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Reactions of Eight-Coordinate Metal Cyanide Complexes. III.[1,2] Synthesis and Structure of Iodohexakis(*tert*-butyl isocyanide)molybdenum(II) Iodide

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The compound of empirical formula $Mo(CNR)_6I_2$, R = *tert*-butyl, has been isolated from the reaction products of silver octacyanomolybdate(IV) and *tert*-butyl iodide. A single-crystal X-ray diffraction study of the red-orange, crystalline material revealed the correct structural formula to be $[Mo(CNR)_6I]I$. In the cation, the coordination geometry of the molybdenum atom is that of a monocapped trigonal prism, with the carbon atoms at the vertices and an iodine atom above one of the square faces. The average Mo–C distances are 2.06 (2) Å trans to the iodine atom and 2.12 (2) Å cis to the iodine atom. The Mo–I distance is 2.862 (3) Å. Steric crowding by the iodine atom may be judged by the average interligand distances and from the distortions of the trigonal prism defined by the isocyanide ligands. The *tert*-butyl groups are disordered in the lattice. The compound crystallizes in the orthorhombic system, with $a = 22.437$ (9) Å, $b = 22.336$ (9) Å, $c = 16.377$ (7) Å, ρ_{calcd} (for $Z = 8$) = 1.374 g/cm³, ρ_{obsd} = 1.38 g/cm³, and space group *Acam*. The molecule has crystallographically imposed mirror symmetry. Full-matrix, anisotropic refinement of all atoms except the *tert*-butyl carbon atoms, which were assigned isotropic thermal parameters, converged at $R_1 = 0.068$ for 1408 independent, observed reflections.

Introduction

Eight-coordinate complexes of general formula MX_4Y_4, where the π-donor and π-acceptor properties of the ligands X and Y are substantially different, are of interest for the reasons discussed previously.[1,3,4] Compounds originally formulated as $K_4[M(CN)_4(OH)_4]\cdot 4H_2O$ (M = Mo, W) have been shown by chemical, spectroscopic, and X-ray diffraction studies to be $K_4[MO_2(CN)_4]\cdot 6H_2O$[1,5] or $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$[6] and therefore do not belong to the MX_4Y_4 class. Subsequently, we have turned our attention to the molecules $M(CN)_4(CNR)_4$ (M = Mo,[7] W[7,8]) which reportedly may be obtained from the reaction between alkyl halides and the silver salt of the appropriate octacyanometalate(IV), eq 1. The tetracyanotetrakis(alkyl isocyanide)molybdenum(IV) complexes are not particularly well characterized.[9] Recently, however, we have been able to prepare crystalline $Mo(CN)_4(CNR)_4$ (R = CH_3, n-C_3H_7, $tert$-C_4H_9) through a modification of the published synthetic procedure,[7] and the crystal structure of $Mo(CN)_4(CNCH_3)_4$ has been determined.[10] In the course of this study, a new material of empirical formula $Mo(CNR)_6I_2$ (R = $tert$-C_4H_9) was isolated in a redox reaction which *tentatively* may be represented by eq 2. The molybdenum(II) isocyanide complex was obtained as beautiful red-orange prisms, and its solid-state structure has been elucidated in a single-crystal X-ray diffraction investigation. While this structure determination was in progress, the synthesis and characterization of the closely related molybdenum(II) isocyanide complexes $Mo(CNR)_5X_2$ (X = Cl, Br) was reported, and the presence of seven-coordinate molybdenum(II) was suggested.[11] Our study reinforces the conclusions drawn by these authors and provides much needed structural information about seven-coordinate complexes of MX_6Y type, where X and Y are both monodentate ligands.[12]

$$Ag_4[M(CN)_8] + 4RX \longrightarrow M(CN)_4(CNR)_4 + 4AgX \quad (1)$$

$$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}C_3H_7,\ tert\text{-}C_4H_9,\ \text{etc.}$$

$$M = Mo,\ W$$

$$Ag_4Mo(CN)_8 + 6RI \longrightarrow [Mo(CNR)_6I]I + 2AgCN + 2AgI + I_2 \quad (2)$$

Experimental Procedure and Results

Collection and Reduction of X-Ray Data.—The compound was prepared by shaking a suspension of silver octacyanomolybdate(IV) in *tert*-butyl iodide for 6 days, extracting the residue with methanol, and crystallizing by slow evaporation from methanol after chromatography on alumina. This synthesis has been reproduced only with great difficulty, and futher studies are in progress. *Anal.* Calcd for $C_{30}H_{54}N_6I_2Mo$: C, 42.46; H, 6.41; N, 9.90. Found (by Galbraith Laboratories, Knoxville, Tenn.): C, 43.0; H, 6.44; N, 9.39.

A rectangular prism of approximate dimensions 0.1 × 0.1 × 0.3 mm was selected from the small crop of red-orange crystals and mounted with clear nail polish on the end of a glass fiber. The mounting axis was the longest of the three and parallel to *c*. The crystal, which has been kept in air for over 2 years without any visible signs of decomposition, was used in all subsequent work reported here. The space group and approximate unit cell parameters were determined using Ni-filtered Cu Kα radiation

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[1] Part I: S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **6**, 1943 (1967).

[2] Part II: M. Allen and S. J. Lippard, *ibid.*, **9**, 991 (1970).

[3] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

[4] S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

[5] S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967).

[6] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **90**, 3374 (1968).

