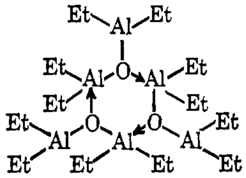

This structure has equal numbers of three- and four-coordinate aluminum atoms and, if a similar structural pattern occurs in the pure compound, could explain the uptake of only one molecule of trimethylamine per two aluminum atoms to form the complex, $(Et_2Al)_2O \cdot NMe_3$. The molecular weight data on the adduct, however, show this to be only slightly associated ($n = 1.325$) in benzene solution. This indicates a breakdown of the postulated trimeric structure of $(Et_2Al)_2O$ either on complex formation or on dissolution of the complex in benzene. The presence of an Al–N absorption mode in the infrared spectrum of the complex occurs at 516 cm^{-1} which is close to the values of previously assigned Al–N vibrations.[24]

A higher degree of polymerization in the case of $(EtAlOEt)_2$ and $(EtAlCl)_2O$ may be attributed to cross-linked structures involving ethoxy- and chloro-bridging groups, or perhaps to the formation of larger rings. The weakness of the complex formed between trimethylamine and the ethoxy derivative may be due in part to this internal satisfying of four coordinancy by the aluminum atoms, and also in part to the shielding effects of the ethoxy group. The stronger complex formed between the chloro derivative and trimethylamine may be accounted for by the electron-withdrawing effect of the halogen atoms which enhances the acceptor properties of the aluminum atoms.

The reactivity toward moist air of the compounds studied followed the expected pattern. Thus, when triethylalane is exposed to the air it immediately inflames, but $(Et_2Al)_2O$, although fuming in moist air and being readily oxidized (as evidenced by the appearance of strong C–O absorption bands in the infrared spectrum of an exposed sample), does not inflame. The substituted derivatives $(EtAlOEt)_2O$ and $(EtAlCl)_2O$ appear to be less prone to attack by moisture in the air but are again readily oxidized by atmospheric oxygen. Finally, with higher percentages of oxygen in the compounds, *e.g.*, EtAlO, the stability toward atmospheric moisture appears to be greater, although a slow oxidation of the ethyl group may still be observed in the infrared spectrum of an exposed sample.

Acknowledgments. We wish to thank the Advanced Research Projects Agency and the National Science Foundation for financial support for this research.

[24] G. W. Fraser, N. N. Greenwood, and B. P. Straughan, *J. Chem. Soc.*, 3742 (1963).

Stereochemistry of Discrete Eight-Coordination. V. The Octacyanomolybdate(IV) Ion[1]

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Received October 5, 1967

Abstract: Accurate stereochemical parameters for the dodecahedral form of the octacyanomolybdate(IV) ion, obtained by analysis of the three-dimensional X-ray data recorded from crystalline $K_4Mo(CN)_8 \cdot 2H_2O$ for $(\sin \theta)/\lambda < 0.82$, are in part as follows. The averaged Mo–C bond length is 2.163 Å, with a mean deviation of 0.005 Å and an esd of 0.007 Å; corresponding data for the C≡N distance are respectively 1.152, 0.006, and 0.009 Å, and for the Mo–N chain length, 3.314, 0.005, and 0.008 Å. Comparison of these results with analogous data for eight-coordinate oxozirconate(IV) complexes and for the octahedral $MoO_2(CN_4)^{4-}$ ion strongly suggests that the net benefits from π bonding are much larger in the d^0 Zr(IV) complexes than in the d^2 Mo(IV) species. The commonly made assumption that the D_{2d} dodecahedron is better adapted than is the D_{4d} antiprism for π bonding is highly questionable. Evidence bearing on the stereochemical form of the $Mo(CN)_8{}^{4-}$ ion in solution, though inconclusive, inclines toward a species having effectively D_{4d} symmetry. It is pointed out that the antiprismatic variant of the quadruply charged complex is clearly the better adapted to stabilizing short-range interactions of a specifically anisotropic nature with contiguous water molecules and/or cations in the immediate environment.

The remarkable octacyanomolybdate(IV) and octacyanotungstate(IV) complexes, known since the turn of the century, have received intensive study during recent years by a variety of modern experimental techniques. The behavior of these complexes, nevertheless, is not yet fully understood and is subject to debatable interpretations. The points at issue can be more sharply defined and, in part, resolved with the aid of accurate bond parameters for the octacyanomolybdate(IV) complex and for some other complexed species that are especially useful for comparative purposes. These data are introduced, as needed, in the general discussion; the reliability of the $Mo(CN)_8{}^{4-}$ data is documented in the Experimental Section of this paper.

The strong presumption that the octacyanomolybdate(IV) and octacyanotungstate(IV) complexes exist

[1] This investigation was supported in part by National Science Foundation Grants G-23470 and GP-6710X, by Public Health Research Grant No. 5-ROI-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

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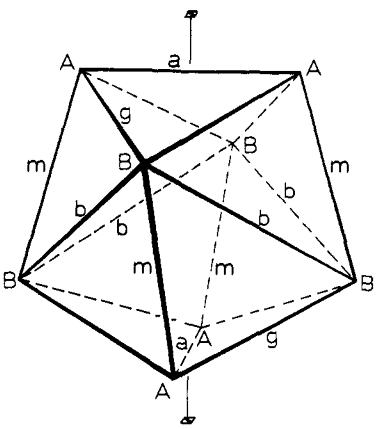

Figure 1. The D_{2d} dodecahedron. The two equivalent trapezoids, BAAB, lie in mutually perpendicular mirror planes that intersect in the $\bar{4}$ axis. Taking the mirror planes as the *xz* and *yz* axial planes in the $\bar{4}m2$ representation, the twofold axes coincide with the lines, $x = \pm y$, and pass through the midpoints of pairs of opposite *b* edges. Just two of the eight *g* edges of general type are labeled.

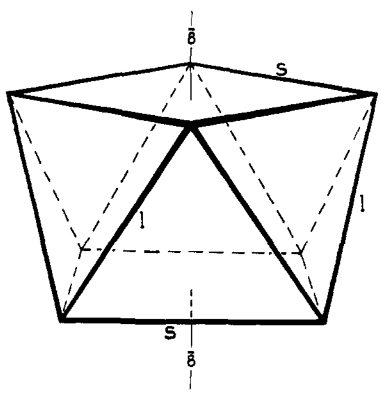

Figure 2. The D_{4d}-$\bar{8}m2$ antiprism. The four vertical mirror planes intersect in the $\bar{8}$ (or *z*) axis. The polyhedron center is the point of intersection of the $\bar{8}$ and four twofold azes. Each twofold axis passes through the midpoint of a pair of opposite *l* edges.

both in aqueous solution and in crystals as eight-coordinate ionic species of relatively high stability dates from Rosenheim's paper of 1907.[3] Comparatively recent work[4] demonstrates that exchange of CN^- between the $Mo(CN)_8{}^{4-}$ species and the solution, quite negligible in the dark, is photocatalyzed, but that, in ordinary light, the $Mo(CN)_8{}^{4-}$ ion acquires a lability that is still extremely small as compared with that generally observed for complexes in which coordination numbers above six are utilized. Prolonged irradiation of the aqueous solution with near-ultraviolet light produces products[5-8] that are of subsequent interest.

