The Reactions of Acetone and of Diacetone Alcohol with $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$. The Formation of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(OEt)]$ and the Structures ‡ of $[\{Mo[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)I\}_2O]$ and a Bicyclic Salt $[C_6H_3Me_5N_2(OH)][I_{\frac{1}{2}}(I_3)_{\frac{1}{2}}]$

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The complex $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (Me_2pz = 3,5-dimethylpyrazolyl) reacted with boiling acetone and with diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) over several days, giving low yields of the salt of the cation $[C_6H_3Me_5N_2(OH)]^+$, $[\{Mo[HB(Me_2pz)_3](NO)I\}_2O]$, and $[Mo\{HB(Me_2pz)_3\}(NO)I(OEt)]$. The structure of an iodide salt of the organic cation, and of the bimetallic species have been determined crystallographically. The organic salt is a bicyclic species derived by fusion of a C_3 fragment (possibly derived from diacetone alcohol) across the N–N bond of 3,5-dimethylpyrazole. The bimetallic species can be described as two distorted, eclipsed octahedra sharing the bridging O atom, where the Mo–O distances are 1.86 and 1.93 Å, and the Mo–O–Mo angle is 171°. Possible routes to the formation of these compounds are discussed.

We have established that $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (Me_2pz= 3,5-dimethylpyrazolyl) reacts with alcohols,[1] phenols,[2] primary amines,[3] 1,1-disubstituted hydrazines,[4] and thiols [5] (RQH; Q = O, S, NH, or NHNR′) affording the air- and moisture-stable species $[Mo\{HB(Me_2pz)_3\}(NO)I(QR)]$, with loss of HI. We have further shown that the precursor di-iodide is reluctant to react with secondary amines (NHRR′) to give $[Mo\{HB(Me_2pz)_3\}(NO)I(NRR')]$, and have attributed this to steric hindrance, despite the ability to lose HI, as $[NH_2R_2]I$.[3]

We were therefore rather surprised to discover that $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ reacted with acetone and with methyl ethyl ketone, apparently with loss of HI, affording green substances. We also observed that green species were formed when the di-iodide was refluxed in hot toluene during recrystallisation procedures. We thought initially that these green materials would be related to the mono-alkoxides, $[Mo\{HB(Me_2pz)_3\}(NO)I(OR)]$ which contain a green chromophore. Our surprise was turned to confusion, however, by our subsequent discovery that $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ is readily reduced [6] to a paramagnetic monoanion, $[Mo\{HB(Me_2pz)_3\}(NO)I_2]^-$, from which I^- dissociates giving the presumably solvated species $[Mo\{HB(Me_2pz)_3\}(NO)I]$, both of which are *green*! Indeed, from preliminary electrochemical studies it is evident that the di-iodide precursor could be reduced by acetone, as it is apparently by ethanol.[6]

In an attempt to rationalise, if not fully explain, these observations, we have investigated, in some detail, the reactions between $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ and acetone. A preliminary account of our work has been given.[7]

Experimental

All reactions were carried out under dry nitrogen, and all solvents and glassware were dried prior to use. The complex $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ was prepared as described elsewhere;[1,8] the di-iodide was used as the toluene solvate following toluene recrystallisation.

Microanalyses were determined by the Microanalytical Laboratory of this Department. Molecular weight determinations and gas-liquid chromatography (g.l.c.) were made using a Mechrolab 301A osmometer, and a PE F11 instrument, respectively. I.r. and 220-MHz ^1H n.m.r. spectra were obtained using PE 297, 180, and R34 spectrometers. Mass spectra were obtained using a Kratos MS-80 instrument in EI mode.

Reaction of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ *with Acetone.*—The complex $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (3.0 g) was dissolved in ethanol-free acetone (100 cm^3; absence of EtOH established by g.l.c. on a Porapak column, temperature progression 5° min^{-1}, 125—180 °C). The mixture was refluxed for 3 d, and on cooling and filtering, a *white organic salt*, compound (1), m.p. 179—182 °C (uncorrected), was collected (Found: C, 40.9; H, 6.0; I, 33.8; N, 8.7. $C_{11}H_{19}IN_2O$ requires C, 41.0; H, 5.9; I, 33.4; N, 8.7%). I.r. (KBr disc): 3 210 cm^{-1} [$\nu(OH)$]. ^1H N.m.r. ($CDCl_3$): δ 8.27 (s, 3 H, Me^a; see Figure 2), 8.04 (s, 3 H, Me^a), 7.95 (s, 3 H, Me^b), 7.53 (s, 3 H, Me^c), 7.37 (s, 3 H, Me^c), 6.80 (AB pair, 2 H, $CH_2{}^d$), 3.65 (s, 1 H, CH^e), and 3.18 (s, 1 H, OH). ^1H N.m.r. (D_2O): δ 8.42 (s, 6 H, Me^a), 8.17 (s, 3 H, Me^b), 7.71 (s, 3 H, Me^c), 7.70 (s, 3 H, Me^c), 7.20 (m, 2 H, $CH_2{}^d$), and 3.75 (s, 1 H, CH^e). Mass spectrum (only peaks $>2\%$ and above 96 a.m.u.): parent ion, $[M]^+$, m/e = 195(2); 194(9), $[M - H]^+$; 180(3), $[M - CH_3]^+$; 179(21), $[M - H - CH_3]^+$; 151(9), $[M - C_2H_4O]^+$; 138(5); 137(22); 98(18); 97(33); and 96(100), $[C_3HMe_2N_2H]^+$.