[7] (a) F. Hoelzl and G. Is. Xenakis, *Monatsh.*, **48**, 689 (1927); (b) F. Hoelzl and N. Zymaris, *ibid.*, **49**, 241 (1928).

[8] H. Latka, *Z. Anorg. Allg. Chem.*, **353**, 243 (1967).

[9] See, for example, L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley–Interscience, New York, N. Y., 1969, pp 66–67.

[10] D. F. Lewis, S. J. Lippard, and M. Novotny, to be submitted for publication.

[11] F. Bonati and G. Minghetti, *Inorg. Chem.*, **9**, 2642 (1970).

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

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS OF THE ATOMS[a,b]

Atom	x	y	z	β_{11}[c] or B[d]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.2817 (1)	0.2880 (1)	0.0	13 (1)	14 (1)	44 (1)	2 (1)	0.0	0.0
I1	0.1911 (1)	0.1978 (1)	0.0	21 (1)	21 (1)	97 (2)	−5 (1)	0.0	0.0
I2	0.0	0.0	0.2201 (2)	25 (1)	29 (1)	84 (2)	4 (1)	0.0	0.0
C1	0.2981 (9)	0.3778 (13)	0.0	7 (6)	24 (8)	55 (17)	4 (5)	0.0	0.0
N1	0.3088 (10)	0.4301 (11)	0.0	32 (7)	19 (7)	71 (17)	−5 (6)	0.0	0.0
C11	0.3158 (12)	0.4942 (11)	0.0	18 (7)	17 (7)	71 (19)	−13 (6)	0.0	0.0
C2	0.3729 (13)	0.3038 (10)	0.0	22 (8)	13 (6)	53 (17)	1 (6)	0.0	0.0
N2	0.4233 (11)	0.3118 (10)	0.0	16 (7)	25 (7)	96 (20)	−4 (5)	0.0	0.0
C21	0.4892 (12)	0.3192 (13)	0.0	20 (8)	29 (8)	50 (17)	−11 (6)	0.0	0.0
C3	0.2270 (8)	0.3234 (8)	0.0919 (13)	14 (5)	23 (5)	45 (12)	−1 (4)	0 (5)	4 (6)
N3	0.1931 (7)	0.3444 (7)	0.1382 (12)	18 (4)	21 (4)	68 (12)	−1 (4)	7 (6)	−5 (5)
C31	0.1458 (8)	0.3752 (9)	0.1821 (14)	21 (5)	26 (5)	53 (13)	5 (4)	14 (7)	3 (7)
C4	0.3170 (8)	0.2323 (8)	0.0936 (13)	16 (5)	18 (5)	53 (13)	−3 (4)	9 (6)	3 (6)
N4	0.3383 (7)	0.1982 (8)	0.1391 (11)	28 (5)	26 (5)	51 (11)	2 (4)	−2 (6)	5 (6)
C41	0.3677 (10)	0.1522 (10)	0.1870 (17)	31 (7)	28 (7)	87 (19)	4 (5)	−11 (9)	17 (9)
C111	0.2639 (20)	0.5220 (19)	0.0406 (26)	7.5 (13)					
C112	0.3616 (33)	0.5112 (28)	0.0519 (42)	12.9 (21)					
C113	0.3190 (19)	0.5171 (18)	−0.0908 (27)	5.7 (10)					
C211	0.5121 (19)	0.2605 (20)	0.0369 (26)	7.7 (13)					
C212	0.5040 (24)	0.3519 (27)	0.0702 (36)	8.9 (15)					
C213	0.5084 (23)	0.3102 (27)	−0.0895 (36)	8.8 (14)					
C311	0.1058 (24)	0.4134 (24)	0.1187 (38)	9.6 (15)					
C312	0.1697 (19)	0.4281 (20)	0.2323 (31)	6.8 (11)					
C313	0.1068 (24)	0.3317 (24)	0.2185 (37)	9.1 (15)					
C314	0.1501 (18)	0.3607 (19)	0.2701 (29)	6.0 (10)					
C315	0.0883 (21)	0.3564 (20)	0.1421 (32)	7.2 (12)					
C316	0.1529 (17)	0.4431 (17)	0.1668 (26)	4.8 (9)					
C411	0.4022 (23)	0.1103 (22)	0.1149 (37)	9.0 (14)					
C412	0.4193 (21)	0.1788 (21)	0.2351 (33)	6.7 (12)					
C413	0.3255 (19)	0.1113 (20)	0.2240 (30)	6.2 (11)					
C414	0.3467 (21)	0.1663 (22)	0.2797 (34)	7.8 (13)					
C415	0.3402 (24)	0.0973 (24)	0.1629 (36)	8.5 (14)					
C416	0.4315 (22)	0.1610 (22)	0.1869 (34)	7.1 (13)					

[a] Atoms are labeled as indicated in Figure 1. The *tert*-butyl groups are disordered as described in the text and are numbered accordingly. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is given in the text. Values reported are ×10^4. [d] $\beta_{11} = B$ Å^2, for all methyl carbon atoms of the disordered *tert*-butyl groups.

