Crystal and Molecular Structure of Dicarbonyl-π-cyclopentadienyl[tetrakis(pyrazol-1-yl)borato]molybdenum

By **Elizabeth M. Holt** * and **Smith L. Holt**, Chemistry Department, University of Wyoming, Laramie, Wyoming 82070, U.S.A.

The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray diffraction data measured by counter techniques. Crystals are monoclinic, space group *C*2/*c* with $Z = 8$ in a unit cell of dimensions $a = 37{\cdot}06(7)$, $b = 8{\cdot}747(10)$, $c = 12{\cdot}961(16)$ Å and $\beta = 93° 45(7)'$. Solved from Patterson and Fourier syntheses, the structure was refined by full-matrix least-squares methods to R 9·2% for 1926 non-zero independent reflections. The tetrakis-(1-pyrazolyl)borate group acts as a bidentate ligand *via* co-ordination through one nitrogen atom from each of two pyrazolyl rings while the remainder of the molybdenum co-ordination sphere consists of two σ-bonded CO groups and the π-bonded C_5H_5 group.

TROFIMENKO has reported the syntheses and physical properties of more than 40 molybdenum–pyrazolylborate complexes.[1-5] Several of these [6-8] have recently been subjected to *X*-ray structural investigation with an eye to elucidating for each the conformation of the pyrazolylborate ligand, the mode of ligand co-ordination and the molecular geometry.

---

[1] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675.

[2] S. Trofimenko, *J. Amer. Chem. Soc.*, 1968, **90**, 4754.

[3] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 588.

[4] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 3183.

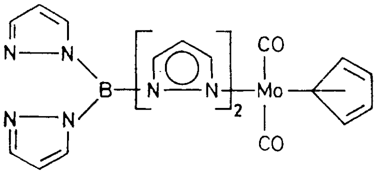
[5] S. Trofimenko, *Inorg. Chem.*, 1970, **9**, 2493.

[6] C. Kosky, P. Ganis, and G. Avitabile, *Acta Cryst.*, 1971, **B27**, 1958.

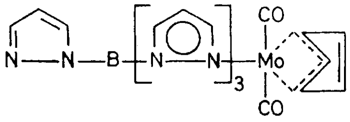
[7] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725.

[8] E. M. Holt, F. Cavallito, S. L. Holt, and K. J. Watson, unpublished data.

The structure analysis of the compound reported here was undertaken to provide information about the conformation of the tetrakis-(1-pyrazolyl)borate ligand and to ascertain whether or not $[(C_3N_2H_3)_4B](C_5H_5)Mo(CO)_2$ possesses the structure suggested by Trofimenko,[3] with the tetrakis-(1-pyrazolyl)borate group serving as a bidentate ligand as in (I), rather than a terdentate ligand as in (II).



(I)



(II)

While this manuscript was in preparation, a report of a structure determination of this material appeared for which 889 data were used. The present investigation provides evidence that the previous assignment[9] of two of the atoms adjacent to one of the nitrogen atoms co-ordinated to boron was incorrect.

EXPERIMENTAL

Crystal Data.—$C_{19}H_{17}BMoN_8O_2$, $M = 494{\cdot}9$, Monoclinic, $a = 37{\cdot}06(7)$, $b = 8{\cdot}747(10)$, $c = 12{\cdot}961(16)$ Å, $\beta = 93° 45(7)'$, $U = 4192{\cdot}2$ Å^3, $D_m = 1{\cdot}591(1)$ (by flotation), $Z = 8$, $D_c = 1{\cdot}57$. Space group $C2/c$ from systematic absences: hkl $h + k = 2n$, $h0l$ $l = 2n$ $(h = 2n)$, and $0k0$ $k = 2n$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 7·22 cm^{-1}.

