Reactions of Eight-Coordinate Metal Cyanide Complexes. IV.[1] Synthesis and Spectroscopic and Structural Properties of Tetracyanotetrakis(alkyl isocyanide)molybdenum(IV) Complexes

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Received January 21, 1972

Abstract: The compounds $(RNC)_4Mo(CN)_4$ (R = CH_3, n-C_3H_7, t-C_4H_9, and allyl) and $[(C_6H_5)_2CHNC]_4Mo(CN)_4 \cdot CHCl_3$ were prepared from the reaction between silver octacyanomolybdate(IV) and the corresponding alkyl halide. The basic geometry was determined in a single-crystal X-ray diffraction study of the methyl derivative. The complex crystallizes in space group $C2/c$ of the monoclinic system with four molecules per unit cell and a = 12.916 (8) Å, b = 10.442 (8) Å, c = 11.826 (6) Å, β = 96.86 (6)°, ρ_{obsd} = 1.52 g/cc, ρ_{calcd} = 1.528 g/cc. The structure, refined to a conventional R factor of 0.046, consists of eight carbon atoms at the apices of a triangular dodecahedron with the four cyanide ligands at the A positions ($Mo-C_{av}$ = 2.177 (8) Å) and the four methyl isocyanide ligands at the B positions ($Mo-C_{av}$ = 2.148 (8) Å). In this particular isomer the better π-acceptor (isocyanide) ligands are positioned to accept electron density from the filled $d_{x^2-y^2}$ orbital of the molybdenum atom, a situation anticipated for MX_4Y_4 molecules by Orgel in 1960. Temperature-dependent ^{13}C nmr studies of the *tert*-butyl derivative in chloroform down to −47°, a complete set of infrared and Raman spectral data in the C≡N stretching frequency region, and the electronic spectra of the $(RNC)_4Mo(CN)_4$ complexes are reported and discussed.

Calculations[2,3] based on ligand–ligand repulsion energies show that there is essentially no potential energy difference nor barrier between the two common coordination polyhedra (D_{4d} square antiprism and D_{2d} triangular dodecahedron, Figure 1) for MX_8 complexes,[4] where X is a monodentate ligand and M is a transition metal. This conclusion is substantiated by the limited amount of available X-ray structural information.[4,5] It is therefore of interest that, for reasons based either on symmetry arguments[6] or the expectation of "stoichiometric control of stereochemistry,"[2b] eight-coordinate molecules of the MX_4Y_4 type are predicted to have dodecahedral geometries with the ligands sorted into the appropriate A and B sites (Figure 1) according to their relative π-donor/acceptor properties and the electronic configuration of the transition metal atom.[7] Continuing our search[9] for experimental verification of this idea using compounds free from the constraints of chelating ligands, the system $(RNC)_4Mo(CN)_4$[10] has been investigated.

Complexes of the type $(RNC)_4Mo(CN)_4 \cdot nH_2O$ (R = CH_3, C_2H_5) were originally[10] prepared by the alkylation of silver octacyanomolybdate(IV), eq 1.

$$Ag_4Mo(CN)_8 + 4RX \longrightarrow (RNC)_4Mo(CN)_4 + 4AgX \quad (1)$$

The tungsten analogs were reported shortly thereafter[11] and recently a more detailed synthesis, and characterization, of the tungsten compounds has appeared.[12] Attempts in our laboratory to run the alkylation reaction 1 under the conditions originally described for molybdenum[10] usually resulted in poor yields. Moreover, the reproducibility of the reaction was poor, leading in some cases to the products of reductive alkylation, $[Mo(CNR)_6I]I$, discussed previously.[1] The synthesis of these seven-coordinate molybdenum(II) complexes from octacyanomolybdate(IV) is still not fully understood, and further studies of the reaction are in progress.[13] The present report describes reproducible preparative routes to several $(RNC)_4Mo(CN)_4$ complexes, the crystal structure determination of the methyl derivative, a fairly complete electronic and vibrational spectroscopic characterization, and the results of a variable temperature ^{13}C nmr investigation of the *tert*-butyl derivative.

Experimental Procedure

Synthetic Work. All compounds were prepared from commercially available starting materials. Potassium octacyanomolybdate(IV) dihydrate, $K_4Mo(CN)_8 \cdot 2H_2O$, was synthesized by the method of van de Poel and Neumann.[14] The yields of the $(RNC)_4Mo(CN)_4$ compounds were found to be very sensitive to the purity of the starting materials, especially silver octacyanomolybdate(IV), and therefore special care was exercised in preparing this compound (*vide infra*). The decomposition temperatures of the samples were determined using a Thomas-Hoover capillary melting point apparatus and are only rough estimates because no sharp color

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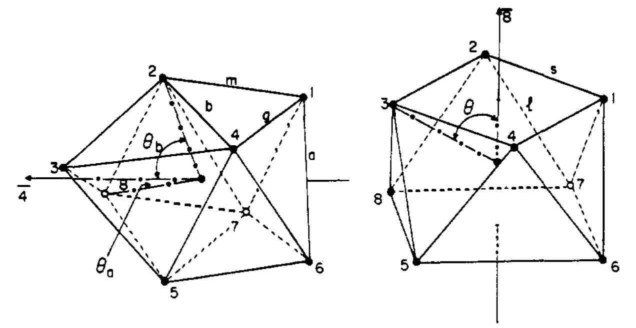

Figure 1. The idealized dodecahedral configuration (left) and the corresponding square antiprism showing the usual[3] angle- and edge-labeling scheme (reproduced from ref 23). The A and B vertices of the dodecahedron are numbered 1,3,6,8 and 2,4,5,7, respectively.

changes occurred. Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Silver Octacyanomolybdate(IV), $Ag_4Mo(CN)_8$. A solution was prepared by dissolving 5.0 g (29.4 mmol) of silver nitrate in 7 ml of water and cooled in an ice bath. *The following procedures were then carried out in the dark* to prevent photodecomposition of $[Mo(CN)_8]^{4-}$ in solution[15] as well as the final product. A solution containing 3.37 g (6.8 mmol) of potassium octacyanomolybdate(IV) dihydrate dissolved in 50 ml of water and cooled to ice temperature was added dropwise to the cooled solution of silver nitrate. The precipitate which formed was immediately filtered off, washed with water (until the washings showed a negative test for the silver ion), methanol, and then ethyl ether, and dried overnight *in vacuo* over P_2O_5. The yield was 4.3 g (86%) of yellow powder which is light-sensitive, especially when wet.

Anal. Calcd for $Ag_4Mo(CN)_8$: C, 13.0; N, 15.2. Found: C, 12.2; N, 14.4.

Despite the low values for the carbon and nitrogen analyses, the infrared spectra of Nujol mulls of this compound, prepared at several different times, showed no evidence for water of crystallization.

