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Complexes of Polypyrazolylborate Ligands. IV.[1] Boron-Hydrogen-Molybdenum Bridge Bonding in the So-Called Sixteen Electron Complex [Dihydrobis-(3,5-dimethyl-1-pyrazolyl)borate]-(trihaptocycloheptatrienyl)dicarbonylmolybdenum in the Crystal[2]

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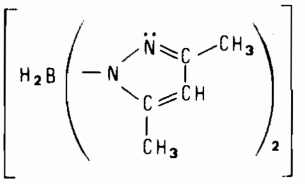
The crystal and molecular structure of [bis(3,5-dimethylpyrazolyl) dihydroborate] (h^3-cycloheptatrienyl) dicarbonylmolybdenum has been determined by single crystal X-ray diffraction methods. The asymmetric unit contains two molecules which are virtually mirror images of each other. The cycloheptatriene ring is found as a trihapto *species, and the pyrazolylborate ligand is bidentate. The MNNBNN ring has a pronounced boat conformation with one of the hydrogen atoms on the boron atom approaching the molybdenum atom closely, forming a B–H–Mo 3-center, 2-electron bond. The average H–B (terminal), B–H (bridge) and H–Mo distances in the two independent molecules are 1.05 Å, 1.26 Å, and 2.14 Å; each individual distance to a hydrogen atom has an esd of 0.06 Å and the members of each equivalent pair differ by less than this. The molybdenum atom achieves an effective 18-electron configuration when the two electrons of the B–H–Mo bond are counted. The puzzling stability of "16-electron" configurations is thus explained. The crystal data are: space group $P\bar{1}(C_i^1$, no. 2), $a = 10.354(4)$ Å, $b = 19.783(8)$ Å, $c = 10.318(5)$ Å, $\alpha = 96.83(2)^\circ$, $\beta = 86.93(2)^\circ$ and $\gamma = 107.16(1)^\circ$; the density (by flotation): 1.47 ± 01 g/cm^3; (calculated for $Z = 4$) 1.477 g/cm^3. The intensities of 4121 reflections collected with MoKα radiation on a counter diffractometer were used to solve and refine the structure. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods to final unweighted and weighted residuals, 0.044 and 0.059, respectively. When hydrogen atoms were included in the calculated structure factors, R_1 and R_2 were reduced to 0.032 and 0.045, respectively.*

Introduction

The polypyrazolylborate ligands and their complexes were discovered and first investigated by S. Trofimenko.[5] Among the more intriguing complexes prepared by Trofimenko is the one which is the subject of this report, [bis-(3,5-dimethylpyrazolyl)dihydroborate](h^3-cycloheptatrienyl)dicarbonylmolybdenum $[H_2B(3,5\text{-}Me_2pz)_2][h^3\text{–}C_7H_7)(CO)_2Mo$, where $H_2B(3,5\text{–}Me_2pz)_2$ represents the ligand, (1).



(1)

This complex is of unusual interest with respect to its dynamical behavior, several aspects of its structure and its electronic structure. A thorough structural and dynamical investigation of it was therefore undertaken in these Laboratories. As a necessary basis for dynamical studies the structure of the molecule as it occurs in the crystal was determined and the results are reported here. Studies of the dynamical behavior in solution are described elsewhere.[6]

With respect to molecular and electronic structure, the greatest interest centers around the related questions of whether this molecule truly has only a sixteen-electron configuration and what is the mode of attachment of the C_7H_7 ring to the metal. There is considerable precedent for M–(h^3–C_7H_7) bonding;[7-11] however, this would appear to connote a sixteen-electron configuration, since the H_2BPz_2, 2CO, h^3–C_7H_7 and Mo, each treated as a neutral entity, contribute 3, 4, 3, and 6 electrons, respectively. One obvious way to in-

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[1] (a) For Part III, See Ref. 6. (b) For a preliminary communication of this work, and that in Part III, see J.L. Calderon, F.A. Cotton, M. Jeremic, and A. Shaver, *Chem. Comm.*, 1972, 777.

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(4) Visiting Scholar, Committee on International Exchange of Persons (Fulbright-Hayes Program) 1969-1971.

(5a.) S. Trofimenko, *J. Amer. Chem. Soc.*, *88*, 1842 (1966).

(5b.) *Idem.*, *ibid.*, *89*, 3170 (1967).

(5c.) *Idem. ibid.*, *91*, 3183 (1967).

(5d.) *Idem.*, *Inorg. Chem.*, 9, 2493 (1970).

(5e.) *Idem.*, *Accounts Chem. Res.*, *4*, 17 (1971).

(6) J.L. Calderon, F.A. Cotton and A. Shaver, *J. Organometal. Chem.*, Submitted for publication.

(7) J.W. Faller, *Inorg. Chem.*, *8*, 767 (1969).

(8) D. Ciappenelli and M. Rosenblum, *J. Amer. Chem. Soc.*, *91*, 6876 (1969).

(9) M.A. Bennett, R. Bramley and R. Watt, *ibid.*, *91*, 3089 (1969).

(10) F.A. Cotton and C.R. Reich, *ibid.*, *91*, 847 (1969).

(11) F.A. Cotton B.G. DeBoer and M.D. LaPrade, Special Lectures XXIIIrd International Congress of Pure and Applied Chemistry, Boston, 1971, Volume 6, page 1.

crease the electron count to 18 is to assume that the cycloheptatrienyl ring is h^5–C_7H_7. While this form of bonding seems less likely, there is now at least one reasonably certain example of *pentahapto* cycloheptatrienyl group.[12]

It will be shown here that the Mo–(h^3–C_7H_7) portion of the structure is present, but that the molybdenum atom need not be considered to have a 16-elctron configuration since a B–H–Mo 2e–3c bond is also present.