A two-dimensional X-ray analysis of crystalline structure dating from 1939 for the salt $K_4Mo(CN)_8 \cdot 2H_2O$ provides the following stereochemical description of the complex anion.[9] The coordination polyhedron utilized by the eight-coordinate $Mo(CN)_8{}^{4-}$ is the dodecahedron, with triangular faces and the ideal or maximum symmetry of D_{2d}-$\bar{4}m2$, that is represented by Figure 1. (Only the symmetry of C_s-m is required in the crystal.) Averaged bond lengths of Mo—C = 2.15 and C≡N = 1.15 Å, but no reliable estimate of the relative values of the bond lengths for the symmetry-nonequivalent bond types, Mo–C^A and Mo–C^B, are provided by the two-dimensional analysis. In respect of steric merit[9-11] there is little to choose between the D_{2d} dodecahedron and the square antiprism of D_{4d}-$\bar{8}m2$ symmetry (Figure 2), but it is important to note that nonbonding repulsions must affect the bond-length ratio, M–A/M–B, in the dodecahedron.[10] Thus, for example, in a dodecahedral oxozirconate(IV) coordination group that utilizes only monodentate ligands, the destabilizing energy associated with the nonbonding repulsions between ligand pairings of O^A–O^A type is estimated to be ~8 kcal/mole larger than that associated with repulsions of the O^B–O^B type.

Our three-dimensional reanalysis and refinement of the $K_4Mo(CN)_8 \cdot 2H_2O$ structure now demonstrate that the coordination polyhedron, of required C_s symmetry, has shape parameters that differ measureably from those of the ideal D_{2d} dodecahedron, but that, such distortions notwithstanding, there are no objectively significant variations in either the Mo–C or the C≡N bond lengths. The averaged Mo–C bond distance of 2.163 Å carries a mean deviation of ±0.005 Å as compared with the estimated standard deviation (esd) for an individual bond length of 0.007 Å; corresponding data for the C≡N bond distance and the Mo–N separation are, respectively, 1.152 ± 0.006 with an esd of 0.009 Å, and 3.314 ± 0.005 with an esd of 0.008 Å. The bond distances display no tendency toward a division into the A and B types (Figure 1) that are symmetry-nonequivalent in D_{2d}. MoCN chains are nearly linear with MoCN angles that average to 177.5 ± 0.9°.

The virtual equality of the Mo–C^A and Mo–C^B complexing bond lengths implies a corresponding near-equality of binding energies and of force constants; an analogous conclusion applies, of course, to the symmetry-nonequivalent classes of C≡N bonds. Inasmuch as the adverse effects of the ligand nonbonding repulsions weigh more heavily upon the Mo–C^A bonds, it is probable that the direct bonding interactions are compensatingly stronger for this bond type. It is clear, however, that virtual equality of the M–A and M–B bond types in respect to strength and length is not a general requirement for stabilization of dodecahedral coordination relative to the antiprismatic alternative. In the known eight-coordinate dodecahedral oxozirconate(IV) complexes of accurately determined structures, the Zr–O^B bonds are definitely shorter than those of Zr–O^A type by 0.06–0.14 Å, with ~0.10 Å as the expectation value in the absence of unduly large stereochemical complication.[12]

Treatments of the bonding problem, first in the very general terms of the group-theoretical conditions,[13]

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(3) A. Rosenheim, *Z. Anorg. Chem.*, 54, 97 (1907), who cites references to still earlier studies.

(4) A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, 72, 4030 (1950).

(5) A. W. Adamson and J. R. Perumareddi, *Inorg. Chem.*, 4, 247 (1965).

(6) (a) W. Jakób, A. Samotus, and Z. Stasicka, Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm, June 1962; (b) W. Jacób and Z. Jacób, *Roczniki Chem.*, 36, 593 (1962).

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

(8) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 6, 1943 (1967).

(9) J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, 61, 2853 (1939).

(10) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

(11) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).

(12) J. L. Hoard, E. W. Silverton, and J. V. Silverton, *J. Am. Chem. Soc.*, 90, 2300 (1968).

and later by way of hybrid valence-bond discussions of the σ-bonding patterns,[14,15] suggest that both the D_{2d} dodecahedron and the D_{4d} antiprism are suitable coordination polyhedra for the eight-coordination complexes formed by a central atom that, in the cationic form corresponding to its oxidation state, retains a d^0, d^1, or d^2 electron configuration in its valence shell. The suggestion[16,17] that "back" π bonding in d^1 and d^2 complexes, most specifically in the diamagnetic d^2 $Mo(CN)_8{}^{4-}$, has both the required selectivity and the sufficient magnitude to stabilize dodecahedral coordination relative to the antiprismatic alternative implies two distinct premises, both of doubtful validity: (1) that d^0 complexes normally are more stable in antiprismatic coordination, but (2) that d^1 and d^2 complexes normally prefer dodecahedral coordination. Thus the assumption, implicit in the earlier ligand-field discussions of the problem, that dodecahedral coordination is improbable for the most numerous class of d^0 complexes has been roundly disproved by X-ray analyses of crystalline structure for many such species.[18] Furthermore, it is highly probable that in aqueous solution the d^1 $Mo(CN)_8{}^{3-}$ and $W(CN)_8{}^{3-}$ ions are antiprismatic species,[19,20] and similar behavior on the part of the d^2 $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ species seems not unlikely (*vide infra*).

These reservations notwithstanding, the rather ill-defined role played by π bonding in discrete eight-coordination retains a good deal of interest. Having first conceded that π bonding cannot properly be treated as an independent phenomenon, we look for comparative data in which significant differences are confidently attributable to differences in the nature and/or the magnitude of the π bonding. This condition is most nearly satisfied by the structural data that are available for the dodecahedral $Mo(CN)_8{}^{4-}$ and oxozirconate(IV) species.

