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Structural Studies of Three Seven-Coordinate Isocyanide Complexes of Molybdenum(II) and Tungsten(II)[1,2]

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The structures of heptakis(cyclohexyl isocyanide)molybdenum(II) hexafluorophosphate, $[Mo(CNC_6H_{11})_7](PF_6)_2$ (**1**), cyanohexakis(*tert*-butyl isocyanide)molybdenum(II) hexafluorophosphate, $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (**2**), and heptakis(*tert*-butyl isocyanide)tungsten(II) hexafluorophosphate, $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (**3**), are reported. Compound **1** crystallizes in the trigonal crystal system, space group *P*31*c*, with $a = b = 11.543$ (4) Å and $c = 24.353$ (4) Å. The molybdenum atom is situated on a crystallographic threefold axis, and the geometry of the cation 11.543 that of a distorted capped octahedron. The capping ligand is disordered and situated slightly off the crystallographic threefold axis, thereby distorting the inner coordination sphere from perfect C_{3v} symmetry. The Mo–C bond lengths are 2.145 (8) Å for the uncapped face, 2.088 (8) Å for the capped face, and 2.049 (28) Å for the capping ligand. The hexafluorophosphate anions also lie on threefold axes and are disordered. Compound **2** crystallizes in the orthorhombic crystal system, space group *Cmca*, with $a = 16.712$ (3) Å, $b = 22.689$ (5) Å, and $c = 22.807$ (3) Å. It is isomorphous with the compounds $[M(CN\text{-}t\text{-}C_4H_9)_6X]X$, where M = Mo or W and X = Cl, Br, or I. The geometry of the cation is that of a capped trigonal prism with cyanide ion as the capping ligand. The complex has approximate overall C_{2v} symmetry with a crystallographically required mirror plane passing through it. The Mo–CN bond length is 2.191 (9) Å while the $Mo\text{–}CN\text{-}t\text{-}C_4H_9$ distances are 2.114 (6) and 2.111 (7) Å for the capped face and 2.081 (10) and 2.050 (10) Å for the unique edge ligands. The structure of compound **3** was refined in the nonstandard monoclinic space group *F*2/*m* with $a = 25.260$ (3) Å, $b = 11.629$ (1) Å, $c = 38.008$ (6) Å, and $\beta = 90.81$ (1)°. It is isomorphous with the molybdenum analogue. The capped trigonal-prismatic geometry of the cation is characterized by W–C bond lengths of 2.142 (8) Å for the unique ligand, 2.115 (5) and 2.123 (5) Å for the capped face, and 2.069 (6) Å for the unique edge ligands. Various criteria for choosing the best idealized geometry for these and related seven-coordinate complexes are discussed. Examination of a list of angles at the metal atom, ordered according to decreasing magnitude, is shown to be a quick and useful approach to the problem. It is concluded that crystal packing forces are often the dominant factor in determining the seven-coordinate geometry adopted by a particular $[\text{metal(unidentate ligand)}_7]^{x\pm}$ complex in the solid state.

Introduction

The stereochemistry of seven-coordinate molecules is a subject that has attracted considerable recent attention.[4-6] It has even been stated that "seven-coordination is possibly the most complicated subject in the structural and dynamic stereochemical aspects of coordination chemistry".[7] Traditionally, structures have been referenced to one of three high-symmetry coordination polyhedra, the D_{5h} pentagonal bipyramid, the C_{3v} capped octahedron, and the C_{2v} capped trigonal prism. As the number of seven-coordinate complexes that have well-defined geometries increased, however, the existence of a fourth, lower symmetry and previously recognized[4-6] structure, the C_s 4:3 piano stool,[2,8,9] emerged.

What are the factors that determine which of these polyhedral forms will be adopted by a particular complex? Theoretical calculations have shown that the potential energy surface describing seven-coordinate complexes has shallow minima[5] and that chelating ligands can help to dictate the final structure.[6] One particularly well-characterized series of complexes that appeared to be useful for studying the factors that influence the stereochemistry of seven-coordination is the molybdenum(II) and tungsten(II) alkyl isocyanides, ML_7^{2+}, ML_6X^+, and ML_5X_2, where M = Mo or W, L = RNC, X = Cl, Br, I or CN.[2,10-16] These compounds are especially amenable to such an investigation because of the low steric requirements of the isocyanide ligand and the fact that all the ligands are unidentate.

Initially it appeared that, perhaps for electronic reasons, this family of compounds would all adopt capped trigonal-prismatic structures. X-ray diffraction results for $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$,[11] $[Mo(CN\text{-}t\text{-}C_4H_9)_6Br]Br$,[12b] and $[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$[13] revealed nearly perfect C_{2v} symmetry for all three cations, and the structure of the product of the reductive coupling reaction, $[Mo(CN\text{-}t\text{-}C_4H_9)_4(t\text{-BuHNCCNH-}t\text{-Bu})I]I$, was also that of a capped trigonal prism.[17] Subsequent work showed, however, that $[Mo(CNCH_3)_7](BF_4)_2$ had a distorted geometry, described as a capped octahedron,[14] and that $[W(CN\text{-}t\text{-}C_4H_9)_7](W_6O_{19})$ was a severely distorted capped trigonal prism that could also be characterized as a 4:3 piano stool.[16] Moreover, in the analysis of the geometries of these and related molecules, interesting questions were raised about the criteria for choosing a coordination polyhedron.[4,8,14,18] It was therefore decided that it would be valuable to obtain structural information about additional members of the ML_7^{2+}/ML_6X^+ [M = Mo(II), W(II)] family of compounds.

The present article describes structural studies of three complexes, $[Mo(CNC_6H_{11})_7](PF_6)_2$ (**1**), $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (**2**), and $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (**3**). The existing criteria for classifying the geometry of a seven-coordinate

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(1) Part 11 of a continuing series of higher coordinate cyanide and isocyanide complexes. For part 10 see ref 2.

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Table I. Experimental Details of the X-ray Diffraction Studies of $[Mo(CNC_6H_{11})_7](PF_6)_2$ (1), $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (2), and $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (3)

(A) Crystal Parameters[a] at 26 °C

	1	2	3		1	2	3
a, Å	11.543 (4)	16.712 (3)	25.260 (3)	cryst system	trigonal	orthorhombic	monoclinic
b, Å	11.543 (4)	22.689 (5)	11.629 (1)	space group	*P*31*c*	*Cmca*	*F*2/*m*[b]
c, Å	24.353 (4)	22.807 (3)	38.008 (6)	*Z*	2	8	8
β, deg			90.81 (1)	ρ(calcd), g cm^{-3}	1.359	1.176	1.256
V, Å^3	2810.1	8647.9	11164.8				
mol wt	1150.1	765.7	1055.7	ρ(obsd), g cm^{-3}	1.35 (1)[c]	1.16 (1)[c]	1.26 (1)[c]

(B) Measurement of Intensity Data

	1	2	3
takeoff angle, deg	2.5	2.5	2.0
scan width, variable, $\Delta\omega = (A + 0.35 \tan\theta)^\circ$	$A = 0.8$	$A = 0.8$	$A = 0.7$
standards, three reflections measured every 3600 s of X-ray exposure time	$(5\bar{4}0)$, $(22\bar{4})$, $(3\bar{1}\bar{4})$[d]	(0,14,0), $(1\bar{9}\bar{5})$, $(5\bar{3}\bar{9})$[d]	(4,0,18), (10,2,8), $(11,1,\bar{9})$[e]
no. of reflctns collected (non space group extinguished)	4849 [$3 \leqslant 2\theta \leqslant 55^\circ$ ($\pm h, \pm k, +l$)]	4093 [$3 \leqslant 2\theta \leqslant 50^\circ$ ($+h, +k, +l$)]	7607 [$3 \leqslant 2\theta \leqslant 25^\circ$ ($-h, -k, \pm l$); $3 \leqslant 2\theta \leqslant 55^\circ$ ($+h, +k, \pm l$)]

