

Crystal and Molecular Structure of Dicarbonylnitrosyl[hydrotris-(pyrazol-1-yl)borato]molybdenum, $\text{HB}(\text{C}_3\text{N}_2\text{H}_3)_3\text{Mo}(\text{CO})_2\text{NO}$

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The crystal structure of dicarbonylnitrosyl[hydrotris(pyrazol-1-yl)borato]molybdenum, $\text{HB}(\text{C}_3\text{N}_2\text{H}_3)_3\text{Mo}(\text{CO})_2\text{NO}$, has been determined from X-ray single crystal diffractometer data and refined to a final *R* factor of 4.7 % (1572 independent reflections). The material crystallizes in a unit cell $a=b=11.435(5)$, $c=8.054(4)$ Å of space group $P\bar{3}$, $Z=2$. Coordination of the molybdenum is roughly octahedral and that of the boron tetrahedral. The dicarbonyl, nitrosyl disorder has been described using a composite scattering factor.

The structures of a series of metal complexes with the tridentate pyrazolyl borate ligand have been reported. Two of these have involved coordination to molybdenum: $\text{HB}(\text{pz})_3(\text{C}_4\text{H}_7)(\text{CO})_2\text{Mo}$ ¹ and $\text{HB}(\text{pz})_3\text{Mo}(\text{CO})_2\text{NNC}_6\text{H}_5$ ² and three have involved tridentate coordination of a trispyrazolyl borate ligand to other metals: $[\text{HB}(\text{pz})_3]_2\text{Co}$ ³, $\text{HB}(\text{pz})_3(\text{COCH}_3)(\text{CO})_2\text{Fe}$ ⁴ and $\text{HB}(\text{pz})_3(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{CH}_3)\text{Pt}$ ⁵. In several of these materials a skewing of the planes of the pyrazolyl rings relative to the metal-boron axis has been noted. This skewing has been observed to take different forms. The structure determination of dicarbonylnitrosyl[hydrotris-(pyrazol-1-yl)borato]molybdenum was undertaken to provide a structure in which the geometry of the pyrazolyl ring system might be observed without the steric interference of other bulky coordination groups.

EXPERIMENTAL

Crystal data. $\text{HB}(\text{C}_3\text{N}_2\text{H}_3)_3\text{Mo}(\text{CO})_2\text{NO}$, $M=384.22$, trigonal, $P\bar{3}$, $a=b=11.435(5)$, $c=8.054(4)$ Å, $V=912.0(3)$ Å³, $D_m=1.55$ (by float-

ation), $Z=2$, $D_c=1.50$ g cm⁻³, no systematic absences, $\text{MoK}\alpha$ radiation, $\lambda=0.71069$ Å, $\mu(\text{MoK}\alpha)=8.066$ cm⁻¹.

Preliminary photography showed the material to crystallize in a trigonal space group with no systematic absences. The determination of $Z=2$ established that the molybdenum and boron atoms must lie on a line of three-fold symmetry with the two carbonyls and one nitrosyl disordered. A crystal needle-like in shape and of approximate size $0.20 \times 0.20 \times 0.30$ mm³ was mounted on a Picker automated four circle diffractometer. Cell parameters were determined by least squares refinement of the angular positions of 12 independent reflections measured during alignment procedures.

3664 Bragg positions were measured with $\text{MoK}\alpha$ radiation using a 1.66° 2θ -scan at a speed of 1° min⁻¹ with backgrounds counted for 10 s at each extreme of the scan range. Three standard reflections were measured after every 50 reflections and their intensities were constant to within 5 % over the whole data measurement period. Of the data, 1557 were classed as non-zero [$|F_o|/\sigma|F_o| > 1.5$]. Corrections for Lorentz and polarization factors were made in the usual manner.

Of the possible trigonal space groups in accord with $Z=2$ and the lack of systematic absences, $P\bar{3}$ was chosen. Solution and refinement proceeded without difficulty.⁶ Examination of the Harker line $2/3, 1/3, w$ for the special position $1/3, 2/3, z$ allowed assignment of the z coordinate for the heavy atom. Three cycles of refinement of this coordinate ($R=27.9\%$) and a subsequent difference Fourier allowed location of the other eight unique non-hydrogen atoms. Anomalous dispersion corrections were made for molybdenum. Three cycles of least squares refinement of the positional and isotropic thermal parameters for all nine atoms gave an agreement factor of 11.4 %. Because a difference Fourier showed the presence of thermal motion, the isotropic temperature

factors were converted to their anisotropic equivalents and were refined for three cycles. The anisotropic thermal parameters for molybdenum and boron were constrained by the relationships $B_{11} = B_{33} = 2B_{12}$, $B_{23} = B_{13} = 0$.