Tetracyanotetrakis(methyl isocyanide)molybdenum(IV), $(CH_3NC)_4Mo(CN)_4$. About 100 g (~0.7 mol) of methyl iodide, predried with calcium chloride, was distilled under nitrogen over P_2O_5 onto 4.1 g (5.6 mmol) of freshly prepared, finely ground silver octacyanomolybdate(IV). The mixture was refluxed under nitrogen in the dark for about 15 hr, filtered off, washed with ethyl ether, and dried under reduced pressure on a fritted funnel. About 7 g of a yellow precipitate was obtained to which 60 ml of glacial acetic acid was added. The mixture was refluxed under nitrogen for 20 min and the yellow solution filtered while hot. An excess (*ca.* 300 ml) of anhydrous ethyl ether was added to this solution and the mixture was allowed to cool for several hours at 0°. When precipitation was complete, the yellowish-white crude product was filtered and collected for further purification. In some cases, recrystallization from hot methanol was sufficient to produce small yellow crystals. If not, the methanol solution was run through a silica gel chromatography column. Addition of anhydrous ethyl ether to the first band eluted with methanol resulted in crystals (yield, 0.85 g of 42% based on Mo). The crystalline form of the compound, which smells strongly of methyl isocyanide, is fairly stable in air. When heated it slowly changes color from pale yellow to brown (mp 180° dec) and, upon irradiation by X-rays (*vide infra*) over a period of several days, it turns brown.

Anal. Calcd for $C_{12}H_{12}N_8Mo$: C, 39.6; H, 3.32; N, 30.8. Found: C, 39.1; H, 3.43; N, 30.2.

Ir (KBr pellet): 3082 (w), 3072 (w), 3023 (m), 3003 (m), 2947 (m), 2923 (m, br), 2852 (w), 2251 (vs), 2234 (vs), 2196 (sh), 2145 (s), 1733 (w, br), 1493 (w), 1450 (m), 1437 (sh), 1416 (m), 1401 (s), 1115 (w, br), 1026 (w, br), 953 (m), 938 (sh), 750 (m, br), 694 (m), 665 (vw), 539 (w, br), 498 (m), 454 (w), 444 (sh), 409 (m), 399 (s), 371 (vw), 346 (m), 330 (w), 322 (w).

Tetracyanotetrakis(*n*-propyl isocyanide)molybdenum(IV), $(n\text{-}C_3H_7NC)_4Mo(CN)_4$. A solution containing 100 g (~0.8 mol) of *n*-propyl bromide and 4.0 g (5.4 mmol) of silver octacyanomolybdate(IV) was prepared and refluxed under the conditions described above for 15 hr. The hot mixture was quickly filtered in air and an excess of anhydrous ethyl ether added to the yellow filtrate. Small yellow crystals appeared immediately. Cooling to 0° produced further crystallization, and the product was filtered off under nitrogen, washed with ethyl ether, and dried *in vacuo*. This compound smells strongly of *n*-propyl isocyanide and is the least stable of those reported here. Decomposition starts at ~125°.

Anal. Calcd for $C_{20}H_{28}N_8Mo$: C, 50.4; H, 5.92; N, 23.5. Found: C, 49.6; H, 5.83; N, 22.7.

Ir (KBr pellet): 2980 (s), 2953 (s), 2939 (s), 2889 (m), 2862 (m), 2227 (vs), 2189 (sh), 2145 (s), 1735 (w, br), 1472 (m), 1466 (sh), 1455 (s), 1440 (sh), 1436 (s), 1395 (m), 1340 (s), 1275 (s), 1256 (m), 1137 (w), 1113 (w), 1096 (w), 1045 (m), 920 (s), 894 (m), 853 (m), 766 (m), 695 (w), 539 (m), 495 (m, br), 435 (w), 383 (s), 343 (m).

Tetracyanotetrakis(*tert*-butyl isocyanide)molybdenum(IV), $(t\text{-}C_4H_9NC)_4Mo(CN)_4$. About 85 g (~0.6 mol) of *tert*-butyl bromide was mixed and refluxed under the conditions described above with 4.2 g (5.7 mmol) of silver octacyanomolybdate(IV). After refluxing for 15 hr the hot mixture was filtered and an excess of *n*-hexane was added to the yellow filtrate. A yellow precipitate appeared immediately which was filtered after a few hours, washed with *n*-hexane, dried, and redissolved in a small amount of chloroform. The solution was purified on an alumina column (Merck and Co. reagent grade aluminum oxide, suitable for chromatographic absorption) and the first band eluted with chloroform was collected. Addition of anhydrous ether to the chloroform solution gave yellow hexagonal needles after a few hours. The crystals get cloudy and appear to lose their crystalline character when removed from the solution and dried (mp 139° dec). The yield was ~0.8 g (26% based on Mo).

Anal. Calcd for $C_{24}H_{36}N_8Mo$: C, 54.1; H, 6.81; N, 21.0. Found: C, 53.8; H, 6.99; N, 21.0.

Ir (KBr pellet): 2995 (sh), 2988 (s), 2944 (s), 2909 (w), 2879 (w), 2212 (vs), 2181 (sh), 2144 (s), 1917 (w, br), 1477 (s), 1456 (s), 1403 (m), 1376 (s), 1237 (s), 1190 (vs, br), 1043 (m), 932 (w), 849 (m), 722 (m), 695 (vw), 665 (vw), 537 (s), 481 (m), 430 (w), 425 (vw), 378 (s), 347 (m), 332 (m).

Tetracyanotetrakis(allyl isocyanide)molybdenum(IV), $(CH_2CHCH_2NC)_4Mo(CN)_4$. Approximately 100 g of 3-bromopropene, predried with $CaCl_2$, was distilled under nitrogen from P_2O_5 onto 4 g (5.4 mmol) of silver octacyanomolybdate(IV). The mixture was refluxed under nitrogen in the dark for 15 hr and filtered while hot. After addition of ~3:1 excess of ethyl ether to the filtrate, the mixture was allowed to stand for several hours at 0° to produce yellow-green crystals. The product was purified by dissolution in chloroform followed by column chromatography on silica gel using a $CHCl_3$–CH_3OH solution (97/3 by volume) as the eluent. The first fraction off the column was concentrated under reduced pressure at room temperature and crystallized at 0° after the addition of excess ethyl ether. The yield of yellow crystals after drying *in vacuo* was 10% based on molybdenum.

Anal. Calcd for $C_{20}H_{20}N_8Mo$: C, 51.3; H, 4.30; N, 23.9. Found: C, 51.2; H, 4.50; N, 23.7.

Ir (KBr pellet): 3100 (w, br), 3045 (w, br), 3000 (w), 2972 (m), 2951 (m), 2937 (m), 2233 (vs), 2195 (sh), 2145 (m), 1650 (m), 1448 (m), 1440 (sh), 1433 (s), 1421 (s), 1351 (sh), 1345 (m), 1334 (s), 1320 (sh), 1295 (m), 1287 (sh), 1253 (w), 1238 (w), 1139 (w), 1029 (w), 991 (s), 946 (sh), 938 (s), 898 (vw), 826 (w), 751 (w, br), 692 (w, br), 627 (m), 569 (m), 560 (m), 498 (m), 449 (w), 390 (s), 344 (m).

