		2.49	2.596	3.47
Nb_6F_{15}[7]	2.80		2.05	2.11	2.89
$[(CH_3)_4N]_2Nb_6Cl_{18}$[8]	3.02		2.42	2.46	3.40

[a] All distances refer to average values. [b] Tetragonal flattening.

of molecular orbital studies of the $M_6X_{12}{}^{n+}$ species.[16,17]

Infrared spectra of these polynuclear subhalides with $n = 3$ or 4 have been interpreted on the basis of tighter binding in the M–Y(terminal) bond.[18]

It would be reasonable to assume that the six waters and two protons reside in the approximately 9-Å "holes" in the structure, but with no preferred ordering. This would account for the fact that there were no peaks found on the difference map above a value of 1 $e^-/Å^3$, although no oxygen atoms had been included in the structure factor calculation.

In $HNb_6I_8{}^{3+}$,[19] the hydrogen atom was found to reside in the center of the Nb_6 cluster, but chemical evidence[20] seems to rule out a similar position for the proton in this case.

(16) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(17) R. F. Schneider and R. A. Mackay, *J. Chem. Phys.*, **42**, 843 (1968).

(18) P. B. Fleming and R. E. McCarley, *Inorg. Chem.*, **9**, 1347 (1970).

(19) A. Simon, H. G. Schnering, and H. Schafer, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).

(20) R. E. McCarley, private communication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN 48202

The Stereochemistry of the Chloropentaaquoterpyridylpraseodymium(III) Ion[1]

BY LEWIS J. RADONOVICH[2] AND MILTON D. GLICK*

Received January 26, 1970

The crystal structure of $Pr(C_{15}H_{11}N_3)Cl_3(H_2O)_8$ has been determined by single-crystal X-ray diffraction techniques employing Patterson and Fourier syntheses. The compound crystallizes in the space group Cm ($Z = 2$) with dimensions $a = 7.482$ (2), $b = 16.602$ (7), $c = 9.723$ (3) Å, and $\beta = 90.13$ (1)°. The structure was refined to a discrepancy factor of 0.022 for 2005 diffractometer data. The coordination sphere about the Pr(III) ion consists of three nitrogen atoms from the terpyridyl ligand, one chloride ion, and five oxygen atoms from water molecules in the form of a monocapped square-antiprismatic polyhedron.

Introduction

In recent years a large number of rare earth complexes with donor nitrogen atoms have been prepared using nonbasic nitrogen-containing ligands. Prominent among these are complexes of polypyridyl ligands which include $Ln(terpy)Cl_3(H_2O)_n$,[3,4] $Ln(terpy)(NO_3)_3(H_2O)_n$,[5] $Ln(bipy)_2(NO_3)_2(H_2O)_n$,[6,7] $Ln(bipy)_2Cl_3$-

(1) (a) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 17, 1969. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (No. 841-G), and to the National Science Foundation (GP-15070).

(2) (a) National Defense Education Act Fellow, 1966–1969; Petroleum Research Fund Fellow, 1969–1970. (b) This article is based in part on a dissertation submitted by L. J. Radonovich to the Graduate School of Wayne State University in partial fulfillment of the requirements for the Ph.D. degree.

(3) S. P. Sinha, *Z. Naturforsch. A*, **20**, 552 (1965).

(4) Ln denotes the series of lanthanide(III) ions. Terpyridyl is denoted by terpy.

(5) S. P. Sinha, *Z. Naturforsch. A*, **20**, 1661 (1965).

(6) S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).

(7) D. S. Moss and S. P. Sinha, *Z. Phys. Chem.* (*Frankfurt am Main*), **63**, 190 (1969).

$(H_2O)_n$,[6] and $Ln(terpy)_3(ClO_4)_3(H_2O)_n$.[8] In almost all of these compounds it was not possible to distinguish which atoms were present in the coordination sphere of the metal. As part of a continuing study of the stereochemistry and bonding in rare earth complexes, a crystallographic investigation of a hydrated praseodymium(III) terpyridyl trichloride is reported.

Experimental Section

The compound was synthesized according to the preparation given by Sinha.[3] Ethanol solutions of hydrated praseodymium trichloride and 2,2′,2′′-terpyridyl were refluxed for approximately 20 min, precipitating the light green powder of hydrated praseodymium terpyridyl trichloride. The following results of microanalysis were found for the powdered sample. *Anal.* Calcd for $Pr(terpy)Cl_3(H_2O)_2$: N, 8.1; C, 34.8; H, 2.9. Found: N, 7.7; C, 35.9, H, 2.7. This microanalysis is in excellent agreement with that reported on the powder by Sinha.[3]

Single crystals were first formed by the vapor diffusion method using an inner solvent of methanol and an outer solvent of ethanol. This method produced excellent crystals; however, these crystals rapidly became opaque after exposure to air. Crystals were then formed, with difficulty, by a slow evaporation (to dryness) of a methanol solution of the complex. These crystals were quite stable in air. The crystal used for precession pictures and preliminary data collection was mounted on a glass fiber using Kodak 910 adhesive with the [010] direction approximately coincident with the spindle axis. The crystal used for final data collection was cut from a larger crystal under a microscope to a nondescript crystal of the approximate dimensions 0.27 mm × 0.27 mm × 0.30 mm and was mounted on a glass fiber using Silastic adhesive, with the [110] direction approximately coincident with the spindle axis.

Microanalysis of the crystals yielded the following results. *Anal.* Calcd for $Pr(terpy)Cl_3(H_2O)_8$: N, 6.73; C, 28.83; H, 4.32. Found: N, 6.9; C, 29.2; H, 4.3. The experimental density (flotation method) of the crystalline material was 1.73 (3) g/cm^3.

Precession photographs taken with Mo Kα radiation (λ 0.7107 Å) showed the crystals to have Laue symmetry $2/m$ with a systematic absence of all reflections with $h + k$ odd, indicating the possible space groups $C2/m$, $C2$, or Cm. The lattice constants preliminarily obtained from precession photographs were refined by least squares[9] from 23 reflections whose angles were accurately determined at 22° on the Picker four-circle card-controlled diffractometer using Mo Kα_1 radiation (λ 0.70926 Å). The refined lattice constants are a = 7.482 (2) Å, b = 16.602 (7) Å, c = 9.723 (3) Å, and β = 90.13 (1)°. The unit cell volume is 1208 Å^3 and the calculated density for two formula weights of $PrCl_3O_8N_3C_{15}H_{27}$ per unit cell is 1.71 g/cm^3.

Final intensity data were collected with Mo Kα radiation using a moving-crystal, moving-counter (θ–2θ) scan technique[10] with a takeoff angle of 1.7°. A symmetric scan of 2° was used with an allowance for spectral dispersion and a scan rate of 2°/min. Stationary background counts of 15 sec were taken at both ends of the scan. A zirconium filter of 1-mil thickness was used for all data with a 2θ greater than 12° and a filter of 2-mil thickness was used for data less than 12°. Attenuators were inserted for any reflection in which the counting rate exceeded 9000 cps. The pulse height analyzer was set to accept approximately 90% of the pulse generated and the counter aperture was 29.9 cm from the crystal for all data.

A total of 2013 independent data, excluding systematic absences, were collected, partially in the quadrant $\pm h, k, l$ and partially in the quadrant $h, k, \pm l$, to a limiting 2θ of 62.5° ($(\sin\theta)/\lambda \leq 0.756$). Four standard reflections were inserted after every 100 reflections to check for crystal and instrument stability. These standards varied less than 5% during the entire course of data collection.

The intensity data were corrected for background, Lorentz, and polarization effects. Standard deviations for F^2 were assigned according to the formula

$$\sigma(F^2) = [P + (B_1 + B_2)\Delta(2\theta) + (0.05I)^2]^{1/2}$$

where P is the gross intensity, B_1 and B_2 are the background counts, $\Delta(2\theta)$ is the scan length, and I is the net intensity. The data were then scaled to account for the different β filters and the use of attenuators. Of the 2013 data examined, 2005 of these were found to have net intensities greater than one standard deviation and were used for the structure solution and refinement.

The linear absorption coefficient with Mo Kα radiation is 2.39 mm^{-1}. The lack of well-defined faces precluded absorption corrections; however, calculations assuming an extreme case, a cube with the faces corresponding to the crystal axes, showed the transmission factor to vary from 0.54 to 0.66. A more realistic model would lead to less variation in transmission.