Preliminary unit-cell and space group data were obtained from Weissenberg photographs. A rectangular platelet of dimensions 0·3 × 0·2 × 0·04 mm was mounted on a Picker four-circle automated diffractometer. Zirconium-filtered Mo-K_α radiation was used for data collection. During the alignment procedure, unit-cell dimensions were determined by least-squares fit of the angular positions of twelve independent reflections. All independent reflections to sin $\theta_{max.}$ 0·42 were sampled by use of the θ—2θ scan procedure, the 2θ scan being over a range of 1·66° at 1° min^{-1}. Background measurements were made for 10 s each on either side of the calculated peak-angle. Two standard reflections were measured after every hundred reflections. The net counts of these standards were constant to within 5% over the whole data measurement period. The intensities of 2739 lattice points were measured of which 1926 reflections had $|F_o|/\sigma(|F_o|) > 1{\cdot}5$ and were considered observed. Corrections for Lorentz and polarization effects, but not for absorption, were applied.

Determination of the Structure and Refinement.—Successive difference-Fourier, full-matrix least-squares cycles based upon the contributions from increasing numbers of postulated atoms led to the determination of all non-hydrogen atom positions (atomic scattering factors were taken from ref. 10 with the real part of the anomalous scattering contribution for molybdenum included). Individual atomic temperature factors were converted to their anisotropic equivalents, and were refined with the other parameters by full-matrix least-squares cycles, to R 0·092. The maximum ratio of the shift of a parameter to its corresponding estimated standard deviation was 0·03 so refinement was terminated. No attempt was made to locate hydrogen atom positions. A final difference-Fourier map showed no peak $> 0{\cdot}4$ eÅ^{-3}. Unit weights for all reflections were used throughout, this choice being justified by the fact that, at the conclusion of the analysis, the values of $\langle\Sigma(|F_o| - |F_c|)^2\rangle$ for 20 sets of reflections grouped in increasing $|F_o|$ did not differ by more than a factor of 1·9.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20739 (3 pp., 1 microfiche).*

The results of the other investigation[9] were seen to differ from those of the analysis described here in the assignment of carbon and nitrogen to the atoms adjacent to one of the nitrogen atoms co-ordinated to boron. The ambiguity was resolved by observing the effect upon the isotropic thermal parameters of the structure by use of the data of this present analysis but with the atom assignment published, when these were refined by least-squares methods. Table 1 shows the results. The temperature factors of C(19) and N(8) increased and decreased to 'unreasonable' values, when postulated as being first nitrogen and then carbon atoms. Furthermore, this was exactly the same effect as when a corresponding interchange was made with C(16) and N(6), analogous atoms on the other pyrazolyl ring bound only to boron. These tests show that the assignment made in this analysis is correct.

TABLE 1

Effect of atom assignment on temperature factors

Present work		Ref. 9		Test, present work	
Atom	B/Å^2	Atom	B/Å^2	Atom	B/Å^2
C(19)	3·9	'N(19)'	6·1	C(19)	3·9
N(8)	4·5	'C(8)'	2·6	N(8)	4·6
C(16)	5·4	C(16)	5·2	'N(16)'	8·2
N(6)	5·3	N(6)	5·4	'C(6)'	3·2

DISCUSSION OF THE STRUCTURE

The molecular conformation viewed from the crystallographic b axis is shown in the Figure. Final atomic co-ordinates are listed in Table 2, anisotropic thermal parameters in Table 3, and interatomic distances and angles in Tables 4 and 5.

The molybdenum atom is co-ordinated to two nitrogen atoms from the pyrazolylborate ligand, two carbonyl atoms and a penta*hapto*-cyclopentadienyl group. Co-ordination about the boron atom is roughly tetrahedral with the N–B–N angles ranging from 107—111°.

The cyclopentadienyl ring is planar and Mo–C(ring) distances are: C(9) 2·29(2), C(10) 2·39(2), C(11) 2·41(2), C(12) 2·32(2), and C(13) 2·26(2) Å. The difference

---

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

[9] J. L. Calderon, F. A. Cotton, A. Shaver, *J. Organometallic Chem.*, 1972, **37**, 127.