Tetracyanotetrakis(diphenylmethyl isocyanide)molybdenum(IV)·Chloroform, $[(C_6H_5)_2CHNC]_4Mo(CN)_4\cdot CHCl_3$. Approximately 100 ml of chloroform, predried with $CaCl_2$, was distilled under nitrogen over P_2O_5 onto a mixture containing 2.0 g (2.8 mmol) of freshly prepared, finely ground silver octacyanomolybdate(IV) and 3.0 g (12.2 mmol) of benzhydryl bromide. The resultant mixture was refluxed under nitrogen for about 1 hr and filtered while hot. To the filtrate was added a threefold excess of anhydrous ethyl ether. After standing for a few hours at 0° the solution was filtered. The precipitate was redissolved in chloroform and purified on alumina. Addition of an excess of ethyl ether to the first band eluted with chloroform yielded thin yellow crystals (~0.24 g, yield ~8% based on Mo) which were shown by analysis to contain a chloroform molecule of crystallization.

Anal. Calcd for $C_{61}H_{45}N_8Cl_3Mo$: C, 67.1; H, 4.15; N, 10.3; Cl, 9.74. Found: C, 66.9; H, 4.40; N, 10.0; Cl, 9.79.

Ir (KBr pellet): 3109 (sh), 3091 (w), 3065 (m), 3034 (m), 3005 (m), 2985 (w), 2930 (m, br), 2218 (vs), 2183 (sh), 2144 (s), 2138 (sh?), 1955 (w, br), 1885 (w, br), 1809 (w), 1745 (m, br), 1599 (m), 1588 (m), 1494 (s), 1454 (s), 1380 (w, br), 1345 (s), 1333 (m), 1301 (m), 1279 (m), 1234 (w, br), 1184 (sh), 1178 (m), 1156 (w), 1110

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[15] A. G. MacDiarmid and N. F. Hall, *J. Amer. Chem. Soc.*, **75**, 5204 (1953).

(w, br), 1080 (m), 1029 (m), 1001 (m), 959 (m), 919 (m, br), 851 (m, br), 816 (w), 755 (s), 739 (vs), 694 (s, br), 664 (m), 648 (s), 623 (s), 613 (s), 559 (s, br), 498 (m), 466 (w), 448 (w), 395 (sh), 377 (m), 359 (sh), 349 (w).

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer calibrated with polystyrene film. Solids were examined both as Nujol mulls and KBr pellets, with no differences being observed between the two methods. Raman spectra were obtained at Hunter College using a Spex Industries Model 1401 double monochromator. The excitation source was a He–Ne laser (632.8 nm), with transfer optics yielding 50 mW of power at the sample. Emission lines from the laser were used for the calibration of frequency shifts. Samples were illuminated in thin-walled capillaries. Photodecomposition was observed for some of the samples, a problem which usually could be avoided either by (1) slight rotation of the sample tube and rapid remeasurement of the portion of the spectrum of interest or (2) the use of Kodak variable neutral density filters. Electronic spectra were recorded on a Cary Model 14 recording spectrophotometer using 1-cm pathlength matched quartz cells. Variable-temperature ^{13}C nmr spectra were obtained at the laboratory of Bruker Scientific, Inc., Elmsford, N. Y., using pulsed Fourier transform techniques and broad band proton decoupling to enhance the signal-to-noise ratio.

Collection and Reduction of X-Ray Data for $(CH_3NC)_4Mo(CN)_4$. Crystals suitable for X-ray study can be obtained either by slow evaporation from methanol or by slow cooling of a hot methanolic solution. Pale yellow crystals grow in at least two forms as diamond-shaped prisms and as needles. Both forms were found to be chemically and crystallographically identical. A diamond-shaped prism was selected and mounted along the longest dimension, parallel to c^*, with clear nail polish on the end of a glass fiber. The space group and approximate unit cell parameters were determined on the precession camera using Ni-filtered Cu Kα radiation (λ 1.5418 Å). From the Laue symmetry $2/m$ and observed extinctions hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, the space group was determined to be either the centric $C2/c$ (no. 15) or the acentric Cc (no. 9).[16]

Under prolonged radiation on the precession camera the color of the first crystal had changed to brown and there was a possibility that internal decomposition had occurred. Subsequent studies were therefore carried out on a new crystal, which also darkened (*vide infra*), a needle of approximate size 0.07 × 0.08 × 0.22 mm mounted along c^* nearly parallel to the needle axis. This crystal was mounted on a Picker four-circle automated diffractometer. Using Ni-filtered Cu Kα radiation, 20 reflections were then carefully centered on the diffractometer and the setting angles were used to determine the unit cell parameters by a least-squares process.[17] The results are $a = 12.916\ (8)$ Å, $b = 10.442\ (8)$ Å, $c = 11.826\ (6)$ Å, and $\beta = 96.86\ (6)°$. The experimentally determined density (1.52 ± 0.01 g/cc), measured by flotation in a mixture of carbon tetrachloride and *n*-hexane, closely corresponds to the density calculated on the basis of four molecules per unit cell (1.528 g/cc).

Using GSET-4[17] the diffractometer settings were computed from the cell constants and crystal orientation matrix for more than 1000 reflections. Room-temperature intensity data were taken at a takeoff angle of 2° and a scan angle of 1.25° in 2θ plus an allowance for the Kα_1–Kα_2 separation. The scan angle was symmetric with respect to the Bragg position and the scan speed was 1°/min. At both ends of the scan for each reflection stationary 10-sec background counts were taken. Reflections having count rates over 9000 cps were automatically attenuated by inserting copper foil into the diffracted beam path until the intensity was reduced to less than that value. After every 100 reflections four standard reflections were measured and no systematic trends or significant fluctuations apart from normal counting statistics were observed. Thus, despite the irradiation-induced darkening of the crystal noted above, there appeared to be no gross change in the crystallinity of the sample.

The data were corrected by ACAC-3[17] for background, use of attenuators, absorption, and Lorentz and polarization effects, but no correction was made for secondary extinction. In the reduction of data the "ignorance factor" used in the computation of $\sigma(I)$[18] was set equal to 0.05. With a linear absorption coefficient of 71 cm^{-1}, the transmission factors varied from 0.50 to 0.62. The data were then placed on an approximately absolute scale by means of a Wilson plot[17] which produced values for $|F_o|^2$ and $|F_o|$. The calculated mean value for B was 2.43 Å^2. Scattering factors for the zerovalent molybdenum, carbon, nitrogen, and hydrogen atoms were obtained from the International Tables,[19] and the calculated structure factors were appropriately corrected for the effects of anomalous dispersion.[20] Of the 1065 total, independent reflections collected for $0 \leqslant \sin\theta \leqslant 0.866$, the 994 for which $I > 3\sigma(I)$ were defined as observable and used in the final refinement of the structure.