Structure Analysis

The presence of two formula units in any of the possible space groups requires the presence of molecular symmetry. Stereochemical constraints indicated the most likely space group to be Cm, with the praseodymium(III) ion located in the mirror plane ($y = 0$) and the x and z coordinates arbitrary. Successive electron density maps starting with the praseodymium(III) at the origin with a preliminary set of data, which was limited in scope ($(\sin\theta)/\lambda \leq 0.55$), led to an accurate description of the coordination sphere; the presence of 1.5 lattice waters per asymmetric unit was readily apparent ($\rho \approx 3e^-/\text{Å}^3$) from electron density maps using the final, more complete set of data. Full-matrix isotropic least-squares refinement on F of all nonhydrogen atoms, including anomalous dispersion effects for praseodymium, resulted in a conventional discrepancy factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.061 and a weighted discrepancy factor, $wR = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.086 for the image chosen. The alternate image, related by an inversion center, could be rejected at the 0.005 significance according to the Hamilton R value test.[11]

Anisotropic refinement of all nonhydrogen atoms led to discrepancy factors of R = 0.022 and wR = 0.026 with an error of fit of 0.98. The largest peak on the final difference map was 0.5 e$^-$/Å^3 and was near the metal position. Other residual peaks were smaller than 0.4 e$^-$/Å^3. A search for hydrogen atoms confirmed electron density at the expected positions but did not allow unambiguous placement of every hydrogen atom. A comparison of calculated and observed structure factors is given in Table I and is based upon the atomic parameters (in a right-handed coordinate system) given in Table II. Distances and angles with standard deviations estimated from the full variance–covariance matrix are listed in Table III.

The thermal parameters for the lattice waters [O(4) and O(5)] are significantly higher than for all other atoms. In order to test whether these sites might be partially vacant, occupancy factors for these atoms were varied. The resulting occupancy factors were

---

(8) D. A. Durham, G. H. Frost, and F. A. Hart, *J. Inorg. Nucl. Chem.*, **31**, 833 (1969).

(9) Local versions of the following programs were used in the solution and refinement of this structure: PICK 2—J. A. Ibers' least-squares program for lattice constants and orientation angles based on W. C. Hamilton's MODE1; DACOR—D. L. Smith's program for the correction of diffractometer data and estimation of standard deviations; FORDAP—A. Zalkin's Fourier program; ORFLS and ORFFE—W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP—C. K. Johnson's program for drawing of crystal structures. Scattering factors for Pr(III) were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), and those for the remaining atoms were taken from "The International Tables for X-Ray Crystallography," Vol. III, C. H. MacGillavry, G. D. Rieck, and K. Lonsdale, Ed., Kynoch Press, Birmingham, England, 1962, p 201.

(10) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., 1966, p 144.