The pattern of σ bonding in the symmetry-nonequivalent sets of four M–A and four M–B bonds utilizes eight of the nine $4d^55sp^3$ orbitals in the valence shell of Mo(IV) or Zr(IV); no realistic estimates, absolute or relative, of the associated binding energies are given by approximate theory in any of its several forms. For the M(IV) atom in dodecahedral coordination, the most stable of the valence-shell orbitals,[16] d_{xy} in the $\bar{4}m2$ representation of D_{2d} employed in Figure 1, has its four lobes directed along the twofold axes that bisect pairs of opposite *b* edges of the polyhedron. Thus barred from σ bonding,[13] the d_{xy} orbital can be used for π bonding with, predominantly, the four B ligands; such bonding builds up electron density between contiguous pairs of B ligands within the equatorial layer that envelops the *b* edges and the B vertices of the dodecahedron.

The structural data show that in the dodecahedral d^0 oxozirconate(IV) complexes the M–B bonds are shorter (by ~0.10 Å) and, consequently, are stronger than the M–A bonds, whereas in the d^2 $Mo(CN)_8{}^{4-}$ complex the two bond types approach virtual equality in length and, presumably, in strength. The effects of ligand nonbonding repulsions, markedly unfavorable on the M–A bonds, cannot be very dissimilar for the d^0 and the d^2 complexes under scrutiny.[10,12] The theoretical treatment of the σ bonding for both the M–A and the M–B bond types in the d^2 complex is completely parallel to that accorded the d^0 complexes. Consequently, we may conclude that the *net* benefits from π bonding are substantially smaller in the d^2 $Mo(CN)_8{}^{4-}$ ion than in the d^0 oxozirconate(IV) complexes. Indeed, the differential effect on the four M–B distances of what, in approximate theory, is a modification in the character of a single molecular orbital is quite impressive. It is probable that π bonding is a significant factor in stabilizing the d^0 complexes and, whenever mixed ligands are involved, in directing atoms that are π donors to the B positions.[21]

In the Zr(IV) complexes the π bonding transfers charge from the $p\pi$ orbitals of oxygen to the lowest lying d orbital in the valence shell of the Zr(IV) atom, but in the $Mo(CN)_8{}^{4-}$ ion the "back" π bonding transfers charge from the filled, most stable, d orbital of Mo(IV) to the unfilled $p\Pi^*$ antibonding orbitals of the cyanide groups. The energy of the bonding molecular orbital in the $Mo(CN)_8{}^{4-}$ ion cannot be far below that which calls for an "inert pair" of electrons in the d_{xy} orbital of Mo(IV). One, but not both, of these electrons can be removed to give, with retention of the principal structural features, the less stable $Mo(CN)_8{}^{3-}$ ion. The need for at least one, but preferably two quasi-inert electrons in the d_{xy} orbital of the molybdenum atom to stabilize the species is reminiscent of the octahedral hexachloro and hexabromo complexes of Se(IV) and Te(IV) in which the lowest lying valence-shell orbitals, 4s and 5s, of the respective central atoms are occupied by inert pairs.[23]

Stereochemical data[24] for the octahedral *trans*-dioxotetracyanomolybdate(IV) ion, $MoO_2(CN)_4{}^{4-}$, as derived from the crystalline structure of the salt, $NaK_3MoO_2(CN)_4 \cdot 6H_2O$, also are pertinent to this discussion. The red $MoO_2(CN)_4{}^{4-}$ ion, a secondary product of the photolytic hydrolysis of the $Mo(CN)_8{}^{4-}$ species or of the reductive hydrolysis of the d^1 $Mo(CN)_8{}^{3-}$ species, is stabilized in the ordered positive field provided by the cations in a crystalline salt. Interatomic distances with their estimated standard deviations in this complex of effectively D_{4h} symmetry are Mo—N = 3.377 ± 0.011, Mo—C = 2.207 ± 0.012, C≡N = 1.170 ± 0.017, and Mo—O = 1.839 ± 0.009 Å. Instead of the anticipated shortening by $\gtrsim 3\%$ of the Mo—C bond length in the octahedral complex relative to that in the eight-coordinate $Mo(CN)_8{}^{4-}$, an increase of ~2% is observed—this despite the fact that the factors usually considered to affect the bond strength, including

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(13) G. E. Kimball, *J. Chem. Phys.*, 8, 188 (1940).

(14) G. Racah, *ibid.*, **11**, 214 (1943).

(15) (a) G. H. Duffey, *ibid.*, 18, 746 (1950); (b) *ibid.*, 18 1444 (1950). It is of interest to note that in the dodecahedron the M–A σ hybrids carry a larger fraction of d character and a slightly greater "strength" than do the M–B σ hybrids.

(16) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

(17) R. J. Gillespie in "Advances in the Chemistry of the Coordination Compounds," The Macmillian Co., New York, N. Y., 1961, p 34.

(18) *Cf.* E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **51**, 109 (1967), for a listing, essentially complete through 1966, of authenticated dodecahedral and antiprismatic complexes.

(19) B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966).

(20) R. G. Hayes, *J. Chem. Phys.*, **44**, 2210 (1966).

(21) Presumably the dodecahedral $TiCl_4$,2diars molecule[18,22] (diars = *o*-phenylenebisdimethylarsine) gains partial stabilization from such π bonding of the chloride ligands at B vertices with the Ti(IV) atom. It is, nonetheless, the small "bite" of the bidentate diars ligands and, equally, their unique positioning to span the short *a* edges of the dodecahedron that allows this otherwise improbable complex to exist.[10]

(22) R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *Nature*, **199**, 559 (1963).

(23) *Cf.* L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(24) V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, in press.

back π bonding to the cyanide groups, seem uniformly to be more favorable in the $MoO_2(CN)_4{}^{4-}$ ion. The more detailed considerations presented elsewhere[24] suggest that the equilibrium bond length must be quite sensitive to the concentration within a small volume of the very large resultant charge (four electronic units for each complex), that this is a more serious problem in the more compact $MoO_2(CN)_4{}^{4-}$ ion, and that Coulombic repulsions of substantially different magnitudes are predominant in determining the relative values of the Mo—C bond lengths. Also to be noted in this connection is the observation that the Mo—O bond length of 1.84 Å in $MoO_2(CN)_4{}^{4-}$, short though it be in consequence of forward π bonding, is still $\sim$0.10 Å longer than the 1.736 ± 0.005 Å observed for the $Mo^{VI}{=}O$ double bond in the MoO_3 moiety as this is stabilized, with the Mo(VI) atom in octahedral coordination, by complexing either with diethylenetriamine[25] or with the ethylenediaminetetraacetate ion.[26]