Determination and Refinement of the Structure. From the corrected data a three-dimensional Patterson map was computed and successfully solved for the positions of all atoms excluding hydrogen. The space group was assumed to be the centrosymmetric $C2/c$, a choice which appears to be justified by the successful refinement of the structure, requiring the molybdenum atom to occupy the special position 4e and the complex to have a twofold symmetry axis. After a few cycles of least-squares refinement of the overall scale factor and positional parameters and anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ for the Mo, C, and N atoms, a set of phased structure factors was computed for a difference Fourier synthesis. The Fourier map revealed the locations of several hydrogen atoms, but attempts to refine their positional parameters resulted in bond distances and angles that were chemically less reasonable than obtained from the original positions. Therefore the most reasonable initial coordinates of one hydrogen atom for each methyl group were chosen and the coordinates of the remaining hydrogens were calculated on the basis of an assumed threefold symmetry axis along the N–C bond. Refinement was continued with the hydrogen positions fixed and assigned isotropic thermal parameters of 4 Å^2. In the final stages of refinement the weights w were set equal to $1/\sigma^2$, where $\sigma = 0.026F + 0.51$, an empirical function which was found to improve slightly the constancy of $w\Delta^2$ for the various classes of reflections[21] compared to the weights derived from the raw data.[18] In the last refinement cycle the parameters varied by no more than 0.1% of their estimated standard deviations and the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ converged at values of 0.046 and 0.070, respectively. A final difference Fourier map did not show any peaks higher than 0.390 e/Å^3 on a scale where the value for a carbon atom lies between 2.4 and 3.1 e/Å^3.

Results

Synthesis and Stability of $(RNC)_4Mo(CN)_4$ Complexes. Compounds of the type $(RNC)_4Mo(CN)_4$ were prepared by a modification of the method of Hoelzl and Xenakis[10] in reasonable yields (25–50%). Attempts to run the alkylation under the conditions originally described, which require long reaction times and (in our hands) a tedious purification procedure, usually gave poor yields and in some cases led to the formation of reduction products such as $[Mo(CNR)_6I]I$.[1] Reproducible results were obtained when freshly prepared silver octacyanomolybdate(IV) was alkylated under nitrogen in the absence of light with the appropriate halide (CH_3I, n-C_3H_7Br, t-C_4H_9Br, CH_2CHCH_2Br, $(C_6H_5)_2CHBr$). The best temperature for the alkylation seemed to be around 70°. In certain cases the

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[16] "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, pp 89, 101.

[17] Calculations were performed on an IBM 360-91 computer using the following programs: MODE-1, the Brookhaven diffractometer setting program and cell constant and orientation angle refinement program; GSET, 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; and MEAN PLANE, the Pippy–Ahmed best planes program.

[18] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

[19] See ref 16, Vol. III, 1st ed, 1962, pp 202–211.

[20] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

[21] D. W. J. Cruickshank in "Computing Methods of Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, pp 112–115.

Table I. Final Positional and Thermal Parameters of the Atoms[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.0	0.15936 (6)	0.25	45.5 (6)	58.4 (10)	29.7 (7)	0.0	−3.2 (4)	0.0
C(1)	0.0724 (6)	0.2123 (7)	0.4161 (6)	56 (5)	68 (7)	58 (6)	−13 (5)	2 (4)	9 (5)
N(1)	0.1061 (5)	0.2390 (6)	0.5071 (5)	81 (5)	82 (6)	40 (5)	−14 (5)	−8 (4)	−5 (4)
C(11)	0.1416 (8)	0.2661 (9)	0.6248 (7)	113 (8)	115 (10)	44 (6)	−29 (7)	−18 (5)	−12 (6)
C(2)	0.1374 (6)	0.1090 (7)	0.1738 (6)	66 (6)	63 (7)	42 (5)	−1 (5)	−6 (4)	2 (5)
N(2)	0.2107 (5)	0.0910 (6)	0.1325 (5)	58 (4)	85 (6)	50 (5)	5 (4)	10 (4)	1 (4)
C(21)	0.3022 (7)	0.0818 (9)	0.0712 (7)	64 (6)	138 (10)	73 (7)	17 (6)	26 (5)	9 (6)
C(3)	0.0565 (6)	−0.0098 (7)	0.3449 (5)	57 (5)	83 (8)	38 (5)	−9 (5)	−7 (4)	−8 (5)
N(3)	0.0865 (6)	−0.1027 (6)	0.3896 (5)	90 (6)	82 (7)	56 (5)	18 (5)	−6 (4)	18 (5)
C(4)	0.0882 (7)	0.3290 (7)	0.2117 (6)	66 (6)	79 (8)	44 (6)	−1 (5)	3 (5)	−9 (5)
N(4)	0.1331 (6)	0.4175 (7)	0.1908 (6)	98 (6)	91 (7)	83 (6)	−32 (6)	24 (5)	−3 (5)

Hydrogen atoms[d]

	C(11)				C(21)		
Atom	x	y	z	Atom	x	y	z
C(11)HA	0.086	0.251	0.679	C(21)HA	0.271	0.050	−0.010
C(11)HB	0.205	0.212	0.658	C(21)HB	0.331	0.177	0.074
C(11)HC	0.165	0.360	0.640	C(21)HC	0.350	0.015	0.120

[a] Atoms are labeled as indicated in Figure 2. Hydrogen atoms are labeled to correspond to the methyl carbon atoms (C(11) or C(21)) to which they are attached. [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 for β_{ij} are $\times 10^4$. [d] Hydrogen atoms were not refined and were assigned an isotropic thermal parameter of 4.0 Å^2

alkyl bromides were found to be more suitable because they were more stable than the corresponding iodides. The benzhydryl derivative crystallizes with a molecule of lattice chloroform and is a somewhat more stable solid than the other complexes.

The complexes were found to be fairly stable in air when dry and in highly crystalline form but slowly pick up water and smell of isocyanide when finely powdered. The infrared spectra of older samples contained characteristic water bands (~3440–3600 and ~1620 cm^{-1}) which also appeared in the products when the reaction was not run under sufficiently dry conditions. Once absorbed, the water was difficult to remove, and, in one instance, a sample of the *tert*-butyl derivative was isolated which appeared from chemical analysis to contain two water molecules of crystallization. Since the absorption of water may be accompanied by partial decomposition of the sample, no attempt was made to prepare and characterize the hydrates. In chloroform solution the compounds were sufficiently stable to carry out physical measurements but on prolonged standing color changes were noticed.