(11) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

TABLE I

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

	H	FO	FC
K= 0,L=-13	4	238	233
K= 0,L=-10	2	332	318
K= 0,L= -9	2	469	471
	4	251	240
	8	343	345
K= 0,L= -8	2	469	485
	4	499	500
K= 0,L= -7	2	934	922
	4	459	482
	6	447	449
K= 0,L= -6	2	665	661
	4	582	562
	6	420	423
K= 0,L= -5	2	545	499
	4	431	426
	6	498	507
	10	323	319
K= 0,L= -4	2	1000	982
	4	436	427
	6	640	640
K= 0,L= -3	2	1176	1062
	4	638	633
	6	425	428
K= 0,L= -2	2	1222	1161
	4	520	521
	6	746	742
K= 0,L= -1	2	1140	1080
	4	714	696
	6	617	599
	8	591	589
K= 0,L= 0	2	645	793
	4	1014	986
	6	238	239
	8	615	612
	10	326	331
K= 0,L= 1	-10	276	268
	0	1183	1296
	2	2505	2843
	4	784	778
	6	643	647
	8	522	519
	10	204	207
K= 0,L= 2	-10	271	285
	-8	264	264
	0	803	837
	2	1072	967
	4	1537	1534
	6	672	673
	8	600	598
	10	265	266
K= 0,L= 3	-10	318	321
	-8	431	422
	0	1106	1170
	2	1164	1088
	4	143	136
	6	846	837
	8	446	447
	10	315	312
K= 0,L= 4	-10	383	388
	-8	447	455
	0	852	816
	2	1523	1544
	4	350	354
	6	232	230
	8	420	422
	10	314	316
K= 0,L= 5	-8	421	426
	0	870	912
	2	680	665
	4	619	612
	6	323	334
	8	261	272
	10	311	296
K= 0,L= 6	-8	381	386
	0	779	769
	2	519	536
	4	137	131
	6	517	523
	8	360	385
K= 0,L= 7	-8	280	283
	0	783	773
	2	522	506
	4	361	372
	6	295	290
	8	391	389
K= 0,L= 8	-8	300	304
	-6	293	300
	0	722	716
	2	551	558
	4	376	378
	6	354	353
	8	212	211
K= 0,L= 9	-6	255	288
	0	460	474
	2	606	609
	4	365	378
	6	349	353
	8	215	217
K= 0,L= 10	-6	321	323
	-4	249	242
	0	520	524
	2	335	342
	4	336	342
	6	249	246
K= 0,L= 11	-6	111	110
	-4	343	356
	-2	320	316
	0	435	441
	2	301	301
	4	204	203
	6	223	218
K= 0,L= 12	-4	125	128
	-2	334	350
	0	324	329
	2	225	227
	4	205	204
K= 0,L= 13	-2	126	125
	0	288	290
	2	231	227
	4	209	202
K= 0,L= 14	0	135	136
K= 1,L=-14	1	126	123
K= 1,L=-10	1	362	353
K= 1,L= -9	1	463	463
	3	352	388
K= 1,L= -8	1	493	498
	3	533	531
	5	528	528
	9	245	236
K= 1,L= -7	1	658	709
	3	576	561
	5	653	665
K= 1,L= -6	1	623	631
	3	838	815
	5	556	558
K= 1,L= -5	1	694	664
	3	716	709
	5	649	621
	7	421	424
K= 1,L= -4	1	1126	1095
	3	866	844
	5	565	542
	7	531	537
K= 1,L= -3	1	335	345
	3	555	556
	5	707	697
	7	450	451
K= 1,L= -2	1	963	947
	3	1177	1134
	5	842	829
	7	401	401
K= 1,L= -1	1	722	656
	3	1392	1380
	5	788	762
	7	428	430
K= 1,L= 0	1	1400	1401
	3	1372	1346
	5	780	751
	7	422	436
	9	266	286
K= 1,L= 1	-9	241	242
	1	1237	1262
	3	1176	1183
	5	684	671
	7	456	469
	9	280	264
K= 1,L= 2	-9	196	205
	1	241	214
	3	1199	1159
	5	988	987
	7	434	443
	9	261	254
K= 1,L= 3	-9	228	231
	1	1164	1150
	3	569	570
	5	1044	1031
	7	425	431
	9	293	292
K= 1,L= 4	-9	239	241
	1	1072	1020
	3	956	939
	5	564	570
	7	392	393
	9	299	295
K= 1,L= 5	-9	264	266
	1	732	740
	3	709	667
	5	671	674
	7	209	207
	9	266	263
K= 1,L= 6	-9	217	217
	-7	358	355
	1	736	742
	3	545	540
	5	482	491
	7	402	398
	9	163	162
K= 1,L= 7	-9	188	189
	-7	274	280
	1	340	335
	3	659	655
	5	420	427
	7	366	361
	9	204	205
K= 1,L= 8	-7	238	238
	1	396	397
	3	564	579
	5	422	414
	7	270	262
	9	153	150
K= 1,L= 9	-7	313	312
	-5	383	387
	1	424	424
	3	523	534
	5	374	373
	7	219	221
K= 1,L= 10	-7	230	232
	-5	372	378
	-3	333	329
	1	364	367
	3	426	425
	5	339	333
	7	203	206
K= 1,L= 11	-5	250	256
	-3	411	413
	-1	261	261
	1	339	343
	3	261	262
	5	293	258
K= 1,L= 12	-5	186	195
	-3	295	297
	-1	282	282
	1	236	239
	3	266	261
	5	245	232
K= 1,L= 13	-3	176	179
	-1	181	195
	1	224	220
	3	232	233
K= 1,L= 14	1	172	170
K= 2,L=-13	4	206	205
K= 2,L=-10	2	426	418
K= 2,L= -9	2	384	380
	4	340	339
	6	308	305
K= 2,L= -8	2	604	608
	4	310	255
K= 2,L= -7	2	495	472
	4	562	554
K= 2,L= -6	2	799	772
	4	408	396
	6	468	471
K= 2,L= -5	2	1009	959
	4	515	493
	6	617	618
	10	269	264
K= 2,L= -4	2	812	767
	4	604	569
	6	550	557
K= 2,L= -3	2	1192	1150
	4	331	327
	6	656	661
K= 2,L= -2	2	846	826
	4	671	676
	6	426	419
K= 2,L= -1	2	1352	1362
	4	612	623
	6	472	473
K= 2,L= 0	0	1151	1174
	4	694	682
	6	414	401
	8	542	541
	10	246	253
K= 2,L= 1	-10	303	310
	-8	416	413
	0	1102	1131
	2	512	488
	4	284	289
	6	403	389
	8	513	500
	10	297	302
K= 2,L= 2	-10	306	315
	-8	474	475
	0	1589	1764
	2	934	904
	4	587	576
	6	512	503
	8	406	395
	10	289	287
K= 2,L= 3	-10	297	307
	-8	437	435
	0	616	678
	2	1258	1241
	4	594	587
	6	651	649
	8	435	427
	10	259	252
K= 2,L= 4	-10	327	333
	-8	391	392
	0	1189	1210
	2	821	844
	4	653	636
	6	507	507
	8	451	458
	10	297	290
K= 2,L= 5	-8	446	448
	0	959	949
	2	948	953
	4	409	401
	6	451	446
	8	386	388
	10	281	284
K= 2,L= 6	-8	333	336
	0	966	959
	2	634	622
	4	538	537
	6	397	406
	8	369	371
K= 2,L= 7	-8	350	353
	-6	292	284
	0	775	773
	2	546	538
	4	405	408
	6	434	426
	8	354	355
K= 2,L= 8	-8	323	319
	-6	361	365
	0	486	460
	2	553	559
	4	341	345
	6	327	328
	8	278	286
K= 2,L= 9	-6	324	327
	0	583	593
	4	331	342
	6	293	287
	8	222	221
K= 2,L= 10	-6	271	270
	-4	305	315
	0	433	432
	2	431	436
	4	213	221
	6	264	262
K= 2,L= 11	-6	207	208
	-4	250	257
	-2	368	375
	0	414	435
	2	298	293
	4	276	270
	6	108	105
K= 2,L= 12	-4	246	239
	-2	253	256
	0	372	372
	2	238	242
	4	223	223
K= 2,L= 13	-2	233	241
	0	237	241
	2	248	252
	4	176	177
K= 2,L= 14	0	229	226
K= 3,L=-14	1	214	214
K= 3,L=-12	5	263	261
K= 3,L=-10	1	278	281
K= 3,L= -9	1	413	411
	3	377	383
K= 3,L= -8	1	598	605
	3	484	472
	5	389	383
K= 3,L= -7	1	399	405
	3	696	678
	5	543	536
	9	250	244
K= 3,L= -6	1	742	721
	3	524	508
	5	639	633
K= 3,L= -5	1	466	458
	3	947	903
	5	455	455
K= 3,L= -4	1	813	760
	3	863	833
	5	721	699
	7	297	301
K= 3,L= -3	1	1559	1439
	3	938	894
	5	759	737
	7	445	446
K= 3,L= -2	1	367	370
	3	1322	1273
	5	798	784
	7	412	421
K= 3,L= -1	1	1161	1163
	3	398	401
	5	1050	1028
	7	373	387
K= 3,L= 0	1	742	748
	3	1223	1191
	5	527	516
	7	549	551
	9	220	222
K= 3,L= 1	-9	285	279
	1	386	383
	3	1154	1136
	5	845	838
	7	345	350
	9	290	290
K= 3,L= 2	-9	295	301
	1	1065	1118
	3	749	787
	5	683	666
	7	464	477
	9	185	191
K= 3,L= 3	-9	224	217
	1	475	452
	3	964	976
	5	523	510
	7	353	356
	9	223	218
K= 3,L= 4	-9	235	239
	1	1208	1199
	3	548	542
	5	723	728
	7	279	288
	9	246	249
K= 3,L= 5	-9	185	198
	-7	419	420
	1	833	862
	3	930	924
	5	553	565
	7	367	365
	9	213	208
K= 3,L= 6	-9	181	183
	-7	341	344
	1	358	354
	3	803	796
	5	636	647
	7	319	324
	9	217	213
K= 3,L= 7	-7	258	261
	1	674	667
	3	478	487
	5	502	510
	7	345	339
	9	188	190