Experimental Section

A sample of the compound prepared according to the method of Trofimenko[5] was kindly provided by Mr. J. L. Calderon.

Single crystals suitable for X-ray work were grown by controlled evaporation of solvent by passing a slow stream of dry nitrogen over the solution. The best crystals were obtained from a mixture of carbon disulfide and hexane in a ratio of 1:1 by volume. A single crystal, bounded by the 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, and $00\bar{1}$ faces, with approximate dimensions of 0.45×0.35×0.30 mm, was mounted on a glass fiber along the c* axis. Weissenberg (hk0, hkl) and precession (h0l, 0kl) photographs showed triclinic symmetry, implying space groups ($P1(C_1$, no. 1) or $P\bar{1}(C_i$, no. 2). Preliminary cell dimensions determined from these photographs were: a = 10.35 Å, b = 19.80 Å, c = 10.35 Å, α = 96.80°, β = 86.90°, and γ = 107.20°. The crystal was then transferred to a General Electric XRD-6 automatic diffractometer and aligned so that the c* axis was coincident with Φ.

Accurate cell constants were determined by careful centering of 32 strong reflections. Least squares refinement of these gave the following results: a = 10.354(4), b = 19.783(8), c = 10.318(5), α = 96.83(2)°, β = 86.93(2)°, and γ = 107.16(1)°. The observed density of 1.47±0.01 g/cm^3 obtained by the flotation method in aqueous potassium iodide solution, agrees well with the calculated value of 1.477 g/cm^3 for Z = 4. This implies that there are two molecules per asymmetric unit in space group $P\bar{1}$. A Delauney[13] reduction did not reveal any higher symmetry nor did an extensive search by X-ray methods.

Data were taken with MoKα radiation on the XRD-6 automated diffractometer with Datex control. A unique data set of 4998 reflections out to $\lambda^{-1}\sin\theta = 0.52$ ($2\theta = 45°$) was collected. A standard 2θ–θ scan technique was employed with the scan range extending from 0.66° below $2\theta(K\alpha_1)$ to 0.66° above $2\theta(K\alpha_2)$. The scan rate was 2°/min and stationary background counts of 20 sec were taken at each end of the scan. Instrument stability and decomposition were monitored by measuring a set of four reflections, widely separated in reciprocal space, after every 75 reflections.

The measured data were converted to observed structure factors (F_o) by means of DIFDAR, a data reduction program written by Dr. Alan Parkes. Standard deviations (in dekacounts) were assigned to the integrated net intensity measurements (I) according to the formula

$$\sigma(I) = [(CNT + k^2 \cdot B)/10.0 + 0.0001 I^2]^{1/2}$$

where CNT is the intensity measured during the scan, B is the sum of the two background measurements ($B_1+B_2+0.90$), k is a correction factor for variable scan width, and I is equal to CNT–k · B+0.45. The quantities 0.45 and 0.90 arise because the scalar readings are in dekacounts; they represent, respectively, the expectation value and twice the expectation value of counts between 0.1 and 0.9 dekacounts which are not actually recorded. A reflection was considered to be observed and subsequently used in the refinement if $I/\sigma(I) \geq 2.0$. A total of 4121 reflections were accepted as non-zero. No systematic change in the intensities of the standard reflections was observed. They fluctuated by ±2% randomly.

Solution and Refinement

A three-dimensional Patterson[14] function was computed and solved for the Mo atoms in space group $P\bar{1}$. Two cycles of least-squares refinement with two molybdenum atoms assigned isotropic temperature factors gave for the residuals $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ values of 0.39 and 0.40, respectively. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weights, w, were the reciprocals of $\sigma^2(|F_o|)$. The scattering factors employed were those for neutral Mo (and subsequently for neutral O, N, C, and B) given by Cromer and Waber.[15] An anomalous dispersion correction was applied using the values of $\Delta f'$ and $\Delta f''$ of Comer.[16] A three-dimensional electron density difference map was now calculated and 17 atoms were located. Two cycles of least-squares refinement gave R_1 = 0.28 and R_2 = 0.29. A second electron density difference map revealed all molybdenum atoms. Four more cycles of least-squares refinement lowered the residuals to R_1 = 0.060 and R_2 = 0.075. Five more cycles of least-squares refinement in which all atoms were given anisotropic temperature factors converged to R_1 = 0.044 and R_2 = 0.059. Anisotropic refinement was done by a block diagonal program in order to reduce computing costs. Finally one cycle of full-matrix least-squares was performed to check the refinement No parameter shifted more than one-third of its standard deviation and residuals remained the same.

A difference electron density map was now computed, and peaks assignable to all 46 hydrogen atoms were found. The largest peaks not assignable to hydrogen atoms were found near the molybdenum atom. The peaks had maxima of 0.25e/Å^3 and 0.24e/Å^3, compared with a maximum of 0.26e/Å^3 for the lowest peak assigned to a hydrogen atom. The posi-

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(12) T.H. Whitesides and R.A. Budnick, *Chem. Comm.*, *1971*, 1514.

(13) B. Delaunay, Z. *Krist.*, *84*, 109 (1933).

(14) Computer programs used in this work were: PICK2, J.A. Ibers, cell constants refinement and diffractometer settings; DIFDAR, A. Parkes, data reduction; FORDAP, A. Zalkin, Fourier synthesis; SFLS5 (local version), C.T. Prewitt, full matrix least squares refinement; REFINE, Jung Ja Kim block diagonal least squares refinement; STANI, B.G. DeBoer, distances, angles and e.s.d.'s; ORTEP, C.K. Johnson, thermal ellipsoid drawings; PUBTAB, R.C. Elder, structure factor tables.

