spectroscopy: tris(triethylphosphine)platinum(0) (**10**), δ 41.7 (t, J_{Pt-P} = 4226 Hz; lit.[16] δ 42, J_{Pt-P} = 4220 Hz); (3,3-dimethyl-1-butene)bis(triethylphosphine)platinum(0) (**11**), δ 16.0 (d of t, J_{Pt-P} = 3159 Hz, J_{P-P} = 57 Hz), δ 20.9 (d of t, J_{Pt-P} = 3697 Hz, J_{P-P} = 57 Hz); bis(3,3-dimethyl-1-butene)(triethylphosphine)platinum(0) (**12**), δ 21.0 (t, J_{Pt-P} = 3552 Hz).[18] Addition of excess triethylphosphine to the reaction mixture consumed **11** and **12** and yielded **10**. The thermolysis of **9** was repeated in decane by using cyclopentane as internal standard and the decomposition followed by GLC using a 20-ft, $^1/_8$-in. 10% column of SE-30 on Anakrom; equimolar quantities of 2,2-dimethylbutane and 3,3-dimethyl-1-butene were produced throughout the course of reaction which at completion yielded 1 equiv of each/equiv of **9**.

Acknowledgment. Rates of decomposition of **9** were obtained by T. McCarthy and R. Nuzzo.

Registry No. 2, 70620-74-5; **3**, 76722-29-7; **3**-d_6, 79827-23-9; **4**, 79816-36-7; **4a**-d_2, 79816-37-8; **4b**-d_3, 79816-38-9; **5**, 76722-30-0; **5**-d_4, 79816-39-0; **6a**, 79816-51-6; **6a**-*d*, 79816-52-7; **6b**, 79816-53-8; **6b**-d_2, 79816-54-9; **6c**, 79816-55-0; **6c**-d_2, 79816-56-1; **7**, 79816-57-2; **8**, 79816-58-3; **9**, 79816-59-4; **10**, 39045-37-9; **11**, 79816-60-7; **12**, 79816-61-8; dichloro(1,5-cyclooctadiene)platinum(II), 12080-32-9; 1-bromo-2,2-dimethylpentane, 79803-29-5; 2,2-dimethyl-1-pentanol, 2370-12-9; 2-methylpropanal-2-methyl-2-propanimine lithium salt, 52278-93-0; 1-bromopropane, 106-94-5; 1-bromoethane, 74-96-4; 2,2,4,4-tetramethyl-1-pentanol, 79803-30-8; 3,3-dimethyl-1-butanol, 624-95-3; 1,5-dichloro-2,2-dimethylpentane, 79803-31-9; 2,2-dimethyl-1,5-pentyl di-*p*-toluenesulfonate, 62718-14-3; 5-chloro-4,4-dimethyl-1-pentene, 79803-32-0; 4,4-dimethyl-1-penten-5-ol tosylate, 79803-33-1; 1,4-dichloro-2,2-dimethylpentane, 79803-34-2; bis(triethylphosphine)platinum(II) dichloride, 14177-93-6; 2,2,4,4-tetramethylpentanoic acid, 3302-12-3.

Crystal Structure of the Homoleptic Seven-Coordinate Complex Heptakis(*tert*-butyl isocyanide)chromium(II) Hexafluorophosphate, $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[1,2]

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Abstract: The structural characterization of the first homoleptic seven-coordinate chromium complex, $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$, is reported. The geometry of the cation is close to that of the 4:3 (C_s) piano stool with Cr–C distances ranging from 1.966 (8) Å to 2.016 (6) Å. The chromium atom lies on a crystallographically required mirror plane that also contains three of the *tert*-butyl isocyanide ligands, one of which belongs to the trigonal face, the other two being in the tetragonal face of the 4:3 geometry. Crystal data are: a = 16.952 (3) Å, b = 20.795 (4) Å, c = 28.702 (6) Å, V = 10117.9 Å^3, Z = 8, orthorhombic, space group *Cmca*, final R = 0.069 for 2647 X-ray diffractometer data with $F_o > 6\sigma(F_o)$.