K= 3,L= 8	-7	358	368
	1	482	487
	3	663	683
	5	335	337
	7	300	303
K= 3,L= 9	-7	261	260
	-5	505	518
	1	401	411
	3	376	379
	5	461	452
	7	213	220
K= 3,L= 10	-7	263	262
	-5	302	305
	-3	544	544
	1	431	435
	3	335	337
	5	294	252
	7	234	234
K= 3,L= 11	-5	317	318
	-3	311	312
	-1	374	384
	1	265	264
	3	347	349
	5	277	274
K= 3,L= 12	-3	316	310
	-1	220	222
	1	326	328
	3	252	250
	5	253	252
K= 3,L= 13	-3	235	246
	-1	245	240
	1	208	208
	3	277	269
K= 3,L= 14	1	175	173
K= 4,L=-11	4	161	161
K= 4,L= -9	2	411	413
	4	249	242
K= 4,L= -8	2	559	559
	4	246	241
K= 4,L= -7	2	353	361
	4	419	421
K= 4,L= -6	2	524	471
	4	418	417
	6	364	360
K= 4,L= -5	2	811	770
	4	557	550
	6	451	466
	10	191	197
K= 4,L= -4	2	702	661
	4	716	712
	6	626	626
	10	263	260
K= 4,L= -3	2	1377	1385
	4	436	437
	6	585	583
K= 4,L= -2	2	940	913
	4	691	686
	6	486	477
K= 4,L= -1	2	1164	1081
	4	503	556
	6	678	683
K= 4,L= 0	0	951	968
	2	1116	1115
	4	628	656
	6	617	618
	8	523	517
	10	290	298
K= 4,L= 1	-10	317	319
	-8	481	481
	0	1403	1478
	2	995	974
	4	738	726
	6	518	524
	8	457	450
	10	326	322
K= 4,L= 2	-10	333	332
	-8	508	506
	0	1293	1316
	2	1133	1125
	4	313	307
	6	558	544
	8	303	303
	10	326	323
K= 4,L= 3	-8	422	415
	0	1082	1079
	2	1109	1121
	4	404	399
	6	367	379
	8	415	420
	10	273	276
K= 4,L= 4	-8	392	389
	0	1299	1334
	2	639	643
	4	592	576
	6	439	452
	8	377	374
	10	239	241
K= 4,L= 5	-6	378	380
	0	707	698
	2	788	764
	4	486	495
	6	492	493
	8	422	417
	10	196	191
K= 4,L= 6	-8	333	338
	0	945	988
	2	473	461
	4	608	616
	6	293	296
	8	385	384
K= 4,L= 7	-8	391	397
	-6	242	245
	0	753	727
	2	616	621
	4	381	394
	6	361	357
	8	286	287
K= 4,L= 8	-8	301	298
	-6	359	350
	0	484	481
	2	473	478
	4	326	327
	6	303	311
	8	300	299
K= 4,L= 9	-6	288	290
	-4	339	337
	0	543	547
	2	323	331
	4	243	239
	6	292	288
	8	256	253
K= 4,L= 10	-6	271	263
	-4	303	306
	-2	441	435
	0	334	347
	2	403	393
	4	184	191
	6	259	251
K= 4,L= 11	-6	261	271
	-4	221	223
	-2	360	368
	0	342	349
	2	280	280
	4	259	257
	6	190	192
K= 4,L= 12	-4	259	261
	-2	212	224
	0	357	362
	2	258	266
	4	206	206
K= 4,L= 13	-2	275	277
	0	238	237
	2	262	262
	4	172	168
K= 4,L= 14	0	253	252
K= 5,L=-13	3	212	207
K= 5,L=-12	5	240	230
K= 5,L=-10	7	230	227
K= 5,L= -9	1	302	307
	3	404	409
K= 5,L= -8	1	422	438
	3	427	432
K= 5,L= -7	1	457	471
	3	503	505
	5	394	389
	9	200	202
K= 5,L= -6	1	346	351
	3	732	720
	5	478	465
K= 5,L= -5	1	731	719
	3	753	726
	5	721	733
K= 5,L= -4	1	680	671
	3	1070	1051
	5	592	590
	7	420	421
K= 5,L= -3	1	1293	1250
	3	792	746
	5	800	800
	7	273	272
K= 5,L= -2	1	1275	1223
	3	781	767
	5	774	761
	7	404	402
K= 5,L= -1	1	1100	1035
	3	727	715
	5	964	962
	7	433	441
K= 5,L= 0	1	358	387
	3	956	951
	5	809	803
	7	462	468
	9	259	259
K= 5,L= 1	-9	316	312
	1	528	568
	3	1064	1076
	5	705	691
	7	399	399
	9	190	185
K= 5,L= 2	-9	266	263
	1	997	934
	3	1127	1130
	5	534	513
	7	413	413
	9	200	200
K= 5,L= 3	-9	317	324
	1	936	905
	3	1032	1027
	5	567	558
	7	432	445
	9	258	262
K= 5,L= 4	-9	230	222
	1	684	691
	3	739	729
	5	708	707
	7	415	420
	9	237	239
K= 5,L= 5	-9	172	172
	-7	349	343
	1	498	498
	3	715	689
	5	642	651
	7	381	372
	9	208	208
K= 5,L= 6	-9	185	191
	-7	328	335
	1	738	744
	3	633	630
	5	538	546
	7	262	268
	9	186	183
K= 5,L= 7	-7	325	336
	1	445	448
	3	643	656
	5	461	451
	7	247	248
	9	155	160
K= 5,L= 8	-7	280	281
	-5	392	398
	1	432	449
	3	344	338
	5	379	372
	7	262	263
K= 5,L= 9	-7	235	239
	-5	350	347
	-3	363	374
	3	318	311
	5	289	288
	7	211	210
K= 5,L= 10	-5	318	322
	-3	393	392
	-1	303	312
	1	290	283
	3	334	335
	5	334	328
	7	168	161
K= 5,L= 11	-5	290	294
	-3	314	316
	-1	228	226
	1	316	317
	5	300	300
K= 5,L= 12	-3	236	250
	-1	248	248
	1	256	248
	3	308	307
	5	178	179
K= 5,L= 13	-1	233	225
	1	213	210
	3	248	226
K= 6,L=-13	2	167	182
K= 6,L=-11	6	193	195
K= 6,L= -9	2	525	534
	8	221	226
K= 6,L= -8	2	354	354
	4	369	368
K= 6,L= -7	2	745	745
	4	261	261
K= 6,L= -6	2	378	359
	4	717	729
	6	343	338
K= 6,L= -5	2	342	355
	4	519	520
	6	515	522
K= 6,L= -4	2	1091	1068
	4	305	307
	6	373	375
	10	260	262
K= 6,L= -3	2	865	834
	4	743	721
	6	241	243
	10	318	318
K= 6,L= -2	2	878	852
	4	384	384
	6	643	646
K= 6,L= -1	2	732	730
	4	358	349
	6	474	486
K= 6,L= 0	0	1453	1513
	2	991	936
	4	615	599
	6	458	471
	8	390	392
	10	224	225
K= 6,L= 1	-8	557	548
	0	734	718
	2	1577	1575
	4	528	519
	6	646	653
	8	316	320
	10	254	263
K= 6,L= 2	-8	390	345
	0	1299	1292
	2	969	945
	4	456	464
	6	475	487
	8	465	468
	10	274	267
K= 6,L= 3	-8	370	370
	0	1181	1111
	2	705	695
	4	251	274
	6	533	550
	8	433	431
	10	309	302
K= 6,L= 4	-8	445	449
	0	891	900
	2	652	642
	4	453	453
	6	355	357
	8	453	449
	10	260	258
K= 6,L= 5	-8	391	386
	0	1012	1036
	2	466	451
	4	625	612
	6	308	309
	8	370	373
K= 6,L= 6	-8	404	405
	0	557	538
	2	667	683
	4	478	498
	6	357	357
	8	308	305
K= 6,L= 7	-8	329	319
	-6	355	344
	0	687	679
	2	366	365
	4	396	410
	6	273	273
	8	329	321
K= 6,L= 8	-8	255	254
	-6	244	253
	0	845	867
	2	426	449
	4	230	233
	6	264	265
	8	261	257
K= 6,L= 9	-6	324	323
	-4	272	281
	0	265	266
	2	568	599
	4	238	237
	6	270	272
	8	211	207
K= 6,L= 10	-6	280	279
	-4	278	273
	-2	418	425
	0	365	372
	2	229	231
	4	349	354
	6	293	282
K= 6,L= 11	-4	237	244
	-2	301	301
	0	338	340
	2	337	324
	4	145	143
	6	265	257
K= 6,L= 12	-4	167	162
	-2	251	253
	0	305	302
	2	287	283
	4	211	206
K= 6,L= 13	0	257	260
	2	154	154
K= 7,L=-13	3	217	216
K= 7,L=-10	7	184	179
K= 7,L= -9	1	349	354
K= 7,L= -8	1	544	546
	3	523	517
K= 7,L= -7	1	780	806
	3	600	590
	5	473	470
	9	191	190
K= 7,L= -6	1	80	79
	3	868	869
	5	518	508
	9	168	168
K= 7,L= -5	1	522	495
	3	298	281
	5	755	753
K= 7,L= -4	1	682	661
	3	828	822
	5	204	201
K= 7,L= -3	1	610	582
	3	753	730
	5	682	654
	7	143	131
K= 7,L= -2	1	837	820
	3	295	293
	5	695	699
	7	358	351
K= 7,L= -1	1	1197	1196
	3	627	627
	5	554	558
	7	375	377
K= 7,L= 0	1	870	892
	3	1043	1035
	5	742	745
	7	291	286
	9	235	237
K= 7,L= 1	-9	275	265
	1	888	888
	3	1181	1162
	5	730	724
	7	415	418
	9	158	159
K= 7,L= 2	-9	188	185
	1	480	490
	3	1094	1080
	5	599	602
	7	414	423
	9	223	217
K= 7,L= 3	-9	280	284
	1	351	351
	3	535	552
	5	570	565
	7	434	436
	9	245	253
K= 7,L= 4	-9	210	216
	-7	445	460
	1	701	684
	3	489	495
	5	437	442
	7	361	351
	9	218	216
K= 7,L= 5	-9	214	216
	-7	367	375
	1	566	572
	3	740	721
	5	507	515
	7	236	224
	9	184	185
K= 7,L= 6	1	566	562
	3	542	545