The composition of the solvent mixture was established by g.l.c. (FFAP Column, temperature progression 5° min^{-1}, 60—210 °C), being acetone (*ca.* 60%), mesityl oxide (*ca.* 35%) and diacetone alcohol (*ca.* 5%). The percentage of H_2O was not determined but no ethanol was present.

The filtrate from above was partially evaporated *in vacuo* and light petroleum (b.p. 50—60 °C, 100 cm^3) added. An oily olive-green solid precipitated which was recrystallised from

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‡ μ-Oxo-bis{iodo(nitrosyl)[tris(3,5-dimethylpyrazol-1-yl)borato]molybdenum} and 6-hydroxy-2,4,6,8,8-pentamethyl-5-aza-1-azoniabicyclo[3.3.0]octa-1,3-diene iodide–tri-iodide (0.5/0.5).

Supplementary data available (No. SUP 23663, 44 pp.): structure factors, thermal parameters, H-atom co-ordinates, bond distances and angles of pyrazolyl fragments and CH_2Cl_2 [for (2)], least-squares planes [for (2)]. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

dichloromethane–di-isopropyl ether, giving deep green crystals of compound (2) (yields variable but *ca.* 20%) (Found: C, 32.4; H, 3.9; I, 23.0; N, 17.3. $C_{30}H_{44}B_2I_2Mo_2N_{14}O_3$ requires C, 32.3; H, 4.0; I, 22.7; N, 17.6%). I.r. (KBr disc): 1 682 and 1 663 [ν(NO)], 744 cm^{-1} [ν(MoOMo)]. I.r. ($CHCl_3$): 1 694 and 1 661 cm^{-1} [ν(NO)]. ^1H N.m.r. (CD_2Cl_2): δ 9.03 (s, 3 H, CH_3), 9.01 (s, 3 H, CH_3), 7.73 (s, 6 H, $2CH_3$), 7.63 (s, 3 H, CH_3), 7.62 (s, 3 H, CH_3), 7.60 (s, 6 H, $2CH_3$), 7.56 (s, 3 H, CH_3), 7.51 (s, 3 H, CH_3), 6.82 (s, 3 H, CH_3), 6.77 (s, 3 H, CH_3), 4.55 (s, 1 H, $C_3\mathit{H}N_2Me_2$), 4.42 (s, 1 H, $C_3\mathit{H}N_2Me_2$), 4.29 (s, 1 H, $C_3\mathit{H}N_2Me_2$), 4.22 (s, 1 H, $C_3\mathit{H}N_2Me_2$), 4.08 (s, 1 H, $C_3\mathit{H}N_2Me_2$), and 3.98 (s, 1 H, $C_3\mathit{H}N_2Me_2$). Molecular weight ($CHCl_3$) Found: 1 078. Calc.: 1 116.08. Mass spectrum [based on ^{11}B and ^{92}Mo, only peaks of intensity >3% (except for the most significant), and above 389 a.m.u.]: parent ion [*MOM* $[\{Mo[HB(Me_2pz)_3](NO)I\}_2O]^+$, *m/e* = 1 108(<1); 1 078(<1), $[\mathit{MOM} - NO]^+$; 981(10), $[\mathit{MOM} - I]^+$; 824(3), $[\mathit{MOM} - 2I - NO]^+$; 546(41), $[\mathit{M}]^+$; 532(36), $[Mo\{HB(Me_2pz)_3\}IO]^+$; 530(35), $[Mo\{HB(Me_2pz)_3\}IN]^+$; 516(40), $[\mathit{M} - NO]^+$; 405(100), $[Mo\{HB(Me_2pz)_3\}O]^+$; 403(93), $[Mo\{HB(Me_2pz)_3\}N]^+$; 389(37), $[\mathit{M} - NO - I]^+$.

