Triangular Dodecahedral Stereochemistry of $Mo(CH_3NC)_4(CN)_4$; an *X*-Ray Study

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Summary *X*-Ray diffraction shows that the co-ordination of eight carbon atoms about molybdenum is a slightly distorted triangular dodecahedron; the tungsten compound is isomorphous.

X-RAY studies of eight-co-ordination compounds of molybdenum and tungsten[1] show two types of co-ordination polyhedra: the square antiprism ($\bar{8}2m$ symmetry) and the triangular dodecahedron ($\bar{4}2m$ symmetry). However results cannot yet be classified,[2] and both geometries occur in distorted forms. We have studied the simplest complex of the related series $M(RNC)_4(CN)_4$.

The light yellow crystals of two compounds (R = CH_3; M = Mo, W) of the series are isomorphous; by photographic measurements the cell dimensions of the W compound agree with those of the Mo compound within 0·02 Å. The molybdenum compound is monoclinic, space group $C2/c$, with $a = 12{\cdot}901(3)$, $b = 10{\cdot}424(2)$, $c = 11{\cdot}795(3)$ Å and $\beta = 76{\cdot}75(2)°$, $Z = 4$, $D_o = 1{\cdot}5$ and $D_c = 1{\cdot}534$ g cm^{-3}.

1137 non-zero reflections were recorded on an automatic Hilger–Watts four-circle diffractometer. Absorption and extinction corrections were not applied. Neutral atomic scattering factors and anomalous dispersion corrections for the Mo atom were used. The structure was solved from the Patterson function. Refinement of parameters has converged at an *R*-factor of 0·06.

The crystal structure consists of discrete molecules separated by normal intermolecular contacts. The molecular configuration is illustrated in the Figure by the (010) and (100) projections. In the Figure, A denotes a carbon atom of a CN group, and B an inner carbon atom of a CH_3NC group. Average distances for CN groups are Mo–C 2·17, C–N 1·14 Å, and for CH_3NC groups Mo–C 2·14, C–N 1·13, N–CH_3 1·44 Å. Estimated standard deviations are slightly less than 0·01 Å; rotational corrections, which may amount to 0·01 Å, have not been applied to the above distances. The Mo–C–N and C–N–CH_3 angles lie in the range 180° to 174°.

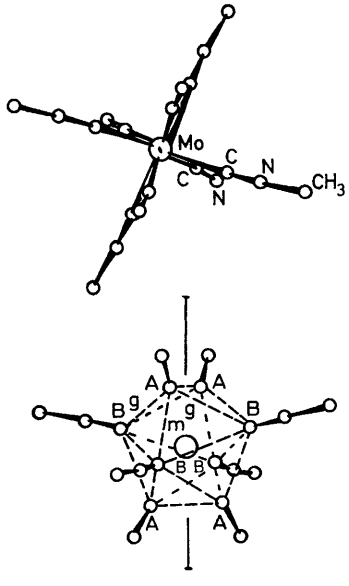

FIGURE. *The structure of* $Mo(CH_3NC)_4(CN)_4$. *Above* (010) *projection; below* (100) *projection.*

The molybdenum atom is surrounded by eight carbon atoms in a slightly distorted triangular dodecahedral configuration Each molecule has a two-fold crystallographic axis, as compared with the ideal $\bar{4}2m$ symmetry The average values of the structural angular shape parameters[3] θ_A and θ_B are 35 4° and 75 4°, these values are typical for dodecahedral coordination The distortions from ideal symmetry are in general small The angle between the least-squares planes through the two AABB carbon trapezoids is 2° different from the ideal 90° angle, the r m s distance of the carbon atoms from these planes is 0 10 Å The average distances in the dodecahedron are AA 2 52, AB (type *m*) 2 45, AB (type *g*) 2 72, and BB 3 12 Å Except for the two independent BB distances, individual values are within 0 05 Å of their appropriate means There is a small twist of the upper half of the molecule relative to the lower half, associated in part with the two unequal BB distances of 2 98 and 3 26 Å The various small distortions may be due to intermolecular forces

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