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα ($\lambda_{\bar{\alpha}}$ 0.710 73 Å) graphite monochromatized
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm
crystal–detector dist, mm: 173
scan technique: coupled ω(crystal)–2θ(counter)
scan rate, variable: 1–20° min^{-1} in ω
bkgd measurements: moving crystal–moving detector, 25% added to scan width at both ends of each scan

(C) Treatment of Intensity Data

	1	2	3		1	2	3
reduction to F_o and $\sigma(F_o)$:	correction for background, attenuator, and Lorentz–polarization of X-radiation as described previously[f]						
μ, cm^{-1}	3.6	3.8	23.4	no. of reflctns after averaging	2204		5640
transmission factor range[g]	0.80–0.95	0.90–0.95	0.74–0.81	obsd unique data [$F_o > 6\sigma(F_o)$]	1777	2170	4164
averaging, R_{av}[f]	0.038		0.014				

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30°$. [b] A nonstandard setting of space group *C*2/*m* (C_{2h}^3, No. 12) having the general equivalent positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(x, \bar{y}, z)$, $(\bar{x}, y, \bar{z})$ and those generated by adding the translations (0, $^1/_2$, $^1/_2$), ($^1/_2$, 0, $^1/_2$), and ($^1/_2$, $^1/_2$, 0). [c] By suspension in a mixture of CCl_4 and cyclohexane. [d] Showed no decay. [e] Used to scale the data for a 9% anisotropic decay (see: Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* 1974, *13*, 1427). [f] Reference 22. [g] Absorption corrections were performed with the Wehe–Busing–Levy ORABS program.

molecule are reviewed and analyzed, and the factors that dictate the choice of geometry for the ML_7^{2+}/ML_6X^+ family are discussed.

Experimental Procedure and Results

Preparation of Compounds. Heptakis(cyclohexyl isocyanide)molybdenum(II) hexafluorophosphate (**1**), which has been reported previously,[14] was prepared from molybdenum hexacarbonyl by oxidative addition using $PhICl_2$.[19] X-ray-quality crystals were obtained by recrystallization from hot $MeOH/H_2O$ in the dark. Cyanohexakis(*tert*-butyl isocyanide)molybdenum(II) hexafluorophosphate (**2**) was synthesized by metathesis from $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$.[19] Vapor diffusion of diethyl ether into a methanolic solution of the complex in the dark gave X-ray quality crystals. Crystals of heptakis(*tert*-butyl isocyanide)tungsten(II) hexafluorophosphate (**3**) were obtained as reported previously.[12b]

Collection and Reduction of X-ray Data. Heptakis(cyclohexyl isocyanide)molybdenum(II) Hexafluorophosphate, $[Mo(CNC_6H_{11})_7](PF_6)_2$ (1). The large yellow crystal used in the diffraction study was a hexagonal plate with approximate dimensions 0.70 mm × 0.70 mm × 0.70 mm × 0.15 mm. A limited data set consisting of reflections from all the octants having indices $|h| \leq 4$, $|k| \leq 4$, and $|l| \leq 4$ was collected. Inspection of these data revealed trigonal symmetry with systematic absences $h,h,2\bar{h},l$ when $l \neq 2n + 1$, consistent with the space group *P*31*c* (C_{3v}^4, No. 159).[20a,21] Further details of the data collection and reduction appear in Table I and ref 22.

Cyanohexakis(*tert*-butyl isocyanide)molybdenum(II) Hexafluorophosphate, $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (2). The yellow crystal used in the diffraction study, a rectangular prism of dimensions 0.15 mm × 0.30 mm × 0.30 mm, was mounted on a glass fiber and examined on the diffractometer. Systematic absences and unit-cell parameters indicated that the crystal was isomorphous with the $[M(CN\text{-}t\text{-}C_4H_9)_6X]X$ analogues, where M = Mo or W and X = Cl, Br, or I,[12b] crystallizing in the orthorhombic space group *Cmca* (D_{2h}^{18}, No. 64).[20b] Details of the data collection and reduction are given in Table I and ref 22.

Heptakis(*tert*-butyl isocyanide)tungsten(II) Hexafluorophosphate, $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (3). A yellow monoclinic prism, with dimensions ranging from 0.17 mm to 0.32 mm, was examined on the diffractometer and shown to be isomorphous with the molybdenum analogue.[13] Data were collected, and the structure was refined in space group *F*2/*m*, a nonstandard setting of space group *C*2/*m* (C_{2h}^3, No

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(19) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics*, in press.

(20) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. I: (a) p 265; (b) p 153; (c) p 95.

(21) The systematic absences $h,h,2\bar{h},l$, $l = 2n + 1$, occur for both space groups *P*31*c* and $P\bar{3}1c$. Statistics and symmetry considerations led us to choose the former, noncentrosymmetric one. In $P\bar{3}1c$ the twofold special positions have either 32 or $\bar{3}$ point symmetry, both of which would require further disordering of the cation.

(22) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *11*, 3379.

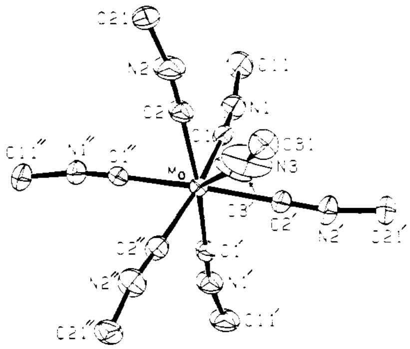

Figure 1. View of the $[Mo(CNC_6H_{11})_7]^{2+}$ cation in **1** approximately down the crystallographic threefold axis. Only the Mo atom lies on this axis. Ligand 1 is disordered over three sites, only one of which is shown. For clarity, only the first atom of each cyclohexyl group is shown. Primed atoms are related to those unprimed by threefold symmetry. Thermal ellipsoids are depicted at the 30% probability level.

12),[20c] with unit-cell constants and crystal parameters as given in Table I.

Structure Solution and Refinement. $[Mo(CNC_6H_{11})_7](PF_6)_2$ (1). From the observed density and unit-cell constants it was determined that there were two $[Mo(CNC_6H_{11})_7](PF_6)_2$ molecules per unit cell (Table I). The molybdenum atom must therefore occupy a threefold special position in the space group $P31c$. In this space group the special positions on the threefold axis at $(^1/_3, {}^2/_3, z)$ and $(^2/_3, {}^1/_3, {}^1/_2 + z)$ require that if $h - k = 3n$, then $l = 2n$. Inspection of the data with $h - k = 3n$ revealed that reflections with $l = 2n + 1$ were systematically weaker than the data with $l = 2n$. The molybdenum atom was therefore placed at this special position. The z coordinate was fixed at 0.0 to define the origin in this polar space group. Since the cyclohexyl isocyanide ligand does not have threefold symmetry, it was realized that the complex would have capped octahedral geometry with a threefold disordering of the capping ligand.