(λ 1.5418 Å) on the precession and Weissenberg cameras. From the Laue symmetry, *mmm*, and observed extinctions, *hkl*, $k + l \neq 2n$, *h*0*l*, $h \neq 2n$, and 0*kl*, $l \neq 2n$, the space group was determined to be either the centric *Acam* (standard group[13a] *Cmca*, no. 64) or acentric *Aba*2 (no. 41).[13b] The unit cell parameters were determined from the 2θ values of axial reflections carefully centered in the counter window of a Picker full-circle automated X-ray diffractometer. The results are a = 22.437 (9) Å, b = 22.336 (9) Å, and c = 16.377 (7) Å. From the density of 1.38 ± 0.01 g/cm^3 measured by flotation in a mixture of carbon tetrachloride and dimethyl malonate, the number of formula units of $C_{30}H_{54}N_6I_2Mo$ per unit cell was computed to be 8 (ρ_{calcd} = 1.374 g/cm^3).

Using Mo Kα radiation (λ 0.7107 Å), the intensities of 2150 reflections were measured within the octant of recriprocal space in which *h*, *k*, and *l* are all positive, and $(\sin \theta)/\lambda \leqslant 0.5$. The diffractometer settings were computed from the cell constants and crystal orientation matrix using Prewitt's program, GSET-4.[14] A takeoff angle of 2° afforded good intensity and narrow peaks (width of 2θ at half-height, 0.2°). Zirconium foil was used to filter out the unwanted Kβ radiation. The scan angle was 1.25° in 2θ, plus an allowance for the $K\alpha_1$–$K\alpha_2$ separation, and was symmetric with respect to the Bragg position. The scan speed was 1°/min, and stationary background counts of 10 sec were taken at both ends of the scan range. The temperature was 20 ± 1°. Four standard reflections, well separated in reciprocal space, were measured after every 100 data points in order to monitor crystal and instrument stability. In no case did a standard vary by more than ±2% of its mean value for the entire run.

The total counts in the peak plus background, E, observed for a time T_E, were corrected for attenuators and for background counts B_1 and B_2 observed for times T_B to give the integrated intensity, $I = E - (B_1 + B_2)(T_E/2T_B)$. The standard deviation in I, $\sigma(I)$, was obtained from the expression[15] $\sigma(I) = [E + (T_E/2T_B)^2 \cdot (B_1 + B_2) + (\epsilon I)^2]^{1/2}$, with the "ignorance" factor[15c] set equal to 0.05 to prevent excessive weighting of the strong reflections. The integrated intensities and their standard deviations were then corrected for Lorentz and polarization effects using ACAC-3[14] to produce values of F_o^2 and $\sigma(F_o^2)$. In view of the small linear absorption coefficient, μ = 18.6 cm^{-1}, absorption corrections were not applied. Scaling of F_o^2 and $\sigma(F_o^2)$ using a Wilson plot was accomplished by XDATA.[14] Scattering factors for the zerovalent Mo, I, N, and C atoms were obtained from ref 16 with corrections for the effects of anomalous dispersion being included in calculating the contributions of the molybdenum and iodine atoms to the structure factors. Reflections for which $F_o^2 \leqslant 3\sigma(F_o^2)$ were excluded from the refinement; the approximately 1400 remaining reflections were used in the structure determination. Although no systematic attempt was made to correct for secondary extinction, the (200), (020), and (022) reflections were excluded from the final refinement cycles, since these appeared to be seriously affected by extinction effects.

Determination and Refinement of the Structure.—From the corrected data, a three-dimensional Patterson map was computed and solved for the coordinates of the molydenum and two iodine atoms. Assuming the space group to be the centrosymmetric *Acam*, the molybdenum and one iodine atom were located on special positions 8f having a mirror plane of symmetry, and the other iodine atom was located on special position 8d having a twofold symmetry axis.[13a] Using the atomic coordinates for

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[13] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962: (a) p 153; (b) p 127.

[14] Calculations were performed on an IBM 360-91 computer using the following programs: GSET-4, the Prewitt diffractometer setting program; ACAC-3, a revised version of the Prewitt absorption correction and data reduction program; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS); ORFFE, the Busing–Martin–Levy molecular geometry and error function program; ORTEP, the Johnson thermal ellipsoid plotting program.

[15] (a) G. M. Brown and H. A. Levy, *J. Phys. (Paris)*, **25**, 497 (1964); (b) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965); (c) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[16] See ref 13, Vol. II, pp 201-246.

these atoms, a set of phased structure factors was computed for a difference Fourier synthesis.

While the difference map clearly revealed all the linear C–N–C atom groupings of the *tert*-butyl isocyanide ligands, the location of the methyl carbon atoms was ambiguous. With the addition of the 12 light atoms to aid the phasing, a new difference Fourier was calculated. From this map it was evident that the methyl carbon atoms in each of the *tert*-butyl isocyanide ligands were disordered. For every *tert*-butyl group it was possible to locate six methyl carbon atoms. In each ligand these atoms could be divided into two sets of three, each set showing the configuration expected for a *tert*-butyl group. Refinement of the positional parameters and individual temperature factors for the 15 ordered and 18 disordered (each disordered atom was given an occupancy factor of 0.5) atoms converged at values of 0.126 and 0.129 for the indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively. During the refinement the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$.

A difference Fourier calculated at this stage revealed residual peaks around the atoms indicative of some anisotropic thermal motion. Accordingly refinement was continued with the "ordered" atoms being assigned an anisotropic temperature factor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Several cycles of full-matrix, least-squares refinement reduced the residuals to 0.068 and 0.083 for R_1 and R_2, respectively. During the final refinement cycle no variable changed by more than 7% of its deviation. In view of the disorder, no attempt was made to locate the hydrogen atoms of the methyl groups or to refine them anisotropically.