X-Ray Structural Results for $(CH_3NC)_4Mo(CN)_4$. The final positional and thermal parameters, with their standard deviations derived from the inverse matrix of the final least-squares refinement cycle, are reported in Table I.[22] Principal intramolecular distances and angles and their standard deviations are summarized in Tables II and III. The root-mean-square amplitudes of thermal vibration appear in Table IV. A drawing of the molecule showing the orientation of the thermal ellipsoids and the atom-labeling scheme is presented in Figure 2, and the packing of molecules in the unit cell is depicted in Figure 3.

Table II. Dimensions of the Mo–C≡N and Mo–C≡N–CH$_3$ Chains[a]

Bond	Distance, Å	Angle	Deg
Mo–C(1)	2.145 (7)	Mo–C(1)–N(1)	176.3 (6)
Mo–C(2)	2.151 (8)	Mo–C(2)–N(2)	175.4 (6)
Mo–C(3)	2.172 (7)	Mo–C(3)–N(3)	176.4 (6)
Mo–C(4)	2.182 (8)	Mo–C(4)–N(4)	179.1 (8)
C(1)–N(1)	1.146 (9)	C(1)–N(1)–C(11)	175.1 (8)
C(2)–N(2)	1.132 (9)	C(2)–N(2)–C(21)	175.4 (6)
C(3)–N(3)	1.151 (9)		
C(4)–N(4)	1.136 (10)		
N(1)–C(11)	1.44 (1)		
N(2)–C(21)	1.46 (1)		

[a] The standard deviation of the last significant figure is given in parentheses.

Table III. Dimensions of the Coordination Polyhedron[a]

Edge	Length, Å	Type[b]	Angle	Deg
C(3)–C(3′)	2.53 (1)	*a*	C(3)–Mo–C(3′)	71.1 (3)
C(4)–C(4′)	2.55 (2)	*a*	C(4)–Mo–C(4′)	71.6 (4)
Mean	2.54		Mean	71.3
C(1)–C(2)	3.26 (1)	*b*	C(1)–Mo–C(2)	98.9 (3)
C(1)–C(2′)	2.99 (1)	*b*	C(1)–Mo–C(2′)	88.3 (3)
Mean	3.125		Mean	93.5
C(1)–C(3)	2.47 (1)	*m*	C(1)–Mo–C(3)	69.8 (2)
C(2)–C(4)	2.44 (1)	*m*	C(2)–Mo–C(4)	68.5 (3)
Mean	2.455		Mean	69.15
C(1)–C(4)	2.74 (1)	*g*	C(1)–Mo–C(4)	78.4 (3)
C(1)–C(4′)	2.71 (1)	*g*	C(1)–Mo–C(4′)	77.4 (3)
C(2)–C(3)	2.69 (1)	*g*	C(2)–Mo–C(3)	76.9 (3)
C(2)–C(3′)	2.78 (1)	*g*	C(2)–Mo–C(3′)	80.1 (3)
Mean	2.73		Mean	78.2

[a] See footnote *a*, Table II. [b] See Figure 1 for nomenclature.

Spectroscopic Studies. The infrared spectral bands of the $(RNC)_4Mo(CN)_4$ complexes in the 4000–300-cm^{-1} frequency range are reported in the Experimental Section for each individual compound. Table V contains a summary of the infrared and Raman bands in the 2000–2300-cm^{-1} region in which the C≡N and RN≡C stretching frequencies occur. In Table VI are collected the electronic spectral absorption maxima and molar extinction coefficients of methanol or chloroform solutions of the $(RNC)_4Mo(CN)_4$ complexes and, for

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(22) 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 code number JACS-72-6961. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table IV. Root-Mean-Square Amplitudes of Thermal Vibration, Å[a,b]

Atom	Minimum	Intermediate	Maximum
Mo	0.140 (2)	0.180 (2)	0.202 (1)
C(1)	0.17 (1)	0.20 (1)	0.236 (9)
N(1)	0.16 (1)	0.210 (8)	0.274 (8)
C(11)	0.15 (1)	0.25 (1)	0.33 (1)
C(2)	0.16 (1)	0.19 (1)	0.24 (1)
N(2)	0.184 (9)	0.210 (8)	0.227 (8)
C(21)	0.19 (1)	0.24 (1)	0.29 (1)
C(3)	0.15 (1)	0.21 (1)	0.234 (9)
N(3)	0.16 (1)	0.232 (9)	0.286 (9)
C(4)	0.17 (1)	0.21 (1)	0.24 (1)
N(4)	0.20 (1)	0.235 (9)	0.307 (9)

[a] Taken along the principal axes of the thermal ellipsoids. The relative orientation of these axes may be seen from Figure 2. [b] See footnote *a*, Table II.

Table V. Infrared and Raman Spectral Results for $(RNC)_4Mo(CN)_4$ Complexes in the C≡N Stretching Frequency Region[a,b]

	Infrared		Raman		
R	KBr pellet[c]	Solution	Solid	Solution	Assignment
CH_3	2145 (m)	2152 (w)	2143 (s)		ν_{CN}
	2234 (s)		2235 (m)	*e*	ν_{CNR}
	2251 (s)	2249 (s)	2257 (m)		ν_{CNR}
n-C_3H_7	2145 (m)	2152 (w)	2141 (s)[d]	2150 (m, pp)	ν_{CN}
	2227 (s)	2235 (s)	2225 (m)[d]	2231 (m, dp)	ν_{CNR}
			2241 (w)[d]	2249 (m, p)	ν_{CNR} (A_1)
t-C_4H_9	2144 (m)	2150 (w)	2141 (m)	2150 (m, pp)	ν_{CN}
	2212 (s)	2219 (s)	2211 (m)	2215 (s, dp)	ν_{CNR}
			2230 (m)	2234 (s, p)	ν_{CNR} (A_1)
CH_2CHCH_2	2145 (m)	*e*	*e*	*e*	ν_{CN}
	2233 (vs)				ν_{CNR}
$(C_6H_5)_2CH$	2138 (sh)		2137 (sh)		
	2144 (m)	2150 (vw)	2142 (m)	*e*	ν_{CN}
	2218 (s)	2226 (s)	2217 (s)		ν_{CNR}
			2238 (m)		ν_{CNR}

[a] Frequencies are reported in reciprocal centimeters and are accurate to ±2 cm^{-1}. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; p, polarized; pp, partly polarized; dp, depolarized. [c] ~0.25 mg of sample in 200 mg of KBr. [d] Kodak variable neutral density filter was used to prevent photodecomposition. [e] Not measured.