A difference Fourier map, calculated by using phases based only on the molybdenum atom, resulted in a value of 0.294 for R_1.[23] The phosphorus atoms of the two hexafluorophosphate anions were located from this map. One phosphorus atom was found at the threefold special position $(^1/_3, {}^2/_3, z)$, with $z = 0.41$, while the other was at the threefold special position $(0, 0, z)$, with $z = 0.21$. Subsequent difference Fourier maps revealed the positions of the atoms of the two unique, ordered cyclohexyl isocyanide ligands, the fluorine atoms of the anions, and the atoms of the disordered cyclohexyl isocyanide ligand. The fluorine atoms of the PF_6^- anions are also disordered about the crystallographic threefold axis.

Least-squares refinement of this model minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1.000/[\sigma^2(F_o) + 0.000625F_o^2]$, resulted in poor geometry for the disordered capping ligand and the two disordered PF_6^- anions. Several different models were tested, including the use of rigid groups with anisotropic temperature factors. The latter became nonpositive definite for the cyclohexyl group atoms and very large ($U \sim 0.8$ Å^2) for the fluorine atoms. It was finally decided to allow the PF_6^- groups to refine without constraint, with an acceptance of their resulting poor geometries, and to constrain[24] the geometry of the threefold disordered capping cyclohexyl ligand so that the individual bond distances and angles within the cyclohexyl group could vary but with restrictions that prevented the geometry of the group from becoming grossly distorted due to the close proximity (0.5–0.7 Å) of atoms from the other two positions of the disordered ligand.

Anisotropic thermal parameters were employed for the molybdenum atom, all the atoms of the two ordered isocyanide ligands, and the phosphorus atoms of the anions. Isotropic temperature factors were used for the remaining atoms. Hydrogen atoms, for the two ordered ligands, were placed in calculated positions (C–H = 0.95 Å) and were allowed to ride on the carbon atom to which they are attached.[24] All hydrogen atoms were assigned a common isotropic temperature factor that converged at $U = 0.154$ (13) Å^2.

Full-matrix least-squares refinement[24,25] of 240 variables converged with $R_1 = 0.058$ and $R_2 = 0.071$.[23] The largest parameter shift was less than 0.2σ and the largest peak on a final difference Fourier map

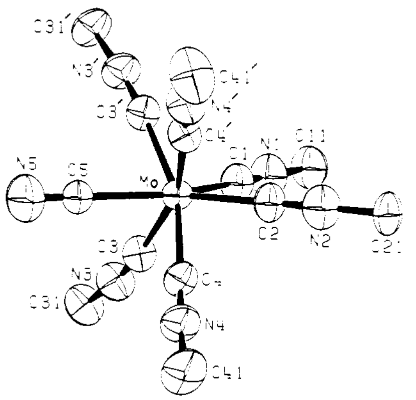

Figure 2. View of the $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)]^+$ cation in **2**. The Mo atom and ligands 1, 2, and 5 lie on a crystallographic mirror plane that relates primed atoms to those unprimed. Terminal methyl groups of the *tert*-butyl isocyanide ligands have been omitted for clarity. Thermal ellipsoids are depicted at the 50% probability level.

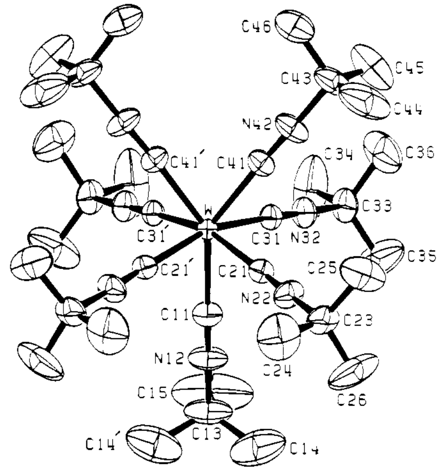

Figure 3. View of the $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ cation in **3**. The W atom and atoms of ligand 1 [except for C(14)] lie on a crystallographically required mirror plane that relates primed atoms to those unprimed. Thermal ellipsoids are depicted at the 30% probability level. Atoms are labeled in a similar fashion to those of the isomorphous molybdenum analogue.[13]

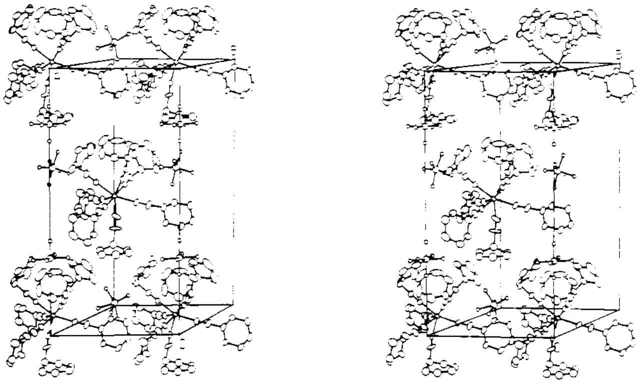

Figure 4. Stereoview of the unit-cell packing diagram for $[Mo(CNC_6H_{11})_7](PF_6)_2$ (**1**).

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

(24) Except where otherwise noted, all calculations were performed on a DEC VAX-11/780 computer using SHELX-76: Sheldrick, G. M. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, 1978; pp 34–42.

(25) Neutral-atom scattering factors and anomalous dispersion corrections were taken from: "International Tables for X-ray Crystallography" Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99 and 149.

Table II. Final Positional Parameters for the Nonhydrogen Atoms of $[Mo(CNC_6H_{11})_7](PF_6)_2$ (1)[a,b]

atom	x	y	z
Mo	0.3333	0.6667	0.0
P(1)	0.3333	0.6667	0.4138(2)
P(2)	0.0	0.0	0.2058(2)
F(11)	0.353(11)	0.653(12)	0.4793(10)
F(12)	0.322(4)	0.727(4)	0.3564(15)
F(13)	0.355(3)	0.812(3)	0.4358(11)
F(14)	0.173(3)	0.615(4)	0.4310(13)
F(15)	0.284(3)	0.534(3)	0.3807(14)
F(16)	0.486(3)	0.753(3)	0.4188(13)
F(21)	0.0	0.0	0.1407(6)
F(22)	0.0	0.0	0.2693(7)
F(23)	-0.152(2)	-0.055(3)	0.1983(10)
F(24)	-0.025(3)	-0.152(2)	0.1999(9)
F(25)	0.168(2)	0.056(3)	0.2082(10)
F(26)	0.038(3)	0.150(2)	0.2154(10)
C(1)	0.4853(7)	0.6791(7)	-0.0543(4)
N(1)	0.5643(8)	0.6899(7)	-0.0854(4)
C(11)	0.6774(10)	0.7279(11)	-0.1218(5)
C(12)	0.6246(14)	0.6824(16)	-0.1773(6)
C(13)	0.5580(15)	0.752(3)	-0.1975(6)
C(14)	0.641(2)	0.907(3)	-0.1950(12)
C(15)	0.7019(17)	0.9507(15)	-0.1400(11)
C(16)	0.7691(10)	0.8798(13)	-0.1185(6)
C(2)	0.5012(8)	0.8444(9)	0.0252(5)
N(2)	0.5966(9)	0.9460(9)	0.0358(5)
C(21)	0.7002(10)	1.0823(10)	0.0479(5)
C(22)	0.8310(11)	1.1080(11)	0.0215(5)
C(23)	0.9438(12)	1.2499(14)	0.0347(7)
C(24)	0.9535(12)	1.2784(11)	0.0948(6)
C(25)	0.8275(11)	1.2407(10)	0.1238(5)
C(26)	0.7148(11)	1.1013(11)	0.1081(4)
C(3)	0.381(3)	0.677(7)	0.0815(12)
N(3)	0.402(3)	0.695(12)	0.1298(8)
C(31)	0.439(3)	0.728(4)	0.1955(17)
C(32)	0.380(4)	0.586(4)	0.215(2)
C(33)	0.234(4)	0.504(3)	0.209(2)
C(34)	0.153(3)	0.567(4)	0.208(2)
C(35)	0.215(3)	0.710(5)	0.2126(20)
C(36)	0.361(4)	0.796(4)	0.211(2)