The mother-liquor from the crystallisation of (2) above was evaporated to dryness *in vacuo*, the residue dissolved in dichloromethane and light petroleum (b.p. 40—60 °C) added until light green crystals of $[Mo\{HB(Me_2pz)_3\}(NO)I(OEt)]$ precipitated (yields variable but *ca.* 7—15%). The compound was identified by spectroscopic comparison (i.r., ^1H n.m.r., and mass spectrometry) with an authentic sample.[1]

Reaction of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ *with Diacetone Alcohol*, $Me_2C(OH)CH_2COMe$.—$[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (2.0 g) was dissolved in diacetone alcohol (50 cm^3) and the mixture refluxed for 2 d (the reflux temperature decreased rapidly from 160 °C to 95—100 °C). On cooling to room temperature and filtering, crude compound (2) was recovered as a deep green powder (*ca.* 25%). At this point g.l.c. analysis (see above) of the reaction solvent established its composition as acetone (traces), diacetone alcohol (*ca.* 25%), and mesityl oxide (*ca.* 75%); water was not estimated but there were no traces of ethanol.

The filtrate from above was cooled at −10 °C overnight and a white precipitate of the organic salt (1) was obtained (*ca.* 0.10 g). On partial evaporation of the solution, a red organic salt (3), m.p. 166—169 °C (uncorrected), was recovered (*ca.* 0.15 g) on filtration (Found: C, 27.7; H, 3.6; I, 52.7; N, 6.3. $C_{11}H_{19}I_2N_2O$ requires C, 29.4; H, 4.3; I, 56.5; N, 6.2%. I.r. (KBr disc): 3 260 and 3 200 cm^{-1} [ν(OH)]. ^1H N.m.r. [$(CD_3)_2CO$]: δ 8.16 (s, 3 H, Me^a; see Figure 2), 8.12 (s, 3 H, Me^a), 7.90 (s, 3 H, Me^b), 7.43 (s, 3 H, Me^c), 7.38 (s, 3 H, Me^c), 7.14 (s, 3 H, possibly H_2O), 6.87 (AB pair, 2 H, $CH_2{}^d$), 3.41 (s, 1 H, CH^e), and 2.83 (s, 1 H, OH). ^1H N.m.r. [$(CD_3)_2CO + D_2O$]: δ 8.17 (m, 6 H, Me^a), 7.92 (s, 3 H, Me^b), 7.43 (m, 6 H, Me^c), 6.98 (m, 2 H, $CH_2{}^d$), and 3.41 (broad t, 1 H, CH^e).

On complete evaporation of the filtrate from above, a complex mixture of solids was obtained. Small amounts of $[Mo\{HB(Me_2pz)_3\}(NO)I(OEt)]$ were present (yields up to 10%) but further separation and characterisation of this mixture proved impossible.

Crystallographic Studies.—Crystal data for $[C_6H_3Me_5N_2(OH)][I_{\frac{1}{2}}(I_3)_{\frac{1}{2}}]$ (3). $C_{11}H_{19}I_2N_2O$, *M* = 449.1 (crystallises from dichloromethane as red, elongated needles, crystal dimensions 0.49 × 0.18 × 0.16 mm), Triclinic, $a = 7.752(5)$, $b = 9.394(4)$, $c = 11.424(9)$ Å, $\alpha = 91.21(5)$, $\beta = 93.24(6)$, $\gamma = 110.26(4)^\circ$, $U = 778.5(9)$ Å^3, $D_m = 1.90$, $Z = 2$, $D_c = 1.916$ g cm^{-3}, $F(000) = 426$, space group $P\bar{1}$ (C_i, no. 2) (assumed and confirmed by the analysis), Mo-K_α radiation (graphite-monochromated) $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 39.79$ cm^{-1}.

Table 1. Atomic positional parameters with estimated standard deviations in parentheses for $[C_6H_3Me_5N_2(OH)][I_{\frac{1}{2}}(I_3)_{\frac{1}{2}}]$ (3)

Atom	*X/a*	*Y/b*	*Z/c*
I(1)	0.254 18(14)	0.314 26(11)	−0.013 13(8)
I(2)	0.000 00	0.000 00	0.000 00
I(3)	0.000 00	0.500 00	0.500 00
O(1)	0.759 7(11)	0.161 2(9)	0.352 7(7)
N(1)	0.466 9(12)	0.157 0(10)	0.284 0(7)
N(2)	0.343 5(12)	0.014 4(10)	0.290 7(7)
C(1)	0.491 6(20)	0.429 0(15)	0.322 7(13)
C(2)	0.391 4(17)	0.259 3(13)	0.320 6(9)
C(3)	0.215 4(17)	0.176 6(14)	0.350 5(9)
C(4)	0.186 1(16)	0.020 5(14)	0.331 7(9)
C(5)	0.022 1(18)	−0.110 4(16)	0.348 1(12)
C(6)	0.738 3(21)	0.279 3(16)	0.167 9(12)
C(7)	0.651 1(15)	0.156 4(13)	0.252 1(9)
C(8)	0.585 4(16)	−0.008 2(13)	0.195 3(9)
C(9)	0.421 0(14)	−0.106 7(12)	0.261 9(9)
C(10)	0.283 4(19)	−0.233 6(16)	0.182 4(11)
C(11)	0.477 1(17)	−0.167 1(13)	0.372 8(10)

Atoms I(1) and I(2) are the unique atoms of the centrosymmetric tri-iodide ion and atom I(3) is the iodide ion. Since atoms I(2) and I(3) are constrained to lie on crystallographic inversion centres, their positional parameters are quoted without estimated standard deviations.