Table VI. Electronic Spectral Results for $(RNC)_4Mo(CN)_4$ Complexes[a]

Compound	Frequency, ν, cm^{-1}	Molar extinction coefficient, ϵ_{max}
$(CH_3NC)_4Mo(CN)_4$[b]	26,000 (sh)	130
	30,000 (sh)	350
	41,500	15,700
	43,800 (sh)	11,000
$(t\text{-}C_4H_9NC)_4Mo(CN)_4$[b]	26,000 (sh)	150
	30,000 (sh)	420
	41,200	15,500
	43,700 (sh)	10,700
$[(C_6H_5)_2CHNC]_4Mo(CN)_4$[c]	26,000 (sh)	200
	30,000 (sh)	600
	39,700	22,500
	41,600 (sh)	16,000
$K_4Mo(CN)_8 \cdot 2H_2O$[d]	23,200	69
	27,200	170
	32,450	262
	37,400	1,350
	41,670	15,540

[a] sh indicates the band was a shoulder, resulting in some uncertainty in the values quoted for ν and ϵ_{max}. [b] Methanol solution. [c] Chloroform solution. [d] Aqueous solution; data from J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, **85**, 249 (1963).

the sake of comparison, a spectrum of potassium octacyanomolybdate(IV) dissolved in water. Fourier-transform ^{13}C nmr spectral results are summarized in Table VII together with data for potassium octacyanomolybdate(IV).

Discussion

Description of the $(CH_3NC)_4Mo(CN)_4$ Structure. It is readily apparent from Figure 2 that the tetracyanotetrakis(methyl isocyanide)molybdenum(IV) complex adopts the dodecahedral configuration with the four cyanide ligands at the A positions and the four isocyanide ligands at the B positions (Figure 1). The best least-squares planes through the central atom and the atoms defining the two intersecting trapezoids (Figure 2) were computed and the mean displacements and interplanar angles evaluated. The resultant values of d_T (0.06, 0.10 Å) and the interplanar angle (87.8°) substantiate the choice of the dodecahedron as the most suitable polyhedron; attempts to fit the structure to a

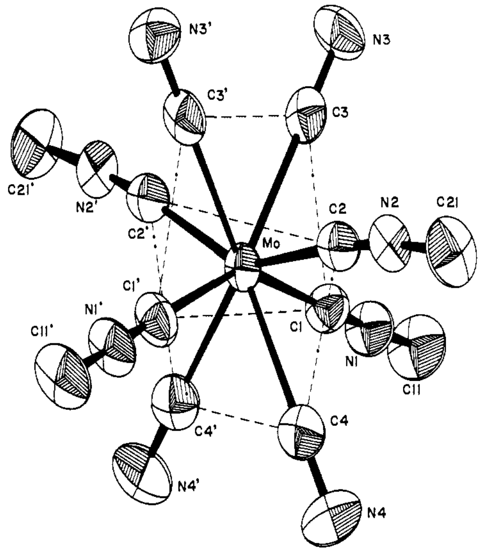

Figure 2. Molecular structure of tetracyanotetrakis(methyl isocyanide)molybdenum(IV) showing the atom-labeling scheme and the 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity, and dashed lines denote the intersecting trapezoids formed by the *mam* dodecahedral edges (Figure 1).

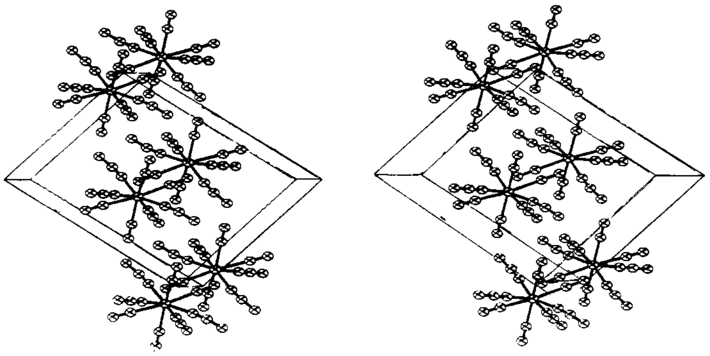

Figure 3. Stereoscopic view of the unit cell packing diagram of $(CH_3NC)_4Mo(CN)_4$.

Table VII. Fourier-Transform ^{13}C Nmr Results for $(t\text{-}C_4H_9NC)_4Mo(CN)_4$ and $K_4Mo(CN)_8$

Complex	T, °C	Chemical shift[a] C≡N	 C≡NR	 $CNC(CH_3)_3$	 $CNC(CH_3)_3$
$(t\text{-}C_4H_9NC)_4Mo(CN)_4$	40	52.5[b]	66.8	135.2	165.4
in $CDCl_3$[c]	−12	54.6	65.3	134.7	165.3
	−47	55.3	64.8	134.6	165.2
$K_4Mo(CN)_8$ in H_2O[d]	3	41.7			

[a] Parts per million upfield from carbon disulfide. [b] Sharpens considerably as T decreases (line width at half-height about 45 and 8 Hz at 40 and −47°, respectively). [c] Deuterium lock signal. Chemical shifts standardized with the deuterated chloroform ^{13}C peak. Assignments of C≡N and C≡NR resonances must be regarded as tentative (see ref 40a). [d] D_2O added for lock signal; methanol added as internal standard.

square-antiprismatic polyhedron resulted in "square" faces with d_S values greater than 0.2 Å.[23] Polyhedral shape parameters,[3] derived from the results of Tables II and III, are summarized in Table VIII along with the corresponding values for $K_4[Mo(CN)_8]\cdot 2H_2O$ and the "most favorable" values for these parameters. From Table VIII it may be seen that the dodecahedral coordination polyhedron of $(CH_3NC)_4Mo(CN)_4$ conforms reasonably well to expectations based on the analysis of Hoard and Silverton.[3] Alkylation of octacyanomolybdate(IV), at least by methyl iodide, therefore does not appear to distort grossly the octacyanomolybdate(IV) structure.

Table VIII. Average Normalized Polyhedron Shape Parameters for Dodecahedral Molecules[a]

Shape parameter[b]	$(CH_3NC)_4$-$Mo(CN)_4$	$Mo(CN)_8^{4-}$ [c]	"Most favorable" [d]
a, Å	1.17	1.18	1.17
b, Å	1.44	1.47	1.49
m, Å	1.13	1.16	1.17
g, Å	1.26	1.24	1.24
θ_A, deg	35.7	36.0	35.2
θ_B, deg	75.7	72.9	73.5
M-A/M-B	1.01	1.00	1.03

[a] Distances are normalized by the average M–C bond length. [b] See Figure 1. [c] J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, **90**, 3177 (1968). [d] Reference 3.

The intraligand geometry (Table II) in the complex is normal and compares favorably with structural results for similar cyano and alkyl isocyanide compounds.[1,5,24] Examination of an extensive list of nonbonded inter- and intramolecular contacts revealed no unusually short distances, the packing of molecules in the unit cell (Figure 3) being determined by van der Waals interactions.