Until this point the nitrosyl dicarbonyl disorder was approximated by one full occupancy carbon and one full occupancy oxygen. Because the parameters are so closely correlated, refinement using one nitrogen at one-third occupancy and one carbon at two-thirds occupancy was not successful. Final refinement was carried out designating the disordered position as CN and using for that atom a weighted averaged form factor (the carbon scattering factor plus one-third of the difference between carbon and nitrogen scattering at each $\sin \theta/\lambda$). In as much as the difference between a nitrosyl NO bond and a carbonyl CO bond is 0.03 Å, the oxygen was refined as a single and full occupancy atom.

In the final cycles of refinement a weighting scheme was introduced to reduce the weight of the high-intensity observations. Unit weights were retained for reflections $|F_o| < 15.0$ and weights of $(15.0/|F_o|)^2$ were applied to those of greater intensity. At the conclusion of the analysis, the values of $\sum(|F_o| - |F_c|)^2$ for the reflections grouped in 20 sets of increasing $|F_o|$ did not differ by more than a factor of 2.0.

The final *R* factor was 4.7%. The maximum ratio of the shift of a parameter to its corresponding estimated standard deviation was 0.003. A final difference Fourier map showed no peak greater than 0.3 e Å⁻³. No attempt was made to locate the hydrogen atoms.

DISCUSSION OF THE STRUCTURE

Fig. 1 shows the structure in projection on the *ac* plane from the positional parameters of Table 1. Table 2 gives the anisotropic temperature factors and Table 3 the pertinent bond lengths and angles. Standard deviations were calculated from the least squares matrix. Lists of observed and calculated structure factors may be obtained from the authors on request.

Coordination of the boron is roughly tetrahedral. Coordination to molybdenum is close to octahedral as evidenced by bond angles

Table 1. Positional parameters, with estimated standard deviations in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mo	0.3333	0.6666	0.21881(6)
O	0.1153(5)	0.4445(5)	-0.0026(6)
N1	0.2108(3)	0.6732(3)	0.5629(4)
N2	0.1876(3)	0.6696(3)	0.3972(4)
CN	0.1948(4)	0.5278(5)	0.0812(5)
C1	0.1129(4)	0.6817(4)	0.6457(6)
C2	0.0240(4)	0.6833(4)	0.5311(7)
C3	0.0734(4)	0.6744(4)	0.3777(6)
B	0.3333	0.6666	0.6309(8)

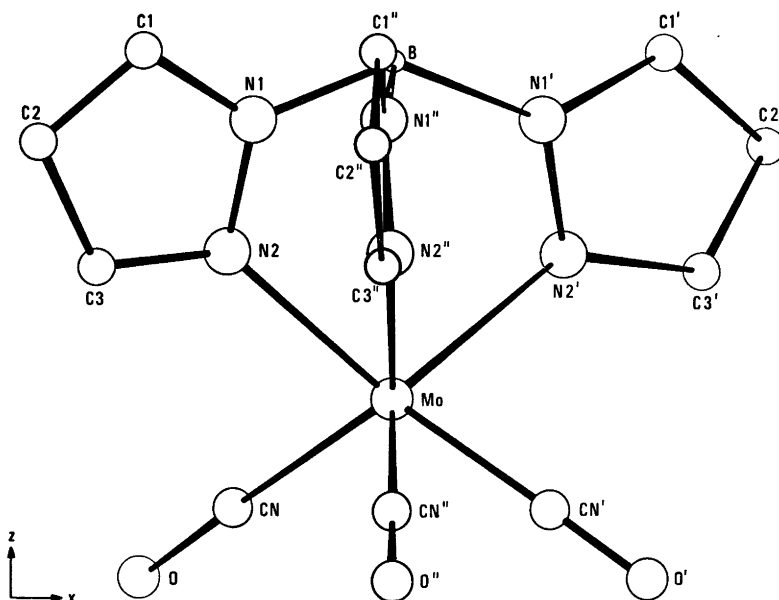


Fig. 1. The molecular conformation as viewed down the *b* axis.

Table 2. Thermal parameters. $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ with estimated standard deviations in parentheses.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.00663(7)	0.00663	0.0657(7)	0.00331	0.0	0.0
O	0.0133(5)	0.0154(6)	0.0157(7)	0.0022(4)	-0.0041(5)	-0.0057(5)
N1	0.0055(2)	0.0059(2)	0.0081(4)	0.0027(2)	-0.0007(2)	-0.0002(2)
N2	0.0055(2)	0.0063(3)	0.0083(4)	0.0032(2)	0.0010(2)	-0.0007(2)
CN	0.0100(4)	0.0110(5)	0.0084(5)	0.0050(4)	-0.0005(4)	-0.0007(4)
C1	0.0061(3)	0.0075(4)	0.0136(6)	0.0032(3)	0.0026(4)	-0.0002(4)
C2	0.0049(3)	0.0078(4)	0.0193(9)	0.0030(3)	0.0010(4)	-0.0008(4)
C3	0.0051(3)	0.0067(3)	0.0158(7)	0.0028(3)	-0.0021(4)	-0.0010(4)
B	0.0066(5)	0.0066	0.0065(7)	0.0033	0.0	0.0

near to 90° at molybdenum. The bond lengths and angles in this structure are consistent with those in other structures of molybdenum pyrazolyl borates.