X-Ray diffraction data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet/Syntex R3 diffractometer working in omega-scan mode. 2 021 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz, polarisation and absorption effects. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares to a final *R* 0.0513. Hydrogen atoms were detected and included in structure factor calculations [C–H 0.95, O–H 0.91 Å, C–C–H(methyl) 110°, $B = 7.0$ Å^2]: allowance was made for the anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of iodine. A secondary extinction coefficient[9] was refined during the latter stages of refinement [3.3(3) for $F_{hkl}^{\text{calc.}}$ on an absolute scale of electrons]. Table 1 lists the atomic positional parameters with estimated standard deviations.

Crystal data for $[\{Mo[HB(Me_2pz)_3](NO)I\}_2O]$ (2). $C_{30}H_{44}B_2I_2Mo_2N_{14}O_3 \cdot 0.5CH_2Cl_2$, *M* = 1 158.6 (1 116.1 excluding solvent), crystals from dichloromethane–di-isopropyl ether (green, irregular bricks), Triclinic, $a = 12.220(6)$, $b = 13.352(10)$, $c = 14.094(5)$ Å, $\alpha = 96.38(5)$, $\beta = 93.12(4)$, $\gamma = 96.78(5)^\circ$, $U = 2\,264(2)$ Å^3, $D_m = 1.62$, $Z = 2$, $D_c = 1.70$ g cm^{-3}, $F(000) = 1\,117$, space group $P\bar{1}$ (C_i, no. 2) (assumed and confirmed by the analysis), Mo-K_α radiation (graphite-monochromated), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 19.9$ cm^{-1}.

Data were collected ($3.5 < 2\theta < 50^\circ$) and processed (1 932 independent reflections, no absorption corrections applied) as for compound (3) above with the addition that a correction was made for substantial (75%) crystal decay which was monitored during data collection. The structure was solved by Patterson, image-seeking and Fourier methods and refined by block-diagonal least squares (anisotropic thermal parameters for iodine and molybdenum only, anomalous scattering allowance for iodine, molybdenum, and chlorine). Hydrogen atoms were detected and included in the structure factor calculations [C–H 0.97, B–H 1.13 Å, C–C–H(methyl) 112°,

Table 2. Atomic positional parameters with estimated standard deviations in parentheses for [{Mo[HB($Me_2pz)_3$](NO)I}$_2$O] (2)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I(1)	0.126 1(3)	0.420 0(2)	0.326 7(2)
I(2)	0.239 0(3)	−0.029 4(2)	0.186 7(2)
Mo(1)	0.282 2(3)	0.376 1(2)	0.197 4(2)
Mo(2)	0.367 8(3)	0.137 5(2)	0.283 8(2)
O(1)	0.446(2)	0.513(2)	0.327(2)
O(2)	0.215(3)	0.129(2)	0.438(2)
O(3)	0.316(2)	0.253(2)	0.233(2)
N(1)	0.382(3)	0.455(2)	0.273(2)
N(2)	0.280(3)	0.136(2)	0.376(2)
N(3)	0.228(2)	0.502(2)	0.125(2)
N(4)	0.191(3)	0.477(2)	0.026(2)
N(5)	0.386(3)	0.378(2)	0.079(2)
N(6)	0.335(3)	0.369(2)	−0.013(2)
N(7)	0.147(3)	0.277(2)	0.100(2)
N(8)	0.143(3)	0.288(2)	0.006(2)
N(9)	0.470(3)	0.027(2)	0.343(2)
N(10)	0.573(3)	0.032(2)	0.318(2)
N(11)	0.497(2)	0.232(2)	0.369(2)
N(12)	0.601(3)	0.219(2)	0.346(2)
N(13)	0.478(2)	0.133(2)	0.162(2)
N(14)	0.585(3)	0.134(2)	0.178(2)
B(1)	0.216(4)	0.373(3)	−0.036(3)
B(2)	0.632(5)	0.123(4)	0.281(4)
C(1)	0.252(4)	0.654(4)	0.244(4)
C(2)	0.214(3)	0.600(3)	0.146(2)
C(3)	0.173(4)	0.637(3)	0.066(3)
C(4)	0.158(3)	0.559(3)	−0.006(3)
C(5)	0.105(4)	0.557(4)	−0.102(3)
C(6)	0.569(4)	0.379(3)	0.154(3)
C(7)	0.493(3)	0.373(3)	0.070(3)
C(8)	0.517(3)	0.366(3)	−0.022(3)
C(9)	0.420(3)	0.360(3)	−0.073(3)
C(10)	0.384(4)	0.343(3)	−0.180(3)
C(11)	0.045(3)	0.167(3)	0.210(2)
C(12)	0.074(3)	0.196(3)	0.113(3)
C(13)	0.033(3)	0.155(3)	0.021(3)
C(14)	0.075(4)	0.210(3)	−0.044(3)
C(15)	0.057(4)	0.200(3)	−0.142(3)
C(16)	0.333(4)	−0.090(3)	0.418(3)
C(17)	0.445(3)	−0.056(2)	0.384(2)
C(18)	0.538(4)	−0.105(3)	0.383(3)
C(19)	0.621(4)	−0.054(3)	0.348(3)
C(20)	0.742(4)	−0.067(4)	0.332(3)
C(21)	0.402(4)	0.347(3)	0.483(3)
C(22)	0.497(3)	0.311(3)	0.438(3)
C(23)	0.608(4)	0.351(3)	0.459(3)
C(24)	0.679(4)	0.291(4)	0.405(3)
C(25)	0.804(4)	0.306(4)	0.400(3)
C(26)	0.353(4)	0.123(3)	0.010(3)
C(27)	0.465(3)	0.131(3)	0.063(2)
C(28)	0.566(3)	0.132(3)	0.022(3)
C(29)	0.642(3)	0.136(3)	0.097(2)
C(30)	0.765(5)	0.139(4)	0.091(4)
C(31)	−0.049(10)	0.691(8)	0.403(8)
Cl(1)	−0.153(3)	0.623(3)	0.362(3)
Cl(2)	0.013(3)	0.796(3)	0.408(3)