Our analysis suggests that the magnitude of the net contribution from π bonding to stabilization of the dodecahedral $Mo(CN)_8{}^{4-}$ ion has been overrated in earlier studies.[16,17] But even if this conclusion be discounted, it remains quite doubtful whether π bonding acts selectively to favor dodecahedral coordination in this complex or, indeed, in any other eight-coordinate species in which the ligand atoms either are chemically identical or do not differ materially in their capacities for engaging in π bonding. The observed distribution[18] of the oxo complexes of Zr(IV) between antiprismatic and dodecahedral coordination carries no hint that π bonding influences the selection of coordination type. Indeed, it is not clear that the geometry of the antiprism is less suited to π bonding than is that of the dodecahedron. Referring to the perspective view of the antiprism in Figure 2, we first note that the symmetry (D_{4d}-$\bar{8}m2$) of the σ-bonding pattern is theoretically compatible with two low-lying electron configurations, d^5p^3 and d^4sp^3, in the valence shell of the central atom.[13] Minimization of the nonbonding repulsions for neon-shell ligands gives, in excellent agreement with experimental data for d^0 complexes, a value of 57° for the angle made by a complexing bond with the $\bar{8}$ or z axis.[10] The d_{z^2} orbital of the central atom, with its principal lobes extending along $\pm z$ and an equatorial doughnut centered on the xy plane, has a nodal angle of 54.7°, and, consequently, is of little or no use for σ bonding. The utility of the d_{z^2} orbital for π bonding has usually been deprecated because the angle $\sim$57° between the axis of a principal lobe and that of a contiguous σ bond is clearly less favorable to π overlap than is the corresponding angle of 45° for π bonding in the octahedral case. Such overlap, however, occurs with eightfold multiplicity in the antiprismatic geometry. We then recognize that the angle of $\sim$33° between the axis of any σ bond and the plane of the equatorial doughnut of the d_{z^2} orbital is especially favorable for π overlap and that, for the unperturbed orbital, the doughnut carries 38.5% of the electron density. It appears also that the neglect of electron correlations in considering the full pattern of σ–π bonding is rather less serious with antiprismatic coordination.

Configuration of the $Mo(CN)_8{}^{4-}$ Ion in Solution

The further experimental data that are pertinent to the stereochemistry of the $Mo(CN)_8{}^{4-}$ ion in solution are summarized below. Electron spin resonance (esr) studies[19,20] of the paramagnetic d^1 $Mo(CN)_8{}^{3-}$ ions in aqueous solutions at 25° and in frozen glycerol at −196° provide data that are generally compatible with a single structural type in which the d_{z^2} orbital is the lowest lying of the valence-shell orbitals of the M(V) atom. This result is indicative of the D_{4d} antiprism as coordination polyhedron. Crystalline $K_4Mo(CN)_8\cdot 2H_2O$ provides comparatively rich infrared[27] and Raman[28] spectra from the C≡N stretching modes; the spectra fit well with dodecahedral $Mo(CN)_8{}^{4-}$ under the site symmetry of C_s. The Raman and infrared spectra given to the $Mo(CN)_8{}^{4-}$ ions in solution are compatible with D_{4d} symmetry,[27–29] although it is unfortunate that just one of the two allowed infrared C≡N stretching bands seem to be reliably observed.[27] D_{2d} symmetry cannot, of course, be excluded by the spectroscopic evidence, but D_{4d} seems a good deal more probable.[28,29] The electronic spectra of the $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ ions in solution have been inconclusively interpreted on both antiprismatic[30] and dodecahedral[31] models. Finally, the observation that the $Mo(CN)_8{}^{4-}$ species in aqueous solution gives a single sharp ^{13}C nuclear magnetic resonance is, as pointed out by the investigator,[32] compatible with three distinctive possibilities for the geometry of the coordination group: (1) antiprismatic coordination; (2) dodecahedral coordination with a negligible difference in the chemical shifts associated with the two symmetry-nonequivalent bond types; and (3) intramolecular conversion of configuration between dodecahedral and antiprismatic coordination, without benefit of dissociation,[4,32] at too high a frequency to be followed by the nmr technique.

The esr studies of the d^1 complexes speak firmly for D_{4d} symmetry; all studies of the d^2 complexes in solution are permissive, at least, of either D_{4d} or D_{2d} symmetry. In connection with the ^{13}C nmr result,[32] we note that the bond data for dodecahedral $Mo(CN)_8{}^{4-}$ suggest a negligible difference in the chemical shifts associated with the two bond types. The possibility of rapid intramolecular conversion of coordination types is particularly interesting, because this phenomenon unquestionably occurs in numerous other cases, *e.g.*, in the phosphorus pentahalogenides.[32]

There are striking similarities, but there are also some rather fundamental differences, between the configurational intraconversion, trigonal bipyramid $\rightleftarrows$ square pyramid, that occurs in the phosphorus halogenides and the intraconversion, D_{2d} dodecahedron $\rightleftarrows$ D_{4d} antiprism, that is of present interest. The characteristically low potential barrier to intraconversion of the five-coordinate species is associated with the fact that,

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[25] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964); F. A. Cotton and R. M. Wing, *ibid.*, **4**, 867 (1965).

[26] M. D. Glick, J. J. Park, and J. L. Hoard, "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz-Bad, Switzerland, Sept 5–9, 1966, p 424. Two MoO_3 moieties are thus stabilized in the binuclear complex.

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

[28] H. Stammreich, private communications, 1964 and 1965.

[29] H. Stammreich and O. Sala, *Z. Elektrochem.*, **64**, 741 (1960); **65**, 149 (1961).

[30] E. König, *Theoret. Chim. Acta*, **1**, 23 (1962).

[31] J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

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

structurally speaking, both configurations are residues obtained by excising one ligand from the sterically excellent octahedral configuration; otherwise put, the addition of a sixth ligand to either five-coordination group requires essentially no change in bond distances nor any very significant increase in the nonbonding repulsions. The packing of the ligands in the eight-coordinate $Mo(CN)_8{}^{4-}$ species is, by contrast, very tight. While it is true that the movement of just four carbon atoms, each by $\sim$0.75 Å, suffices to convert one coordination polyhedron into the other,[10] a rather substantial potential barrier to intraconversion is still probable. We note, in this connection, that the root-mean-square amplitudes of vibration of the carbon atoms in crystalline $K_4Mo(CN)_8 \cdot 2H_2O$ at room temperature are $\sim$0.16 Å. We remark further that freely occurring intraconversion, unbiased by an energy difference between the limiting forms of the complex, assigns statistical weights that favor the dodecahedral form in a 2:1 ratio. It seems more plausible than not that the d^2 $Mo(CN)_8{}^{4-}$ and the d^1 $Mo(CN)_8{}^{3-}$ ions should behave similarly in respect to configurational intraconversion, but the esr results for the d^1 complex are incompatible with any very significant contribution from a D_{2d} dodecahedral form except, perhaps, on the quite improbable basis that, even at −196°, the intraconversion is a fast process on the esr time scale.[32,33]

The experimental evidence bearing upon the stereochemical form of the $Mo(CN)_8{}^{4-}$ ion in solution, when considered *in toto*, is largely permissive and, consequently, inconclusive. It seems, nonetheless, that whenever the evidence carries a somewhat positive cast it favors an antiprismatic stereochemistry. There are quite general grounds, we now suggest, for accepting this interpretation of the data, at least in its essential features.