(15) D.T. Cromer and J.T. Waber, *Acta Crystallogr.*, *18*, 104 (1965).

(16) D.T. Cromer, *ibid.*, *18*, 17 (1965).

tional parameters of hydrogen atoms as obtained from the difference map are recorded in Table Va. A structure factor calculation in which the hydrogen contributions were included, and each was assigned an isotropic temperature parameter equal to 1.10 times that for the carbon atom to which it is attached, was carried out. The residuals were $R_1 = 0.032$ and $R_2 = 0.045$.

Since an examination of the structure revealed that the positions of the four hydrogen atoms attached to the boron atoms were of exceptional importance, refinement of these four hydrogen atoms was carried out in the following way. Three cycles of full-matrix refinement were run. The parameters varied in each run were the following: (1) All non-hydrogen atoms and the two hydrogen atoms of interest in molecule 1 of the asymmetric unit. (2) All non-hydrogen atoms and the two hydrogen atoms of interest in the second molecule constituting the asymmetric unit. In these two cycles the non-hydrogen atoms were assigned anisotropic temperature parameters, while the two hydrogen atoms were refined isotropically. (3) Only the four hydrogen atoms of interest were refined, using isotropic temperature factors. The changes which

Table I. Final Positional Parameters [a].

Atom	x	y	z
1Mo	0.73129(4)	0.88449(3)	0.21414(5)
2Mo	0.81236(5)	0.32415(3)	0.17949(5)
1O1	0.6591(5)	0.0217(2)	0.3260(5)
1O2	0.4213(4)	0.8420(3)	0.1636(5)
2O1	0.0878(5)	0.4063(3)	0.3016(5)
2O2	0.7523(6)	0.3041(3)	0.4746(5)
1N1	0.6780(4)	0.8290(3)	0.3879(5)
1N2	0.7322(5)	0.7723(3)	0.3765(5)
1N3	0.9402(5)	0.8982(3)	0.2860(5)
1N4	0.9550(5)	0.8312(3)	0.2791(5)
2N1	0.7035(5)	0.4028(3)	0.2286(5)
2N2	0.5929(5)	0.3876(3)	0.1491(5)
2N3	0.8249(5)	0.3664(3)	—0.0127(5)
2N4	0.6973(6)	0.3500(3)	—0.0600(5)
1C1	0.6922(6)	0.9716(4)	0.2839(6)
1C2	0.5372(6)	0.8567(4)	0.1794(6)
1C3	0.5998(6)	0.8255(4)	0.4975(6)
1C4	0.5247(7)	0.8764(4)	0.5383(7)
1C5	0.6046(7)	0.7651(4)	0.5572(6)
1C6	0.6883(7)	0.7335(4)	0.4770(7)
1C7	0.7268(8)	0.6669(4)	0.4906(8)
1C8	0.0813(7)	0.8357(4)	0.3166(6)
1C9	0.1263(8)	0.7701(4)	0.3190(8)
1C10	0.1505(7)	0.9075(4)	0.3476(7)
1C11	0.0575(6)	0.9443(4)	0.3265(6)
1C12	0.0790(7)	0.0239(4)	0.3481(7)
1C13	0.8601(6)	0.9743(4)	0.0818(6)
1C14	0.8340(6)	0.9026(4)	0.0229(6)
1C15	0.6993(6)	0.8619(4)	—0.0159(6)
1C16	0.6060(6)	0.8887(4)	—0.0845(7)
1C17	0.6088(7)	0.9564(5)	—0.0970(7)
1C18	0.8034(7)	0.0278(4)	0.0460(6)
1C19	0.7014(8)	0.0217(4)	—0.0342(7)
2C1	0.9858(7)	0.3753(4)	0.2522(6)
2C2	0.7729(7)	0.3083(4)	0.3623(7)
2C3	0.6976(7)	0.4575(4)	0.3166(7)
2C4	0.8027(9)	0.4874(4)	0.4209(7)
2C5	0.5834(7)	0.4782(4)	0.2950(7)
2C6	0.5207(6)	0.4318(4)	0.1893(7)
2C7	0.3922(8)	0.4292(5)	0.1175(9)
2C8	0.7019(8)	0.3737(4)	—0.1780(7)
2C9	0.5760(9)	0.3623(5)	—0.2563(8)
2C10	0.8346(8)	0.4063(4)	—0.2097(7)
2C11	0.9106(7)	0.4006(3)	—0.1036(6)
2C12	0.0601(7)	0.4271(4)	—0.0839(8)
2C13	0.9633(7)	0.2636(4)	0.0585(7)
2C14	0.8316(7)	0.2219(3)	0.0784(6)
2C15	0.7820(7)	0.2035(3)	0.2071(7)
2C16	0.8569(7)	0.1849(4)	0.3083(6)
2C17	0.9925(8)	0.1943(3)	0.3130(7)
2C18	0.0872(7)	0.2620(4)	0.1194(7)
2C19	0.0995(7)	0.2306(4)	0.2247(7)
1B	0.8261(8)	0.7706(4)	0.2554(7)
2B	0.5835(9)	0.3245(4)	0.0418(8)

[a] Estimated standard deviations occurring in the last significant figure are given in parentheses.