Six groups of five consecutive carbon atoms from C(1) to C(30) constitute the six pyrazolyl rings. Atoms C(31), Cl(1), and Cl(2) comprise the dichloromethane.

B = 10.0 Å^2] with the exception of those on the half-occupancy dichloromethane solvent molecule. The refinement converged at R 0.0794. Table 2 lists the atomic positional parameters with estimated standard deviations. Scattering factors are taken from ref. 10; unit weights were used throughout the refinements; computer programs formed part of the Sheffield *X*-ray system.

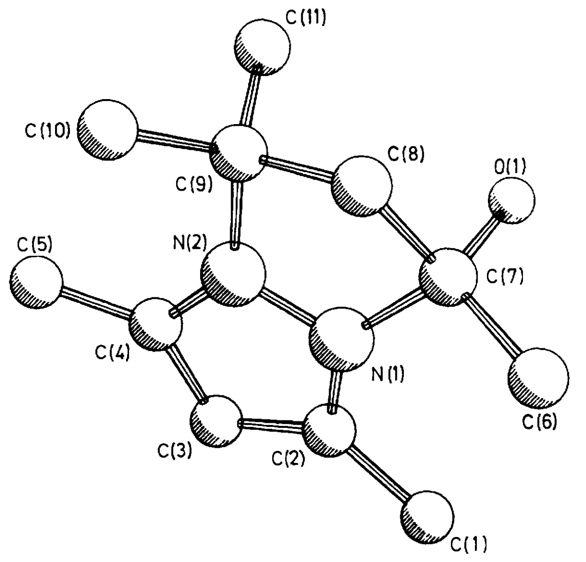


Figure 1. The molecular geometry, with atom labelling, of the bicyclic cation [$C_6H_3Me_5N_2(OH)$]$^+$

Results and Discussion

After refluxing [Mo{HB($Me_2pz)_3$}(NO)I_2] in degassed ethanol-free acetone for 3 d, we were able to isolate, albeit in low yields, three compounds. The first, (1), was a white organic cation, isolated as an iodide. The second, (2), the largest amount of a pure compound recovered, was identified as a bimetallic species. The third pure substance isolated was [Mo{HB($Me_2pz)_3$}(NO)I(OEt)]. The identity of the last was established by comparison with an authentic sample,[1] and both it and the bimetallic species (2) are green, although of different shades, the former being apple green and the latter olive green.

Because of the formation of the ethoxide, the constitution of the solvent before and after the reaction was established by g.l.c. We could detect no ethanol, but observed that diacetone alcohol, mesityl oxide, and water were present after the reaction was stopped.

In view of the occurrence of significant amounts of diacetone alcohol in the system described above, we investigated the behaviour of [Mo{HB($Me_2pz)_3$}(NO)I_2] with that compound. It was clear that, after refluxing had begun, the diacetone alcohol was progressively and substantially dehydrated to mesityl oxide. Again, the white salt (1), together with an apparently related red salt, (3), also an iodide, was formed as well as (2) and some [Mo{HB($Me_2pz)_3$}(NO)I(OEt)]. At the end of the reaction, g.l.c. analysis of the solvent revealed acetone (traces), the original diacetone alcohol (only *ca.* 25%), but substantial amounts of mesityl oxide (*ca.* 75%). Water was also present, but no evidence for methanol or ethanol could be obtained.