The assignment of an occupancy factor of 0.5 for each of the disordered atoms is warranted by the fact that the final average temperature factors for each of the two sets of three atoms for each *tert*-butyl group are nearly identical. Thus refinement of the individual occupancy factors did not appear to be of any value and was not pursued.

A trial refinement of the structure in the noncentric space group *Aba*2 resulted in a model having poor internal consistency with respect to bond lengths and angles. Moreover, it was not possible to refine simultaneously the parameters of several atoms related by the mirror plane in the centric space group without high correlations. This evidence, in addition to the successful refinement in the centric group, substantiates the choice of the space group *Acam*, although an absolute assignment is not claimed.

A final difference Fourier map showed no significant electron density except for a residual peak about two-thirds the height of a carbon atom at $x = 0$, $y = 0$, $z = 0.41$, a loosely packed region of the unit cell. Introduction of an oxygen atom at half-weight into the structure factor calculation and refinement improved both residuals slightly but did not affect the coordination geometry by as much as one standard deviation. The peak might correspond to a water molecule of crystallization at half-occupancy. On the other hand, an oxygen atom at the position indicated would result in several short nonbonded contacts (I2···O and methyl···O distances of ~3.1 Å), and the peak could have arisen from improper phasing in the region of disordered *tert*-butyl groups and heavy iodide ions. It was therefore not included in the computation of the results presented below, although we do not exclude the possibility that there might be residual water in the lattice.

The molecular structure of the $[(tert\text{-BuNC})_6\text{MoI}]^+$ cation is shown in Figure 1, while Figure 2 shows a stereoscopic view of the molecular packing in the crystal. The iodide ion is not included in Figure 1 since it is remotely situated with respect to the complex cation, and its position appears to be influenced only by normal van der Waals packing forces (Figure 2). The final positional and thermal atomic parameters are given in Table I. A summary of important bond distances and angles is given in Table II, and Table III contains the dimensions of the minimum, medium, and maximum axes of the ellipsoid of thermal vibration for those atoms that were allowed anisotropic temperature factors.[17]

TABLE II

Molecular Geometry of the $[(tert\text{-}C_4H_9NC)_6MoI]^+$ Cation[a,b]

Bond Distances, Å		Interbond Angles, Deg	
Mo–I1	2.862 (3)	I1–Mo–C3	81.4 (5)
Mo–C1	2.04 (3)	I1–Mo–C4	81.6 (5)
Mo–C2	2.07 (3)	C1–Mo–C2	69.7 (9)
Mo–C3	2.10 (2)	C1–Mo–C3	74.6 (6)
Mo–C4	2.13 (2)	C1–Mo–C4	120.5 (6)
C1–N1	1.19 (3)	C2–Mo–C3	120.8 (6)
C2–N2	1.15 (3)	C2–Mo–C4	74.5 (6)
C3–N3	1.17 (2)	C3–Mo–C4	85.5 (7)
C4–N4	1.17 (2)	C3–Mo–C3′	88.4 (7)
N1–C11	1.44 (3)	C4–Mo–C4′	92.2 (7)
N2–C21	1.49 (3)	C3–Mo–C4′	163.0 (7)
N3–C31	1.45 (2)	N1–C1–Mo	178.8 (21)
N4–C41	1.45 (3)	N2–C2–Mo	179.0 (25)
		N3–C3–Mo	174.5 (17)
Interbond Angles, Deg		N4–C4–Mo	173.5 (18)
I1–Mo–C1	145.2 (6)	C11–N1–C1	174.7 (27)
I1–Mo–C2	145.1 (6)	C21–N2–C2	177.6 (27)
		C31–N3–C3	169.0 (21)
		C41–N4–C4	173.2 (22)

Average Interatomic Distances and Angles within the *tert*-Butyl Groups[c]

Central Atom	C–C distance, Å		C–C–C angle, deg	
	Group A	Group B	Group A	Group B
C11	1.48 (8, 6)	1.48 (8, 6)[d]	109 (4, 7)	109 (4, 7)[d]
C21	1.49 (8, 7)	1.49 (8, 7)[d]	109 (15, 24)	109 (15, 24)[d]
C31	1.53 (7, 9)	1.51 (3, 3)	109 (7, 11)	109 (3, 3)
C41	1.55 (10, 12)	1.50 (7, 9)	109 (7, 9)	109 (7, 11)

[a] See footnotes *a* and *b*, Table I. [b] Reported values have not been corrected for thermal motion. [c] Numbers in parentheses are ± standard deviations from the mean and range of values, respectively, in the last significant figure. Groups A and B are defined in Figure 4. [d] Related to group A by the crystallographic mirror plane (see Figure 4).

