Journal of Organometallic Chemistry, 226 (1982) 57—62
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAETHYLAMMONIUM HYDROTRIS(3,5-DIMETHYLPYRAZOLYL)BORATOTRICARBONYLMOLYBDENUM(0), $[NEt_4][Mo(CO)_3HB(C_5H_7N_2)_3]$

C.P. MARABELLA and J.H. ENEMARK *
Department of Chemistry, University of Arizona, Tucson, Arizona 85721 (U.S.A.)

(Received June 5th, 1981; in revised form September 3rd, 1981)

Summary

The crystal and molecular structure of tetraethylammonium hydrotris(3,5-dimethylpyrazolyl)boratotricarbonylmolybdenum(0), $[N(C_2H_5)_4][Mo(CO)_3$-$HB(3,5\text{-}Me_2pz)_3]$ has been determined from intensity data collected using counter methods. The salt crystallizes in space group $Pna2_1$ with parameters $a = 18.038(6)$, $b = 9.956(3)$, $c = 16.881(3)$ Å, $V = 3031.4(20)$ Å^3, $Z = 4$, $d_{calc} = 1.33$ g/ml and $d_{obs} = 1.33$ g/ml. Final convergence yielded a conventional $R = 0.042$ and a "goodness of fit" of 2.07. The steric pocket formed by the 3-methyl hydrogens of the pyrazolyl moiety is discussed.

Introduction

Following the initial report of Trofimenko [1] concerning the preparation of polypyrazolylborates, a rich and extensive transition metal chemistry of these ligands quickly emerged [2,3]. More recently, McCleverty and coworkers [4] have used the hydrotris(3,5-dimethylpyrazolyl)borate [hereafter designated $HB(Me_2pz)_3^-$] to stabilize a variety of Mo^{II} complexes containing alkoxide, hydrazido, amido and nitrosyl groups. We have shown that the $HB(Me_2pz)_3^-$ ligand stabilizes oxomolybdenum(V) complexes [5]. The relative stability of these compounds is attributed to the steric bulk of the 3-methyl substituent on the pyrazolyl ligand. The structures of several low-symmetry Mo^{II} complexes of the $HB(Me_2pz)_3^-$ ligand have been determined. However, the structure of the parent $[Mo(CO)_3HB(Me_2pz)_3]^-$ anion, which is the starting material for a variety of derivatives, has not been previously reported.

0022—328X/82/0000—0000/$02.75

Experimental

The title compound was prepared following the procedure of Trofimenko [6]. Recrystallization in CH_3CN yielded large, yellow prismatic crystals suitable for single crystal X-ray analysis.

The data crystal was mounted on a glass fiber and transferred to a Syntex $P2_1$ four circle autodiffractometer. Initial omega scans indicated a satisfactory mosaicity of less than 0.25° width at half height, and unit cell parameters were determined from 25 random, centered peaks [7] with a 2θ range of 5.0—25.0°. During the three days of data collection the intensities of the three standard check reflections showed no significant fluctuations. Additional crystallographic details are given in Table 1.

Solution and description of structure

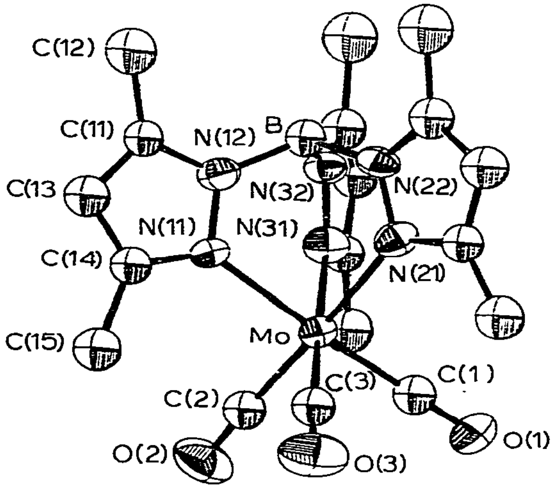
Data reduction was handled as described earlier [8] and the molybdenum atom was located applying the standard Patterson method. Non-hydrogen atoms were located in successive difference Fourier maps and standard computational programs were used throughout the solution [9]. The distribution of intensities suggested that the correct space group was $Pna2_1$. This was confirmed by successful refinement of the structure. The absolute stereochemistry of the crystal could not be determined from the unique octant of data because no significant difference was observed in R or R_w for the two possible enantiomers. Several methyl hydrogen atoms on both the anion and cation were located