The White and Red Organic Salts, (1) *and* (3).—The nature of these species was established primarily by a single-crystal *X*-ray analysis of the red salt, (3). This was identified as containing a bicyclic cation, [$C_6H_3Me_5N_2(OH)$]$^+$ and a 1 : 1 mixture of I^- and I_3^-. The structure of the cation is illustrated in Figure 1 with the atom labelling used in the associated Tables: bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables 3 and 4. The unsaturated five-membered ring of the bicyclic cation is closely planar (r.m.s. deviation 0.002 Å), with coplanar methyl substituents, whereas the

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

I(1)–I(2)	2.940 1(10)	N(1)–C(7)	1.495(15)
N(1)–N(2)	1.357(13)	N(2)–C(9)	1.498(14)
N(1)–C(2)	1.356(15)	O(1)–C(7)	1.377(14)
N(2)–C(4)	1.350(15)	C(6)–C(7)	1.514(19)
C(1)–C(2)	1.511(19)	C(7)–C(8)	1.564(16)
C(2)–C(3)	1.383(17)	C(8)–C(9)	1.543(16)
C(3)–C(4)	1.414(17)	C(9)–C(10)	1.532(18)
C(4)–C(5)	1.456(19)	C(9)–C(11)	1.502(16)
N(2)–N(1)–C(2)	109.5(9)	N(1)–C(7)–O(1)	109.5(9)
N(2)–N(1)–C(7)	112.1(8)	N(1)–C(7)–C(6)	111.8(10)
C(2)–N(1)–C(7)	138.0(10)	N(1)–C(7)–C(8)	97.7(8)
N(1)–N(2)–C(4)	109.9(9)	O(1)–C(7)–C(6)	114.3(10)
N(1)–N(2)–C(9)	113.1(8)	O(1)–C(7)–C(8)	108.5(9)
C(4)–N(2)–C(9)	136.7(10)	C(6)–C(7)–C(8)	113.9(10)
N(1)–C(2)–C(1)	123.1(11)	C(7)–C(8)–C(9)	107.6(9)
N(1)–C(2)–C(3)	106.6(10)	N(2)–C(9)–C(8)	97.7(8)
C(1)–C(2)–C(3)	130.3(11)	N(2)–C(9)–C(10)	111.0(9)
C(2)–C(3)–C(4)	108.4(11)	N(2)–C(9)–C(11)	110.0(9)
N(2)–C(4)–C(3)	105.7(10)	C(8)–C(9)–C(10)	112.0(10)
N(2)–C(4)–C(5)	125.2(11)	C(8)–C(9)–C(11)	113.7(9)
C(3)–C(4)–C(5)	129.1(12)	C(10)–C(9)–C(11)	111.6(10)

Non-bonded contacts

I(3) $\cdots$ O(1) [$x - 1, y, z$]	3.428(8)
I(3) $\cdots$ O(1) [$1 - x, 1 - y, 1 - z$]	3.428(8)
I(3) $\cdots$ H(O1) [$x - 1, y, z$]	2.52
I(3) $\cdots$ H(O1) [$1 - x, 1 - y, 1 - z$]	2.52

Table 4. Details of planar fragments of compound (3). Equations of mean planes are of the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to orthogonal axes a, b^*, c'. Deviations (Å) of atoms from the mean planes are given in square brackets

Plane A: N(1), N(2), C(2)–C(4) (r.m.s. deviation 0.002 Å)

p	q	r	d
−0.3410	0.0365	−0.9394	−3.9339

[N(1) 0.001, N(2) 0.001, C(2) −0.002, C(3) 0.002, C(4) −0.002, C(1) 0.016, C(5) 0.025, C(7) −0.153, C(8) 0.322, C(9) −0.118]

Plane B: N(1), N(2), C(7), C(9) (r.m.s. deviation 0.006 Å)

p	q	r	d
−0.2502	0.0088	−0.9682	−3.8044

[N(1) 0.007, N(2) −0.007, C(7) −0.004, C(9) 0.004, C(8) 0.534, C(2) −0.117, C(3) −0.205, C(4) −0.140, O(1) −1.304, C(6) 0.898, C(10) 0.975, C(11) −1.389]

Plane C: C(7)–C(9)

p	q	r	d
−0.7224	0.2314	−0.6517	−4.6764

[N(1) 0.812, N(2) 0.794, C(2) 1.453, C(3) 1.847, C(4) 1.419, O(1) −1.288, C(6) 0.667, C(10) 0.736, C(11) −1.367]

Angles (°) between planes: A–B 5.7; A–C 29.9; B–C 35.5

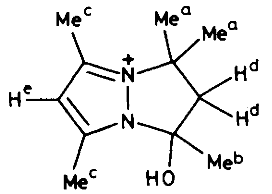


Figure 2. Structure of the bicyclic cation $[C_6H_3Me_5N_2(OH)]^+$, with labelling for n.m.r. assignments