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF THERMAL VIBRATION (Å)[a,b]

Atom	Min	Intermed	Max
Mo	0.172 (4)	0.194 (4)	0.245 (4)
I1	0.206 (3)	0.256 (3)	0.363 (3)
I2	0.243 (3)	0.281 (3)	0.338 (3)
C1	0.13 (6)	0.25 (4)	0.27 (4)
N1	0.21 (4)	0.29 (3)	0.31 (4)
C11	0.11 (7)	0.28 (4)	0.31 (4)
C2	0.18 (4)	0.24 (4)	0.27 (4)
N2	0.20 (4)	0.26 (3)	0.36 (4)
C21	0.18 (5)	0.26 (4)	0.30 (4)
C3	0.19 (3)	0.23 (3)	0.26 (3)
N3	0.21 (3)	0.22 (2)	0.31 (3)
C31	0.18 (3)	0.25 (3)	0.31 (3)
C4	0.17 (3)	0.22 (3)	0.28 (3)
N4	0.23 (3)	0.27 (2)	0.28 (3)
C41	0.21 (4)	0.29 (3)	0.37 (4)

[a] Taken along the principal axes of the thermal ellipsoids. The orientation of these axes may be seen from Figure 1. [b] See footnotes *a* and *b*, Table I.

Discussion

The coordination geometry of the molybdenum atom may be described as that of a distorted, monocapped trigonal prism with the capping atom, iodine, lying above the square face defined by the atoms C3, C3′, C4, C4′ (Figures 1 and 3). The cation possesses crystallographically required mirror symmetry and the atoms Mo and I1, together with the ligands C1–N1–C11 and C2–N2–C21, lie on this mirror plane. The symmetry of the immediate coordination sphere of the molybdenum atom is very close to the C_{2v}, which is the point group of a regular capped trigonal prism.

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[17] A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to the author, title of article, volume, and page number. Remit $3.00 for photocopy and $2.00 for microfiche.

TABLE IV

DISTRIBUTION OF DISCRETE SEVEN-COORDINATE STRUCTURES AMONG THE THREE BASIC POLYHEDRA[a,b]

	Pentagonal bipyramid D_{5h}	Capped trigonal prism C_{2v}	Capped octahedron C_{3v}
MX_7[c]	UF_7^{3-} ZrF_7^{3-} HfF_7^{3-} } ?	NbF_7^{2-} TaF_7^{2-}	...
MX_6Y	$Sn(trop)_3Cl$[d] $Sn(trop)_3OH$[d] $Zr(acac)_3Cl$[e]	$[Mo(CNR)_6I]^+$[f] $Yb(acac)_3(H_2O)$[g] $Yb(acac)_3(Hacim)$[h]	$NbOF_6^{3-}$[c] $Ho(dbm)_3(H_2O)$[i] $Y(bza)_3(H_2O)$[j]
MX_5Y_2	$UO_2F_5^{3-}$[c]	...	...
MX_4Y_3	$[Ti_2(ox)_3(OH_2)_6]$[k]	...	...
MX_3Y_3Z	...	...	$[Ni(tren\text{-}py)]^{2+}$[l]
Other	$[Fe(EDTA)(OH_2)]^-$[c]	$[Fe(DCTA)(OH_2)]^-$[c] $[Mn(EDTA)(OH_2)]^{2-}$[c] $[Pr(dpm)_3]_2$[m] $[W(CO)_3(GeBr_3)(bipy)Br]$[n]	...

[a] This compilation contains a representative but not a complete set of known heptacoordinate structures. [b] Abbreviations: trop, tropolonato; acac, acetylacetonato; Hacim, acetylacetonimine; dbm, dibenzoylmethanato; bza, benzoylacetonato; ox, oxalato; tren-py, tris[1-(2-pyridyl)-2-azabuten-4-yl]amine; EDTA, ethylenediaminetetraacetato; DCTA, 1,2-diaminocyclohexanetetraacetato; dpm, dipivaloylmethanato; bipy, bipyridyl. [c] Data taken from ref 12, which may be consulted for citation of the original literature. [d] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3636 (1970). [e] R. B. Von Dreele, J. J. Stezowski, and R. C. Fay, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, No. INOR-43. [f] This work; R = *tert*-C_4H_9. [g] J. A. Cunningham, D. E. Sands, W. F. Wagner, and M. F. Richardson, *Inorg. Chem.*, **8**, 22 (1969); E. D. Watkins, J. A. Cunningham, T. Phillips, D. E. Sands, and W. F. Wagner, *ibid.*, **8**, 29 (1969). [h] M. F. Richardson, P. W. R. Corfield, D. E. Sands, and R. E. Sievers, *ibid.*, **9**, 1632 (1970). [i] A. Zalkin and D. H. Templeton, Abstracts, American Crystallographic Association Summer Meeting, Minneapolis, Minn., 1967, p 98. [j] F. A. Cotton and P. Legzdins, *Inorg. Chem.*, **7**, 1777 (1968). [k] M. G. B. Drew, G. W. A. Fowles, and D. F. Lewis, *Chem. Commun.*, 876 (1969). [l] L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6041 (1968). [m] C. S. Erasmus and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **26**, 1843 (1970). [n] E. M. Cradwick and D. Hall, *J. Organometal. Chem.*, **25**, 91 (1970).