TABLE 1

$[N(Et)_4][Mo(CO)_3HB(3,5\text{-}Me_2pz)_3]$: CRYSTALLOGRAPHIC INFORMATION [a]

	$[N(C_2H_5)_4][Mo(CO)_3HB(C_5H_7N)_3]$
F.W.	607.50
Color	yellow
Radiation	Mo-K_α
d_{calc} (g/ml)	1.33
d_{obs} (g/ml)	1.33
Cell dimensions:	
a (Å)	18.038(6)
b (Å)	9.956(3)
c (Å)	16.881(3)
V (Å^3)	3031.4(20)
Z (molecules/unit cell)	4
Space group	$Pna2_1$
Data collection mode	$2\theta : \theta$
Scan rate (min, max)	3.0, 29.3
Background/scan time	0.5
μ (cm^{-1})	4.67
Abs. correction	empirical
NO($I > 3\sigma(I)$)/NV	2406/207
p	0.04
R_{final}	0.042
R_w final	0.056
GOF	2.07

[a] NO, NV, p, R, R_w and GOF are defined in reference 8.



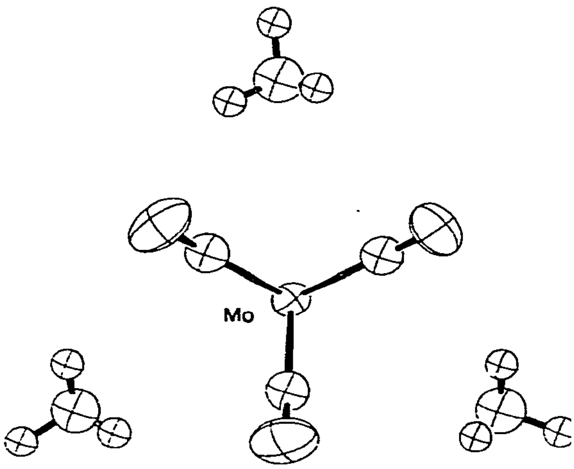


Fig. 1. View of anion. Hydrogen atoms omitted for clarity.

Fig. 2. View down pseudo-three fold axis of anion showing "pocket" formed by 3-methyl substituents on pyrazolyl groups. Thermal parameters for hydrogens set artifically small.

from the final difference map. The remaining hydrogen atoms were input at idealized positions (C—H = 0.95 Å) and entered as fixed contributors in the structure factor calculation.

Hydrotris(3,5-dimethylpyrazolyl)borate acts as a tridentate ligand occupying facial octahedral sites. The remaining sites are taken up by three CO groups, yielding the expected slightly distorted octahedral coordination characteristic of Mo^0 complexes (Fig. 1). The resulting distances and angles have unexceptional values (Tables 2 and 3) and equivalent distances and angles yield acceptable σ_{av} values.

The $Mo—N_{avg}$ distance of the title compound (2.263(5) Å) are marginally longer than the comparative Mo—N distance *trans* to the NO group (2.239(8) Å) reported [4a] for $Mo[HB(3,5-Me_2-4-Cl-pz)_3](NO)Cl(OPr^i)$. The Mo—N distances

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) FOR $[Mo(CO)_3HB(3,5-Me_2pz)_3]^-$