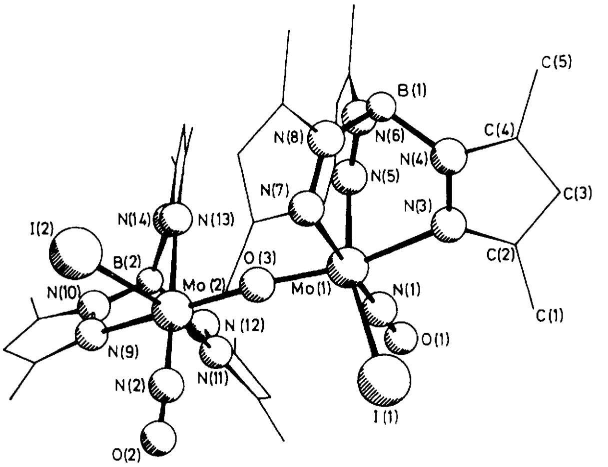


Figure 3. The molecular geometry of the bimetallic complex $[\{Mo[HB(Me_2pz)_3](NO)I\}_2O]$ (2). For clarity, the pyrazolyl rings are shown only in outline and only ring 1 is labelled: the labelling of the remaining rings comprises sequential sets of five carbon atoms; C(6)—C(10), C(11)—C(15), C(16)—C(20), C(21)—C(25), and C(26)—C(30)

saturated ring adopts an envelope conformation, being folded about the C(7) $\cdots$ C(9) line by 35.5°. There is also a fold about the N(1)–N(2) common bond of 5.7° which is in the opposite sense to that within the saturated ring, giving the molecular skeleton an overall zigzag shape. Bond lengths show no unexpected features: the N–N bond is 1.357 Å; there is a rather short contact between the oxygen atom and the iodide ion (3.43 Å) situated on the inversion centre at [0,0.5,0.5] and the hydrogen atom was detected between these two atoms; the second counter anion is a tri-iodide ion situated across the inversion centre at the origin of the unit cell; the bond length is 2.940 Å.

The cation is derived formally by fusing a C_3 fragment, presumably derived from diacetone alcohol or mesityl oxide, across the N–N bond of a 3,5-dimethylpyrazole ring. This red species is virtually identical spectroscopically to (1), except that the latter is clearly a mono-iodide. The ^1H n.m.r. spectra of the two species are given in the Experimental section; assignments of the resonances are based on Figure 2.

While (1) was very soluble in water, (2) was not, but in boiling acetone, de-iodination of (3) occurred, giving small amounts of (1).

The Bimetallic Complex (2).—The nature of this compound was also established crystallographically. The structure of the bimetallic complex is illustrated in Figure 3 with the atom labelling used in Table 5 which lists selected bond lengths and angles with estimated standard deviations.

The two molybdenum co-ordination polyhedra in the complex are each approximately octahedral, are mutually eclipsed (see Figure 4), and are linked by a bridging oxygen atom. The bridging system is slightly asymmetric, with Mo–O 1.86(2) and 1.93(2) Å, respectively, bond lengths which are shorter than might have been expected for a Mo–O single bond in systems containing molybdenum in oxidation states +2, +3, or +4. Thus a degree of π-bonding between the O and the two Mo atoms must occur ($p_\pi \longrightarrow d_\pi$ donation). This is entirely consistent with our related structural findings in $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ [X = OPr^i, Y = OPr^i or OEt; X = I, Y = $O(CH_2)_3Br$] and $[Mo\{HB(4\text{-}Cl\text{-}3,5\text{-}Me_2C_3N_2\}(NO)Cl(OPr^i)]$,[1,11] where the Mo–O distance falls between 1.86 and 1.92 Å. The π-interaction within the Mo–O–Mo system is also enhanced by the near eclipsing of the two octahedral units.

Table 5. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for compound (2)