The complex $K_4[V(CN)_7]\cdot 2H_2O$ is thus far the only homoleptic seven-coordinate first-row transition-metal complex to have been structurally characterized by X-ray diffraction.[4] Recently, we described the synthesis of the title compound,[5] a homologue of the compounds $[M(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ (M = Mo, W), the structures of which have been previously studied.[6,7] Although the molybdenum and tungsten analogues are isomorphous and have C_{2v} capped trigonal prismatic geometries, the chromium complex is shown here to crystallize in a different space group and to have a different solid state structure.

The number of structurally characterized homoleptic seven-coordinate complexes has recently seen considerable growth, the two largest groups being complexes with isocyanide and cyanide ligands. The isocyanide complexes are $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$,[6] $[W(CN\text{-}t\text{-}Bu)_7](PF_6)_2$,[7] $[W(CN\text{-}t\text{-}Bu)_7](W_6O_{19})$,[8] $[Mo(CNCH_3)_7](BF_4)_2$,[9] and $[Mo(CNC_6H_{11})_7](PF_6)_2$,[7] while the cyanide complexes include $K_5[Mo(CN)_7]\cdot H_2O$,[10] $Na_5[Mo(CN)_7]\cdot 10H_2O$,[10] $NaK_3[Mo(CN)_7]\cdot 2H_2O$,[11] $K_4[Re(CN)_7]\cdot 2H_2O$,[12] and $K_4[V(CN)_7]\cdot 2H_2O$.[4] Other homoleptic seven-coordinate complexes for which structural information is available include the three fluoride compounds IF_7,[13] $(NH_4)_3[ZrF_7]$,[14] and $K_2[NbF_7]$,[15] and the complexes $[Ca(H_2O)_7](I_{10})$,[16] $[Sr(H_2O)_7](I_{12})$,[16] and $[Er(dmp)_7](ClO_4)_3$,[17] where dmp = 2,6-dimethyl-4-pyrone.

Seven-coordinate chromium compounds are not unknown although most examples contain multidentate ligands.[18,19] Two cases where all the ligands are unidentate are $Cr[P(OMe)_3]_5H_2$[20] and the present compound. Our previous studies[6,7] and those of others[8,9] on the stereochemistry of [metal(unidentate isocyanide)$_7$]$^{2+}$ complexes have revealed cations with geometries having C_{2v} (capped trigonal prismatic), C_{3v} (capped octahedral), and C_s (4:3 piano stool) symmetries. The present work shows that the title compound has a stereochemistry close to that of the 4:3 (C_s) piano stool geometry.

Experimental Section and Results

Collection and Reduction of X-ray Data. The synthesis of $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ has been described previously.[5] The orange crystal used in the diffraction study, grown from *tert*-butyl isocyanide, had approx-

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[1] Part 13 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 12 see ref 2.

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Table I. Experimental Details of the X-ray Diffraction Study of $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$

(A) Crystal Parameters[a] at 26 °C

a = 16.952 (3) Å
b = 20.795 (4) Å
c = 28.702 (6) Å
V = 10117.9 Å^3
mol wt = 923.9
space group = *Cmca*
Z = 8
ρ(calcd) = 1.213 g cm^{-3}
ρ(obsd)[b] = 1.21 (1) g cm^{-3}