[10] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

TABLE 2

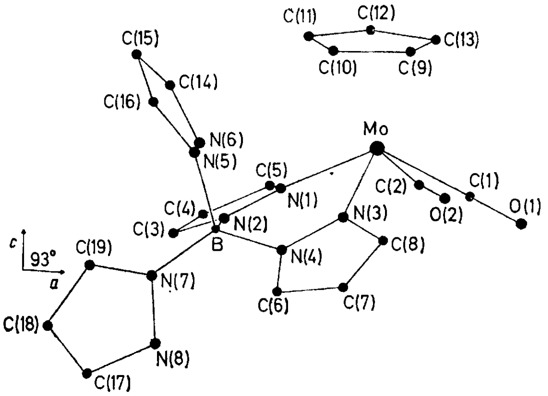
Positional parameters, with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Mo	0·1798(0)	0·4542(3)	0·2163(2)
O(1)	0·2540(4)	0·4006(22)	0·1210(13)
O(2)	0·2146(5)	0·7626(23)	0·1518(20)
N(1)	0·1304(4)	0·5548(24)	0·1466(12)
N(2)	0·1010(4)	0·4915(16)	0·0979(12)
N(3)	0·1618(5)	0·2644(21)	0·1132(14)
N(4)	0·1306(5)	0·2442(21)	0·0569(13)
N(5)	0·0848(4)	0·2523(21)	0·1898(10)
N(6)	0·0891(5)	0·0983(22)	0·2026(14)
N(7)	0·0659(4)	0·2859(16)	0·0050(11)
N(8)	0·0684(5)	0·3383(26)	−0·0927(15)
C(1)	0·2271(7)	0·4146(47)	0·1575(19)
C(2)	0·2010(7)	0·6576(37)	0·1681(21)
C(3)	0·0752(5)	0·5956(24)	0·0697(17)
C(4)	0·0901(7)	0·7405(30)	0·1003(16)
C(5)	0·1242(5)	0·7123(23)	0·1490(13)
C(6)	0·1297(5)	0·1132(27)	−0·0043(17)
C(7)	0·1632(7)	0·0568(33)	0·0093(14)
C(8)	0·1832(6)	0·1535(31)	0·0841(18)
C(9)	0·1940(6)	0·3061(33)	0·3592(18)
C(10)	0·1555(7)	0·2942(34)	0·3509(18)
C(11)	0·1433(6)	0·4456(46)	0·3691(18)
C(12)	0·1741(8)	0·5535(42)	0·3866(17)
C(13)	0·2080(6)	0·4537(43)	0·3785(15)
C(14)	0·0720(7)	0·0564(35)	0·2833(20)
C(15)	0·0552(7)	0·1911(38)	0·3240(18)
C(16)	0·0643(6)	0·3301(30)	0·2566(19)
C(17)	0·0347(8)	0·2986(39)	−0·1418(25)
C(18)	0·0130(8)	0·2024(41)	−0·0787(23)
C(19)	0·0333(6)	0·2198(35)	0·0157(19)
B	0·0970(5)	0·3168(27)	0·0801(19)