Table II. Anisotropic Temperature Parameters [a,b] ($\times 10^4$).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
1Mo	58.8(6)	18.0(2)	69.0(6)	13.4(3)	0.1(4)	2.3(3)
2Mo	76.4(6)	18.0(2)	67.8(6)	13.1(3)	—12.0(4)	1.3(3)
1O1	167(7)	25(2)	143(7)	36(3)	31(6)	0(3)
1O2	74(6)	51(3)	141(7)	11(3)	—4(5)	16(3)
2O1	113(7)	36(2)	147(7)	139(1)	—48(5)	—17(3)
2O2	214(9)	55(3)	104(7)	63(4)	11(6)	12(3)
1N1	74(6)	22(2)	79(6)	15(3)	—6(5)	4(3)
1N2	90(7)	20(2)	87(6)	16(3)	—4(5)	10(3)
1N3	70(6)	21(2)	85(6)	18(3)	—6(5)	0(3)
1N4	74(6)	24(2)	88(6)	23(3)	—6(5)	3(3)
2N1	97(7)	23(2)	77(6)	19(3)	—6(5)	2(2)
2N2	73(6)	23(2)	113(7)	16(3)	—6(5)	5(3)
2N3	76(6)	22(2)	81(6)	9(3)	—22(5)	0(3)
2N4	112(7)	22(2)	73(6)	17(3)	—20(5)	3(3)
1C1	84(8)	29(3)	74(8)	14(4)	7(6)	8(3)
1C2	70(8)	28(3)	78(8)	14(4)	—4(6)	0(3)
1C3	73(8)	31(3)	73(7)	11(4)	—6(6)	3(4)
1C4	108(9)	36(3)	112(9)	32(4)	20(7)	7(4)
1C5	88(8)	33(3)	81(8)	15(4)	—5(6)	10(3)
1C6	91(9)	24(2)	101(8)	7(4)	—41(7)	7(4)
1C7	182(12)	23(3)	134(10)	27(5)	—11(9)	11(4)
1C8	89(8)	34(3)	71(7)	24(4)	—2(6)	8(3)
1C9	119(10)	42(3)	129(10)	46(5)	—13(8)	14(4)
1C10	92(9)	37(3)	92(9)	20(4)	—6(7)	11(4)
1C11	80(8)	27(3)	69(7)	15(4)	—3(6)	3(3)
1C12	109(10)	25(3)	127(10)	4(4)	—6(8)	—2(4)
1C13	74(8)	23(2)	84(8)	8(3)	13(7)	8(3)
1C14	82(8)	21(2)	73(7)	15(3)	10(6)	0(3)
1C15	85(9)	30(3)	57(7)	13(4)	5(6)	0(3)
1C16	84(8)	37(3)	89(8)	14(4)	—9(6)	4(4)
1C17	115(10)	50(4)	82(8)	37(5)	2(7)	19(4)
1C18	97(8)	24(3)	89(8)	19(4)	25(6)	10(3)
1C19	129(10)	32(3)	95(9)	31(4)	21(7)	16(4)
2C1	107(9)	25(3)	79(8)	20(4)	—12(7)	—3(4)
2C2	117(10)	28(3)	84(8)	31(4)	0(7)	3(4)
2C3	125(10)	27(3)	89(8)	24(4)	3(7)	10(4)
2C4	186(10)	40(3)	97(8)	38(4)	—49(7)	—23(4)
2C5	113(10)	31(3)	132(10)	27(4)	0(8)	7(4)
2C6	70(8)	29(3)	142(10)	14(4)	—9(7)	12(4)
2C7	91(10)	45(4)	230(14)	28(5)	—47(10)	—3(6)
2C8	150(9)	29(3)	86(8)	34(4)	—40(7)	3(3)
2C9	190(9)	55(3)	127(10)	46(4)	—29(8)	—3(4)
2C10	152(11)	31(3)	87(8)	30(5)	—13(8)	5(4)
2C11	116(11)	19(3)	87(8)	18(4)	—5(8)	4(3)
2C12	95(14)	29(4)	141(10)	6(6)	—3(9)	12(5)
2C13	119(10)	28(3)	85(8)	26(4)	6(7)	0(4)
2C14	126(9)	17(2)	85(8)	20(4)	—20(7)	—5(3)
2C15	123(10)	16(2)	117(9)	12(4)	—20(7)	0(4)
2C16	124(10)	22(3)	102(8)	24(4)	—33(7)	—3(4)
2C17	184(12)	22(3)	92(8)	38(4)	—26(8)	—10(4)
2C18	128(10)	32(3)	98(9)	33(4)	—14(7)	—17(4)
2C19	113(10)	34(3)	112(9)	35(4)	—29(7)	—18(4)
1B	90(10)	24(3)	73(8)	17(4)	—4(7)	2(4)
2B	112(11)	23(3)	109(10)	14(5)	—27(8)	1(4)

[a] Estimated standard deviations occurring in the least significant figure appear in parentheses. [b] Anisotropic temperature factors are defined as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + hkl\beta_{23})]$.

occurred in positional parameters of non-hydrogen atoms in the first two cycles were negligible. In the third cycle, the parameters of the 4 hydrogen atoms changed by less than their esd's.

The refined positions of the four hydrogen atoms are listed in part B of Table V. The distances previously reported[1b] for bonds to these hydrogen atoms were based on the unrefined positional parameters in Part A of Table V.

Table III. Interatomic Distances[a] (Å).