	5	537	545
	7	258	259
	9	146	152
K= 7,L= 7	-7	301	311
	1	344	354
	3	568	579
	5	390	396
	7	275	274
K= 7,L= 8	-7	268	269
	-5	402	398
	1	763	784
	3	399	404
	5	364	361
	7	233	233
K= 7,L= 9	-7	260	262
	-5	385	388
	-3	468	464
	1	402	405
	3	569	568
	5	353	356
	7	237	212
K= 7,L= 10	-5	360	359
	-3	331	325
	-1	351	350
	1	210	208
	3	358	359
	5	422	419
	7	200	205
K= 7,L= 11	-5	223	233
	-3	335	335
	-1	215	215
	1	356	357
	3	207	211
	5	262	262
K= 7,L= 12	-3	191	186
	-1	272	271
	1	200	200
	3	330	323
K= 7,L= 13	-1	182	186
	1	190	191
	3	188	188
K= 8,L=-13	2	205	204
K= 8,L=-12	4	212	206
K= 8,L= -9	2	442	438
K= 8,L= -8	2	420	432
	4	283	281
K= 8,L= -7	2	578	569
	4	346	353
K= 8,L= -6	2	594	586
	4	481	477
K= 8,L= -5	2	432	417
	4	528	532
	6	428	423
K= 8,L= -4	2	617	611
	4	332	328
	6	385	386
K= 8,L= -3	2	724	705
	4	432	443
	6	353	360
	10	272	271
K= 8,L= -2	2	678	672
	4	411	421
	6	446	443
	10	256	250
K= 8,L= -1	2	779	774
	4	372	371
	6	402	402
	10	220	220
K= 8,L= 0	0	928	907
	2	719	741
	4	554	536
	6	362	373
	8	381	390
	10	277	274
K= 8,L= 1	-8	435	431
	0	961	1006
	2	725	718
	4	510	502
	6	497	510
	8	344	349
	10	248	247
K= 8,L= 2	-8	341	335
	0	953	969
	2	824	822
	4	409	417
	6	497	513
	8	387	388
	10	238	235
K= 8,L= 3	-8	370	368
	0	659	690
	2	746	727
	4	450	460
	6	422	429
	8	406	404
	10	259	257
K= 8,L= 4	-8	398	398
	0	769	764
	2	476	482
	4	418	421
	6	405	407
	8	355	355
K= 8,L= 5	-8	387	378
	0	745	735
	2	539	540
	4	377	381
	6	317	320
	8	348	344
K= 8,L= 6	-8	315	318
	-6	350	341
	0	432	426
	2	484	487
	4	401	409
	6	292	289
	8	300	298
K= 8,L= 7	-8	293	291
	-6	290	287
	0	688	697
	2	403	408
	4	320	320
	6	305	309
	8	267	267
K= 8,L= 8	-6	288	281
	-4	309	307
	0	566	566
	2	476	482
	4	246	244
	6	286	279
	8	254	247
K= 8,L= 9	-6	315	316
	-4	254	255
	0	342	344
	2	449	457
	4	279	284
	6	255	259
K= 8,L= 10	-6	187	198
	-4	265	274
	-2	331	336
	0	386	383
	2	303	305
	4	284	277
	6	256	257
K= 8,L= 11	-4	157	167
	-2	303	313
	0	316	309
	2	305	301
	4	182	176
K= 8,L= 12	-2	189	190
	0	321	314
	2	218	212
	4	204	196
K= 8,L= 13	0	198	196
	2	184	190
K= 9,L=-13	1	172	170
K= 9,L=-11	5	231	228
K= 9,L= -9	7	176	168
K= 9,L= -8	1	394	397
	3	383	375
K= 9,L= -7	1	373	378
	3	506	507
K= 9,L= -6	1	559	580
	3	548	556
	5	441	446
	9	146	146
K= 9,L= -5	1	420	428
	3	664	676
	9	169	168
K= 9,L= -4	1	437	424
	3	593	590
	5	525	523
K= 9,L= -3	1	928	920
	3	681	676
	5	537	548
K= 9,L= -2	1	361	355
	3	1021	1007
	5	632	653
K= 9,L= -1	1	865	839
	3	444	435
	5	753	751
K= 9,L= 0	1	675	642
	3	819	790
	5	374	371
	7	394	387
	9	245	239
K= 9,L= 1	-9	224	224
	-7	371	[illegible]
	1	[illegible]	482
	3	796	789
	5	619	[illegible]
	7	258	260
	9	208	212
K= 9,L= 2	-9	159	158
	-7	309	306
	1	[illegible]	741
	3	594	606
	5	605	622
	7	408	403
	9	171	175
K= 9,L= 3	-9	226	218
	-7	366	372
	1	811	803
	3	842	831
	5	518	523
	7	348	350
	9	231	234
K= 9,L= 4	-9	231	224
	-7	397	404
	1	833	845
	3	505	508
	5	656	667
	7	283	288
	9	224	221
K= 9,L= 5	-7	352	357
	3	608	622
	5	424	439
	7	313	322
	9	176	183
K= 9,L= 6	-7	275	287
	1	386	399
	3	517	522
	5	440	440
	7	233	238
	9	205	196
K= 9,L= 7	-7	201	203
	-5	403	410
	1	421	421
	3	376	379
	5	387	390
	7	255	254
K= 9,L= 8	-7	278	282
	-5	337	327
	1	285	299
	3	425	427
	5	281	285
	7	249	246
K= 9,L= 9	-5	398	407
	-3	264	262
	-1	323	326
	3	341	343
	5	286	289
	7	160	158
K= 9,L= 10	-5	233	236
	-3	352	359
	-1	226	222
	1	321	327
	3	300	299
	5	250	254
K= 9,L= 11	-3	225	224
	-1	290	295
	1	225	219
	3	275	272
	5	220	220
K= 9,L= 12	-3	43	227
	-1	203	201
	1	239	237
	3	201	207
K= 9,L= 13	1	163	163
K= 10,L=-10	6	191	185
K= 10,L= -8	2	459	448
K= 10,L= -7	2	364	360
	4	283	281
K= 10,L= -6	2	495	482
	4	300	305
K= 10,L= -5	2	691	684
	4	285	283
K= 10,L= -4	2	850	861
	4	424	424
K= 10,L= -3	2	816	815
	4	326	331
	6	514	522
K= 10,L= -2	2	846	831
	4	620	630
	6	387	393
K= 10,L= -1	2	[illegible]	695
	4	[illegible]	950
	6	418	420
K= 10,L= 0	0	946	934
	2	752	746
	4	453	453
	6	377	385
	8	444	444
K= 10,L= 1	-8	369	366
	0	1075	1065
	2	418	418
	4	549	542
	6	332	346
	8	430	427
K= 10,L= 2	-8	386	376
	0	818	818
	2	665	668
	4	310	317
	6	443	456
	8	339	337
K= 10,L= 3	-8	348	344
	0	580	568
	2	671	657
	4	428	429
	6	325	332
	8	310	313
K= 10,L= 4	-8	317	317
	-6	364	361
	0	873	856
	2	636	639
	4	460	467
	6	356	349
	8	252	258
K= 10,L= 5	-8	299	298
	-6	318	312
	0	566	558
	2	698	714
	4	256	259
	6	343	343
	8	303	297
K= 10,L= 6	-8	230	226
	-6	292	291
	0	636	640
	2	361	370
	4	364	371
	6	252	251
	8	295	297
K= 10,L= 7	-6	218	212
	-4	368	359
	0	456	460
	2	409	410
	4	244	241
	6	341	337
	8	226	229
K= 10,L= 8	-6	319	306
	-4	210	209
	0	316	319
	2	358	358
	4	276	277
	6	273	272
K= 10,L= 9	-6	239	243
	-4	263	263
	-2	273	274
	0	407	401
	2	299	296
	4	235	243
	6	214	210
K= 10,L= 10	-4	225	229
	-2	291	300
	0	284	287
	2	320	313
	4	170	168
	6	182	180
K= 10,L= 11	-4	177	170
	-2	278	287
	0	322	320
	2	193	191
	4	190	183
K= 10,L= 12	-2	176	176
	0	298	298
	2	199	185
K= 11,L=-12	3	264	263
K= 11,L= -8	1	350	353
	3	212	215
K= 11,L= -7	1	355	355
	3	422	410
K= 11,L= -6	1	428	438
	3	427	427
K= 11,L= -5	1	530	555
	3	476	491
	5	336	331
K= 11,L= -4	1	396	416
	3	611	634
	5	415	417
	9	162	165
K= 11,L= -3	1	391	388
	3	548	555
	5	554	566
K= 11,L= -2	1	434	451
	3	691	700
	5	482	483
K= 11,L= -1	1	660	653
	3	723	729
	5	535	543
K= 11,L= 0	1	467	460
	3	667	660
	5	510	520
	7	340	345
	9	193	194
K= 11,L= 1	-9	207	203
	-7	270	274
	1	396	398
	3	477	467
	5	490	496
	7	350	353
	9	227	229
K= 11,L= 2	-9	190	190
	-7	343	348
	1	541	547
	3	465	459
	5	457	459
	7	278	274
	9	191	193
K= 11,L= 3	-9	169	167
	-7	359	362
	1	486	498
	3	578	587
	5	508	509
	7	209	209
	9	145	149
K= 11,L= 4	-7	309	313
	1	626	621
	3	495	500
	5	497	501
	7	235	231
	9	174	166
K= 11,L= 5	-7	288	297
	1	527	533
	3	494	503
	5	397	392
	7	231	228
K= 11,L= 6	-7	218	229
	-5	385	379
	1	410	418
	3	430	439
	5	372	372
	7	243	248
K= 11,L= 7	-7	207	215
	-5	372	377
	1	309	313
	3	411	416
	5	346	355
	7	276	264
K= 11,L= 8	-5	372	372
	-3	296	293
	1	234	231
	3	426	421
	5	299	304
	7	239	232
K= 11,L= 9	-5	350	348
	-3	270	279
	-1	251	251
	1	272	275
	3	326	325
	5	272	275
K= 11,L= 10	-5	229	230
	-3	305	306
	-1	265	265
	1	270	262
	3	247	247
	5	196	199
K= 11,L= 11	-3	235	242
	-1	240	264
	1	249	247
	3	231	223
K= 11,L= 12	-1	165	166
	1	209	209
	3	116	195