Vibrational and Electronic Spectroscopy. From group theory, the infrared spectrum in the C≡N stretching frequency region of solid $(CH_3NC)_4Mo(CN)_4$ (idealized D_{2d} symmetry) should consist of four bands, two from the cyanide and two from the isocyanide ligands. As indicated in Table V, only three bands appear, and the other derivatives (taken in the present discussion to be isostructural) contain even fewer absorptions. To explain these results one must assume that the missing bands are either due to accidental degeneracies or that several absorptions are very weak. The assumption of accidental degeneracy is quite reasonable for the RNC stretching modes since the width of the bands at half-height is greater than 30 cm^{-1}. The failure to observe the splitting of C≡N stretching frequencies in cyano complexes is not unusual.[25] The occurrence of accidental degeneracies in the solid-state infrared spectra of the $(RNC)_4Mo(CN)_4$ complexes prevents a definitive assignment of their geometry. In some cases shoulders were observed ~2190 cm^{-1} which, from their intensities and positions,[26] are attributed to the presence of ^{13}C and ^{15}N isotopes and are not reported in Table V (these are listed in the Experimental Section, however). The assignment of ν_{CN} and ν_{CNR} in Table V was facilitated both by the absorption frequencies[25] and intensities, the latter being generally greater for the isocyanide ligands in which there is more charge separation.[27] The ν_{CN} stretching frequency (2145 cm^{-1}) of the $(RNC)_4Mo(CN)_4$ complexes is shifted to higher energy compared

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(23) For discussion, see S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7, 1686 (1968); *ibid.*, 11, 1446 (1972).

(24) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley-Interscience, New York, N. Y., 1969, p 33.

(25) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, pp 178–186.

(26) S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, 21, 1087 (1965).

(27) Reference 24, p 7.

with the ν_{CN} values in $Mo(CN)_8^{4-}$ (where the highest energy band occurs at (2136 cm^{-1}),[26,28] a result consistent with the decrease in negative charge on the complex. The infrared spectra of the $(RNC)_4Mo(CN)_4$ complexes in methanol solutions are in general agreement with the solid state results (Table V) and thus also do not provide unambiguous structural information. The ν_{CNR} band of the methyl derivative is not split as in the solid state.

There should be six Raman-active C≡N vibrations, three for the cyano and three for the isocyanide ligands ($2A_1 + 2B_2 + 2E$). Again there are several accidental degeneracies in the spectra, precluding a unique structural interpretation. Generally, the ν_{CN} bands are more intense than the ν_{CNR} bands, a result which is ascribed in part to the fact that the intense A_1 mode overlaps the B_2 and E cyano absorption frequencies. The A_1 stretching frequency of the isocyanide ligands is separated out from the other two (degenerate) bands and occurs at slightly higher energies in the Raman spectrum. The assignment of the A_1 modes (both ν_{CN} and ν_{CNR}) was facilitated by the polarization results for methanolic solutions of $(n\text{-}C_3H_7NC)_4Mo(CN)_4$ and $(t\text{-}C_4H_9NC)_4Mo(CN)_4$ (Table V).

Table VI summarizes the electronic spectral bands of $(RNC)_4Mo(CN)_4$ complexes in methanol or chloroform solution compared to the spectrum of $Mo(CN)_8^{4-}$ in water. The high intensity bands around 41,000 cm^{-1} are assigned to a ligand → metal charge-transfer transitions, the energy of which is seen to decrease slightly as the ligands become more readily oxidizable. Because of this strong absorption, only two d-d transitions can be observed for the $(RNC)_4Mo(CN)_4$, the energies of which are not influenced by the choice of R. By analogy to the assignments made for the octacyanomolybdate(IV) ion in aqueous solution,[29] the bands ~26,000 and 30,000 cm^{-1} are assigned to the $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1B_1$ transitions, respectively. Both of these absorptions are more intense and occur at higher energy than for $Mo(CN)_8^{4-}$, which may be attributed to the increased covalency[30] and greater ligand field strength, respectively, of the metal-ligand (isocyanide) bonds.

Evaluation of π Bonding and Choice of Stereoisomer. There are 22 different possible structural isomers for a dodecahedral complex of MX_4Y_4 stoichiometry and another 13 isomers for the square-antiprismatic coordination framework.[31] The fact that $(CH_3NC)_4Mo(CN)_4$ adopts a dodecahedral configuration with the better π-acceptor (methyl isocyanide)[32] ligands at the B positions is the strongest piece of evidence favoring the idea that preferential π back-bonding involving the metal $d_{x^2-y^2}$ orbital might influence the choice of stereoisomer as originally proposed by Orgel[6] for an eight-coordinate d^2 metal complex. The fact that the average Mo-C bond length is slightly shorter (Table II) for the isocyanide compared to the cyanide ligands provides additional support for preferential Mo-C isocyanide π bonding. The total amount of Mo-C π bonding involving isocyanide ligands of $(CH_3NC)_4Mo(CN)_4$ cannot be very great on an absolute scale, however, since the average Mo-C bond distance of 2.148 (8) Å is substantially greater than the mean Mo-C bond length (2.08 Å) in the $[Mo(CNR)_6I]^+$ ion.[1] In the latter complex, strong π bonding can be expected because of the low oxidation state of the molybdenum atom. Thus, the average Mo-C distance of 2.08 Å is clearly shorter than the sum of the Slater single bond Mo and C atomic radii, 2.15 Å,[33] to which the present values (Table II) may be favorably compared.

Conclusions about the extent of Mo → C π bonding derived from infrared spectral criteria are ambiguous. Comparing the measured stretching frequencies of coordinated isocyanides in the complexes $(RNC)_4Mo(CN)_4$ (Table V) with the stretching frequencies of the free RNC ligands (ref 24, p 12), a shift of ~50 cm^{-1} or more to higher energies is readily apparent. This result should not be considered as proof that there is no π bonding between the metal and the ligand, however. Coordination of CN^- or RNC will generally tend to increase the amount of C-N σ-bond character and raise the absorption frequency, whereas π back-bonding will tend to lower the band frequency through population of the C≡N π* orbitals.[24,34,35] Ideally one would like to have a RNC-Y adduct in which no π bonding could occur and for which the group Y has an effective electronegativity identical with that of the complex in question. A shift of the C≡N stretching frequency in the latter could then be properly ascribed to π back-bonding.[35] The chief difficulty here is the lack of an appropriate reference compound, as may be assessed by comparing the ν_{CNR} values for the following possible "standards" in which π back-bonding would not be expected: $(C_6H_5)_3B\text{-}CN(C_6H_{11})$ (ν_{CNR}, 2255 cm^{-1}); $(C_6H_5)_3Al\text{-}CN(C_6H_{11})$ (ν_{CNR}, 2215 cm^{-1}); and $(C_5H_5)_3Y\text{-}CN(C_6H_{11})$ (ν_{CNR}, 2208 cm^{-1}).[36-38]

To summarize, it appears that preferential π bonding between the molybdenum atom and the isocyanide ligands occurs to the extent that the delicate energy balance influencing the choice of stereoisomer[2-5] is affected to produce the one isomer in which such a π interaction is maximized.[6] The π interaction must be a weak one, however, judging from the absence of definitive, confirmatory structural or infrared spectroscopic evidence. Further synthetic and structural studies of MX_4Y_4 complexes involving monodentate ligands will be of interest.