Atoms	Molecule 1	Molecule 2
Mo-N1	2.173(5)	2.175(5)
Mo-N3	2.233(5)	2.222(5)
Mo-C1	1.933(7)	1.925(7)
Mo-C2	1.961(6)	1.951(7)
Mo-C13	2.405(6)	2.444(7)
Mo-C14	2.207(6)	2.221(6)
Mo-C15	2.385(6)	2.364(6)
C1-O1	1.171(8)	1.162(8)
C2-O2	1.162(8)	1.175(9)
N1-N2	1.384(7)	1.380(7)
N1-C3	1.354(8)	1.341(8)
N3-N4	1.371(7)	1.368(8)
N3-C11	1.340(8)	1.356(8)
N2-C6	1.343(8)	1.330(8)
N4-C8	1.358(8)	1.348(8)
C3-C4	1.499(10)	1.512(10)
C3-C5	1.421(9)	1.398(10)
C6-C7	1.508(10)	1.540(11)
C6-C5	1.392(9)	1.392(9)
C8-C9	1.508(10)	1.516(11)
C8-C10	1.396(10)	1.375(10)
C11-C10	1.406(9)	1.415(10)
C11-C12	1.515(9)	1.498(10)
B-N2	1.545(9)	1.552(10)
B-N4	1.518(9)	1.545(10)
C14-C13	1.428(8)	1.399(10)
C14-C15	1.440(9)	1.445(9)
C16-C15	1.476(9)	1.474(10)
C16-C17	1.353(11)	1.364(10)
C18-C13	1.444(9)	1.468(10)
C18-C19	1.345(9)	1.343(10)
C17-C19	1.464(10)	1.466(10)
Nonbonded Contacts		
Mo-C16	3.426(7)	3.550(8)
Mo-C18	3.374(7)	3.418(7)

[a] Estimated standard deviations occurring in the least significant figure appear in parentheses. All intermolecular contacts are greater than 3.30 Å.

Results

The fractional coordinates and anisotropic thermal parameters of all non-hydrogen atoms are given in Tables I and II, respectively. The structures of the two molecules in the asymmetric unit are depicted in Figure 1 together with the numbering scheme. This figure shows a projection of molecule 1 on the xy plane rotated 10° clockwise about the z axis. The two molecules are thus not shown in the relationship they have in the crystal; there was no way in which a pair could be viewed which did not entail serious overlapping of atoms in one or the other of the molecules. Table III and IV contain interatomic distances and bond angles involving non-hydrogen atoms. The position of hydrogen atoms found on the difference Fourier map are given in Table V. Table VI defines some mean planes and gives the dihedral angles between them. Table VII contains observed and calculated structure factors in units of 0.1 electrons. Figures 2 and 3 show the conformation of the chelate ring and the coordination around the molybdenum atom. Figure 4 shows details of the B-H-Mo bridge bonding.

Table IV. Bond Angles[a] (Degrees).

Atoms	Molecule 1	Molecule 2
N1-Mo-N3	80.5(2)	80.4(2)
N1-Mo-C1	97.8(3)	100.3(3)
N1-Mo-C2	87.1(3)	82.4(3)
N1-Mo-C13	156.7(2)	158.6(2)
N1-Mo-C14	153.3(2)	152.4(3)
N1-Mo-C15	139.4(2)	137.7(3)
N3-Mo-C1	103.9(2)	102.3(3)
N3-Mo-C2	167.2(2)	162.8(3)
N3-Mo-C13	80.5(2)	79.4(2)
N3-Mo-C14	84.6(2)	89.6(3)
N3-Mo-C15	117.2(2)	124.6(2)
C1-Mo-C2	80.7(3)	80.5(3)
C1-Mo-C13	74.0(3)	77.4(3)
C1-Mo-C14	107.3(3)	106.9(3)
C1-Mo-C15	111.2(3)	105.6(3)
C13-Mo-C14	35.8(2)	34.2(3)
C13-Mo-C15	62.6(2)	61.8(3)
C14-Mo-C15	36.3(2)	36.6(3)
C2-Mo-C13	112.3(2)	117.6(3)
C2-Mo-C14	105.6(3)	105.9(3)
C2-Mo-C15	70.9(2)	69.7(3)
Mo-C1-O1	175.2(6)	177.0(6)
Mo-C2-O2	177.1(6)	175.3(6)
Mo-N1-N2	109.4(4)	109.8(4)
N2-N1-C3	107.8(5)	107.4(5)
Mo-N3-N4	106.4(4)	108.7(4)
N4-N3-C11	107.2(5)	106.7(5)
N1-N2-B	113.2(4)	114.2(5)
N1-N2-C6	109.7(4)	108.9(6)
N3-N4-B	115.3(4)	114.1(5)
N3-N4-C8	109.7(5)	110.2(5)
N2-B-N4	108.1(5)	107.3(6)
N1-C3-C5	108.1(6)	109.6(6)
N1-C3-C4	122.7(6)	121.6(6)
C3-C5-C6	106.1(6)	104.8(6)
N2-C6-C7	122.4(6)	121.1(6)
N2-C6-C5	108.3(6)	109.4(6)
N4-C8-C9	121.4(6)	122.4(7)
N4-C8-C10	108.0(6)	108.5(6)
C8-C10-C11	105.0(6)	105.6(6)
N3-C11-C10	110.0(6)	109.0(6)
N3-C11-C12	122.5(6)	121.5(6)
C14-C13-C18	127.0(6)	128.3(6)
C13-C14-C15	120.4(6)	121.1(6)
C14-C15-C16	125.1(6)	126.9(6)
C15-C16-C17	129.8(7)	128.0(6)
C16-C17-C19	127.1(7)	128.3(7)
C13-C18-C19	130.1(6)	128.6(7)
C17-C19-C18	127.9(7)	128.3(7)

[a] Estimated standard deviations occurring in the least significant figure appear in parentheses.

Discussion

The molecular structure lacks any element of symmetry and the crystallographic asymmetric unit consists of two molecules which are virtually, although not crystallographically, enantiomorphous. These are illustrated in Figure 1. As can be seen in Table III, there are no chemically significant differences between corresponding dimensions of the two molecules.

The most important result of this investigation is the discovery that although the molecule contains a Mo–(h^3–C_7H_7) moiety, it should not be considered a 16-electron complex. The BNNMoNN chelate ring is bent into a severe boat configuration which allows one of the hydrogen atoms on the boron atom to approach the molybdenum atom very closely. The B-H-Mo group can be regarded as a hydrogen-bridged 2e-3c bonding arrangement.