TABLE 3

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

Atom	$10^5\beta_{11}$	$10^4\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^4\beta_{23}$
Mo	54(1)	106(2)	405(8)	−6(4)	12(2)	−4(1)
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
O(1)	5(1)	341(31)	120(14)	−5(4)	12(3)	−33(17)
O(2)	7(1)	199(25)	184(21)	−18(5)	1(4)	70(20)
N(1)	4(1)	94(19)	58(10)	−1(4)	−1(3)	6(13)
N(2)	4(1)	72(15)	52(8)	−3(3)	2(2)	−10(9)
N(3)	7(1)	104(22)	54(11)	1(4)	−1(3)	−2(14)
N(4)	5(1)	125(23)	51(9)	−4(4)	2(3)	−26(14)
N(5)	50(1)	124(21)	44(7)	−3(4)	6(2)	−1(11)
N(6)	14(2)	102(27)	74(14)	−9(6)	−1(4)	16(16)
N(7)	7(1)	132(19)	42(10)	−1(4)	−3(3)	−18(11)
N(8)	12(2)	5(58)	47(13)	−16(9)	8(4)	52(23)
C(1)	6(2)	180(101)	65(14)	8(10)	6(4)	15(31)
C(2)	6(2)	183(47)	89(15)	−15(7)	−4(4)	22(23)
C(3)	3(1)	62(17)	88(15)	3(4)	1(3)	−9(13)
C(4)	9(2)	167(39)	72(11)	−9(7)	5(4)	38(18)
C(5)	4(1)	112(29)	70(9)	4(4)	−3(2)	7(13)
C(6)	6(1)	102(26)	92(15)	−1(5)	7(4)	−37(18)
C(7)	9(3)	142(33)	91(12)	2(8)	5(4)	−32(19)
C(8)	10(2)	132(41)	96(14)	14(8)	5(4)	−52(21)
C(9)	7(1)	193(34)	42(13)	−1(5)	1(3)	27(17)
C(10)	7(2)	225(35)	53(12)	2(6)	3(4)	59(17)
C(11)	7(2)	225(45)	52(12)	9(8)	3(3)	−1(22)
C(12)	8(2)	281(49)	49(14)	−4(9)	3(4)	−11(24)
C(13)	7(2)	236(41)	45(10)	−3(7)	−2(3)	13(20)
C(14)	17(3)	238(49)	74(18)	−31(10)	−1(6)	30(27)
C(15)	15(3)	359(56)	44(20)	−49(12)	7(6)	24(29)
C(16)	11(2)	275(49)	43(17)	−21(9)	9(5)	−52(25)
C(17)	1(3)	101(68)	60(38)	−33(12)	2(9)	40(43)
C(18)	10(3)	121(78)	123(19)	−28(12)	11(6)	53(33)
C(19)	3(2)	324(103)	103(26)	−13(11)	−1(6)	2(44)
B	3(1)	8(19)	65(16)	1(4)	1(4)	20(16)



FIGURE

TABLE 4

Bond distances (Å) with estimated standard deviations in parentheses

Mo–C(1)	1·96(2)	C(7)–C(6)	1·34(3)
Mo–C(2)	1·99(2)	B–N(2)	1·58(2)
Mo–N(3)	2·23(2)	B–N(4)	1·51(2)
Mo–N(1)	2·22(1)	B–N(5)	1·52(2)
Mo–C(9)	2·29(2)	B–N(7)	1·54(2)
Mo–C(12)	2·32(2)	N(5)–N(6)	1·36(2)
Mo–C(10)	2·39(2)	N(5)–C(16)	1·37(3)
Mo–C(11)	2·41(2)	N(6)–C(14)	1·32(3)
Mo–C(13)	2·26(2)	C(14)–C(15)	1·46(4)
Mo–B	3·63(2)	C(15)–C(16)	1·51(3)
C(2)–O(2)	1·12(2)	N(7)–N(8)	1·36(2)
C(1)–O(1)	1·13(2)	N(8)–C(19)	1·38(2)
N(2)–N(1)	1·34(2)	C(17)–C(18)	1·40(4)
N(1)–C(5)	1·35(2)	C(18)–C(19)	1·46(4)
N(2)–C(3)	1·35(2)	N(8)–C(17)	1·41(3)
C(4)–C(3)	1·38(3)	C(12)–C(13)	1·46(3)
C(5)–C(4)	1·37(2)	C(13)–C(9)	1·41(3)
N(3)–N(4)	1·34(2)	C(9)–C(10)	1·41(2)
N(3)–C(8)	1·32(2)	C(10)–C(11)	1·39(3)
N(4)–C(6)	1·36(2)	C(11)–C(12)	1·42(3)
C(8)–C(7)	1·44(3)		