[a] Atoms are labeled as shown in Figure 1. The cyclohexane ring attached to N(1) is labeled C(11)–C(16) with C(11) being attached to N(1). Other rings are labeled similarly. F(11)–F(16) are attached to P(1) and F(21)–F(26) are attached to P(2). Ligand 3 is disordered over three positions as are atoms F(11)–F(16) and F(23)–F(26). An occupancy factor of 0.3333 was applied to these atoms. [b] Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

was ca. 0.5 e Å^{-3}. At the end of the refinement the fact that the correct hand of the structure had been chosen was confirmed by inspection of a listing of $|F_o|$ vs. $|F_c|$ for Friedel pairs with $|hkl| \leq |444|$ and by the Hamilton R-factor test. The hand reported here was confirmed at the 99.5% probability level.

Final nonhydrogen atomic positional parameters for **1**, together with their estimated standard deviations, are reported in Table II while Table V lists interatomic distances and angles. The coordination geometry and atom labeling scheme of the $[Mo(CNC_6H_{11})_7]^{2+}$ cation are shown in Figure 1 and a unit-cell packing diagram appears in Figure 4.

$[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (2). Initial coordinates for the molybdenum atom and the –C≡N– atoms of the four independent *tert*-butyl isocyanide ligands were taken from the published values of $[Mo(CN\text{-}t\text{-}C_4H_9)_6Br]Br$.[12b] A difference Fourier map phased by using these atoms revealed the positions of the *tert*-butyl groups of the four isocyanide ligands, the cyanide ligand, and the hexafluorophosphate ion, which was found to be situated on a mirror plane at (x, $^1/_2$, 0). Least-squares refinement of this model, followed by another difference Fourier map, revealed that the *tert*-butyl groups of three of the four isocyanide ligands, including two ligands situated on a mirror plane, were disordered over two sites. The disordered atoms were refined with equal site occupancy factors. All atoms were assigned anisotropic temperature factors. Hydrogen atoms were not included in the refinement. Least-squares refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1.000/[\sigma^2(F_o) + 0.000625F_o^2]$, converged at final values of $R_1 = 0.050$ and $R_2 = 0.066$.[23] In the final cycle of refinement the maximum shift/error was less than 0.1. The maximum peak on the final difference Fourier map was ca. 1.0 e Å^{-3} in the vicinity of the ordered *tert*-butyl isocyanide ligand. All remaining peaks were less than 0.35 e Å^{-3}.

Final positional parameters for **2** are listed in Table III while Table VI contains a list of interatomic distances and angles. Figure 2 displays the coordination geometry and atom labeling scheme for the $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)]^+$ cation.

Table III. Final Positional Parameters for the Nonhydrogen Atoms of $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (2)[a]

atom	x	y	z
Mo	0.0	0.28660(3)	0.28381(3)
P	0.28523(19)	0.5	0.0
F(1)	0.3785(5)	0.5	0.0
F(2)	0.1932(5)	0.5	0.0
F(3)	0.2845(4)	0.4355(2)	0.0234(3)
F(4)	0.2850(5)	0.4767(3)	-0.0637(2)
C(1)	0.0	0.3769(4)	0.2998(4)
N(1)	0.0	0.4276(4)	0.3066(4)
C(11)	0.0	0.4912(4)	0.3162(5)
C(111)	0.0	0.5008(19)	0.3817(13)
C(112)	-0.0796(20)	0.5149(11)	0.2977(17)
C(113)	0.0	0.5176(12)	0.2564(14)
C(114)	-0.069(3)	0.5058(15)	0.352(3)
C(2)	0.0	0.3008(4)	0.3726(4)
N(2)	0.0	0.3066(4)	0.4232(4)
C(21)	0.0	0.3140(5)	0.4881(4)
C(211)	0.0	0.2538(14)	0.5132(13)
C(212)	0.076(2)	0.344(2)	0.5055(15)
C(213)	0.0	0.3810(14)	0.5002(16)
C(214)	0.078(2)	0.292(2)	0.5095(11)
C(3)	0.0907(4)	0.3209(3)	0.2289(3)
N(3)	0.1351(4)	0.3403(2)	0.1953(3)
C(31)	0.1776(5)	0.3705(3)	0.1481(3)
C(311)	0.2669(9)	0.3577(11)	0.1564(8)
C(312)	0.1590(17)	0.4349(6)	0.1547(11)
C(313)	0.1470(14)	0.3446(10)	0.0912(7)
C(314)	0.1119(14)	0.401(2)	0.1096(16)
C(315)	0.229(3)	0.3275(13)	0.1133(19)
C(316)	0.230(2)	0.4171(18)	0.1734(10)
C(4)	0.0927(4)	0.2328(3)	0.3167(3)
N(4)	0.1409(4)	0.2003(3)	0.3340(3)
C(41)	0.1898(6)	0.1551(4)	0.3623(4)
C(411)	0.1973(9)	0.1680(5)	0.4254(4)
C(412)	0.2797(8)	0.1674(7)	0.3377(7)
C(413)	0.1701(11)	0.0985(4)	0.3355(6)
C(5)	0.0	0.2187(4)	0.2155(4)
N(5)	0.0	0.1829(5)	0.1798(5)

[a] Atoms are labeled as shown in Figure 2. Methyl groups attached to C(11) are labeled C(111)–C(114). Other methyl groups are labeled similarly. Methyl groups of ligands 1–3 are disordered over two sites and were assigned an occupancy factor of 0.5. See footnote *b*, Table II.

Table IV. Final Positional Parameters for the Nonhydrogen Atoms of $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (3)[a]