(B) Measurement of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα (λ_{α_1} = 0.70930 Å; $\lambda_{\bar{\alpha}}$ = 0.71073 Å) graphite monochromatized
takeoff angle: 2.0°
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm
crystal-detector distance: 173 mm
scan technique: coupled ω(crystal) – 2θ(counter)
scan width: variable, $\Delta\omega$ = (0.7 + 0.35 tan θ)°
scan rate: variable from 0.91 to 6.71° min^{-1} in ω
prescan rejection limit: 1σ
prescan acceptance limit: 100σ
maximum counting time: 75 s
background measurements: moving crystal–moving detector, 25% added to scan width at both ends of each scan
standards: three reflections (400), (008), and (222), measured every 3600 s of X-ray exposure time, showed no decay
no. of reflections collected: [3° ≤ 2θ ≤ 50° (+h, +k, +l)] 4608 unique, non-space-group extinguished
reorientation control: the three reflections (2,0,22), (6,4,18), and (6,14,2) were recentered every 250 data and if the position of any scattering vector deviated by more than 0.05° from its calculated position a new orientation matrix was calculated based on the recentering of 19 more reflections

(C) Treatment of Intensity Data

reduction to F_o and $\sigma(F_o)$: correction for background, attenuator, and Lorentz-polarization of monochromatized X radiation as described previously[c]
absorption correction: not applied, μ = 3.51 cm^{-1}; estimated[d] transmission factor range 0.88–0.90
observed data: 2647 unique reflections with $F_o > 6\sigma(F_o)$ were used in the structure refinement

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30°$. [b] By suspension in aqueous ZnI_2. [c] Reference 22. [d] Performed with the Wehe-Busing-Levy ORABS program.

Table II. Final Positional Parameters for the Nonhydrogen Atoms of $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[a]

atom	x	y	z
Cr	0.00	0.67447(5)	0.37194(4)
P(1)	0.25	0.05882(18)	0.25
P(2)	0.00	0.00	0.00
P(3)	0.50	0.00	0.00
F(11)	0.25	-0.0097(5)	0.25
F(12)	0.25	0.1261(6)	0.25
F(13)	0.1807(5)	0.0552(5)	0.2821(3)
F(14)	0.1959(6)	0.0611(7)	0.2112(3)
F(21)	0.00	0.0324(9)	0.0418(5)
F(22)	0.0628(4)	0.0448(4)	-0.0183(4)
F(31)	0.50	-0.0355(6)	-0.0448(4)
F(32)	0.5624(5)	-0.0473(3)	0.0146(4)
N(11)	0.00	0.6803(3)	0.2626(2)
N(21)	0.00	0.5313(3)	0.3410(2)
N(31)	0.00	0.7131(3)	0.4783(2)
N(41)	-0.1624(3)	0.6202(2)	0.40669(16)
N(51)	-0.1171(3)	0.7907(2)	0.35705(16)
C(11)	0.00	0.6767(4)	0.3027(3)
C(12)	0.00	0.6894(4)	0.2120(3)
C(13)	0.00	0.6238(6)	0.1900(4)
C(14)	-0.0746(6)	0.7264(4)	0.1994(3)
C(21)	0.00	0.5834(4)	0.3535(3)
C(22)	0.00	0.4640(4)	0.3256(3)
C(23)	0.00	0.4635(5)	0.2726(4)
C(24)	0.0738(5)	0.4334(3)	0.3464(3)
C(31)	0.00	0.6974(3)	0.4399(3)
C(32)	0.00	0.7330(4)	0.5265(3)
C(33)	0.00	0.8056(5)	0.5277(4)
C(34)	-0.0717(6)	0.7057(4)	0.5497(3)
C(41)	-0.1026(3)	0.6385(2)	0.39272(18)
C(42)	-0.2378(3)	0.5989(3)	0.4256(2)
C(43)	-0.3028(4)	0.6314(4)	0.3966(3)
C(44)	-0.2400(5)	0.5265(3)	0.4205(3)
C(45)	-0.2415(5)	0.6177(4)	0.4766(3)
C(51)	-0.0762(3)	0.7477(3)	0.36243(18)
C(52)	-0.1696(5)	0.8454(3)	0.3514(3)
C(53)	-0.2212(8)	0.8486(6)	0.3920(5)
C(54)	-0.1194(8)	0.9054(5)	0.3484(5)
C(55)	-0.2098(12)	0.8382(8)	0.3084(6)