within one standard deviation of that corresponding to 100% occupancy and there was no effect on the agreement factors.

Description of Structure

The crystalline structure consists of chloropentaaquoterpyridylpraseodymium(III) complex ions, $Pr(terpy)Cl(H_2O)_5{}^{2+}$ each of which shares half of each of the four surrounding uncoordinated Cl^- ions (Figure 1) and three uncoordinated water molecules to give the neutral formula $Pr(terpy)Cl_3(H_2O)_8$. The praseodymium(III) ion is coordinated to nine species: three nitrogens from the terpyridyl group, five oxygen atoms from water molecules, and one Cl^- ion. Figure 2 shows a view of the $Pr(terpy)Cl(H_2O)_5{}^{2+}$ ion with the crystallographic mirror plane bisecting the terpyridyl group. The metal–nitrogen bond distances (Figure 3) are equivalent at 2.630 (3) Å (average), which may be compared with the lanthanum–nitrogen distance of 2.665 (16) Å found by Al-Karaghouli and Wood[12] in bis(bipyridyl)lanthanum nitrate. The average metal–water distance of 2.513 (3) Å is compared with the lanthanum–water distances of 2.59 (4) Å found by Hoard, *et al.*,[13] and 2.605 (11) Å found by Al-Karaghouli and Wood.[12] These values are in good agreement with the difference in the ionic radii which indicates that praseodymium(III) is 0.05 Å smaller than lanthanum(III).[14]

The praseodynium–nitrogen distance is significantly shorter, after allowing for the lanthanide contraction, than the lanthanum–nitrogen distances of 2.85 (5) and 2.755 (6) Å found by Hoard.[13] Similar results were found by Moss and Sinha[7] in $Tb(bipy)_2(NO_3)_3$.

Sinha has studied the visible and near-infrared spectra of several neodymium complexes.[15] He proposes a parameter of covalency δ (in per cent) which is expressed as $\delta = 100(1 - \beta)/\beta$, where β is the average value of

---

[12] A. R. Al-Karaghouli and J. S. Wood, *J. Amer. Chem. Soc.*, **90**, 6548 (1968).

[13] (a) M. D. Lind, B. Lee, and J. L. Hoard, *ibid.*, **87**, 1611 (1965); (b) J. L. Hoard, B. Lee, and M. D. Lind, *ibid.*, **87**, 1612 (1965).

[14] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

[15] S. P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).

TABLE II

POSITIONS IN FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) WITH THE ESTIMATED STANDARD DEVIATIONS OF THE LAST DIGIT IN PARENTHESES[a]

	x	*y*	*z*
Pr	0.0	0.0	0.0
Cl(1)	0.38437 (15)	0.0	−0.0064 (14)
Cl(2)	−0.20658 (23)	0.15656 (11)	0.38847 (14)
N(1)	0.1111 (5)	0.0	−0.2570 (4)
N(2)	0.0456(5)	0.1401 (2)	−0.1200 (4)
C(1)	0.0016 (7)	0.2086 (3)	−0.0539 (6)
C(2)	0.0067 (7)	0.2839 (3)	−0.1161 (1)
C(3)	0.0624 (9)	0.2891 (3)	−0.2500 (8)
C(4)	0.1071 (7)	0.2198 (3)	−0.3194 (6)
C(5)	0.0992 (5)	0.1451 (2)	−0.2518 (4)
C(6)	0.1515 (5)	0.0702 (2)	−0.3202 (3)
C(7)	0.2410 (7)	0.0713 (4)	−0.4470 (4)
C(8)	0.2867 (12)	0.0	−0.5081 (8)
O(1)	−0.2548 (5)	0.0	−0.1632 (4)
O(2)	0.0990 (4)	0.0916 (2)	0.1921 (3)
O(3)	−0.2518 (4)	0.0861 (3)	0.0961 (4)
O(4)	0.3999 (8)	0.1742 (4)	0.2635 (7)
O(5)	−0.2639 (13)	0.0	−0.4325 (8)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pr	64.2 (3)	20.0 (1)	45.9 (2)		3.4 (1)	
Cl(1)	65 (1)	29.8 (4)	91 (1)		3 (1)	
Cl(2)	243 (3)	53 (1)	92 (1)	16 (1)	17 (1)	−19 (1)
N(1)	86 (6)	25 (1)	56 (3)		3 (3)	
N(2)	132 (5)	23 (1)	82 (3)	−4 (2)	−1 (3)	2 (1)
C(1)	175 (8)	23 (1)	124 (5)	7 (2)	−11 (5)	−5 (2)
C(2)	187 (9)	20 (1)	198 (9)	1 (2)	−60 (7)	−6 (2)
C(3)	212 (11)	27 (1)	181 (9)	−9 (3)	−57 (8)	27 (3)
C(4)	190 (9)	32 (1)	123 (5)	−11 (3)	−20 (5)	−28 (2)
C(5)	109 (5)	27 (1)	81 (3)	−8 (2)	−15 (3)	−12 (2)
C(6)	112 (5)	31 (1)	56 (3)	−5 (2)	−1 (3)	6 (1)
C(7)	187 (8)	50 (2)	65 (3)	−17 (3)	29 (4)	12 (2)
C(8)	189 (14)	69 (5)	65 (7)		32 (8)	
O(1)	90 (5)	51 (2)	65 (3)		2 (3)	
O(2)	124 (5)	46 (1)	89 (3)	2 (2)	−7 (3)	−23 (2)
O(3)	107 (5)	54 (2)	121 (4)	7 (2)	7 (3)	−36 (2)
O(4)	231 (10)	60 (3)	208 (8)	−33 (4)	23 (7)	−28 (4)
O(5)	353 (2)	76 (4)	86 (7)		−27 (10)	

[a] The anisotropic thermal parameters are of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE III

BONDED AND NONBONDED DISTANCES AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS OF THE LAST DIGIT IN PARENTHESES[a]

Bonded Distances, Å

Pr–N(1)	2.635 (4)	C(6)–C(5)	1.464 (6)
Pr–N(2)	2.625 (3)	C(7)–C(8)	1.368 (7)
Pr–Cl(1)	2.876 (2)	N(2)–C(1)	1.349 (5)
Pr–O(3)	2.544 (3)	N(2)–C(5)	1.346 (5)
Pr–O(2)	2.519 (3)	C(1)–C(2)	1.390 (7)
Pr–O(1)	2.477 (4)	C(2)–C(3)	1.371 (11)
N(1)–C(6)	1.351 (4)	C(3)–C(4)	1.376 (9)
C(6)–C(7)	1.404 (5)	C(4)–C(5)	1.405 (5)

Possible Hydrogen Bond Distances, Å

O(1)···Cl(1)$^{\mathrm{VI}}$	3.132 (4)	O(3)···Cl(1)$^{\mathrm{VI}}$	3.214 (4)
O(1)···O(5)	2.620 (9)	O(4)···Cl(2)$^{\mathrm{II}}$	3.163 (7)
O(2)···O(4)	2.725 (6)	O(4)···Cl(2)$^{\mathrm{III}}$	3.196 (7)
O(2)···Cl(2)	3.171 (4)	O(5)···Cl(2)$^{\mathrm{IV}}$	3.158 (5)
O(3)···Cl(2)	3.092 (4)	O(5)···Cl(2)$^{\mathrm{V}}$	3.158 (5)

Polyhedral Edges, A

O(2)···O(2)$^{\mathrm{I}}$	3.040 (8)	N(2)···Cl(1)	3.629 (4)
O(3)···O(3)$^{\mathrm{I}}$	2.860 (9)	O(2)···Cl(1)	3.225 (3)
O(3)···O(1)	2.898 (5)	O(2)···N(2)	3.164 (5)
O(2)···O(3)	2.785 (5)	O(3)···N(2)	3.192 (5)
N(2)···N(1)	2.725 (4)	N(1)···O(1)	2.887 (6)
N(2)···O(1)	3.260 (4)	N(1)···Cl(1)	3.221 (4)