atom	x	y	z
W	0.14809(1)	0.0	0.12657(1)
P(1)	0.44388(8)	0.5	0.18011(6)
P(2)	0.37254(10)	0.0	0.03304(8)
F(11)	0.4723(3)	0.5	0.21645(18)
F(12)	0.3898(3)	0.5	0.2005(2)
F(13)	0.4103(3)	0.5	0.14561(16)
F(14)	0.4418(2)	0.3666(4)	0.18096(13)
F(15)	0.4945(3)	0.5	0.1600(2)
F(21)	0.4291(3)	0.0	0.0173(2)
F(22)	0.3969(3)	0.0	0.07059(19)
F(23)	0.3170(3)	0.0	0.0488(2)
F(24)	0.3496(3)	0.0	-0.00413(19)
F(25)	0.3735(3)	0.1292(6)	0.0331(2)
C(11)	0.1670(3)	0.0	0.0716(2)
N(12)	0.1738(3)	0.0	0.04201(16)
C(13)	0.1783(4)	0.0	0.0042(2)
C(14)	0.2112(4)	0.1011(12)	-0.0047(2)
C(15)	0.1269(6)	0.0	-0.0106(3)
C(21)	0.21303(19)	0.1143(5)	0.13038(12)
N(22)	0.24939(18)	0.1734(4)	0.13218(12)
C(23)	0.2950(3)	0.2473(6)	0.13743(17)
C(24)	0.3419(3)	0.1672(10)	0.1476(3)
C(25)	0.2839(3)	0.3246(9)	0.1676(3)
C(26)	0.3059(4)	0.3069(10)	0.1050(2)
C(31)	0.08987(19)	0.1160(4)	0.10680(13)
N(32)	0.05863(18)	0.1762(4)	0.09504(12)
C(33)	0.0179(2)	0.2500(6)	0.07973(17)
C(34)	-0.0253(4)	0.1777(9)	0.0674(4)
C(35)	0.0399(4)	0.3192(10)	0.0519(3)
C(36)	-0.0027(4)	0.3250(9)	0.1087(3)
C(41)	0.1306(2)	0.1043(5)	0.16886(13)
N(42)	0.1217(2)	0.1652(5)	0.19160(13)
C(43)	0.1063(3)	0.2433(7)	0.22002(18)
C(44)	0.1529(4)	0.3127(10)	0.2302(3)
C(45)	0.0609(4)	0.3153(9)	0.2075(3)
C(46)	0.0874(5)	0.1696(9)	0.2502(2)

[a] Atoms are labeled as indicated in Figure 3. This labeling corresponds to that of ref 13. See footnote *b*, Table II.

Table V. Interatomic Distances (Å) and Angles (Deg) for $[Mo(CNC_6H_{11})_7](PF_6)_2$ (1)[a,b]

Coordination Sphere			
Mo-C(1)	2.143(7)	Mo-C(3)	2.049(29)
Mo-C(2)	2.089(8)		
C(1)-Mo-C(2)	77.8(3)	C(2)-Mo-C(2')	111.8(3)
C(1)-Mo-C(3)	113.9(7)	C(3)-Mo-C(1')	132.2(7)
C(1)-Mo-C(2')	159.0(3)	C(3)-Mo-C(1")	135.7(7)
C(1)-Mo-C(2")	79.7(3)	C(3)-Mo-C(2')	87.0(18)
C(1)-Mo-C(1')	86.0(3)	C(3)-Mo-C(2")	68.3(18)
C(2)-Mo-C(3)	64.4(18)		
Ligand Geometry			
C(1)-N(1)	1.14(1)	C(23)-C(24)	1.49(2)
N(1)-C(11)	1.45(1)	C(24)-C(25)	1.47(2)
C(11)-C(12)	1.47(2)	C(25)-C(26)	1.53(1)
C(12)-C(13)	1.45(3)	C(26)-C(21)	1.48(2)
C(13)-C(14)	1.56(3)	C(3)-N(3)	1.20(4)
C(14)-C(15)	1.48(3)	N(3)-C(31)	1.65(5)
C(15)-C(16)	1.48(2)	C(31)-C(32)	1.51(2)
C(16)-C(11)	1.53(2)	C(32)-C(33)	1.48(2)
C(2)-N(2)	1.17(1)	C(33)-C(34)	1.45(2)
N(2)-C(21)	1.45(1)	C(34)-C(35)	1.44(2)
C(21)-C(22)	1.53(2)	C(35)-C(36)	1.46(2)
C(22)-C(23)	1.52(2)	C(36)-C(31)	1.51(2)
Mo-C(1)-N(1)	175.8(8)	C(21)-C(22)-C(23)	110.4(9)
C(1)-N(1)-C(11)	170.0(8)	C(22)-C(23)-C(24)	112(1)
N(1)-C(11)-C(12)	107.7(9)	C(23)-C(24)-C(25)	117(1)
N(1)-C(11)-C(16)	108.5(8)	C(24)-C(25)-C(26)	112.6(9)
C(16)-C(11)-C(12)	112(1)	C(25)-C(26)-C(21)	112.2(9)
C(11)-C(12)-C(13)	111(1)	Mo-C(3)-N(3)	171(7)
C(12)-C(13)-C(14)	116(1)	C(3)-N(3)-C(31)	176(8)
C(13)-C(14)-C(15)	110(2)	N(3)-C(31)-C(32)	97(5)
C(14)-C(15)-C(16)	115(2)	N(3)-C(31)-C(36)	103(4)
C(15)-C(16)-C(11)	111(1)	C(36)-C(31)-C(32)	115(2)
Mo-C(2)-N(2)	176(1)	C(31)-C(32)-C(33)	115(2)
C(2)-N(2)-C(21)	170(1)	C(32)-C(33)-C(34)	120(2)
N(2)-C(21)-C(22)	108.9(9)	C(33)-C(34)-C(35)	120(2)
N(2)-C(21)-C(26)	109(1)	C(34)-C(35)-C(36)	121(2)
C(22)-C(21)-C(26)	111.1(9)	C(35)-C(36)-C(31)	116(2)
Anion Geometry			
min P-F	1.54(3)	mean cis F-P-F	90(2)
max P-F	1.72(2)	min trans F-P-F	155(2)
mean P-F	1.61(3)	max trans F-P-F	180.0
min cis F-P-F	80(3)	mean trans F-P-F	168(2)
max cis F-P-F	114(4)		

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

Table VI. Interatomic Distances (Å) and Angles (Deg) for $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ (2)[a]

Coordination Sphere			
Mo-C(1)	2.081(10)	Mo-C(4)	2.111(7)
Mo-C(2)	2.050(10)	Mo-C(5)	2.191(9)
Mo-C(3)	2.114(6)		
C(1)-Mo-C(2)	70.9(3)	C(3)-Mo-C(4)	84.1(2)
C(1)-Mo-C(3)	75.0(2)	C(3)-Mo-C(5)	80.7(2)
C(1)-Mo-C(4)	120.5(2)	C(3)-Mo-C(3')	91.5(2)
C(1)-Mo-C(5)	144.7(3)	C(3)-Mo-C(4')	161.8(2)
C(2)-Mo-C(3)	121.8(2)	C(4)-Mo-C(5)	81.2(2)
C(2)-Mo-C(4)	74.9(2)	C(4)-Mo-C(4')	94.4(2)
C(2)-Mo-C(5)	144.4(3)		
Ligand Geometry			
C(1)-N(1)	1.16(1)	N(4)-C(4)	1.16(1)
N(1)-C(11)	1.46(1)	N(4)-C(41)	1.46(1)
C(2)-N(2)	1.16(1)	C(5)-N(5)	1.15(1)
N(2)-C(21)	1.49(1)	mean C-C(methyl)	1.51(2)
C(3)-N(3)	1.15(1)	range C-C(methyl)	1.45-1.63
N(3)-C(31)	1.46(1)		
Mo-C(1)-N(1)	177.7(8)	C(4)-N(4)-C(41)	169.5(8)
C(1)-N(1)-C(11)	179(1)	Mo-C(5)-N(5)	179.8(4)
Mo-C(2)-N(2)	177.4(8)	mean N-C-C(methyl)	107(1)
C(2)-N(2)-C(21)	180	range N-C-C(methyl)	104-111
Mo-C(3)-N(3)	174.1(6)	mean C(methyl)-C-C(methyl)	112(2)
C(3)-N(3)-C(31)	169(1)	range C(methyl)-C-C(methyl)	102-127
Mo-C(4)-N(4)	175.9(6)		
Anion Geometry			
P-F(1)	1.558(8)	P-F(3)	1.557(5)
P-F(2)	1.537(8)	P-F(4)	1.547(5)
F(1)-P-F(2)	180	F(3)-P-F(4)	90.1(3)
F(1)-P-F(3)	90.5(3)	F(3)-P-F(3')	179.1(3)
F(1)-P-F(4)	90.1(3)	F(4)-P-F(3')	89.9(3)
F(2)-P-F(3)	89.5(3)	F(4)-P-F(4')	179.7(3)
F(2)-P-F(4)	89.9(3)		

[a] See footnote *a*, Table III, and footnote *b*, Table V. Primed atoms are related to those unprimed by mirror symmetry.