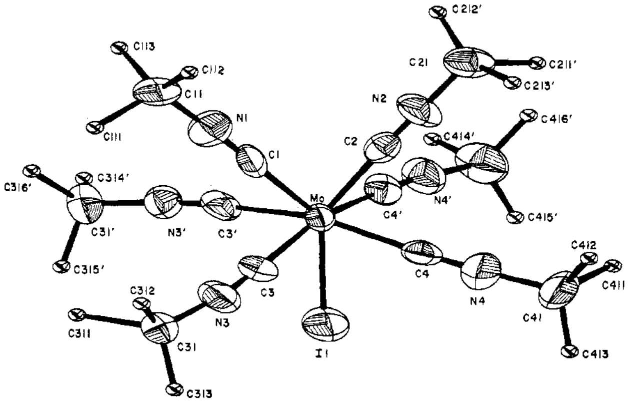

Figure 1.—Structure of the iodohexakis(*tert*-butyl isocyanide)-molybdenum(II) cation showing the atom-labeling scheme and the 50% probability thermal ellipsoids. For clarity, the methyl carbon atoms of the *tert*-butyl groups have all been drawn as spheres, 0.2 Å in diameter. The primed atoms were generated from the coordinates of Table I by setting $z = -z$. The disorder of the *tert*-butyl groups is discussed in the text.

Gillespie[18] has described the three basic polyhedra that may be adopted by a seven-coordinate molecule. These are the "1:5:1" pentagonal bipyramid of D_{5h} symmetry, the "1:4:2" capped trigonal prism of C_{2v} symmetry, and the "1:3:3" capped octahedron of C_{3v} symmetry. The distribution of several classes of crystallographically characterized seven-coordinate complexes among these three basic polyhedra is summarized in Table IV.

The energetic similarities among the three basic polyhedra have been noted by several authors.[12,18,19] The choice of geometry for any given complex is generally dictated by a combination of ligand–ligand nonbonded repulsions, crystal packing energies, and steric constraints in the case of complexes having multidentate chelating ligands. The correspondence between the stoichiometry of a seven-coordinate compound and the polyhedron that it adopts is evident for certain of the mixed-ligand complexes listed in Table IV. For example $[Ni(tren\text{-}py)]^{2+}$, an MX_3Y_3Z type complex, has the "1:3:3" capped octahedral geometry and UO_2F^{3-}, an MX_5Y_2 type complex, has the "1:5:1" pentagonal-bipyramidal geometry. Notable exceptions are the trischelate complexes of the MX_6Y type, for which all three of the idealized structures seem to be equally probable. Intuitively one might expect nonchelated complexes of the MX_6Y type to have a "1:4:2" capped trigonal-prismatic or "1:3:3" capped octahedral structure. As evident from Table IV, the latter geometry is adopted by the $NbOF_6^{3-}$ ion, in which the capping ligand O is of the same approximate size as the donor atoms of the remaining ligands. In the present instance, however, the capping ligand (iodine) is much larger than the other six ligands (*tert*-butyl isocyanide) and the C_{2v} capped trigonal prismatic structure is preferred. The iodohexakis(*tert*-butyl isocanide)molybdenum(II) cation is the only concrete representative of this coordination geometry for an MX_6Y molecule containing only monodentate ligands. For compounds having the widest variety of ligands, for instance $W(CO)_3(GeBr_3)(bipy)Br$, the capped trigonal prism may prove to be the most suitable stereochemistry since it is of lowest idealized symmetry. Other possible geometries for coordination number 7 and further examples are discussed in ref 12.

The Mo–I1 distance of 2.862 (3) Å is consistent with the molybdenum–iodine single-bond length of 2.85 Å computed from the atomic radii calculated by Slater[20] (Mo, 1.45 Å; I, 1.40 Å). As evident from Figures 1 and 3 there are clearly two different chemical environments for the isocyanide ligands, which are reflected in the nonequivalent mean bond lengths Mo–C1(C2) = 2.055 (15) Å and Mo–C3(C4) = 2.115 (15) Å. Whereas the difference between these two sets

(18) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

(19) (a) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3626 (1970); (b) J. J. Park, D. M. Collins, and J. L. Hoard, *ibid.*, **92**, 3636 (1970), and references cited therein.

(20) J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

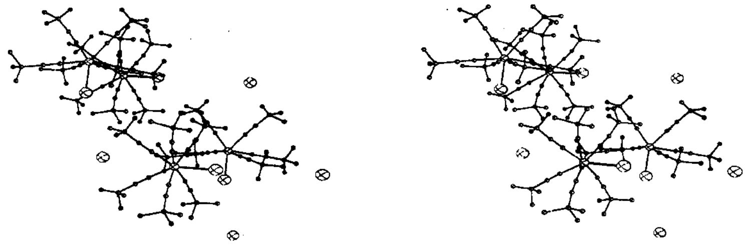

Figure 2.—Stereoscopic view of the crystal packing showing half the contents of a unit cell. Only one of the two possible conformations of the disordered *tert*-butyl groups is shown.

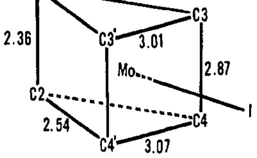

Figure 3.—Geometry of the trigonal-prismatic coordination polyhedron for the $[\mathrm{Mo(CNR)_6I}]^+$ cation. Distances are in ångström units and have estimated standard deviations of 0.03–0.04 Å.

of Mo–C bond distances is barely significant statistically, the shorter bonds are trans to the iodine atom where steric crowding is less severe (Figure 1). It may also be noted that the Mo–C distances are somewhat shorter than the 2.15 Å predicted on the basis of Slater atomic radii,[20] suggesting that the molybdenum–carbon bond orders are greater than 1.