A quantitative theoretical treatment of the nonexistent free $Mo(CN)_8{}^{4-}$ ion would tell us whether the antiprismatic or the dodecahedral form is the more stable—or the less unstable—relative to an arbitrarily chosen zero of energy. Unless, however, this difference in configurational energy is a good deal larger than the observed nonsystematic distribution of the simpler[34] eight-coordinate complexes between the two stereochemical types suggests,[12,18] it follows that the observable form taken by the $Mo(CN)_8{}^{4-}$ ion is determined by the particular physical environment. Both in crystals and in aqueous solution the interactions of the $Mo(CN)_8{}^{4-}$ ion with other species extend to large distances, but with a striking difference of emphasis in these contrasting environments. In the selection of the crystalline arrangement that maximizes the crystal energy the requirement of three-dimensional periodicity (*i.e.*, long-range order) is overriding; the choice of stereochemical form for the $Mo(CN)_8{}^{4-}$ ion and the specification of the constitution and geometry of the coordination shell that immediately surrounds the $Mo(CN)_8{}^{4-}$ core correspond, at best, to a constrained maximum in the localized stabilizing interactions. Thus the occurrence of dodecahedral $Mo(CN)_8{}^{4-}$ in the crystalline potassium salt provides no guarantee that the complex is invariably, or even usually, stabilized as the dodecahedral species in other crystalline salts.

In aqueous solution, by contrast, it is only in the quite specific interactions of the $Mo(CN)_8{}^{4-}$ core with its immediate environment that the differences between antiprismatic and dodecahedral geometry can be reflected in a substantial difference in the over-all stabilizing energy. We then ask in which type of coordination polyhedron, neither of them regular, the quadruply charged $Mo(CN)_8{}^{4-}$ core departs further from a quasi-spherical shape and charge distribution, and is thereby more strongly predisposed to stabilization through anisotropic short-range interactions with contiguous species? The answer is, of course, the antiprism with its pair of curious square faces.

Given the expected angle of $\sim$57° between the axis of an Mo—C$\equiv$N chain and the $\bar{8}$ axis, the area of a square face is more than twice that of a triangular face (the factor is $4/\sqrt{3}$ for the equilateral antiprism corresponding to the hard-sphere model). The configuration of an antiprismatic $Mo(CN)_8{}^{4-}$ can be viewed as a pair of square pyramids that have a common apex at Mo(IV) and the same principal axis, the $\bar{8}$ or *z* axis (Figure 2). Four cyanide groups define the slant edges of the frustum of a pyramid or, alternatively, of a "square vat" with nitrogen atoms at the vertices of the larger, sterically more open, square face. On, in, and just above each vat-like grouping, the electron density is high. It is not only that each such grouping carries half of the resultant charge of the complex: a principal lobe of the d_{z^2} orbital of Mo(IV) extends through the base defined by the four carbon atoms into the vat, and the π-bonding systems of the cyanide groups are well oriented to build up further the electron density within and above the vat.

We now consider how the charge distribution and the geometry of each pyramidal moiety may gain in stability through interactions with the polar H–O bonds of a suitably positioned water molecule that carries the standard HOH angle of 104–105°. A water molecule in which the oxygen atom is centered on the unique axis, $\sim$1.5 Å outside the nitrogen face and $\sim$3.3 Å from the Mo(IV) atom (a nonbonding O–Mo separation[35]), has innumerable stabilizing orientations open to it. There are, however, two quite definite orientations, each conforming to C_{2v}-mm2 symmetry and equivalent to one another through rotation by 90° around the unique axis, that favor highly specific interactions. Each such orientation requires the H–O bonds of the water molecule to be directed almost exactly toward the midpoints of two cyanide groups that define diagonally opposite edges of the vat; the separation, in this direction, of the cyanide axes from the oxygen atom is $\sim$2.9 Å. The polar H–O bonds are positioned for strong interactions with the filled Π-orbital systems of the cyanide groups and, at still shorter range, with the electron density in the Π^* orbitals of the ligands. The stabilization thus provided has both

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(33) Using the representations, $\bar{8}2m$ for D_{4d} and $\bar{4}2m$ for D_{2d}, the conversion, antiprism → dodecahedron, involves the axial conversions, $8 \rightarrow 2$, $2 \rightarrow \bar{4}$, $2 \rightarrow 2$, with the $\bar{4}$ axis appearing along either the *x* or the *y* axis of the antiprismatic description. Superposition of the $d_{y^2-z^2}$ and the $d_{z^2-x^2}$ orbitals, each with half-weight, from the orthogonally oriented pair of dodecahedra (in $\bar{4}2m$ representations) thus obtained would give, for sufficiently rapid intraconversion, esr behavior similar to that provided by the d_{z^2} orbital in the antiprism.

(34) There is little doubt that increasing complexity, chemical and structural, generally favors dodecahedral coordination.[10,12,18]

(35) Neither the dimensional relations nor the electronic structure in an antiprismatic $Mo(CN)_8{}^{4-}$ is compatible with expansion of the coordination number above eight.

cooperative and quasi-internal aspects. Although the water molecule cannot be coordinated to the Mo(IV) atom,[35] neither is it relegated to an incompletely defined outer coordination shell; the water molecule, indeed, is oriented to permit the efficient utilization of its oxide oxygen atom in hydrogen bonding to other molecules in an outer coordination sphere.

Appraisal of the stabilizing interactions of the water molecule with the pyramidal moiety as roughly equivalent to that provided by two good hydrogen bonds gives a crude estimate of ~10 kcal/mole of stabilization for each such moiety or ~20 kcal/mole for the complex as a whole. Although energy from this source is only a fraction of that which stabilizes the complex, it represents, at least in first approximation, additional stabilization that has no apparent counterpart in the interactions that are accessible to the dodecahedral Mo-$(CN)_8^{4-}$ core in solution. This is, of course, the consequence of the much nearer approach to quasi-spherical symmetry that characterizes the dodecahedral core. It is further evident that the antiprismatic core is much the better adapted to intimate pairing with any of the usual cationic species, and that such pairing assumes increasing importance with increasing concentration. Thus it is quite probable that the dominant form of the complex anion in solution is a quasi-antiprismatic species, stabilized by reason of its anisotropic character, as described above.[36] The lability of the water molecules that bear primary responsibility for stabilization of the species must be quite high, especially in respect to reorientations; consequently, the effective symmetry of the species during study by current physical techniques is D_{4d}.