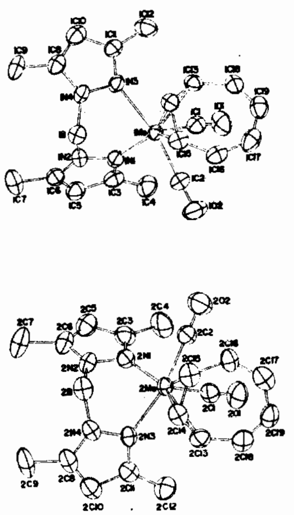

Figure 1. Projections of the two virtually enantiomorphous molecules constituting the crystallographic asymmetric unit. Each molecule is shown in a projection which best shows all the atoms, and the numbering scheme is defined. Prefactory numbers, 1 and 2, identify the molecules; corresponding atoms in the enantiomorphs have otherwise identical numbers. The juxtaposition of the two molecules in the figure does *not* correspond to their packing in the crystal.

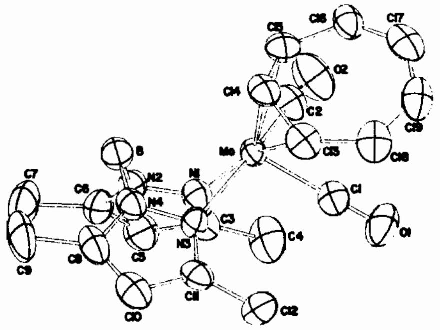

Figure 2. A projection of one molecule chosen particularly to show the tub configuration of the chelate ring.

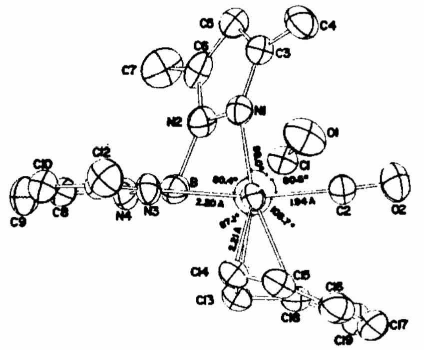

Figure 3. A projection of one molecule chosen particularly to show the roughly square pyramidal arrangement of ligands around the molybdenum atom.

Table V. A. Unrefined Positional Parameters for Hydrogen Atoms [a,b]

Atom	x	y	z
1H4	0.521	0.114	0.533
1H4	0.423	0.092	0.449
1H4	0.515	0.117	0.376
1H5	0.452	0.239	0.376
1H7	0.685	0.652	0.538
1H7	0.810	0.655	0.507
1H7	0.750	0.656	0.417
1H9	0.165	0.810	0.342
1H9	0.056	0.731	0.361
1H9	0.097	0.740	0.217
1H10	0.237	0.929	0.384
1H12	0.142	0.038	0.433
1H12	0.981	0.027	0.351
1H12	0.148	0.031	0.276
1HB	0.847	0.723	0.230
1HB	0.755	0.779	0.164
1H13	0.962	1.006	0.127
1H14	0.895	0.878	0.015
1H15	0.314	0.202	0.039
1H16	0.438	0.130	0.132
1H17	0.459	0.041	0.151
1H18	0.858	0.083	0.096
1H19	0.303	0.931	0.055
2H4	0.801	0.449	0.443
2H4	0.754	0.499	0.515
2H4	0.847	0.516	0.403
2H5	0.569	0.523	0.362
2H7	0.362	0.482	0.142
2H7	0.384	0.408	0.026
2H7	0.325	0.416	0.212
2H9	0.432	0.685	0.260
2H9	0.418	0.662	0.358
2H9	0.510	0.625	0.173
2H10	0.130	0.566	0.270
2H12	0.902	0.606	0.134
2H12	0.904	0.546	0.095
2H12	0.908	0.558	0.003
2HB	0.486	0.312	0.000
2HB	0.618	0.280	0.097
2H13	0.985	0.278	−0.019
2H14	0.775	0.222	0.018
2H15	0.690	0.177	0.218
2H16	0.797	0.161	0.379
2H17	0.022	0.179	0.374
2H18	0.165	0.278	0.083
2H19	0.174	0.231	0.249

B. Refined Positional and Temperature Parameters of Hydrogen Atoms Attached to Boron Atoms [a]

Atom	x	y	z	B
1HB	0.84(4)	0.73(4)	0.24(4)	1.6(9)
1HB	0.77(6)	0.79(6)	0.17(6)	1.9(1.4)
2HB	0.49(6)	0.31(6)	0.01(6)	1.6(1.3)
2HB	0.62(5)	0.28(5)	0.10(5)	1.4(1.1)

[a] Numbers for hydrogen atoms are derived from those of the atoms to which they are bound. [b] The grid of the difference Fourier map was 0.030 for the x and z axes and 0.015 for the y axis.

The Dipyrazolylborate-Molybdenum Chelate Ring. This is only the second such structural unit to be

Table VI. Angles Between Planes and Distances of Atoms from Planes[a].