A calculation of the planarity of the pyrazolyl ring by least squares planes shows the ring to be planar (max. dev. 0.004 Å) with the molybdenum atom 0.113 Å on one side of the plane and the boron atom 0.021 Å on the other side of the plane. Thus the tridentate pyrazolyl borate ligand observed in a situation free of the steric effects of other bulky ligands still

Table 3. Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses.

Mo-N2	2.213(4)
N2-N1	1.357(4)
N1-B	1.546(4)
N2-C3	1.344(6)
C3-C2	1.383(7)
C2-C1	1.380(7)
C1-N1	1.347(6)
Mo-N1	1.930(4)
CN-O	1.150(6)
CN-Mo-CN'	90.45(30)
CN-Mo-N2	94.02(33)
N2-Mo-N2'	82.42(33)
Mo-N2-N1	120.11(34)
N2-N1-B	121.05(36)
C3-N2-N1	107.04(35)
N2-N1-C1	109.39(36)
N1-C1-C2	108.32(41)
C1-C2-C3	105.40(44)
C2-C3-N2	109.83(41)
C3-N2-Mo	132.81(40)
C1-N1-B	129.55(37)
O-CN-Mo	177.88(35)
N1-B-N1'	107.81(28)

shows a skewing of the rings relative to the molybdenum-boron axis.

It may be noted that whereas the two other molybdenum complexes with a tris pyrazolyl borate ligand tend to show this type of skewing of the pyrazole planes relative to the molybdenum-boron axis, two of the tris pyrazolyl borate complexes with other metals show a skewing of the plane of the coordinated ring such that the metal and the boron lie on the same side of the plane of the ring. In $\text{HB}(\text{pz})_3(\text{C}_4\text{H}_7)(\text{CO})_2\text{Mo}^1$ two of the three rings show this twisted skewing [Ring A, max. dev. of ring members from plane (max. dev.) 0.001 Å, Mo 0.010 Å, B -0.078 Å; Ring B, max. dev. 0.006 Å, Mo -0.039 Å, B 0.176 Å] while the third ring (max. dev. 0.011 Å, Mo -0.193 Å, B -0.098 Å) has both coordinated atoms on the same side of the plane. Calculations performed on the position parameters for $\text{HB}(\text{pz})_3\text{Mo}(\text{CO})_2\text{NNC}_6\text{H}_5^2$ show this same pattern. Ring A, max. dev. 0.004 Å, Mo -0.050 Å, B 0.016 Å; Ring B max. dev. 0.006 Å, Mo -0.006 Å, B -0.014 Å and ring C max. dev. 0.005 Å, Mo 0.103 Å, B 0.002 Å.

In contrast the tris pyrazolyl borate complexes with other metals seem to show a flapping type of skewing. The structure of $[\text{HB}(\text{pz})_3]_2\text{Co}^3$ shows the cobalt atom to be 0.042-0.227 Å from the plane of the pyrazolyl rings and the boron atom to be 0.022-0.180 Å from that plane on the same side of the ring. (Deviation of ring members from plane 0.001-0.013 Å). Calculations of planes performed on data published for $\text{HB}(\text{pz})_3(\text{COCH}_3)(\text{CO})_2\text{Fe}^4$ show a similar situation: Ring 1, max. dev. 0.002 Å, Fe 0.129 Å, B 0.087 Å; Ring 2, max. dev.

0.015 Å, Fe 0.090 Å, B 0.008 Å; and Ring 3, max. dev. 0.002 Å, Fe 0.043 Å, B 0.095 Å. In a third non-molybdenum structure, the structure of $\text{HB}(\text{pz})_3(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{CH}_3)_2\text{Pt}$,⁵ the choice of space group has forced one of the pyrazolyl rings to lie on a mirror plane with the platinum and boron. The other two rings are related by the mirror plane. Thus it does not seem valid to look at the skewing of the rings in this structure.

The single crystal structure of $\text{HB}(\text{C}_3\text{N}_2\text{H}_3)_3\text{-Mo}(\text{CO})_2\text{NO}$ is consistent with the other published structures of molybdenum pyrazolyl borates in showing a twisted skewing of the pyrazolyl rings relative to the molybdenum-boron axis as opposed to the flapping type of skewing observed in structures of the ligand coordinated to other metals.

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