Experimental Section

A crystal specimen of $K_4Mo(CN)_8 \cdot 2H_2O$ in the form of an approximate cube of ~0.2-mm edge length was cut from one of the excellent tabular crystals[9] of the 1935 preparation[37] and used for the measurement of three-dimensional X-ray data on a General Electric XRD-3 spectrometer assembly. Reconfirmation of the space group as the orthorhombic Pnma-D_{2h}^{16} was provided by the pattern of systematically absent spectra,[38] by the absence of detectable piezoelectricity, and, of course, by the successful refinement of the structure earlier derived by two-dimensional analysis.[9] Lattice constants of a = 16.64 ± 0.01, b = 11.66 ± 0.007, and c = 8.710 ± 0.005 Å together with a cell content of $4K_4Mo(CN)_8 \cdot 2H_2O$ give a calculated density of 1.952 g/cc as compared with a measured density of 1.94 g/cc.

The measurement of diffracted intensities for all independent $\{hkl\}$ reflections having $(\sin \theta)/\lambda < 0.82$ Å^{-1} utilized Mo Kα radiation and the stationary-crystal stationary-counter technique as described in detail elsewhere.[39] Background corrections to the intensities of all reflections having $2\theta < 20°$ were individually measured. The corrections for all other reflections were read from plots of background count *vs.* 2θ, evaluated at regular intervals in χ for the crystal as mounted; the high quality of the specimen and its clean mounting were conducive to accuracy in using this method.[39] Of the 3868 independent reflections in the range of 2θ that was explored, 3307, or 85.5% of those theoretically allowed, were recorded as above background.

The linear absorption coefficient of the crystal for Mo Kα radiation is 1.74 mm^{-1}, yielding a μR of 0.22 for a spherical crystal having the same volume as the cube-shaped specimen used for intensity measurements. The absorption of X-rays by a spherical crystal having μR = 0.22 is virtually independent of scattering angle, and deviations from this absorption occasioned by the use of the cube-shaped specimen are practically negligible except for a trivial fraction of the reflections. In these circumstances the experimental intensity data were reduced to a corresponding set of relative structure amplitudes, $k|F_o|$, without correction for absorption.

Following confirmation by three-dimensional Fourier methods of the atomic arrangement reported long ago[9] for crystalline $K_4Mo(CN)_8 \cdot 2H_2O$, anisotropic full-matrix least-squares refinements of the structure were carried to convergence for each of the several schemes detailed below for handling the input data. The procedure in all of these refinements was invariant in respect to (1) the exclusion of three reflections that were clearly subject to strong extinction,[40] (2) the atomic form factors employed,[41] (3) the dispersion corrections (real and imaginary) to the form factor of the molybdenum atom,[42] and (4) the use of standard computational programs[43] minimizing the function, $\Sigma w(|F_o| - |F_c|)^2$, in which $|F_o|$ and $|F_c|$ are the respective absolute values of the observed and calculated structure amplitudes for the reflection (hkl). Furthermore, each reflection that was included in a refinement was weighted in accordance with the pattern, $w = 1$ for $|F_o| <$ bp and $\sqrt{w} = \text{bp}/|F_o|$ for $|F_o| >$ bp, wherein bp represents the breakpoint. All refinements except one (no. II below) used a breakpoint of (88–90) electrons so that only the 115 strongest reflections carried reduced weights.

Included in the 3307 independent reflections recorded as above background were some 660 reflections having $|F_o|$ values that were distributed more or less uniformly in the range from 4.5 to 10.0 electrons,[44] *i.e.*, in a range corresponding to ~0.05–0.10% of the theoretical maximum amplitude of 968 electrons—the number of electrons carried by the unit cell of $K_4Mo(CN)_8 \cdot 2H_2O$. The intensities of these weak reflections—much too weak, indeed, to be recorded photographically except, perhaps, by using an oversized crystal that would require gross corrections for absorption—were estimated on the spectrometer assembly with ever decreasing accuracy as $|F_o| \rightarrow 0$; but inasmuch as they came predominantly from beyond the Cu Kα limiting sphere, these weak reflections provided semiquantitative amplitude data of high resolving power.

Refinement I included the amplitude data for 3304 of the 3307 observed reflections; the breakpoint was taken at $|F_o|$ = 89.7 electrons.

Refinement II differed from I only in that the breakpoint was taken at $|F_o|$ = 14.8 electrons, with the attendant danger of giving undue weight to the less accurately measured data.

Refinment III differed from I by the exclusion of all reflections that gave intensity counts of three or less per second. The 477 amplitudes thus excluded were, for the most part, those having $|F_o|$ less than *ca.* nine electrons.

Refinement IV differed from I in two respects: reflections giving intensity counts of two or less per second were excluded, and the intensity counts of all remaining reflections were reduced each by one count per second. The net effects were to eliminate the weakest 326 of the 3307 observed reflections and to require slightly larger values of the general scaling factor for the $|F_o|$ and of the apparent thermal parameters.

Refinement V differed from IV in that the positions of the carbon atoms were interchanged with those of the nitrogen atoms.

The summary of the least-squares refinements given in Table I includes numerical values for both the conventional (unweighted) discrepancy factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and the weighted discrepancy factor, $r = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, for each refinement. The values of both discrepancy factors are, of course,

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(36) The experimentally meaningless question of whether the free $Mo(CN)_8^{4-}$ ion is less unstable in one stereochemical form than in the other is not answered.

(37) H. H. Willard and R. C. Thielke, *J. Am. Chem. Soc.*, 57, 2609 (1935).

(38) "International Tables for X-Ray Crystallography." Vol. I, "Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, p 151.

(39) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, 2, 243 (1963).

(40) The three reflections in question were (020), (040), and (060). The molybdenum atoms and half each of the potassium, carbon, and nitrogen atoms lie in the mirror planes, $y = {}^1/_4$ and $y = {}^3/_4$, and, consequently, scatter exactly in phase for even orders of reflection from (010). The remaining atoms lie in general positions[38] of Pnma: $\pm(x, y, z)$, $\pm({}^1/_2 + x, {}^1/_2 - y, {}^1/_2 - z)$, $\pm(x, {}^1/_2 - y, z)$, $\pm({}^1/_2 + x, y, {}^1/_2 - z)$.

(41) Atomic form factors were from D. T. Cromer and J. T. Waber, *Acta Cryst.*, 18, 104 (1965).

(42) Dispersion corrections were those of D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, "Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962, pp 213–215.

(43) Slightly modified versions of the Busing–Martin–Levy ORFLS and ORFFE programs on a CDC 1604 computer were employed in the final steps of every refinement.

(44) Just 11 reflections recorded as observable had $F_o < 4.5$ electrons.