[a] Atoms of the cation are labeled as indicated in Figure 1. For the anions, F(11)–F(14) are bound to P(1), F(21)–F(22) are bound to P(2), and F(31)–F(32) are bound to P(3). Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

imate dimensions of 0.55 mm × 0.55 mm × 0.53 mm and was sealed in a capillary to minimize decomposition. A large crystal was chosen for this study since data from smaller crystals were too weak. Preliminary oscillation and Weissenberg photographs showed the lattice to have Laue symmetry mmm. The systematic absences, hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$, and $hk0$ when $h \neq 2n$, were consistent with either space group *Cmca* (D_{2h}^{18}, No. 64) or its noncentrosymmetric equivalent *C2ca* (C_{2v}^{17}, No. 41, in a nonstandard setting). The former space group has been confirmed by the successful solution and refinement of the structure. Moreover, refinement in the noncentrosymmetric space group *C2ca* produced a model with geometry substantially worse than that obtained in space group *Cmca*. The quality of the data crystal was checked by taking open-counter ω scans of several strong low-angle reflections and was judged to be acceptable. The average width of the peaks at half-height was 0.11°. Further details of the data collection and reduction appear in Table I and ref 22.

Determination and Refinement of the Structure. The position of the chromium atom was determined from a Patterson map. Subsequent difference Fourier maps and cycles of least-squares refinement revealed the positions of the remaining nonhydrogen atoms. Neutral atom scattering factors and anomalous dispersion corrections for the nonhydrogen atoms were obtained from ref 23. Scattering factors for the hydrogen atoms were those of Stewart et al.[24] All nonhydrogen atoms were refined anisotropically. Although the thermal ellipsoids of the methyl carbon atoms of ligand 5 and some of the fluorine atoms of the PF_6^- groups were suggestive of disorder, inspection of a difference Fourier map failed to reveal reasonable sets of alternative positions for these atoms. Toward the final stages of refinement, methyl hydrogen atoms were set up and refined as rigid groups (C–H = 0.95 Å; H–C–H = 109.5°) pivoting on their respective carbon atoms. A common isotropic temperature factor for all these hydrogen atoms converged toward U = 0.15 Å^2. In the final cycles of refinement the hydrogen atoms were included as invariants with all parameters fixed at the values obtained in the last cycle of rigid group refinement.

Full-matrix least-squares refinement of 286 variables, using SHELX-76,[25] converged to final residual indices of R_1 = 0.069 and R_2 = 0.093.[26] The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.8189/[\sigma^2(F_o) + 0.00081F_o^2]$. In the final cycles of refinement no parameter of the hexafluorophosphate anions shifted by more than 0.028 of its estimated standard deviation, while for the parameters of the cation, the largest shift was 0.004σ. The largest peak on the final difference Fourier map was 0.52 e Å^{-3} on a scale where a typical carbon atom was 4.67 e Å^{-3}. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, (sin θ)/λ, $|h|$, $|k|$, or $|l|$, showed reasonable consistency, and the weighting scheme was considered to be satisfactory.

Final non-hydrogen-atom positional parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and angles, with estimated standard deviations, are given in Table III. A listing of final observed and calculated structure factors, anisotropic thermal parameters, and hydrogen-atom positional parameters are available as Tables S1–S3.[27] Figure 1 shows the geometry of the cation along with the atom-labeling scheme while Figure 2 depicts the unit-cell packing.

Discussion

The structure consists of discrete $[Cr(CN\text{-}t\text{-}Bu)_7]^{2+}$ cations and PF_6^- anions (Figures 1 and 2). In the cations, each chromium atom is surrounded by seven unidentate CN-*t*-Bu ligands in a geometry closely approximating the 4:3 (C_s) piano stool[28] (vide

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(26) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(27) Supplementary material.