Table VII. Interatomic Distances (Å) and Angles (Deg) for $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (3)[a]

Coordination Sphere			
W-C(11)	2.142(8)	W-C(31)	2.123(5)
W-C(21)	2.115(5)	W-C(41)	2.069(6)
C(11)-W-C(21)	83.2(2)	C(21)-W-C(41)	75.8(2)
C(11)-W-C(31)	79.5(2)	C(21)-W-C(41')	119.6(2)
C(11)-W-C(41)	143.9(2)	C(31)-W-C(31')	78.6(2)
C(21)-W-C(21')	77.8(2)	C(31)-W-C(41)	75.3(2)
C(21)-W-C(31)	99.2(2)	C(31)-W-C(41')	119.4(2)
C(21)-W-C(31')	162.7(2)	C(41)-W-C(41')	72.0(2)
Ligand Geometry			
C(11)-N(12)	1.148(9)	N(32)-C(33)	1.459(7)
C(12)-C(13)	1.45(1)	C(41)-N(42)	1.140(7)
C(21)-N(22)	1.147(6)	N(42)-C(43)	1.469(8)
N(22)-C(23)	1.448(7)	mean C-C(methyl)	1.48(1)
C(31)-N(32)	1.143(6)	range C-C(methyl)	1.42-1.55
W-C(11)-N(12)	176.0(7)	W-C(41)-N(42)	177.7(6)
C(11)-N(12)-C(13)	176.4(9)	C(41)-N(42)-C(43)	175.8(7)
W-C(21)-N(22)	178.0(5)	mean N-C-C(methyl)	108(1)
C(21)-N(22)-C(23)	175.9(6)	range N-C-C(methyl)	107-109
W-C(31)-N(32)	177.4(5)	mean C(methyl)-C-C(methyl)	111(1)
C(31)-N(32)-C(33)	177.9(6)	range C(methyl)-C-C(methyl)	108-115
Anion Geometry			
min P-F	1.501(7)	mean cis F-P-F	90.0(4)
max P-F	1.582(9)	min trans F-P-F	174.5(6)
mean P-F	1.540(8)	max trans F-P-F	179.4(6)
min cis F-P-F	87.2(5)	mean trans F-P-F	178.0(6)
max cis F-P-F	93.3(6)		

[a] See footnote *a*, Table IV, and footnote *b*, Table V. Primed atoms are related to those unprimed by mirror symmetry.

$[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (3). Refinement of this structure was initiated by using the nonhydrogen atom positional parameters previously published for the isomorphous molybdenum analogue.[13] Full-matrix least-squares refinement of 281 variables converged at $R_1 = 0.034$ and $R_2 = 0.045$. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 0.9520/[\sigma^2(F_o) + 0.0014F_o^2]$. All nonhydrogen atoms were refined anisotropically. The methyl group hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and included in the refinement as invariants with a common isotropic temperature factor fixed at $U = 0.20$ Å^2. In the final cycle of refinement, no parameter shifted by more than 0.001σ, and the largest peak on the final difference Fourier map was 0.57 e Å^{-3} and was in the vicinity of the tungsten atom.

Final nonhydrogen positional parameters for **3**, together with their estimated standard deviations, appear in Table IV. Bond distances and angles are listed in Table VII, and Figure 3 depicts the coordination geometry and atom labeling scheme for the $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ cation.

Discussion

Description of the Structures. $[Mo(CNC_6H_{11})_7](PF_6)_2$ (1). The structure consists of discrete seven-coordinate $[Mo(CNC_6H_{11})_7]^{2+}$ cations and PF_6^- anions. The molybdenum atom sits on a crystallographic threefold axis, and each cation has approximate capped octahedral geometry. The uncapped face comprises ligands 1, 1′, and 1″ (Figure 1) while the capped face is made up of ligands 2, 2′, and 2″. The capping ligand (ligand 3) lies slightly off the crystallographic threefold axis and is therefore disordered over three positions. This displacement distorts the symmetry of the cation from that of a perfect capped octahedron (C_{3v}).

The disordering of the capping ligand occurs because a cyclohexyl isocyanide ligand lacks threefold symmetry. Figure

Table VIII. Summary of Interbond Angles (Deg) and Metal–Ligand Distances (Å) for Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes[a]

Angle Number	$[Mo(CNR)_7]$–[b] $(PF_6)_2$ R = C_6H_{11}	$[Mo(CNR)_6CN]$–[b] (PF_6) R = $\underline{t}$-C_4H_9	$[W(CNR)_7]$–[b] $(PF_6)_2$ R = $\underline{t}$-C_4H_9	$[Mo(CNR_7]$–[c] $(PF_6)_2$ R = $\underline{t}$-C_4H_9	$[W(CNR)_7]$–[d] (W_6O_{19}) R = $\underline{t}$-C_4H_9	$[Mo(CNR)_7]$–[e] $(BF_4)_2$ R = CH_3	$[Mo(CNR)_6I]$–[f] I R = $\underline{t}$-C_4H_9	$[Mo(CNR)_6Br]$–[g] Br R = $\underline{t}$-C_4H_9	$[Mo(SnCl_3)(CNR)_6]$–[h] $[(Ph_3B)_2CN]$ R = $\underline{t}$-C_4H_9	$W(CNR)_3$–[i] $(CO)_2I_2$ R = $\underline{t}$-C_4H_9
ANGLES										
1	159.0	161.8	162.7	164.0	166.0	163.6	163.0	163.8	176.3	165.8
2	159.0	161.8	162.7	164.0	153.8	156.5	163.0	163.8	155.7	155.1
3	159.0	144.7	143.9	144.2	152.6	154.1	145.2	145.7	155.7	154.4
4	135.7	144.4	143.9	144.2	134.5	134.4	145.1	145.1	132.7	132.0
5	132.2	121.8	119.6	119.0	133.4	130.0	120.8	120.0	132.7	131.5
6	113.9	121.8	119.6	119.0	122.5	120.2	120.8	120.0	122.0	119.7
7	111.8	120.5	119.4	118.8	116.1	119.7	120.5	119.5	111.5	117.5
8	111.8	120.5	119.4	118.8	109.8	111.2	120.5	119.5	103.6	110.5
9	111.8	94.4	99.2	99.0	105.7	105.2	92.2	93.9	103.6	109.2
10	86.0	91.5	99.2	99.0	89.8	89.5	88.4	93.4	95.5	89.5
11	86.0	84.1	83.2	83.7	89.4	87.0	85.5	84.0	95.5	87.9
12	86.0	84.1	83.2	83.7	81.0	81.1	85.5	84.0	81.6	84.7
13	79.7	81.2	79.5	80.3	79.3	81.0	81.6	81.9	81.6	81.1
14	79.7	81.2	79.5	80.3	78.6	79.8	81.6	81.9	78.8	80.8
15	79.7	80.7	78.6	78.8	78.3	78.9	81.4	81.9	78.5	77.1
16	77.8	80.7	77.8	78.6	77.8	78.3	81.4	81.9	78.5	76.6
17	77.8	75.0	75.8	75.2	77.7	77.2	74.6	74.8	78.0	75.6
18	77.8	75.0	75.8	75.2	77.3	76.9	74.6	74.8	78.0	75.1
19	87.0	74.9	75.3	75.0	76.5	76.2	74.5	74.6	72.2	74.7
20	68.3	74.9	75.3	75.0	72.7	72.9	74.5	74.6	70.6	74.1
21	64.4	70.9	72.0	71.5	72.5	71.5	69.7	69.2	70.6	72.9
DISTANCES										
	2.049(29)	2.050(10)	2.069(6)	2.051(7)	2.06(2)	2.038(9)	2.04(3)	2.047(13)	2.071(9)	1.959(15)
	2.089(8)	2.081(10)	2.069(6)	2.051(7)	2.07(2)	2.075(9)	2.07(3)	2.051(12)	2.071(3)	1.997(13)
	2.089(8)	2.111(7)	2.115(5)	2.127(7)	2.08(2)	2.095(8)	2.10(2)	2.113(9)	2.071(18)	2.092(13)
	2.089(8)	2.111(7)	2.115(5)	2.127(7)	2.09(2)	2.098(8)	2.10(2)	2.113(9)	2.137(15)	2.099(13)
	2.143(7)	2.114(6)	2.123(5)	2.138(7)	2.10(2)	2.137(9)	2.13(2)	2.119(9)	2.138(8)	2.145(13)
	2.143(7)	2.114(6)	2.123(5)	2.138(7)	2.11(2)	2.145(9)	2.13(2)	2.119(9)	2.138(8)	2.863(1)
	2.143(7)	2.191(9)	2.142(8)	2.171(9)	2.12(2)	2.16(1)	2.862(3)	2.673(2)	2.663(1)	2.865(1)