Table I. Summary of the Several Refinements of Structure

Refinement no.[a]	No. of reflections	Break point[a]	Discrepancy factor R[b]	r[c]
I	3304	89.7	0.072	0.083
II	3304	14.8	0.078	0.179
III	2827	88.8	0.059	0.073
IV	2978	88.4	0.064	0.076
V	2978	88.9	0.078	0.091

[a] See text for description. [b] Unweighted; see text. [c] Weighted; see text.

Table II. Atomic Coordinates in Crystalline $K_4Mo(CN)_8 \cdot 2H_2O$[a]

Atom type	Coordinates 10^4x	10^4y	10^4z
O	8890 (4)	567 (5)	5913 (7)
C_1	381 (3)	1396 (4)	1654 (6)
C_2	1724 (3)	729 (5)	697 (6)
C_3	608 (4)	2500	−1060 (9)
C_4	2168 (4)	2500	−997 (8)
C_5	2589 (5)	2500	1776 (9)
C_6	1403 (4)	2500	3440 (9)
N_1	−136 (3)	833 (5)	2095 (7)
N_2	1921 (4)	−209 (5)	499 (8)
N_3	192 (4)	2500	−2118 (8)
N_4	2591 (5)	2500	−2019 (8)
N_5	3263 (5)	2500	2146 (10)
N_6	1381 (5)	2500	4761 (8)
K_1	1480 (1)	477 (1)	6903 (2)
K_2	8625 (1)	2500	9741 (2)
K_3	9603 (1)	2500	4791 (2)
Mo	10^5x = 13,648 (3)	2500	10^5z = 9680 (6)

[a] Estimated standard deviations of the last figure are given in parentheses. Those values without standard deviations are symmetry required.

Table III. Anisotropic Thermal Parameters in $K_4Mo(CN)_8 \cdot 2H_2O$[a]

Atom type	Thermal parameters, Å B_{11}	B_{22}	B_{23}	B_{12}	B_{13}	B_{23}
O	4.8 (2)	4.0 (2)	3.8 (2)	−0.5 (2)	0.3 (2)	0.7 (2)
C_1	1.8 (1)	1.8 (2)	2.3 (2)	−0.0 (2)	0.3 (1)	−0.3 (1)
C_2	1.8 (1)	2.1 (2)	2.4 (2)	−0.2 (2)	0.2 (1)	0.2 (2)
C_3	1.7 (2)	2.7 (3)	2.0 (2)	0	−0.3 (2)	0
C_4	1.9 (2)	2.0 (2)	1.4 (2)	0	−0.4 (2)	0
C_5	1.6 (2)	4.3 (4)	1.8 (2)	0	−0 1 (2)	0
C_6	2.0 (2)	2.0 (2)	1.9 (2)	0	−0.1 (2)	0
N_1	2.1 (1)	3.2 (2)	4.1 (2)	−1.1 (2)	0.8 (2)	−0.1 (2)
N_2	3.3 (2)	2.0 (2)	5.2 (3)	0.2 (2)	0.1 (2)	−0.2 (2)
N_3	2.0 (3)	5.3 (4)	1.8 (2)	0	−0.1 (2)	0
N_4	3.4 (3)	3.8 (3)	1.9 (2)	0	0.6 (2)	0
N_5	1.9 (2)	9.5 (8)	2.7 (3)	0	0.0 (2)	0
N_6	3.3 (3)	4.9 (4)	1.4 (2)	0	−0.1 (2)	0
K_1	2.5 (1)	3.1 (1)	2.9 (1)	−0.9 (1)	−0.1 (1)	−0.3 (0)
K_2	3.3 (1)	2.1 (1)	2.2 (1)	0	−0.1 (1)	0
K_3	2.5 (1)	2.8 (1)	2.0 (1)	0	−0.5 (1)	0
Mo	1.1 (1)	1.2 (0)	1.1 (0)	0	0.0 (0)	0

[a] The thermal parameters were introduced in the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The parameters reported here are related as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. The estimated standard deviations of the last figures are given in parentheses. Those values without standard deviations are symmetry required.

highly dependent upon the nature and the scope of the data that are included in their calculation. It is to be emphasized, therefore, that the refinements I–IV inclusive provide quantitative descriptions of the $Mo(CN)_8^{4-}$ ion that, by objective criteria, differ quite trivially from one another, and that the primary objective in carrying out the several refinements is thereby accomplished. But it is further to be emphasized that refinement I, which uses all of the observed data as recorded together with a sensible weighting scheme, gives slightly lower values for the estimated standard deviations in the atomic coordinates and the apparent thermal parameters than does any of the other refinements. It is consequently the results of refinement I that are reported in Tables II and III.[45]

The comparison of refinements IV and V provides objective evidence that the complexing bonds from the Mo(IV) atoms are with carbon rather than with nitrogen atoms in the $Mo(CN)_8^{4-}$ ion. We further note that refinement V assigns artifically large values of the apparent thermal parameters to nitrogen atoms and artificially small values to carbon atoms.

The Refined Structure

The atomic coordinates listed in Table II lead to the interatomic distances and angles within the $Mo(CN)_8^{4-}$ ion that are given in Tables IV and V. Bond lengths and Mo–N distances, classified as of A or B type in accordance with the ideal (D_{2d}) symmetry of the dodecahedron (Figure 1), are listed in Table IV. Inasmuch as no Mo—C≡N chain departs by more than 3.4° from strict linearity (Table IV), no Mo—N distance is more than 0.002 Å shorter than the sum of the Mo—C and

Table IV. Dimensions of the Mo—C≡N Chains in the $Mo(CN)_8^{4-}$ Ion

Type A Distances (Å) with Standard Deviations[a]					
Mo—C_1	2.167 (5)	C_1≡N_1	1.149 (7)	Mo—N_1	3.314 (6)
Mo—C_4	2.172 (8)	C_4≡N_4	1.136 (10)	Mo—N_4	3.307 (8)
Mo—C_5	2.155 (8)	C_5≡N_5	1.166 (11)	Mo—N_5	3.320 (9)
Mean	2.165	Mean	1.150	Mean	3.314
Type B Distances (Å) with Standard Deviations[a]					
Mo—C_2	2.163 (6)	C_2≡N_2	1.155 (8)	Mo—N_2	3.317 (7)
Mo—C_3	2.169 (8)	C_3≡N_3	1.153 (10)	Mo—N_3	3.322 (8)
Mo—C_6	2.154 (8)	C_6≡N_6	1.151 (10)	Mo—N_6	3.304 (8)
Mean	2.162	Mean	1.153	Mean	3.315
Averaged Distances (Å) with Mean Deviations[b]					
Mo—C	2.163 (5)	C≡N	1.152 (6)	Mo—N	3.314 (5)
Bond Angles (deg) at Carbon in the Chains					
Range, 176.4–179.6°; average, 177.5°; mean deviation 0.9°; esd, 0.7°					

