Crystal and molecular structure of (2,2'-bipyridine)
pyridine tricarbonyl molybdenum (III)

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Abstract
The crystal and molecular structure of (2,2'-bipyridine) pyridine tricarbonyl molybdenum (III), [(C₁₀H₈N₂)(C₅H₆N)(CO)₃Mo], has been determined from three-dimensional data collected photographically. The space group is Pnam; the unit cell has the dimensions \(a = 14.755 \pm 1\) Å, \(b = 8.344 \pm 1\) Å, \(c = 13.733 \pm 1\) Å (at 20°C) and contains four molecules. The structure has been refined to a residual (R) of 0.073 using least-squares methods on 1394 independent non-zero reflexions.

The molecule has been found to be octahedral in arrangement, with bipyridine and pyridine forming one triangle and the three carbonyl groups forming the opposite triangle of the octahedron. The best fit plane through the pyridine and lower carbonyl groups make an angle of 78° with the equatorial plane. There is evidence of significant distortion from the ideal octahedral angles of 90°.

Within the molecule, no interatomic distance or bond angle departs significantly from accepted values.

Introduction
Recently, much interest has been taken in 2,2'-bipyridyl derivatives of Group VI carbonyls (Hull & Stiddard, 1966; Stiddard, 1962). These have been examined by both chemical and spectroscopic methods, but very little examination by X-ray methods has been made.

This work was extended to a study of carbonyl -allyl complexes of Group VI elements (Hull & Stiddard, 1967). Some of these structures, however, have been analysed using X-ray methods (Oberhausli & Dahl, 1965; Levdik & Porai-Koshits, 1962; Smith, 1965; Davies et al., 1967; Graham & Fenn, 1969). The stereochemical arrangement of ligands about the molybdenum atom in this present complex is therefore of interest, because it belongs to the first group mentioned above, and secondly it is the starting point for the preparation of complexes in the second group.

Experimental
Crystals of (2,2'-bipyridine) pyridine tricarbonyl molybdenum (III) [(C₁₀H₈N₂)(C₅H₆N)(CO)₃Mo], were donated by Dr M. Stiddard. Oscillation and Weissenberg photographs showed the spacegroup to be Pna2₁ or Pnam (aëb setting of Pnma No. 62) with principal axial lengths:

\[
a = 14.755 \pm 1 \text{ Å} \\
b = 8.344 \pm 1 \text{ Å} \\
c = 13.733 \pm 1 \text{ Å (at 20°C)} \\
V = 1690.75 \text{ Å}^3 \\
FW = 416.26
\]
The accurate cell parameters were obtained from Weissenberg photographs, using gold wire (0.25 mm diameter and 99.998% purity) as a calibrating standard (Powell, 1969). The constants used were:

- Cell constant for gold = 4.078504 Å at 25°C (Weyerer, 1956)
- Copper radiation wavelengths: $\lambda_{\text{Cu}} = 1.54051$ Å, $\lambda_{\text{Cu}} = 1.54433$ Å, $\lambda_{\text{Cu}} = 1.54178$ Å, $\lambda_{\text{Cu}} = 1.39217$ Å
- Coefficient of refraction $\beta = 1.86 \times 10^{-4}$ Å
- Coefficient of expansion $\alpha = 14.1 \times 10^{-6}$ deg$^{-1}$

The density of the crystals determined using the method of flotation was 1.61 ± 0.02 g cm$^{-3}$. This compares with a calculated value of 1.631 g cm$^{-3}$ (Z = 4). The linear absorption coefficient for CuKα radiation is 67 cm$^{-1}$.

1394 independent non-zero reflexions were collected from a small unshaped crystal (size about 0.03 × 0.01 × 0.002 cm). Intensities were measured by visual estimation from zero and upper layer equi-inclination Weissenberg photographs taken about [010]. They represent about 72% of the copper sphere. The raw data were corrected for Lorentz and polarization factors and spot distortion (Phillips, 1954). No absorption corrections were applied, and it was estimated that the maximum effect on the intensities was of the order of 4%. The data were placed on the same overall absolute scale using a computer program written by Powell (1969b). This program utilizes the Wilson method (1942), but assumes a parabolic rather than a linear relationship between $\ln(I/ZF^2)$ and $(\sin 2\theta)/\lambda^2$.

Initially, individual layers of data are statistically analysed and each brought to the same scale as the zero layer. A least squares best fit parabola is then deduced and the data brought to the same overall absolute scale. The best fit straight line is used to give a mean isotropic temperature factor.

The computer programs used in this investigation were those forming the Crystallographic program system Crystal '69, written for the ICL 4130 (Griffiths & Powell, 1969).

Structure determination and refinement

The centrosymmetric spacegroup (Pna2₁) was assumed, and subsequent work proved this to be correct. The heavy atom was thus positioned on the mirror plane (x, y, z), and the x and y coordinates were found from a three-dimensional Patterson synthesis.

Three-dimensional Fourier and difference syntheses yielded the coordinates of all light atoms, the difference syntheses also indicating heavy atom anisotropic thermal motion.

Refinement was carried out using a block diagonal least squares program which minimized the function $\Sigma(\omega \cdot \Delta^2) = 2[\omega (K F_o - F_c)^2]$. The weighting factor used was $\omega = 1$ for $|F_o| < FSTAR$, and $\omega = FSTAR/|F_o|$ for $|F_o| > FSTAR$, where $FSTAR \sim 4F_{\text{min}}$ (Hughes, 1941). A weighting scheme analysis of the mean $\Sigma(\omega \cdot \Delta^2)$ for different $|K F_c|$ ranges was examined from time to time, and the value of $FSTAR$ modified as necessary. All reflections for which $|F_o| > 3|F_c|$ were automatically excluded from the least squares calculation.

The scattering factors used for Mo(III) were those obtained from the Thomas–Fermi–Dirac statistical model (International Tables, Vol. III, p. 211).

Several cycles of isotropic refinement including layer scale factor refinement gave a residual of 0.11. Heavy atom anisotropic refinement was then carried out, certain restrictions being placed on the $b_{ij}$ values because of its special position. In the final stages of refinement, all atoms were given anisotropic thermal parameters. Hydrogen atoms were positioned using stereochemical considerations, but were not refined. Refinement was considered complete when the parameter shifts obtained were less than 0.1 times the corresponding estimated standard deviations. At this stage, the residual was 0.073 for the 1394 observed terms. The values of $FSTAR$ used in the last refinement cycle was 20.0. The number of reflexions with $|F_o| < FSTAR$ at this stage was 655, and 7 reflexions had $|F_o| > 3|F_c|$. A final three-dimensional difference synthesis showed no residual peaks in excess of ±0.5 eÅ$^{-3}$. 