The distortion of the trigonal prism described by atoms C1, C2, C3, C3′, C4, and C4′ may be seen by reference to Figure 3. The major cause of the distortion is the nonbonded repulsive interaction between the iodine atom and the four adjacent carbon atoms. As a consequence, the atoms C3, C3′, C4, and C4′ that occupy the corners of the capped square face are displaced toward the C1–C2 edge of the prism. Although the molybdenum atom still lies within the body of the prism, it is only 0.32 Å away from the center of the C3, C3′, C4, C4′ face and yet is 1.69 Å from the midpoint of the C1–C2 edge. In a regular prism the ratio of these distances would be 1:2. In addition, the triangular faces, which would be equilateral in a regular trigonal prism, are now isosceles with the C3–C3′ and C4–C4′ edges adjacent to the iodine atom being enlarged by ~20% (Figure 3).

A further consequence of the displacement of the capped face by the iodine atom is that repulsive intramolecular isocyanide interactions have pushed the atoms C1 and C2 closer together, resulting in (1) a C1–C2 length of 2.36 Å, about 0.5 Å shorter than the C3–C4 edge, (2) a dihedral angle of 14.6 (12)° between the two triangular faces, and (3) nonequivalent bond angles for C3–Mo–C4, 85.5 (7)°, and C1–Mo–C2, 69.7 (9)°. Intramolecular isocyanide repulsions also lead to the elongation of the C3, C3′, C4, C4′ face in a direction perpendicular to the mirror plane (Figure 3), resulting in the angle of 85.5 (7)° for C3–Mo–C4 being smaller than the values of 88.4 (7) and 92.2 (7)° for the angles C3–Mo–C3′ and C4–Mo–C4′, respectively.

From the angles I1–Mo–C1, 145.2 (6)°, I1–Mo–C2, 145.1 (6)°, I1–Mo–C3, 81.4 (5)°, and I1–Mo–C4, 81.6 (5)°, it is apparent that the iodine atom is symmetrically placed with respect to both of the distinguishable sets of carbon atoms C1, C2 and C3, C4, C3′, C4′.

The dimensions of the isocyanide ligands are normal. The C≡N bond lengths, which range from 1.15 (3) to 1.19 (3) Å, are identical within experimental error, and the mean value of 1.17 (2) Å compares favorably with the average distances found in $[\mathrm{Co(CNCH_3)_5}](\mathrm{ClO_4})_2$ (1.15 (4) Å[21]) and $\mathrm{Fe(CN)_2(CNCH_3)_4}$ (1.13 (10) Å[22]). The average value of the N–C(butyl) distances is 1.46 (3) Å, again comparable with the distances of 1.50 (4) and 1.48 (10) Å found for the cobalt and iron compounds, respectively.

The isocyanide ligands C1–N1–C11 and C2–N2–C21 are almost collinear for they have Mo–C–N angles of 178.8 (21) and 179.0 (25)° and C–N–C angles of 174.7 (27) and 177.6 (27)°, respectively. The remaining ligands deviate more noticeably from linearity, however, with the angles Mo–C3–N3, Mo–C4–N4, C3–N3–C31, and C4–N4–C41 being 174.5 (17), 173.5 (18), 169.0 (21), and 173.2 (22)°, respectively. Again the differences may be attributed to the greater steric crowding on the side of the molecule where the iodine atom is coordinated.

The methyl carbon atoms of each of the *tert*-butyl groups are disordered. For every *tert*-butyl group there are six methyl carbon atoms each with an occupancy factor of 0.5. The six methyl carbon atoms are comprised of two groups of three atoms, each of which represents one conformation of the *tert*-butyl group in the lattice (Figure 1). The superposition of the two sets results in an approximate local C_6-symmetry axis collinear with the N–C bond axis of the isocyanide ligands (Figure 4). The *tert*-butyl groups of the two isocyanide ligands situated on the crystallographic mirror plane are disordered so that no one of the methyl carbon atoms actually lies on that plane (*m*----*m* in Figure 4). The variation and individual standard deviations of the bond lengths and angles within the *tert*-butyl ligands are larger than one might ordinarily expect by present day standards (Table II). This behavior is not unusual for disordered structures, however, and may possibly have been eliminated by use of a hindered-rotor model[23,24] rather than the assignment of two fixed conformations of half-weight to the *tert*-butyl groups.

In conclusion, the product of the reductive alkylation of silver octacyanomolybdate(IV) with *tert*-butyl iodide has been shown to be a seven-coordinate molybdenum(II) isocyanide complex with a monocapped trigonal-prismatic coordination geometry. This result substantiates the suggestion of seven-coordination for

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(21) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1495 (1964).

(22) J. B. Wilford, N. O. Smith, and H. M. Powell, *J. Chem. Soc. A*, 1544 (1968).

(23) M. V. King and W. N. Lipscomb, *Acta Crystallogr.*, **3**, 155 (1950).

(24) See, for example, R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966).

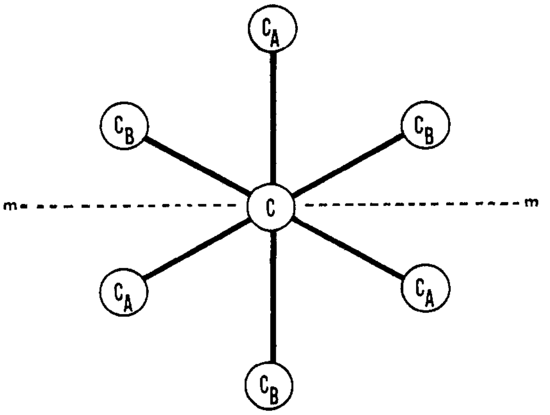

Figure 4.—View down the -C–N–C axis of the isocyanide ligands showing the disorder of the methyl groups. Atoms labeled C_A and C_B belong to the distinct conformations of the disordered *tert*-butyl group. For those ligands that lie on the crystallographic mirror plane (*m*– – – –*m*), the atoms C_A and C_B are related by virtue of that plane.