Table III. Interatomic Distances (Å) and Angles (deg) for $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[a]

		Coordination Sphere	
Cr-C(11)	1.987(7)	Cr-C(41)	1.986(5)
Cr-C(21)	1.966(8)	Cr-C(51)	2.016(6)
Cr-C(31)	2.008(9)		
C(11)-Cr-C(21)	75.7(3)	C(31)-Cr-C(41)	78.3(2)
C(11)-Cr-C(31)	164.1(2)	C(31)-Cr-C(51)	87.3(2)
C(11)-Cr-C(41)	108.0(2)	C(41)-Cr-C(51)	76.4(2)
C(11)-Cr-C(51)	81.2(2)	C(41)-Cr-C(41')	122.4(3)
C(21)-Cr-C(31)	119.3(3)	C(41)-Cr-C(51')	152.5(2)
C(21)-Cr-C(41)	73.6(2)	C(51)-Cr-C(51')	79.7(3)
C(21)-Cr-C(51)	133.7(2)		
		Ligand Geometry	
C(11)-N(11)	1.155(9)	N(21)-C(22)	1.466(9)
C(21)-N(21)	1.143(9)	N(31)-C(32)	1.443(9)
C(31)-N(31)	1.150(9)	N(41)-C(42)	1.458(7)
C(41)-N(41)	1.154(6)	N(51)-C(52)	1.454(8)
C(51)-N(51)	1.142(6)	mean C-C(methyl)	1.503(11)
N(11)-C(12)	1.463(10)	range C-C(methyl)	1.418(15)-1.537(9)
Cr-C(11)-N(11)	177.6(7)	C(31)-N(31)-C(32)	179.8(3)
Cr-C(21)-N(21)	177.2(7)	C(41)-N(41)-C(42)	178.0(6)
Cr-C(31)-N(31)	177.2(6)	C(51)-N(51)-C(52)	178.6(6)
Cr-C(41)-N(41)	176.1(5)	mean N-C-C(methyl)	107.7(6)
Cr-C(51)-N(51)	177.5(5)	range N-C-C(methyl)	106.4(5)-108.5(5)
C(11)-N(11)-C(12)	176.4(8)	mean C(methyl)-C-C(methyl)	111.2(7)
C(21)-N(21)-C(22)	179.1(8)	range C(methyl)-C-C(methyl)	107.9(10)-114.4(11)
		Anion Geometry	
min P-F	1.377(10)	mean cis F-P-F	90.0(6)
max P-F	1.509(6)	min trans F-P-F	174.3(8)
mean P-F	1.454(9)	max trans F-P-F	180.0
min cis F-P-F	85.1(5)	mean trans F-P-F	178.9(17)
max cis F-P-F	94.9(5)		

[a] See footnote *a*, Table II. Distances have not been corrected for thermal motion. Standard deviations, quoted for mean values, are the average of the standard deviation for the individual values. Primed atoms are related to those unprimed by mirror symmetry.

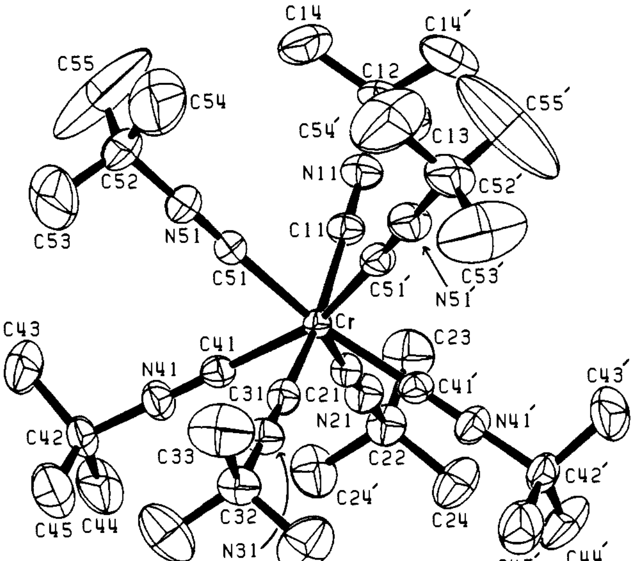

Figure 1. Geometry of the $[Cr(CN\text{-}t\text{-}Bu)_7]^{2+}$ cation showing the atom-labeling scheme. Thermal ellipsoids are depicted at the 40% probability level. Hydrogen atoms have been omitted for clarity. Primed atoms are related to those unprimed by a crystallographically required mirror plane containing Cr and C(11), N(11), C(12), C(13) of ligand 1, C(21), N(21), C(22), and C(23) of ligand 2, and C(31), N(31), C(32), and C(33) of ligand 3.