A. C_7H_7 Ring

1. Ring Planes Calculated
   plane A: C13-C14-C15
   plane B: C13-C15-C16-C18
   plane C: C16-C17-C18-C19

2. Dihedral Angles, Degrees
   φ(A, B): 146.4°
   φ(B, C): 174.7°

3. Displacements, in Angstroms, from Mean Planes

Atoms	Plane A	B	C
C13	0.0	—0.022	—0.165
C14	0.0	—0.395	—0.575
C15	0.0	0.022	—0.092
C16	—0.836	—0.017	0.002
C17	—1.488	—0.111	—0.005
C18	—0.742	0.018	—0.002
C19	—1.429	—0.081	0.005

B. BN_4Mo Chelate Ring

1. Ring Planes Calculated
   plane D: N1-Mo-N3
   plane E: N2-B-N4
   plane F: N1-N2-N3-N4

2. Dihedral Angles, Degrees
   φ(D, F): 121.3
   φ(E, F): 120.9
   φ(D, E): 62.7

3. Displacements, in Angstroms, from Mean Plane

Atom	Plane D	E	F
Mo	0.0	—2.669	—1.437
N(1)	0.0	—1.203	—0.025
N(2)	—1.136	0.0	0.029
N(3)	0.0	—1.134	0.025
N(4)	—1.183	0.0	—0.029
B	—1.959	0.0	—0.771

C. Basal Plane of « Square Pyramid »

1. Plane defined by N1-N3-C2-C14

2. Displacements, in Angstroms:

N1	—0.18	C1	2.15
N3	0.17	C13	1.26
C2	0.16	C15	—0.66
C14	—0.15	N2	—1.39
Mo	0.27	N4	—1.12
		B	—1.93

[a] Calculated using Molecule 1.

studied by X-ray crystallography, the other being the one in $[B(pz)_4](h^5\text{–}C_5H_5)(CO)_2Mo$.[17] Again, as had been anticipated, the ring has a tub conformation. This is most clearly seen in Figure 2, where the chelate ring is viewed nearly edge on. Such a conformation is, in part, imposed by the required coplanarity of each set of B-N-N-Mo bonds. However, as shown in Table VIB, the folding of the ring in this case is quite pronounced, with both dihedral angles being approximately 121°. The reason for this severe folding of the ring will be discussed below.

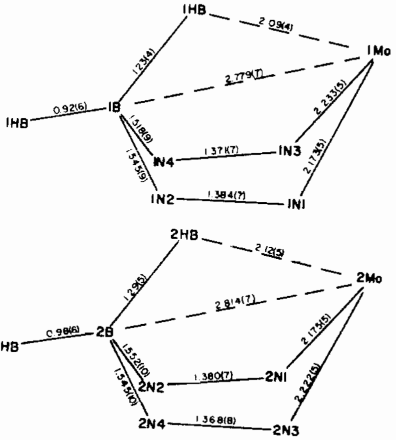

Figure 4. Diagrams showing the dimensions of the H-B-H-Mo portions of the two crystallographically independent (virtually enantiomorphous) molecules.

The Mo-N distances range from 2.173 to 2.222Å, with a mean value of 2.196 Å. This agrees well with the values of 2.18 and 2.23Å found in $[B(pz)_4](h^5\text{–}C_5H_5)(CO)_2Mo$[17] and with the three Mo-N distances for the tridentate tripyrazolylborate ligand in $[HB(pz)_3](CO)_2(N_2C_6H_5)Mo$,[18] namely, 2.21, 2.21 and 2.23 Å. Within the limits of the uncertainties, corresponding N-N, C-N, C-C and B-N distances are the same in all three molecules.

Trihaptocycloheptatrienyl Ring. This is only the second reported structure of an $(h^3\text{–}C_7H_7)$–M group, the previous one being that in $(h^5\text{–}C_5H_5)(CO)_2(h^3\text{–}C_7H_7)Mo$.[11] Corresponding C-C and Mo-C bond distances in the two cases usually differ by less than the sum of their esd's and the ring conformations are almost identical. The dihedral angles between the plane of the bound allylic set of three carbon atoms and the plane of the central four carbon atoms are 144° in the previous case and 146° in the present one. The C_7H_7 rings are fluxional in both molecules. The structure parameters for a fluxional $(h^3\text{–}C_7H_7)Mo$ group would thus seem to be relatively invariant and to be now well established.

Coordination of the Molybdenum Atom. It is of particular interest to examine closely the coordination about the molybdenum atom, since we are dealing here with the case of a purported 16-electron configuration. The coordination sphere (considering for the moment only the non-hydrogen atoms) has a rather irregular arrangement, but it can be approximately described as a square pyramid with C(1)–O(1) occupying the axial position. The angles from the Mo-C(1) bond to the basal bonds are: 107° to Mo–C(14), 103° to Mo–N(3), 98° to Mo–N(1) and 81° to Mo–C(2). In the basal plane the four angles range from

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[17] J.L. Calderon, F.A. Cotton and A. Shaver, *J. Organometal. Chem.*, *37*, 127 (1972).

[18] G. Avitabile, P. Ganis, and M. Nemeroff, *Acta Crystallogr. B27*, 725 (1971).

Table VII. Observed and Calculated Structure Factors in Units of 0.1 Electrons

** H=-8 **

K	L	FOBS	FCAL
2	3	[illegible]	312
2	4	315	[illegible]
2	5	497	496
2	7	317	293
3	0	221	235
3	0	221	239
3	[illegible]	223	226
3	1	223	226
3	[illegible]	162	145
3	3	167	145
3	6	127	87
4	[illegible]	568	612
4	1	568	612
4	2	340	316
4	[illegible]	340	316
4	3	239	236
4	3	239	236
4	4	561	594
4	6	331	331
4	7	265	253
5	[illegible]	90	88
5	[illegible]	90	88
5	4	171	195
5	5	112	124
5	6	270	256
5	7	211	215
6	0	745	741
6	0	745	741
6	1	441	448
6	[illegible]	441	448
6	2	469	462
6	[illegible]	469	462
6	3	524	530
6	3	524	530