MoL_5X_2 (L = isocyanide; X = Cl, Br) compounds prepared by an entirely different route.[11] Seven-coordination has long been postulated[25–29] for Mo(II) complexes containing good π-acceptor ligands, notably carbonyls, and the present study provides direct confirmation of this suggestion by X-ray diffraction.[30–32] Recently cations of general formula $[Mo(CO)_2(D)_2I]^+$ (D = *o*-phen, bipy)[33] and the complex $Mo(CO)_3(dtc)_2$[34] have been reported. The resemblance between the stoichiometries of these MX_4Y_2Z and MX_4Y_3 type of molecules and that of the $[Mo(CNR)_6I]^+$ ion may be noted. Finally, we wish to emphasize that, although the C_{2v} capped trigonal prism has been identified in the solid state for iodohexakis(*tert*-butyl isocyanide)molybdenum(II) iodide, the structure of this compound in solution is as yet unknown. Because of the close energetic similarities between coordination polyhedra for the higher coordination numbers, rearrangement to one of the other structures (Table IV) or stereochemical nonrigidity[35] is entirely possible. Thus, for example, the related heptacyanomolybdate(III) ion is known from its spectroscopic properties to have a seven-coordinate pentagonal-bipyramidal structure in solution, while in the solid potassium dihydrate salt, a capped trigonal-prismatic structure has been proposed.[36] Studies of the solution structure of $[Mo(CNR)_6I]^+$ salts are currently in progress.

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[25] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1806 (1960).

[26] P. C. H. Mitchell, *Coord. Chem. Rev.*, **1**, 315 (1966), and references cited therein.

[27] R. Colton and I. B. Tomkins, *Aust. J. Chem.*, **19**, 1143 (1966).

[28] R. Colton and I. B. Tomkins, *ibid.*, **19**, 1519 (1966).

[29] H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

[30] Note, also, the closely related $[W(CO)_3(bipy)(GeBr_3)Br]$ complex[31] and the discussion in ref 32.

[31] E. M. Cradwick and D. Hall, *J. Organometal. Chem.*, **25**, 91 (1970).

[32] M. G. B. Drew, I. B. Tomkins, and R. Colton, *Aust. J. Chem.*, **23**, 2517 (1970).

[33] H. Behrens, G. Lehnert, and H. Sauerborn, *Z. Anorg. Allg. Chem.*, **374**, 310 (1970).

[34] R. Colton, G. R. Scollary, and I. B. Tomkins, *Aust. J. Chem.*, **21**, 15 (1968); dtc = diethyldithiocarbamate.

[35] E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

[36] G. R. Rossman, Ph.D. Thesis, California Institute of Technology, 1971.

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Some Chemistry of Azido Complexes of Group Ib Metals

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The preparation and characterization of several azido and thiocyanato complexes of group Ib metals of the general formula ML_nX (n = 1, M = Au(I); n = 2, M = Cu(I), Ag(I); L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, $P(o\text{-}CH_3C_6H_4)(C_6H_5)_2$, $P(CH_3O)(C_6H_5)_2$, $P(C_2H_5O)(C_6H_5)_2$; $X^- = N_3^-$, NCS^-), $ML'X$, and $M_2L'_3X_2$ ($L' = (C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$) are reported. The azido complexes react with dipolarophiles such as CS_2 and CF_3CN by 1,3-dipolar cycloaddition to form thiothiatriazolato and perfluoromethyltetrazolato complexes. The CF_3CN adducts are stable while the CS_2 adducts decompose both thermally and photolytically. The thermal decomposition of a solution containing azidobis(triphenylphosphine)copper(I) and CS_2 in a 1:1 ratio yields triphenylphosphine sulfide, CuNCS, and thiocyanatobis(triphenylphosphine)copper(I), while the photolytic decomposition of the above solution leads to the corresponding thiocyanato complex and colloidal sulfur. The same results are observed for the other CS_2 adducts reported here. Thermal or photolytic decomposition of the complex thiothiatriazolato(triphenylphosphine)copper(I) ($Cu(P(C_6H_5)_3)N_3 \cdot CS_2$) in $CHCl_3$ leads to CuNCS and triphenylphosphine sulfide. The azido complexes of Cu(I) and Ag(I) are all photolytically active and their photolysis in chloroform leads to the liberation of N_2, to the abstraction of chlorine atoms from the solvent, and to the formation of complexes such as $[Ag(P(C_6H_5)_3Cl]_4$ and $Cu_2(P(C_6H_5)_3)_3Cl_2$. The geometry of these group Ib metal complexes is discussed in terms of recent X-ray structural results and physical data obtained in solution.

Introduction

The chemistry of coordinated azides has received increased attention during the past several years primarily due to the fact that coordinated azides can be both oxidized and reduced. For example, it was shown that coordinated azides react with metal hydrides to produce amino complexes[1] or with oxygen to produce coordi-

[1] W. Beck and M. Bauder, *Chem. Ber.*, **103**, 583 (1970).