TABLE 5

Bond angles (deg.) with estimated standard deviations in parentheses

C(2)–Mo–C(1)	71(1)	N(1)–N(2)–B	123(1)
C(1)–Mo–N(3)	81(1)	N(3)–N(4)–B	124(1)
C(2)–Mo–N(1)	80(1)	N(2)–B–N(4)	111(1)
N(1)–Mo–N(3)	83(1)	C(3)–N(2)–N(1)	110(1)
Mo–C(1)–O(1)	117(3)	C(6)–N(4)–N(3)	111(1)
Mo–C(2)–O(2)	175(2)	N(2)–B–N(7)	107(1)
C(13)–C(9)–C(10)	108(2)	N(2)–B–N(5)	110(1)
C(9)–C(10)–C(11)	110(2)	N(7)–B–N(4)	111(2)
C(10)–C(11)–C(12)	108(2)	N(7)–B–N(5)	109(1)
C(11)–C(12)–C(13)	107(2)	N(5)–B–N(4)	110(1)
C(12)–C(13)–C(9)	107(2)	N(6)–N(5)–B	118(1)
Mo–N(1)–N(2)	129(1)	N(8)–N(7)–B	123(2)
Mo–N(3)–N(4)	128(1)	C(16)–N(5)–B	127(2)
Mo–N(1)–C(5)	122(1)	C(19)–N(7)–B	126(2)
Mo–N(3)–C(8)	124(1)	N(7)–C(19)–C(18)	107(2)
N(2)–N(1)–C(5)	108(1)	N(5)–C(16)–C(15)	105(2)
N(4)–N(3)–C(8)	108(2)	N(7)–N(8)–C(17)	105(2)
N(1)–C(5)–C(4)	107(2)	N(5)–N(6)–C(14)	106(2)
N(3)–C(8)–C(7)	107(2)	C(17)–C(18)–C(19)	103(3)
N(2)–C(3)–C(4)	106(1)	C(14)–C(15)–C(16)	100(2)
N(4)–C(6)–C(7)	106(2)	C(19)–N(7)–N(8)	111(2)
C(5)–C(4)–C(3)	108(2)	C(16)–N(5)–N(6)	114(2)
C(8)–C(7)–C(6)	108(2)	N(6)–C(14)–C(15)	114(2)
C(3)–N(2)–B	126(1)	N(8)–C(17)–C(18)	112(3)
C(6)–N(4)–B	122(1)		

between the longest and shortest is thus 0·15 Å, the degree of tilt being somewhat greater than that in most documented cases of molybdenum–cyclopentadienyl bonding where the Mo–C distances for any one ring differ by <0·097 Å.[11-14] Each of the five members of the ring has non-bonded contact distances less than the sum of the van der Waals radii involved, *e.g.* C(1) · · · C(9) 3·07(2), N(3) · · · C(10) 3·19(2), N(1) · · · C(11) 3·08(2), C(2) · · · C(12) 3·04(3), C(1) · · · C(13) 2·98(2), and C(2) · · · C(13) 3·18(2) Å. However because C(10) and C(11) are relatively closer to the pyrazolylborate ligand, they have more close non-bonded contacts than the other three members of the ring. C(10), for example, is within 3·93(3) Å from C(1), C(8), C(14), N(4), N(1), N(5), N(6), C(16), and N(3). The tilt of the cyclopentadienyl ring thus represents minimization of the non-bonded contacts within the molecule.

The six-membered ring [Mo, B, N(1)—(4)] is roughly a boat shape with Mo and B in the raised end positions, however the nitrogen atoms are not coplanar, each being 0·18—0·21 Å from the plane formed by the other three.

The Mo–N distances are 2·23(2) and 2·22(1) Å, slightly longer as would be expected, than those found in $[HB(C_3N_2H_3)_3]_2Co$ [2·120(7)—2·140(7) Å].[15]

We thank the National Science Foundation for a grant.

[2/2330 *Received*, 12*th October*, 1972]

---

[11] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **37**, 809.

[12] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.

[13] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

[14] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1967, **6**, 1213.

[15] M. R. Churchill, K. Gold, and C. E. Maw, jun., *Inorg. Chem.*, 1970, **9**, 1597.