[a] Angles and distances are listed in decreasing size. [b] This work. [c] Reference 13. [d] Reference 16. [e] Reference 14. [f] Reference 11. [g] Reference 12b. [h] Reference 2. [i] Reference 8.

1 is a view down the C_3 axis of the inner coordination sphere of the $[Mo(CNC_6H_{11})_7]^{2+}$ cation showing the displacement of the C≡N—C portion of the capping ligand from the threefold axis. The capping ligand is disordered in such a way that the crystallographic threefold axis passes approximately through the pseudothreefold axis of the cyclohexyl ring. The cyclohexyl ring in this model is flattened, owing to the disorder, and only C(31) lies significantly out of the plane of the other five atoms.

All the cyclohexyl rings of the structure adopt the chair conformation. In the ligands of the capped face, the C≡N moiety is bonded to the cyclohexyl ring in the equatorial position, whereas in the capping ligand and the ligands of the uncapped face the attachment is axial. This difference in cyclohexyl ring attachment permits efficient packing of the cations in the unit cell, as may be seen by examination of Figure 4. The cyclohexyl groups of the capped face ligands are interleaved with similar cyclohexyl groups of molecules translated one unit cell in both *a* and *b*.

The geometry of ligands 1 and 2 in the present compound is comparable to the geometry of the cyclohexyl isocyanide ligands in the complex $[Mo(CNC_6H_{11})_5(dpm)](PF_6)_2$.[26] In the present compound the C≡N, N—C, and C(ring)—C(ring) distances, averaged over ligands 1 and 2, are 1.16, 1.45, and 1.50 Å, and in $[Mo(CNC_6H_{11})_5(dppm)](PF_6)_2$ the average values are 1.15, 1.45, and 1.49 Å, respectively. The Mo—C≡N, C≡N—C, N—C—C(ring), and C(ring)-C(ring)-C(ring) angles average 176, 170, 109, and 113° in the present compound and average 175, 173, 110, and 110° in $[Mo(CNC_6H_{11})_5(dppm)](PF_6)_2$. The geometry of ligand 3 is not as good, because it is disordered. The Mo–C bond lengths (Table V) [Mo–C(1) = 2.143 (7) Å, Mo–C(2) = 2.089 (8) Å, Mo–C(3) = 2.049 (29) Å] are all comparable to similar distances observed in other molybdenum(II)–isocyanide complexes[2,11,12b,13,14,26] (Table VIII). The Mo–C distances have the 1:3:3 pattern previously recognized[14] for capped-octahedral structures, and the angles at the molybdenum atom also reflect capped-octahedral symmetry (vide infra).

The hexafluorophosphate groups of the structure also lie on crystallographic threefold axes, but these axes do not coincide with that of either anion. For anion 1 the crystallographic threefold axis passes only through the phosphorus atom, and all of the six fluorine atoms are disordered. In anion 2 the crystallographic threefold axis passes through one *trans*-F–P–F moiety and results in the disorder of the remaining four fluorine atoms. The disordering of these anions can be visualized by reference to the unit-cell packing diagram (Figure 4). The capping cyclohexyl group (ligand 3) is surrounded by PF_6^- anions 1 and 2 in such a manner that its disorder about the threefold axis meshes with that of neighboring PF_6^- anions.

$[Mo(CN$-t-$C_4H_9)_6(CN)](PF_6)$ (2). This structure is isomorphous with those of the $[Mo(CN$-t-$C_4H_9)_6Br]Br$ and $[Mo(CN$-t-$C_4H_9)_6I]I$ compounds[11,12b] and consists of discrete $[Mo(CN$-t-$C_4H_9)_6(CN)]^+$ cations and PF_6^- anions. The cation is isostructural with the bromide and iodide analogues. Its geometry is that of a capped trigonal prism with cyanide as the capping ligand (Figure 2). The capped face is made up of ligands 3, 4, 3′, and 4′ while ligands 1 and 2 comprise the unique edge.[13] The molybdenum atom, the unique edge ligands, and the capping cyanide ligand all lie on a crystallographically required mirror plane.

The individual Mo–C bond lengths to the *tert*-butyl isocyanide ligands [Mo–C(1) = 2.081 (10) Å, Mo–C(2) = 2.050 (10) Å, Mo–C(3) = 2.114 (6) Å, Mo–C(4) = 2.111 (7) Å] are within three standard deviations of those found in the bromide and iodide structures. The Mo–CN bond length of 2.191 (9) Å is comparable to the 2.204 (6) Å value for the similar bond in $[Mo(CN$-t-$C_4H_9)_4(t$-BuHNCCNH-t-Bu)(CN)][B(C_6H_5)_4]$[27] and to the longest such bond [2.201 (7) Å] in $Na_5[Mo(CN)_7]\cdot 10H_2O$.[28] In the structures[28] of $Na_5[Mo(CN)_7]\cdot 10H_2O$ and $K_5[Mo(CN)_7]\cdot H_2O$ the Mo–CN bond lengths average 2.14 Å, apart from one longer bond in the Na^+

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(26) Corfield, P. W. R.; Dewan, J. C.; Wood, T. E.; Walton, R. A.; Lippard, S. J., to be submitted for publication.