Atoms	$n = 1$	2	3	Avg. (σ_{av})
Mo—C(*n*)	1.938(7)	1.940(8)	1.946(8)	1.941(4)
Mo—N(*n*1)	2.269(5)	2.260(6)	2.260(6)	2.263(5)
N(*n*1)—N(*n*2)	1.380(7)	1.376(8)	1.371(8)	1.376(5)
N(*n*1)—C(*n*4)	1.310(10)	1.368(9)	1.346(9)	1.341(30)
N(*n*2)—B	1.544(10)	1.522(10)	1.538(10)	1.535(11)
N(*n*2)—C(*n*1)	1.367(9)	1.373(9)	1.354(9)	1.365(10)
C(*n*1)—C(*n*2)	1.507(11)	1.475(12)	1.501(15)	1.494(17)
C(*n*1)—C(*n*3)	1.361(10)	1.342(11)	1.350(11)	1.351(10)
C(*n*3)—C(*n*4)	1.366(10)	1.380(11)	1.418(11)	1.388(27)
C(*n*4)—C(*n*5)	1.532(11)	1.456(10)	1.455(11)	1.481(44)
C(*n*)—O(*n*)	1.165(8)	1.173(9)	1.163(9)	1.167(5)

TABLE 3.

SELECTED INTERATOMIC ANGLES (deg) FOR $[Mo(CO)_3HB(3,5\text{-}Me_2pz)_3]^-$

Atoms	n =	1			2			3	
	n' = 2		3	1		3	1		2
C(n)—Mo—C(n')	85.1(3)		85.0(3)			83.2(3)			
C(n)—Mo—N(n1)		175.6(3)			176.8(3)			178.4(3)	
C(n)—Mo—N(n'1)	98.0(3)		94.5(3)	96.6(3)		98.3(3)	99.2(3)		96.2(3)
N(n1)—Mo—N(n'1)	80.3(2)		81.2(2)			82.4(2)			
N(n2)—B—N(n'2)	109.4(6)		109.3(6)			108.9(6)			
Mo—C(n)—O(n)		178.4(6)			175.5(7)			176.0(7)	
Mo—N(n1)—N(n2)		119.6(4)			120.9(4)			120.4(4)	
Mo—N(n1)—C(n4)		133.5(5)			132.6(5)			132.1(5)	
N(n2)—N(n1)—C(n4)		106.7(6)			106.6(6)			107.1(6)	
N(n1)—N(n2)—C(n1)		108.5(6)			109.5(6)			109.2(6)	
N(n1)—N(n2)—B		120.8(6)			120.2(5)			120.3(6)	
C(n1)—N(n2)—B		130.5(6)			130.3(6)			130.5(6)	
N(n2)—C(n1)—C(n2)		122.7(6)			122.3(6)			123.0(7)	
N(n2)—C(n1)—C(n3)		107.0(6)			106.8(7)			109.1(7)	
C(n2)—C(n1)—C(n3)		130.3(7)			130.9(8)			127.9(8)	
C(n1)—C(n3)—C(n4)		106.9(7)			109.5(7)			106.0(7)	
C(n3)—C(n4)—C(n5)		127.8(7)			130.6(7)			129.4(7)	
C(n3)—C(n4)—N(n1)		110.7(6)			107.7(6)			108.6(6)	
C(n5)—C(n4)—N(n1)		121.2(7)			121.8(6)			121.9(7)	

TABLE 4.

ATOMIC POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS FOR $[N(C_2H_5)_4][Mo(CO)_3HB(3,5\text{-}Me_2pz)_3]^a$. Thermal parameters reported are X10