infra), also known as the 4:3 tetragonal base–trigonal cap stereochemistry. The tetragonal base is comprised of atoms C(21), C(31), C(41), and C(41′) and atoms C(11), C(51), and C(51′) make up the trigonal cap. The chromium atom lies 0.98 Å from the tetragonal plane and 1.33 Å from the trigonal plane. Each cation has crystallographically required mirror symmetry with the chromium atom situated on the mirror plane. Atoms N(11) and C(11)–C(13) of ligand 1 (Figure 1), N(21) and C(21)–C(23) of ligand 2, and N(31) and C(31)–C(33) of ligand 3 also lie on this mirror plane. The geometry within the CN-*t*-Bu ligands is reasonable when compared to that determined in similar complexes.

Table IV. Summary of Interbond Angles (deg) for Seven-Coordinate Structures[a]

Angle No.	PB (D_{5h})	CO (C_{3v})[b]	CTP (C_{2v})[c]	4:3 (C_s)[b]	$[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[d]
1	180.0	160.0	164.0	170.0	164.1
2	144.0	160.0	164.0	153.6	152.5
3	144.0	160.0	144.2	153.6	152.5
4	144.0	130.0	144.2	130.8	133.7
5	144.0	130.0	119.0	130.8	133.7
6	144.0	130.0	119.0	120.0	122.4
7	90.0	108.9	118.8	120.0	119.3
8	90.0	108.9	118.8	108.8	108.0
9	90.0	108.9	99.0	108.8	108.0
10	90.0	83.1	99.0	89.4	87.3
11	90.0	83.1	83.7	89.4	87.3
12	90.0	83.1	83.7	83.1	81.2
13	90.0	82.0	80.3	83.1	81.2
14	90.0	82.0	80.3	83.1	79.7
15	90.0	82.0	78.8	75.5	78.3
16	90.0	82.0	78.6	75.5	78.3
17	72.0	82.0	75.2	75.5	76.4
18	72.0	82.0	75.2	75.5	76.4
19	72.0	70.0	75.0	73.3	75.7
20	72.0	70.0	75.0	73.3	73.6
21	72.0	70.0	71.5	70.0	73.6

[a] Angles are listed by decreasing size. Abbreviations used are PB, pentagonal bipyramid; CO, capped octahedron; CTP, capped trigonal prism; 4:3, the 4:3 "piano stool" structure. [b] The internal angles of these reference geometries are calculated from the corresponding optimized geometries for d⁴ complexes (ref 36). [c] The structure of $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ (ref 6) is used for the reference geometry. [d] This work.