Angles, Deg

Pr–N(2)–C(5)	121.2 (3)	C(5)–C(6)–C(7)	121.0 (4)
N(2)–C(5)–C(6)	117.4 (3)	Cl(1)–N(2)–O(1)	93.7 (1)
C(5)–C(6)–N(1)	117.7 (3)	N(2)–O(1)–N(2)$^{\mathrm{I}}$	91.0 (2)
C(6)–N(1)–Pr	120.1 (2)	O(2)$^{\mathrm{I}}$–O(2)–O(3)	88.1 (1)
N(2)–C(1)–C(2)	123.0 (5)	O(2)–O(3)–O(3)$^{\mathrm{I}}$	91.85 (12)
C(1)–C(2)–C(3)	118.6 (5)	N(2)–Pr–N(2)	64.40 (8)
C(2)–C(3)–C(4)	119.3 (5)	N(2)–Pr–Cl(1)	82.42 (8)
C(3)–C(4)–C(5)	119.8 (5)	N(2)–Pr–O(1)	79.38 (9)
C(5)–N(2)–C(1)	118.4 (4)	N(2)–Pr–O(3)	76.24 (13)
N(1)–C(6)–C(7)	121.2 (4)	N(2)–Pr–O(2)	75.91 (12)
C(6)–C(7)–C(8)	119.3 (5)	Cl(1)–Pr–O(2)	73.09 (8)
C(7)–C(8)–C(7)$^{\mathrm{I}}$	119.8 (6)	O(2)–Pr–O(2)$^{\mathrm{I}}$	74.26 (19)
C(6)–N(1)–C(6)$^{\mathrm{I}}$	119.1 (4)	O(3)–Pr–O(3)$^{\mathrm{I}}$	68.40 (21)
N(2)–C(5)–C(4)	120.9 (4)	O(3)–Pr–O(2)	66.75 (11)
C(6)–C(5)–C(4)	121.7 (4)	O(3)–Pr–O(1)	70.49 (11)

[a] The superscripts correspond to the following symmetry positions: (I) $x, -y, z$; (II) $^1/_2 + x, {}^1/_2 - y, z$; (III) $1 + x, y, z$; (IV) $x, y, -1 + z$; (V) $x, -y, -1 + z$; (IV) $-1 + x, y, z$.

the ratio $\nu_{\text{complex}}/\nu_{\text{aquo}}$. Depending on the ligands, the value of δ may be either positive (covalent bonding) or negative (ionic bonding). Although he places no significance on the absolute values of δ's, he uses them to express the relative covalent character in complexes. Sinha found that in the solid state terpyridyl and bipyridyl complexes give quite high δ values indicating strongly covalent metal–ligand interactions. The metal–nitrogen bond lengths found in this structure as well as those found by Moss[7] are consistent with a strong, albeit not necessarily covalent, interaction.

The praseodymium–chloride distance of 2.876 (2) Å is much larger than that of 2.72 (1) Å found in the six-coordinate tris(hexamethylphosphoramide)trichloropraseodymium(III).[16] This difference in bond distance may be attributed, on the basis of a purely ionic model, to the differing coordination numbers in the two complexes. Use of the Born–Madelung expression[17] with a Born parameter of 9 to account for the increase in bond distance upon going from coordination number 6 to coordination number 9 leads to a factor of 1.05, consistent with that difference shown in these two complexes. Therefore, one need not invoke bond strength arguments to explain the Pr–Cl bond distance. The sum of the ionic radii, presumably derived for six-coordination, is 2.82 Å, midway between the value found here and the nine-coordinate value.

The symmetry of the terpridyl group is distorted little by complexation. Each pyridyl group is planar (sum of the internal angles in the central ring is 719.9° and in the outer ring is 720.0°). The average C–N distance of 1.349 Å is consistent with that reported in pyridine.[18] The small, but statistically significant, difference in average aromatic C–C bond distances between those bonds involving the carbons para to the nitrogen [C(3) and C(8)], 1.372 Å (average), and the others, 1.400 Å (average), has also been observed in recent work on complexes of acetatoterpyridylcopper(II).[19]

The pyridyl groups are rotated relative to one another with a torsional angle of 12.1 (2)°. In Zn(terpy)Cl_3[20] the torsional angles average 5°. The rings were found to be essentially coplanar in the acetatoterpyridyl-

---

(16) M. D. Glick and L. J. Radonovich, Paper O13, Meeting of the American Crystallographic Association, Ottawa, Ontario, Canada, Aug 16–22, 1970.

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 537–540.

(18) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958).

(19) G. A. Zakrzewski, G. D. Andreetti, and E. C. Lingafelter, Paper O5, Meeting of the American Crystallographic Association, Ottawa, Ontario, Canada, Aug 16–22, 1970.

(20) K. Knox and A. P. Ginsberg, *Inorg. Chem.*, **3**, 555 (1964).

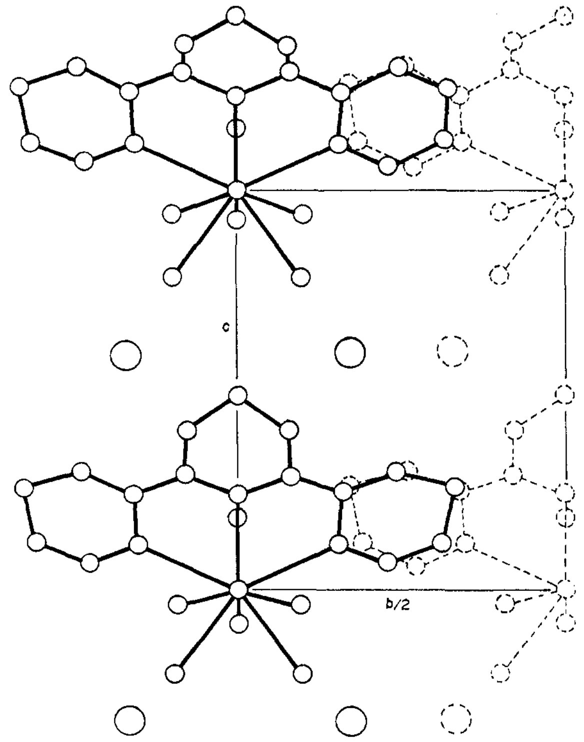

Figure 1.—The structure of $Pr(terpy)Cl_3(H_2O)_8$ projected onto the *bc* plane. The solid lines indicate one formula unit around the Pr(III) ion at 0, 0, 0 and one around the Pr(III) ion at 0, 0, 1. The broken lines indicate the formula units releated by C centering.

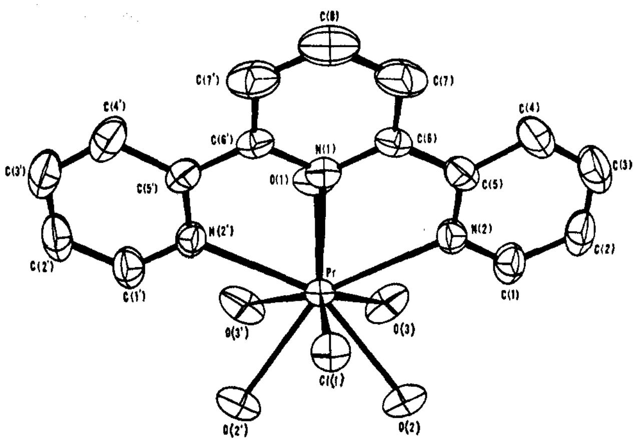

Figure 2.—The $Pr(terpy)Cl(H_2O)_5^{2+}$ complex ion.

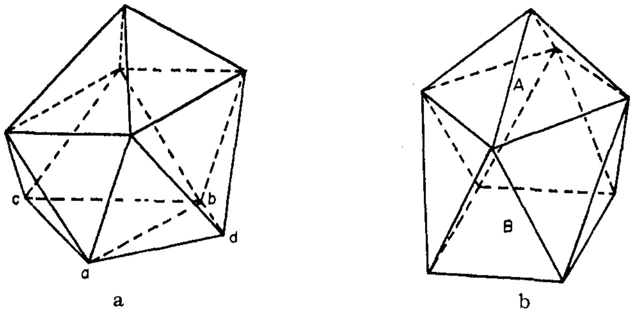

Figure 3.—The two idealized geometries for a nonacoordinate polyhedron: (left) the tricapped trigonal prism; (right) the monocapped square antiprism.

copper(II) complexes.[19] While the torsional angles in the terpyridyl group are related to the coordination geometry to which they must conform, it is difficult to assess the significance of these angles since free terpyridyl may well not be planar as a result of H···H nonbonded interactions. The 12° twist in the complex under discussion here does lead to equivalent distances from the praseodymium ion to the nitrogen. Angles within the terpyridyl group are normal.

Two idealized geometries have been proposed for nine-coordinate polyhedra:[21] the tricapped trigonal prism (Figure 3a) of D_{3h} symmetry and monocapped square antiprism (Figure 3b) of C_{4v} symmetry. The tricapped trigonal-prismatic configuration has been established for ReH_9^{2-} [22] and for $Nd(OH_2)_9^{3+}$ in $Nd(OH_2)_9(BrO_3)_3$[23] as well as for a series of isostructural lanthanide hydroxides.[24] The monocapped square-antiprismatic polyhedron has been found for certain metal cage compounds and for metal tellurides and arsenides and had not been reported for any metal complexes.[21] Recently, Day and Hoard have determined this geometry for tetrakis(tropolonato)-*N*,*N*-′dimethylformamidethorium(IV)[25] and have also commented on its previously unrecognized appearance in the ethylenediaminetetraacetatotriaquolanthanum(III) ion.[13b] As Muetterties and Wright have pointed out,[21] however, the two geometries can be interconverted with relatively minor distortions. The monocapped square antiprism can be generated from the tricapped trigonal prism by raising points a and b, and lowering the two caps c and d so that the four form the basal plane.