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

Table V. Dimensions of the Coordination Polyhedron

Edge length, Å[a]			Angle, deg, at Mo[a]	
C_1—C_1'	2.575 (11)	Edges of	C_1MoC_1'	72.9 (0.3)
C_4—C_5	2.515 (11)	*a* type	C_4MoC_5	71.1 (0.4)
Mean	2.545		Mean	72.0
C_2—C_3	3.171 (8)	Edges of	C_2MoC_3	94.1 (0.4)
C_2—C_6	3.203 (8)	*b* type	C_2MoC_6	95.8 (0.4)
Mean	3.187		Mean	95.0
C_1—C_2	2.509 (8)	Edges of	C_1MoC_2	70.8 (0.3)
C_3—C_4	2.596 (10)	*m* type	C_3MoC_4	73.5 (0.4)
C_5—C_6	2.448 (11)		C_5MoC_6	69.2 (0.4)
Mean	2.515		Mean	71.1
C_1—C_3	2.719 (9)	Edges of	C_1MoC_3	77.7 (0.3)
C_1—C_6	2.640 (8)	*g* type	C_1MoC_6	75.3 (0.3)
C_2—C_4	2.644 (8)		C_2MoC_4	75.2 (0.3)
C_2—C_5	2.687 (8)		C_2MoC_5	77.0 (0.3)
Mean	2.673		Mean	76.3

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

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(45) A table of observed and calculated structure amplitudes from this refinement has been deposited as Document No. 9778 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

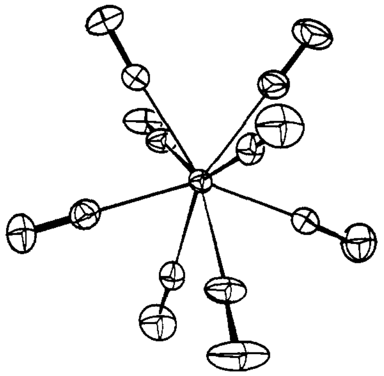

Figure 3. Diagram in perspective of the dodecahedral $Mo(CN)_8^{4-}$ ion to indicate the relative thermal motions of the atoms in the complex as it exists in the crystal.

C≡N bond lengths; indeed the Mo—N distances carry fully as much weight as do the Mo—C bond lengths in arriving at the conclusion that the eight Mo—C≡N chains are, within very narrow limits, dimensionally equivalent. No tendency for either the Mo—C or the C≡N bond lengths to separate into A and B classes is evident in the data of Table IV, even though such a separation is freely permitted by the maximum ideal symmetry of D_{2d}.

The geometry of the coordination polyhedron is, by contrast, quite definitely limited to the symmetry of C_s-m, the site symmetry of the complex anion as specified by the space group. Edge lengths of the coordination polyhedron and the angles subtended by these edges at the molybdenum atom, grouped in accordance with the edge types that characterize the ideal D_{2d} dodecahedron (Figure 1), are listed in Table V. The largest departures from D_{2d} symmetry are manifest in a pair of *m* edges that differ in length by a highly significant 0.15 Å, and in the angles subtended by these edge at Mo(IV) that differ by 4.3°. The averaged values for the edge lengths and the bond angles of the several classes are, however, in excellent agreement with expectation;[10] thus the *a* and the *m* edges are short and differ little in length, the *g* edges are 0.10–0.15 Å longer, and the *b* edges are easily the longest of all. Using the averaged dimensions given for the polyhedron in Table V, the angles, θ_A and θ_B, made by bonds of the respective A and B types with the quasi-$\bar{4}$ axis, are 36.0 and 72.9°; values of $\theta_A = 35.2$ and $\theta_B = 73.5°$, from the tetrakis(oxalato)zirconate(IV) ion,[46] were earlier considered to be "most favorable" for d^0 complexes.[10]

The distortion of the coordination polyhedron from D_{2d} symmetry and the departure of the Mo—C≡N chains from strict linearity are both attributable to the complicated packing relations that most directly involve the potassium and the nitrogen atoms. The coordination groups around each of the three structurally distinct classes of potassium ions are not describable as simply distorted versions of familiar polyhedra, but, as the data listed in Table VI demonstrate, the potassium ions are responsible for the stabilization of the crystalline arrangement.[47] The water molecules are used to fill out the coordination groups of two classes of potassium ions; H_2O–N separations range upward from 3.16 Å.

Table VI. Interatomic Separations[a] (Å) Involving the Potassium Ions

K_1–O	2.806 (7)	K_2–N_5	2.778 (9)	K_3–O[b]	2.729 (7)
K_1–N_1	2.844 (7)	K_2–N_2[b]	2.829 (7)	K_3–N_5	2.797 (8)
K_1–N_2	2.946 (7)	K_2–N_4	2.928 (8)	K_3–N_3	2.865 (9)
K_1–N_6	3.011 (6)	K_2–N_3	3.069 (8)	K_3–N_6	2.958 (9)
K_1–N_4	3.141 (9)	K_2–C_3	3.373 (9)	K_3–N_1[b]	3.079 (7)
K_1–C_4	3.197 (9)	K_2–C_5	3.490 (9)	K_3–C_6	3.218 (9)
K_1–C_3	3.288 (9)			K_3–C_1[b]	3.286 (7)

[a] The standard deviation of the last figure is given in parentheses.
[b] Two such distances for each potassium ion.

As may be seen in Figure 3 and Table III, the pattern of thermal vibrations within the $Mo(CN)_8^{4-}$ ion is rather complicated, particularly that for the nitrogen atoms. Much the largest value listed in Table III for a thermal parameter is the 9.5 Å^2 for vibration of an N_5 atom normal to the mirror plane in which this atom is centered (the corresponding root-mean-square amplitude of vibration is 0.35 Å). This vibration is strongly encouraged by the circumstance that, apart from the carbon atom to which it is bonded, an N_5 atom has as near neighbors just two potassium ions (at 2.78 and 2.80 Å), both centered in the common mirror plane; other potassium ions, water molecules, and atoms of other complexes are all more than 3.5 Å distant from an N_5 atom. The main features of the vibrational patterns for the other light atoms in the $Mo(CN)_8^{4-}$ ion are similarly traceable to nonisotropic interactions with the environment.

The averaged isotropic thermal parameter, 2.1 Å^2, for the carbon atoms in the anion corresponds to a root-mean-square amplitude of vibration of 0.16 Å.

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(46) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 2, 250 (1963).

(47) See ref 10 for diagrams of the crystalline arrangement as projected on the (001) and (010) faces of the unit cell.