We have shown previously[7,29] that the stereochemistry about the metal atom in a seven-coordinate complex of stoichiometry $[metal(unidentate)_7]^{x\pm}$ can be fairly quickly identified by listing the 21 angles at the metal in order of decreasing size. Their values are then compared with those calculated for idealized polyhedra. This method has proved useful for previous structure determinations and, for the present case (Table IV), suggests that the geometry of the $[Cr(CN\text{-}t\text{-}Bu)_7]^{2+}$ cation is closer to that of a 4:3 (C_s) piano stool than to any of the other idealized polyhedra (i.e., D_{5h} pentagonal bipyramid; C_{3v} capped octahedron; C_{2v} capped trigonal prism). Dihedral angle calculations,[28] carried out on the coordination geometry normalized to a unit sphere, show that the angle across the diagonals of the tetragonal face defined by C(21), C(31), C(41), and C(41′) is 3.2°. The theoretical value for the 4:3 geometry is 0°. The angle between the tetragonal and trigonal planes is 3.7° which compares well with the theoretical value of 0°. As has been pointed out previously,[7] the 4:3 piano stool geometry has only C_s symmetry at best. This symmetry is that found in the present compound, which contains a crystallographically required mirror plane (Figure 3), and therefore crystallographically imposed C_s symmetry. The expected pattern of bond lengths for the 4:3 geometry might then be 1:1:2:2:1 or 1:2:2:2 with accidental degeneracies raising them to 1:3:3. The present compound displays the 1:3:3 pattern as do the complexes $[Mo(CNCH_3)_7](BF_4)_2$[9] and $[Mo(CN\text{-}t\text{-}Bu)_6(SnCl_3)]^+$,[29] both of which have the 4:3 geometry.

The $[Cr(CN\text{-}t\text{-}Bu)_7]^{2+}$ cation occupies a position between the pentagonal bipyramid and the capped octahedron on the potential energy surface calculated from ligand-ligand repulsions for complexes of stoichiometry $[M(unidentate)_7]^{x\pm}$.[30] The values of ϕ_B and ϕ_C are 119.3° and 165.0°, respectively (Figure 7, ref 30). The general stereochemistry is defined in Figure 6 of ref 30, with position A corresponding to atom C(31) in the present case, B = C(21), C = C(11), D = C(41), E = C(51), F = C(51′), and G = C(41′). The repulsion energy calculations show that there is little or no energy barrier between the pentagonal bipyramid and the capped octahedron for this system and, as we have suggested previously,[7] it appears that crystal packing forces are an important factor in determining just where in this potential energy valley a particular complex will lie. A similar situation exists in

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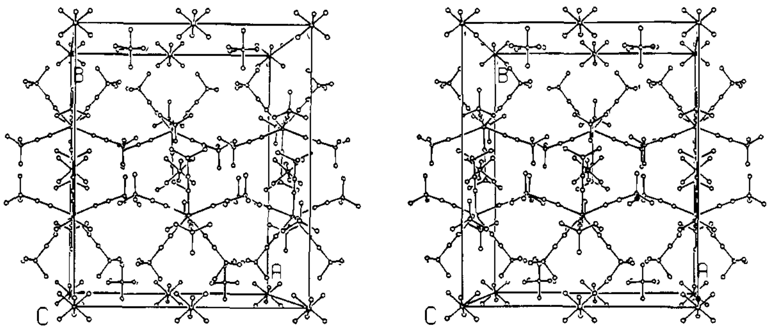

Figure 2. Unit-cell packing diagram for $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$. For clarity, cations and anions related by the C-centering have been omitted.

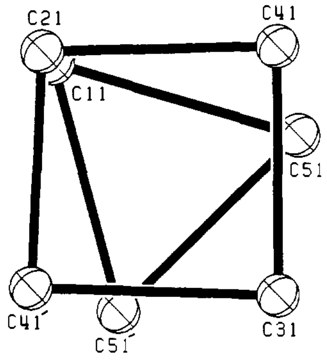

Figure 3. Projection of the tetragonal plane onto the trigonal plane of coordinated atoms, transformed to a unit sphere, in $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$. Lines joining atoms are drawn to define the planes. The chromium atom is omitted. Atoms C(11), C(21), and C(31) lie on a crystallographically required mirror plane.

the [metal(unidentate)$_5$]$^{x\pm}$ system[31] where a very large and shallow minimum exists on the potential energy surface. The compound $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ is a classic case since it crystallizes[32] in such a manner that the lattice contains both trigonal-bipyramidal and square-based-pyramidal $[Ni(CN)_5]^{3-}$ ions. Both of these geometries lie in the potential energy minimum computed for this surface which strongly suggests that crystal packing forces determine the geometry adopted by each anion.