The $Pr(terpy)Cl(H_2O)_5^{2+}$ complex ion is best described as a distorted monocapped square antiprism with N(1) forming the cap. The actual coordination polyhedron is shown in Figure 4. In the idealized monocapped square antiprism atoms O(2), $O(2)^I$, O(3), and $O(3)^I$ would form a square (plane B, Figure 3b) as would atoms Cl(1), N(2), $N(2)^I$, and O(1) (plane A, Figure 3b). In the actual complex ion atoms O(2), $O(2)^I$, O(3), and $O(3)^I$ are required by symmetry to lie in a plane[26] ($0.3352X - 0.9422Z = -1.514$) and the angles between edges are 88.1° and 91.9 (1)°. Atoms Cl(1), N(2), $N(2)^I$, and O(1) are somewhat ruffled with the equation of the mean plane being $0.3090X - 0.9511Z = 1.076$. The deviations from this plane for atoms Cl(1), N(2), $N(2)^I$, and O(1) are 0.13, −0.14, −0.14, and 0.15 Å, respectively. The angles between edges are 91.0 (2), 93.7 (1), and 79.8 (4)°. The mirror planes require the two four-sided figures to have their diagonals 45° to one another when projected down N(1)–Pr. Viewing the monocapped square antiprism with the cap in the vertical position, the praseodymium(III) ion is 1.52 Å above plane B but only 1.06 Å below mean plane A. Mean planes A and B are essentially parallel with a dihedral angle of 1.5°. The deviations from the idealized geometry are due primarily to the length of the praseodymium–chloride bond which is 0.25 Å longer than any of the other metal–ligand bonds. Further, the Cl(1) atom

---

[21] E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

[22] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964); A. P. Ginsberg, *ibid.*, **3**, 567 (1964).

[23] L. Helmholz, *J. Amer. Chem. Soc.*, **61**, 1544 (1939).

[24] D. R. Fitzwater and R. E. Rundle, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **112**, 362 (1959).

[25] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3626 (1970).

[26] The coordinates *X*, *Y*, and *Z* are in units of ångströms and are based on the orthonormal coordinate system $a' = a$, $b' = a \times c$, $c' = a \times b'$.

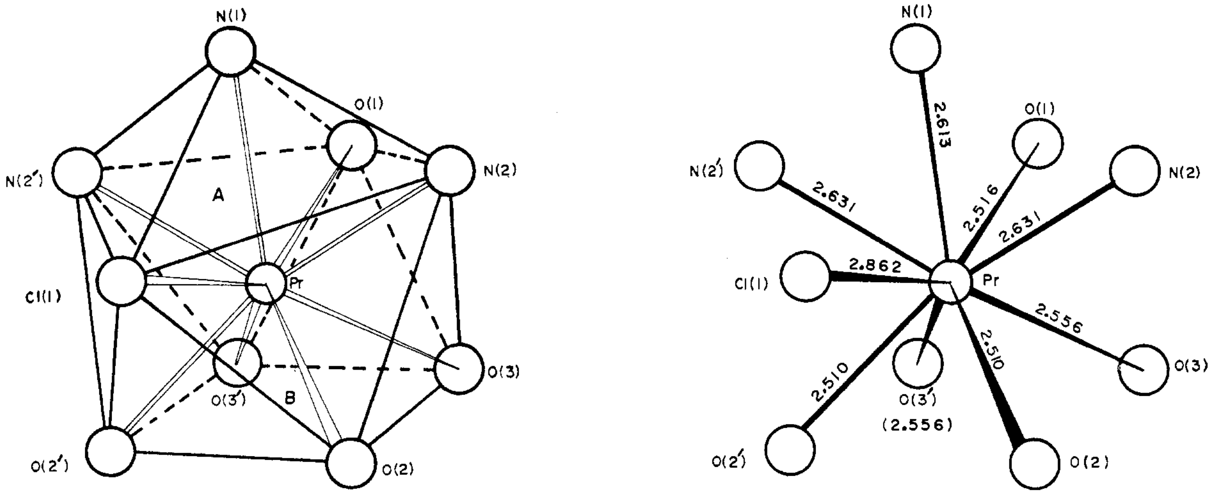

Figure 4.—The coordination polyhedron about the Pr(III) ion showing the monocapped square-antiprismatic configuration.

is bent down toward plane B as can be seen in Figure 3. Since this complex contains constraints of chelating as well as three different kinds of atoms in the coordination sphere, it does not lend itself to detailed analysis of the coordination polyhedron. Day and Hoard[25] have noted that the quasi-C_4 axis [N(1)–Pr] corresponding to the C_{4v} symmetry of the idealized monocapped square antiprism must generate four axes [Pr–N(1), Pr–N(2), Pr–N(2)$^{\mathrm{I}}$, and Pr–Cl(1)] normal to which are observed one-five-three layering of the ligated atoms. Examination of the model does show such layering.

A reasonable pattern of three-dimensional hydrogen bonding (Table III) can be proposed as

$$\begin{aligned} &O(1) \longrightarrow Cl(1)^{\mathrm{VI}} \text{ and } O(5) \\ &O(2) \longrightarrow Cl(2) \text{ and } O(4) \\ &O(3) \longrightarrow Cl(2) \text{ and } Cl(1)^{\mathrm{VI}} \\ &O(4) \longrightarrow Cl(2)^{\mathrm{II}} \text{ and } Cl(2)^{\mathrm{III}} \\ &O(5) \longrightarrow Cl(2)^{\mathrm{IV}} \text{ and } Cl(2)^{\mathrm{V}} \end{aligned}$$

This scheme thus links each complex ion to all six of its neighboring ions *via* hydrogen bonding. This three-dimensional hydrogen bonding is manifested in the excellent crystals corresponding to the octahydrated complex.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA 22901

The Crystal and Molecular Structure of Tris(glycinato)chromium(III) Monohydrate, $Cr(C_2H_4NO_2)_3 \cdot H_2O$

BY ROBERT F. BRYAN,* PETER T. GREENE, PETER F. STOKELY, AND EDMOND W. WILSON, JR.

Received October 29, 1970

The crystal and molecular structure of tris(glycinato)chromium(III) monohydrate, $Cr(C_2H_4NO_2)_3 \cdot H_2O$, has been determined by single-crystal X-ray analysis. The cell constants are a = 6.256 (1), b = 14.649 (1), c = 12.267 (1) Å, and β = 100.39 (1)°. The space group is $P2_1/c$ and with $Z = 4$ the calculated density is 1.755 g/cm^3 compared to the observed 1.76 (1) g/cm^3. Scintillation counter diffractometry was used to measure the intensities of 2631 independent reflections significantly above background. The phase problem was solved by the application of direct methods and the structural parameters refined by a block-diagonal least-squares procedure to a final R of 0.0266. All hydrogen atoms in the structure were located and their positional parameters were refined. Anisotropic thermal parameters were used for all atoms except hydrogen. The chromium ion is octahedrally coordinated by three glycinato ligands so that the three nitrogen atoms are mutually cis. Average bond lengths are as follows (Å): Cr–N, 2.068 (5); Cr–O, 1.965 (2); N–C, 1.479 (3); C–C, 1.517 (2); C–O (coordinated), 1.290 (9); C–O(carbonyl), 1.223 (6). Individual molecules in the crystal are held together by a three-dimensional network of strong hydrogen bonds, including an unusual bifurcated linkage. The uv and visible spectra of the complex are presented and discussed.

Introduction

No crystal structure analysis has been reported for any amino acid complex of chromium(III) though many amino acid complexes with other metal ions have been extensively studied.[1] We give here the results of an accurate three-dimensional single-crystal X-ray analysis of the structure of tris(glycinato)chromium(III) monohydrate and present and discuss the uv and visible spectra of the compound.

Experimental Section

The complex was prepared by refluxing an aqueous solution of

---

(1) For a recent review of metal complexes with amino acids and peptides see H. C. Freeman, *Advan. Protein Chem.*, **22**, 258 (1967).