^{13}C Nmr Spectroscopy. In order to evaluate the possibility that $(RNC)_4Mo(CN)_4$ complexes might be stereochemically nonrigid,[39] the ^{13}C nmr spectrum of the most soluble derivative, $(t\text{-}C_4H_9NC)_4Mo(CN)_4$, was examined over a 90° temperature range in chloroform solution. As indicated in Table VII the four ^{13}C resonances of the complex shift slightly as the temperature is

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(28) K. O. Hartman and F. A. Miller, *Spectrochim. Acta, Part A*, 24, 669 (1968).

(29) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, **85**, 249 (1963).

(30) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, p 135.

(31) L. R. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Amer. Chem. Soc.*, **65**, 329 (1943).

(32) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 754.

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

(34) L. H. Jones, *ibid.*, **41**, 856 (1964).

(35) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

(36) G. Hesse, W. Witte, and G. Bittner, *Justus Liebigs Ann. Chem.*, **687**, 9 (1965).

(37) G. Hesse, H. Witte, and P. Mischke, *Angew. Chem.*, 77, 380 (1965).

(38) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, **6**, 141 (1966).

(39) E. L. Muetterties, *Inorg. Chem.*, 4, 769 (1965).

lowered, and the cyanide resonance sharpens considerably because of reduced nitrogen quadrupolar broadening at the lower temperatures, but no new resonances or splitting of peaks were observed. This behavior is consistent with the presence of only one geometric isomer in solution, but rapid interconversion of isomers at −47° cannot be excluded. The assignments of resonances indicated in Table VII are consistent with the relative ^{13}C chemical shift values quoted for other cyano andis ocyanide metal complexes.[40,40a] The data for potassium octacyanomolybdate(IV) in aqueous solution (Table VII and ref 39) are more suggestive of fluxional behavior,[39] but again a unique interpretation is not yet possible. Recently, stereochemical nonrigidity was conclusively demonstrated for related molecules, $MoH_4(PR_3)_4$, although a topological mechanism was not established.[41,42]

Acknowledgments. We are indebted to the National Science Foundation for support of this research under Grant No. GP 27239X, to Dr. Bernard Bulkin of Hunter College for kindly providing the Raman spectra, to Bruker Scientific Co. for the variable-temperature Fourier-transform ^{13}C nmr spectra, to Professor H. B. Gray for a stimulating discussion, and to the Alfred P. Sloan Foundation for a research fellowship to S. J. L. (1968–1970).

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(40) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).

(40a) Note Added In Proof. The identification of the cyanide resonance, made on the basis of the quadrupolar broadening cited above, must be regarded as tentative. Recent studies of $Mo(CNR)_6I^+$ in solution suggest the assignment of $C{\equiv}N$ and $C{\equiv}NR$ resonances in Table VII may have to be reversed.

(41) (a) J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.*, 93, 5261 (1971); (b) B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *Chem. Commun.*, 1617 (1971).

(42) As indicated previously,[1] the X-ray structure of $(CH_3NC)Mo(CN)_4$ was determined early last year. Publication of the results was delayed pending completion of the chemical and spectroscopic studies reported here. At the time when this paper was being submitted, a completely independent investigation of the $(CH_3NC)_4Mo(CN)_4$ crystal structure appeared as a preliminary communication.[43] The two structural determinations are in good agreement.

(43) F. H. Cano and D. W. J. Cruickshank, *Chem. Commun.*, 1617 (1971).

The Mechanism of the Oligomerization of Hydrogen Cyanide and Its Possible Role in the Origins of Life[1]

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Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received February 8, 1972*

Abstract: Addition of HCN to RN=CHCN (VIII) (R = $(CH_3)_3C$, $(CH_3)_2CH$, C_6H_{11}, C_2H_5) yielded RNHCH(CN)C(NHR)$(CN)_2$ (XI) and (RNH)(NC)C=C(CN)(NH_2) (X). The formation of X and not (RNH)(NC)C=C(CN)(NHR) (XII) demonstrates that the oligomerization of HCN proceeds by stepwise addition of cyanide to cyanide oligomers, HCN + HCN → I, + HCN → VI, + HCN → III, and not by the dimerization of I → III. These results show that I does not exhibit the properties of a carbene. Furthermore, the mechanism of the oligomerization process demonstrates that the so-called "HCN polymer" must be a mixture of low molecular weight compounds. Since it had previously been shown that these compounds do not contain amide links a reinvestigation of the role of HCN in the chemical evolution of amino acids and other biological monomers is warranted.

Hydrogen cyanide may have played an important role in prebiological chemistry.[2] It is known to self-condense to form "polymers." Amino acids and heterocyclic bases are released from these "polymers" on hydrolysis.[3]

Matthews and coworkers[4] first suggested that the dimeric species I was the direct precurser to the "HCN polymer." They suggested that I has the properties of a carbene (II) and that this carbene dimerized to III and polymerized to the "HCN polymer" IV. It was further suggested that mild hydrolysis of IV yielded peptides V, while it was known that vigorous hydrolysis of IV yields amino acids (Scheme I).

The assignment of structure V is based, principally, on the observation that amino acids are released on acid or base hydrolysis. However, glycine is released on hydrolysis of III, a substance which does not contain an amide linkage.[5] Hydrolytic release of amino acids from a compound, or mixture of compounds, does not constitute evidence for the presence of a peptide bond.

The only experimental evidence presented to indicate that the HCN dimer I has the properties of carbene II is the uv–visible spectrum of a yellow substance prepared photochemically at −196° from the lithium salt of 1-cyanoformamide *p*-toluenesulfonylhydrazone.[6] Compounds I or II were not isolated but, instead, III was the only substance obtained in this investigation. In considering the methods used for the generation of carbenes it would appear highly improbable that such a

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(1) Chemical Evolution. IX. For the previous paper in this series see J. P. Ferris, D. B. Donner, and W. Lotz, *Bioorg. Chem.*, in press.

(2) For a recent review see R. M. Lemmon, *Chem. Rev.*, 70, 95 (1970).

(3) C. V. Lowe, M. W. Rees, and R. Markham, *Nature (London)*, 199, 219 (1963).

(4) C. N. Matthews and R. E. Moser, *Proc. Nat. Acad. Sci. U. S.*, 56, 1087 (1966); C. N. Matthews and R. E. Moser, *Nature (London)*, 215, 1230 (1967).

(5) R. A. Sanchez, J. P. Ferris, and L. E. Orgel, *J. Mol. Biol.*, 30, 223 (1967).

(6) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Amer. Chem. Soc.*, 89, 5673 (1967).