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.190029(24)	0.05423(5)	0.000000	25.79(20)	28.67(20)	23.32(19)	1.59(17)	−1.77(29)	−2.31(28)
N(11)	0.1229(3)	−0.0963(6)	−0.0710(3)	33.5(25)	32.8(24)	24.4(24)	−4.3(21)	−0.1(19)	−3.2(20)
N(21)	0.1439(3)	0.1918(6)	−0.0943(3)	29.7(24)	34.6(25)	31.4(25)	2.4(20)	−5.5(19)	−5.0(21)
N(31)	0.2741(3)	0.0083(6)	−0.0955(4)	35.6(27)	37.5(26)	30.5(27)	4.2(23)	1.7(22)	−0.3(23)
N(12)	0.1273(3)	−0.0956(6)	−0.1526(3)	32.1(24)	37.1(25)	28.0(24)	−3.2(21)	−2.6(20)	−4.8(21)
N(22)	0.1414(3)	0.1522(6)	−0.1723(3)	27.6(22)	38.6(26)	26.1(23)	0.5(20)	−3.1(19)	5.3(21)
N(32)	0.2533(3)	0.0059(6)	−0.1736(3)	33.7(25)	36.7(25)	27.0(24)	1.4(22)	3.3(21)	−3.4(22)
N(4)	0.3473(3)	0.4930(6)	−0.1302(4)	34.4(26)	34.1(24)	31.2(25)	−3.1(22)	0.5(21)	2.1(22)
O(1)	0.2895(3)	0.2604(6)	0.0877(3)	61.0(29)	50.3(28)	44.1(27)	−19.4(24)	−8.7(24)	−9.5(25)
O(2)	0.2434(4)	−0.1429(6)	0.1311(4)	78(4)	58(3)	48.1(29)	18.2(28)	−3.1(28)	18.6(28)
O(3)	0.0770(4)	0.1261(8)	0.1323(3)	55(4)	92(4)	39.3(26)	23(3)	17.6(25)	−5.(3)

TABLE 5

ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $[N(C_2H_5)_4][Mo(CO)_3HB(3,5\text{-}Me_2pz)_3]$

Atom	*x*	*y*	*z*	*B*
B	0.1710(5)	0.0150(8)	−0.1966(5)	3.11(14)
C(1)	0.2524(4)	0.1840(7)	0.0537(4)	3.48(13)
C(2)	0.2252(4)	−0.0711(7)	0.0795(5)	3.52(13)
C(3)	0.1172(4)	0.0987(8)	0.0809(5)	3.58(13)
C(11)	0.0842(4)	−0.1975(7)	−0.1813(4)	3.15(12)
C(12)	0.0750(5)	−0.2241(9)	−0.2686(5)	4.71(17)
C(13)	0.0550(4)	−0.2622(7)	−0.1176(5)	3.80(14)
C(14)	0.0807(4)	−0.1980(8)	−0.0515(4)	3.22(13)
C(15)	0.0607(5)	−0.2263(9)	0.0351(5)	4.40(17)
C(21)	0.1088(4)	0.2512(8)	−0.2170(5)	3.88(14)
C(22)	0.0959(6)	0.2362(10)	−0.3028(6)	5.61(20)
C(23)	0.0916(5)	0.3515(8)	−0.1671(5)	4.53(16)
C(24)	0.1125(4)	0.3168(7)	−0.0911(4)	3.30(13)
C(25)	0.1061(4)	0.3907(8)	−0.0171(5)	4.48(16)
C(31)	0.3146(4)	−0.0051(9)	−0.2195(5)	3.91(14)
C(32)	0.3118(6)	−0.0051(13)	−0.3084(7)	6.07(22)
C(33)	0.3750(4)	−0.0127(8)	−0.1724(5)	4.23(15)
C(34)	0.3483(4)	−0.0052(7)	−0.0935(4)	3.25(12)
C(35)	0.3893(5)	−0.0084(9)	−0.0193(5)	4.99(18)
C(41)	0.3421(6)	0.6132(11)	−0.1847(6)	5.83(20)
C(42)	0.2676(8)	0.6287(14)	−0.2241(9)	8.6(3)
C(51)	0.3387(6)	0.3635(10)	−0.1777(6)	5.90(20)
C(52)	0.3995(7)	0.3362(13)	−0.2358(7)	7.70(28)
C(61)	0.4249(6)	0.4986(13)	−0.0931(7)	7.03(24)
C(62)	0.4406(7)	0.3827(14)	−0.0371(8)	7.85(28)
C(71)	0.2878(6)	0.4959(13)	−0.0678(7)	6.14(22)
C(72)	0.2852(7)	0.6190(14)	−0.0177(8)	8.5(3)

trans to the weakly π-bonding ligands Cl and OPr^i are appreciably shorter, 2.172(8) and 2.211(8) Å, respectively. Relatively shorter Mo—N distances (2.213(4) Å) also occur in $Mo(NO)(CO)_2HB(pz)_3$ [10], a complex of an unsubstituted pyrazolylborate ligand. The latter comparison suggests that steric interactions between the 3-methyl substituents and the ancillary ligands are an important factor in the observed Mo—N bond distances.