** H=-6 **

K	L	FOBS	FCAL
1	5	564	660
1	5	664	660
1	6	220	227
1	6	[illegible]	227
1	7	206	176
1	8	104	116
2	0	264	239
2	1	138	117
2	2	546	565
2	3	176	175
2	4	174	173
2	5	479	463
2	6	136	111
2	6	136	111
2	7	274	248
2	9	194	186
2	[illegible]	[illegible]	242
3	0	581	539
3	1	298	294
3	2	667	698
3	4	577	521
3	6	261	247
3	6	241	247
3	7	198	216
4	0	295	286
4	1	350	379
4	2	314	332
4	3	564	558
4	4	595	576
4	5	119	137
4	5	119	137
4	6	694	687
4	6	604	687
4	7	176	171

Table VII. (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -11*				2	1	594	610	-5	2	387	367
4	0	469	[illegible]	2	2	164	163	-5	3	204	209
5	0	457	249	2	3	341	335	-5	4	728	725
5	1	163	145	2	4	399	375	-5	5	390	373
7	1	256	377	2	4	399	375	-5	5	390	373
8	0	440	234	2	5	276	276	-5	6	161	162
9	0	412	[illegible]	2	5	268	278	-5	6	161	162
H = -10*				2	6	470	456	-5	7	301	288
-3	1	205	213	2	7	234	219	-5	8	116	137
-2	2	254	255	2	8	279	[illegible]	-5	9	184	229
-1	1	299	207	3	0	525	528	-4	1	810	798
-1	2	253	250	3	1	102	177	-4	2	653	678
-1	3	116	110	3	2	288	298	-4	3	264	265
0	1	345	347	3	3	243	237	-4	4	201	205
0	2	407	277	3	5	100	95	-4	6	114	92
0	3	318	331	3	5	100	95	-4	6	114	92
1	0	150	135	3	6	115	96	-4	7	109	93
1	1	164	163	3	7	185	183	-4	8	139	153
1	2	407	202	4	0	728	740	-3	1	870	864
2	0	442	444	4	1	336	330	-3	2	398	406
2	1	437	227	4	2	503	497	-3	3	468	484
2	2	270	289	4	3	496	487	-3	4	428	424
2	3	392	391	4	5	172	171	-3	5	274	292
2	4	173	173	4	7	282	287	-3	6	462	449
3	1	427	107	4	8	281	260	-3	6	462	449
3	3	106	91	5	1	268	263	-3	8	256	260
3	4	154	149	5	2	86	84	-3	9	255	249
4	0	467	107	5	4	164	181	-2	2	115	130
4	1	309	351	5	4	164	181	-2	3	157	148
4	2	407	402	5	7	177	168	-2	4	114	95
4	4	307	306	5	8	219	217	-1	1	353	345
5	1	272	269	6	1	375	371	-1	2	839	854
5	2	150	146	6	2	445	456	-1	3	690	676
5	4	274	256	6	3	239	222	-1	4	175	178
6	0	376	387	6	4	691	681	-1	5	561	660

80° to 106°. As shown in Table VIC the four atoms, C(2), N(1), N(3) and C(14) only roughly define a plane; two of them lie above the mean plane by 0.16 Å and two lie below it by 0.16 Å. The molybdenum atom lies 0.266 Å above the mean plane. Part of the difficulty with trying to fit this set of ligands to some simple description of coordination geometry is that the h^3–C_7H_7 group cannot truly be considered as a single ligand in the ordinary sense; it is only a crude approximation to assign it a position in the coordination shell represented simply by the location of the center atom, C(14), of the bound allylic moiety. Such difficulties notwithstanding, the concept of roughly square pyramidal coordination by the non-hydrogen atoms provides a good starting point for consideration of the electron configuration. The metal-ligand bonding which has been discussed up to this point accounts for only 16 electrons in the valence orbitals of the molybdenum atom.

Hydrogen Bridge Bonding. In Figure 4 the arrangements of the BH_2...Mo portions of each of the two crystallographically independent (enantiomorphic) molecules are depicted. The esd's of individual B-H and Mo-H distances are all 0.06Å. However, each of the three pairs of corresponding distances in the two molecules agree to within less than this amount, which substantially enhances our confidence in the validity of this part of the molecular structure. These dimensions lead us to conclude that the molecule contains a B-H-Mo two-electron, three center (2e-3c) bridge bond. There is considerable precedent for B-H-M bonds, where M is a transition metal, in complexes of BH_4^-[19,20] and $B_3H_8^-$[21,22].

The B-H-Mo bond is the additional factor stabilizing the boat form of the chelate ring and is presumably the cause of the severe bending of the ring that occurs in this case; conversely, of course, it is the severe bending which enables the B-H bond to approach the molybdenum atom closely enough for the three-center bond to form.

This structure provides a satisfactory, though unanticipated, explanation for the remarkable stability of this and other purported 16-electron complexes. The molecule we have examined, and presumably the others which have been so described, are not in fact 16-electron complexes. The central atom (Mo) achieves an effective 18-electron configuration by virtue of its share in the electron pair occupying the bonding orbital spread over the three-cented system B-H-Mo.

While this work was being prepared for publication, a paper leading to essentially the same conclusion appeared.[23] Kosky, Ganis and Avitabile determined the structure of $[H_2B(Me_2\text{–}pz)_2]Mo(CO)_2C_3H_5$. Here the organoligand is the three-electron donor *trihapto*allyl. In this case also, a very severely bent boat configuration is found for the chelate ring and the B to Mo distance is essentially the same as the one we have found. In this case the positions of the hydrogen atoms on the boron atom were not determined with very high accuracy (the precision is not explicitly stated) and the pronounced difference between the lengths of terminal and bridging B-H distances is not resolved. However, there seems little if any doubt that in this case the same type of bridging arrangment we have characterized more accurately is also present.

Acknowledgement. We would like to thank Victor W. Day for his interest and assistance in the solution of this structure.

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