The crystal structures of all members of the homologous series of complexes $[M(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ (M = Cr, Mo, W) have now been determined. The Mo[6] and W[7] complexes are isomorphous and isostructural and possess crystallographically imposed symmetry. The Cr complex also has crystallographically imposed symmetry but its crystal and molecular structure differ from those of the Mo and W complexes. The reason for this difference may be the smaller size of Cr compared to Mo and W. In the $[M(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ complexes, the Mo–C and W–C distances are similar and average 2.115 and 2.108 Å, respectively, while the average Cr–C distance is 1.995 Å. These results reveal the expected[33] 0.12 Å difference between the radius of chromium and those of molybdenum and tungsten in a similar environment. The radius of the metal ion seems to be little affected by its coordination geometry. The capped trigonal prismatic PF_6^- salt[7] of $[W(CN\text{-}t\text{-}Bu)_7]^{2+}$ has an average W–C distance of 2.108 Å, similar to the average value of 2.09 Å found in the $(W_6O_{19})^{2-}$ salt,[8] which has the 4:3 geometry.

When the structures of the capped trigonal prismatic complexes $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[6] and $[Mo(CN\text{-}t\text{-}Bu)_6I]I$[34] were determined it was felt that, perhaps for electronic reasons, other similar complexes might adopt this geometry.[7] Indeed, the cations in $[W(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[7] and $[Mo(CN\text{-}t\text{-}Bu)_6Br]Br$[35] are capped trigonal prismatic but recent structure determinations in our own and other laboratories have shown that similar complexes adopt most of the other seven-coordinate geometries as well. For example, the geometry in $[Mo(CNC_6H_{11})_7](PF_6)_2$[7] is close to being capped octahedral, while $[Mo(CNCH_3)_7](BF_4)_2$,[9] $[W(CN\text{-}t\text{-}Bu)_7](W_6O_{19})$,[8] $[Mo(CN\text{-}t\text{-}Bu)_6(SnCl_3)][(Ph_3B)_2CN]$,[29] and the present compound have the 4:3 (C_s) piano stool geometry. Thus far, no pentagonal-bipyramidal isocyanide complex having only unidentate ligands has been reported, although the trichlorostannate complex is distorted in that direction.[29] By contrast, all the homoleptic seven-coordinate cyanide complexes for which structural data are available possess the pentagonal-bipyramidal geometry.[4,10–12] It will be interesting to see whether cyanide complexes with different geometries are detected in future studies. In the case of the seven-coordinate fluoride complexes, $[NbF_7]^{2-}$[15] is capped trigonal prismatic, while IF_7[13] and $[ZrF_7]^{2-}$[14] both have distorted pentagonal-bipyramidal geometries.

All the hexafluorophosphate anions of the structure are located on special positions. Anion 1 has crystallographically required twofold symmetry. Atoms P(1), F(11), and F(12) lie on this axis in a trans F–P–F arrangement. The anion is completed with F(13) and F(14) in general positions. Anions 2 and 3 both have crystallographically required $2/m$ symmetry. In anion 2, P(2) is located at the origin, and in anion 3, P(3) is at ($^1/_2$, 0, 0). For anion 2, atom F(21) lies on a mirror plane and F(22), in a general position, completes the anion. The situation with anion 3 is similar with F(31) on the mirror and F(32) in a general position. In both these anions the crystallographic twofold axis passes through the phosphorus atom and bisects the line joining two adjacent full occupancy fluorine atoms. The crystallographically required mirror plane also bisects the line joining two adjacent full occupancy fluorine atoms. This distribution of ions, over these special positions in the unit cell, ensures a cation:anion ratio of 1:2. The P–F bond lengths observed for the PF_6^- groups are shorter than usual[6,7] because of thermal motion or unresolved disorder.

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Registry No. $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$, 75215-56-4.

Supplementary Material Available: Tables S1–S3 listing, respectively, final observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters (13 pages). Ordering information is given on any current masthead page.

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