The hydrogen atoms of the 3-methyl moiety are directed away from the molybdenum when viewed down the pseudo-three fold axis of the molecule, (Fig. 2) as anticipated from space filling models. Thus, the 3-methyl substituents of $HB(Me_2pz)_3^-$ form a symmetrical pocket which protects the other ligands and the molybdenum atom and confers chemical stability relative to complexes of unsubstituted pyrazolylborates.

The structural results for this highly symmetric Mo^0 derivative should be useful for future comparison with the structural results of other systems in which the chemical reactivity is modified by changes in the pyrazolyl substituents, the oxidation state of the metal or the ancillary ligands.

Acknowledgements

We thank Mr. S. Ballard for technical assistance. We acknowledge financial support by the National Institute of Environmental Health Sciences

(ES00966) and a generous allocation of computer time from the University of Arizona Computer Center. We thank Professor J. McCleverty for helpful discussions.

References

1 S. Trofimenko, J. Amer. Chem. Soc., 88 (1966) 1842.

2 S. Trofimenko, Accounts Chem. Res., 4 (1971) 17, and references cited therein.

3 A. Shaver, Organometal. Chem. Rev., 3 (1977) 157, and references cited therein.

4 (a) J.A. McCleverty, D. Seddon, N.A. Bailey and N.W. Walker, J. Chem. Soc. Dalton, (1976) 898. (b) J.A. McCleverty, A.E. Rae, I. Wolochowicz, N.A. Bailey and J.M.A. Smith, J. Organometal. Chem., 168 (1979) C1. (c) H. Adams, N.A. Bailey, G. Denti, J.A. McCleverty, J.M.A. Smith and A. Wlodarczyk, J. Chem. Soc. Chem. Commun., (1981) 348. (d) A.E. Rae, Ph.D. Thesis, The University Sheffield, England, 1978. (e) A.S. Drane, Ph.D. thesis, The University, Sheffield, England, 1981.

5 C.P. Marabella and J.H. Enemark, Abstracts, 181st ACS National Meeting, Atlanta, GA, 1981, paper INOR 33.

6 S. Trofimenko, J. Amer. Chem. Soc., 91 (1969) 588.

7 Syntex $P2_1$ Fortran Operations Manual, Syntex Analytical Instruments, Cupertino, California, 1975.

8 K. Yamanouchi and J.H. Enemark, Inorg. Chem., 17 (1978) 1981.

9 All computations were performed on the CDC CYBER-175 computer at the University of Arizona computer center. The major programs used in structure determination were FORDAP (Fourier summation program, by A. Zalkin), Ibers' NUCLS (structure factor calculations and full matrix least-squares refinement, itself a modification of ORFLS, by W.R. Busing, K.O. Martin, and H.A. Levy), ORFFE (locally modified calculations of distances angles, and least-squares planes with standard deviations by Busing, Martin, and Levy), and ORTEP (thermal ellipsoid drawing program, by C.K. Johnson).

10 E.M. Holt, S.L. Holt, F. Cavalito and K.J. Watson, Acta Chem. Scand., A30 (1976) 225.

Note added in proof. Other structures of Mo complexes of $HB(Me_2pz)_3^-$ include $HB(Me_2pz)_3Mo(CO)_2(SC_6H_4Cl$-*p*); T. Begley, D. Condon, G. Ferguson, F.J. Lalor and M.A. Khan, Inorg. Chem., in press, and $HB(Me_2pz)_3MoOCl_2$, G. Ferguson, B. Kaitner, F.J. Lalor and G. Roberts, Inorg. Chem., in press. We thank Prof. G. Ferguson for this information.