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salt. This longer bond was attributed to the fact that this C≡N group is involved in three close contacts to Na^+ ions while the remainder are not. In the $[Mo(CN\text{-}t\text{-}C_4H_9)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$ complex, the C≡N group is involved in two hydrogen-bonding interactions. In the present compound, the C≡N moiety is not involved in any interactions with neighboring ions although the long Mo—C bond is consistent with the idea that weaker bonding occurs at the capping position in the capped trigonal prism.[11] The Mo–C bond lengths in the present compound follow the 1:4:2 pattern typical for MoL_6X^+ capped trigonal-prismatic stereochemistries, and the C–Mo–C angles are those of a nearly perfect C_{2v} capped trigonal prism (vide infra).

Three of the four *tert*-butyl isocyanide ligands (ligands 1, 2, 3) were refined by using a disordered model for the methyl carbon atoms. For the fourth ligand (ligand 4) no satisfactory disordered model could be found. This ligand has the poorest *tert*-butyl group geometry, and the largest unaccounted for peak on the final difference Fourier map occurred ~1.8 Å from the center of this group. These results suggest that these methyl carbon atoms are probably also disordered.

The phosphorus and two fluorine atoms of the PF_6^- group lie on a crystallographic twofold axis while the remaining two fluorine atoms are in general positions. The anion is not disordered, and its geometry is normal for a hexafluorophosphate group. The closest $CH_3\cdots F$ interionic contacts of the structure are all >3.1 Å.

$[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (3). The structure is isomorphous and isostructural with the molybdenum analogue[13] and consists of discrete $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ cations and PF_6^- anions. The cation exhibits capped trigonal prismatic geometry (Figure 3) where ligand 1 is the capping ligand. The ligands of the capped face are ligands 2, 3, 2′, and 3′, and the unique edge comprises ligands 4 and 4′. The tungsten atom and ligand 1 lie on a crystallographic mirror plane.

The W–C bond lengths [W–C(11) = 2.142 (8) Å, W–C(21) = 2.115 (5) Å, W–C(31) = 2.123 (5) Å, W–C(41) = 2.069 (6) Å] compare very favorably with those determined in $[W(CN\text{-}t\text{-}C_4H_9)_7](W_6O_{19})$[16] and $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$.[8] The W–C lengths have the 1:4:2 ratio associated with the capped trigonal-prismatic geometry. Compared with those of the molybdenum analogue, the W–C(11), W–C(21), and W–C(31) distances are shorter by 0.029, 0.012, and 0.015 Å while the W–C(41) distance is longer by 0.018 Å. These differences are on the order of three standard deviations in the first case and two standard deviations in the remainder. The *tert*-butyl groups of the cation and the PF_6^- anions are not disordered and have normal geometries. The phosphorus atom and four fluorine atoms of each anion lie on crystallographically required mirror planes with one additional fluorine atom of each anion being in a general position.

Stereochemical Comparison with Other Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes. Table VIII summarizes the metal–ligand bond lengths and angles at the central metal atom for the three structures determined here as well as for $[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$,[13] $[W(CN\text{-}t\text{-}C_4H_9)_7](W_6O_{19})$,[16] $[Mo(CNCH_3)_7](BF_4)_2$,[14] $[Mo(CN\text{-}t\text{-}C_4H_9)_6X]X$ (X = I,[11] Br[12b]), $[Mo(CN\text{-}t\text{-}C_4H_9)_6(SnCl_3)][(Ph_3B)_2CN]$,[2] and $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$.[8] As discussed previously,[2,4] the interbond angles provide the best method for assigning these molecules to one of the four idealized seven-coordinate stereochemistries. The assignments (cf. Table IV, ref 2) are given in Table VIII. Care must be exercised in applying the interbond angle classification method. In the case of $[Mo(CNC_6H_{11})_7](PF_6)_2$, for example, one must be aware that the 87.0° angle (Table VIII) is that between the capping and a capped-face ligand. It therefore should be grouped with the other angles of this type, which are 68.3 and 64.4°. After this adjustment is made, it becomes obvious that the other angles in the cation are characteristic of capped-octahedral symmetry and that the 87.0° angle results from the displacement of the capping ligand from the crystallographic threefold axis.

The fact that the two isomorphous groups of compounds $[M(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (M = Mo, W) and $[Mo(CN\text{-}t\text{-}C_4H_9)_6X]Y$ (X = Y = Br, I; X = CN, Y = PF_6) have nearly perfect C_{2v} capped trigonal-prismatic structures whereas $[Mo(CNCH_3)_7](BF_4)_2$, $[W(CN\text{-}t\text{-}C_4H_9)_7](W_6O_{19})$, and $[Mo(CN\text{-}t\text{-}C_4H_9)_6(SnCl_3)][(Ph_3B)_2CN]$ have 4:3 piano-stool geometries similar to that of $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$ and $[Mo(CNC_6H_{11})_7](PF_6)_2$ has C_{3v} capped octahedral symmetry demonstrates that crystal packing forces are a prime factor in determining the stereochemistry. Similar observations have been made for complexes of other coordination numbers, a notable example being the existence of both trigonal-bipyramidal and square-based-pyramidal structures in the same crystal lattice of a salt of the $[Ni(CN)_5]^{3-}$ ion.[29] Both cyanide and alkyl isocyanide ligands have linear M–C–N–C– fragments that minimize intramolecular nonbonded contacts. Even for *tert*-butyl isocyanide, the nonbonded contacts between methyl groups of adjacent ligands that subtend a small (70°) angle at the metal center are greater than the sum of van der Waals radii for these groups. The influence of crystal packing on structure is therefore even more important for complexes containing these and other linear, multiply bonded ligands (e.g., CO, NO).

Table VIII reveals the pattern of 2:4:1 for the metal–ligand distances in the C_{2v} capped trigonal-prismatic structures and the 1:3:3 pattern for the C_{3v} capped-octahedral structure consistent with their symmetry. Since a 4:3 piano-stool structure has only C_s symmetry at best, a 1:1:2:2:1 (see Figure 3, ref 8) or a 1:2:2:2 pattern of bond lengths might be expected. Accidental degeneracies could raise this pattern to 1:3:3. The complex $[Mo(CNCH_3)_7](BF_4)_2$ in fact has the 1:1:2:2:1 pattern, but a 1:3:3 pattern can also be (and was[14]) recognized for this compound within the error limits of the bond lengths. The $[Mo(CN\text{-}t\text{-}C_4H_9)_6(SnCl_3)]^+$ cation has an even more obvious 1:3:3 bond length distribution. Since the 4:3 piano-stool geometry is on the pathway connecting the capped octahedron and the pentagonal bypyramid,[6] perhaps these structures have undergone angular distortions from C_{3v} symmetry before the energetically more demanding bond length changes. In such a case the observed 1:3:3 bond length distribution would not really be "accidental". It seems clear, however, that, whether you call them 4:3 piano stools or distorted capped octahedra, $[Mo(CNCH_3)_7](BF_4)_2$, $[W(CN\text{-}t\text{-}C_4H_9)_7](W_6O_{19})$, and $[Mo(CN\text{-}t\text{-}C_4H_9)_6(SnCl_3)][(Ph_3B)_2CN]$ comprise a geometrically distinct class of compounds that was recognized for $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$.[8]

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Supplementary Material Available: Listings of final observed and calculated structure factor amplitudes for **1**–**3** (Tables S1–S3), final thermal parameters for **1**–**3** (Tables S4–S6), and final hydrogen atom positional parameters for **1** and **3** (Tables S7 and S8) (41 pages). Ordering information is given on any current masthead page.

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