Mo(1)–I(1)	2.777(5)	Mo(2)–I(2)	2.752(5)
Mo(1)–N(1)	1.74(3)	Mo(2)–N(2)	1.73(3)
Mo(1)–O(3)	1.86(2)	Mo(2)–O(3)	1.93(2)
Mo(1)–N(3)	2.21(3)	Mo(2)–N(9)	2.24(3)
Mo(1)–N(5)	2.15(3)	Mo(2)–N(11)	2.13(3)
Mo(1)–N(7)	2.28(3)	Mo(2)–N(13)	2.23(3)
N(4)–B(1)	1.62(5)	N(10)–B(2)	1.49(7)
N(6)–B(1)	1.48(5)	N(12)–B(2)	1.59(7)
N(8)–B(1)	1.55(6)	N(14)–B(2)	1.56(7)
O(1)–N(1)	1.20(4)	O(2)–N(2)	1.22(4)
I(1)–Mo(1)–N(1)	89.0(10)	I(2)–Mo(2)–N(2)	89.9(11)
I(1)–Mo(1)–O(3)	100.2(8)	I(2)–Mo(2)–O(3)	105.1(7)
I(1)–Mo(1)–N(3)	85.5(7)	I(2)–Mo(2)–N(9)	86.5(8)
I(1)–Mo(1)–N(5)	163.2(9)	I(2)–Mo(2)–N(11)	162.7(7)
I(1)–Mo(1)–N(7)	89.3(8)	I(2)–Mo(2)–N(13)	87.9(7)
N(1)–Mo(1)–O(3)	98.0(13)	N(2)–Mo(2)–O(3)	95.2(13)
N(1)–Mo(1)–N(3)	93.6(12)	N(2)–Mo(2)–N(9)	93.5(13)
N(1)–Mo(1)–N(5)	92.0(13)	N(2)–Mo(2)–N(11)	93.3(13)
N(1)–Mo(1)–N(7)	177.6(13)	N(2)–Mo(2)–N(13)	177.8(13)
O(3)–Mo(1)–N(3)	167.2(10)	O(3)–Mo(2)–N(9)	165.5(11)
O(3)–Mo(1)–N(5)	96.3(11)	O(3)–Mo(2)–N(11)	91.6(10)
O(3)–Mo(1)–N(7)	84.0(11)	O(3)–Mo(2)–N(13)	85.8(10)
N(3)–Mo(1)–N(5)	77.7(11)	N(9)–Mo(2)–N(11)	76.3(11)
N(3)–Mo(1)–N(7)	84.6(10)	N(9)–Mo(2)–N(13)	86.0(11)
N(5)–Mo(1)–N(7)	89.2(11)	N(11)–Mo(2)–N(13)	88.7(10)
N(4)–B(1)–N(6)	104(3)	N(10)–B(2)–N(12)	106(4)
N(4)–B(1)–N(8)	104(3)	N(10)–B(2)–N(14)	111(4)
N(6)–B(1)–N(8)	111(3)	N(12)–B(2)–N(14)	105(4)
Mo(1)–N(1)–O(1)	176(3)	Mo(2)–N(2)–O(2)	176(3)
Mo(1)–O(3)–Mo(2)	171.0(15)		

The Mo–O–Mo bond system is slightly but significantly bent [171.0(15)°]. The great majority of molybdenum complexes containing a single π-oxo bridge have a linear array of the three atoms,[12] although an exception $[\{Mo^{VI}O_2(Me_2NCH_2CH_2NHCH_2CMe_2S)\}_2O]$ (Mo–O–Mo 148°, Mo–O distance 1.92 Å) has recently been reported.[13] The distortion from linearity here must arise as a result of steric restraints imposed by the proximity of the two very bulky HB(Me$_2$pz)$_3$ ligands. Indeed on the basis of molecular models, we would not have expected bimetallic species containing two groups of Mo{HB(Me$_2$pz)$_3$}(NO)I, joined by a single atom bridge, to form. However, the pyrazolyl rings pack together almost like two enmeshed gear wheels, such that if one looks along the Mo · · · Mo axis, three sides of the dimer are occupied by these rings (Figure 4), while the fourth is filled by an NO group and an I atom. Two of the pyrazolyl rings [N(5)N(6),C(6)—C(10) and N(13),N(14),C(26)—C(30)] are almost parallel to each other, and this may have consequences for the ^{1}H n.m.r. spectrum of (2).

Despite the obvious overcrowding of the molecule, many of the features familiar from previous structural studies [1] of molecules of general formula [Mo{HB(Me$_2$pz)$_3$}(NO)I(L)] are evident. The angles between the pyrazolyl rings reflect the bulk of the unidentate ligand which they ' embrace ' (a large interplanar angle above iodine and small above nitrosyl). However, the angle between pyrazolyl rings pz(2′) and pz(3′) (Figure 4) on Mo(2), which ' embrace ' the bridging oxygen atom O(3), is very large (129.2°), reflecting steric interactions between atoms of the two metal co-ordination polyhedra. The methyl substituents are approximately coplanar with their pyrazolyl rings but the molybdenum atoms deviate substantially (up to 0.46 Å from the plane of ring 3) from some mean ring planes. The lengths of the Mo–I bonds suggest a small degree of π-donor character; the Mo–N(pyrazolyl) bond lengths reflect the competitive π-bonding capacity of the *trans* ligand. The level of accuracy of the structure determination precludes useful discussion of other geometric features of the pyrazolyl rings. The molybdenum–nitrosyl fragments are each linear and the two (μ-O)Mo(NO) planes are mutually perpendicular. The geometry of the molecule of dichloromethane of solvation, of approximately 50% occupancy, is not well determined and it seems not to engage in any significantly short interactions to the complex.

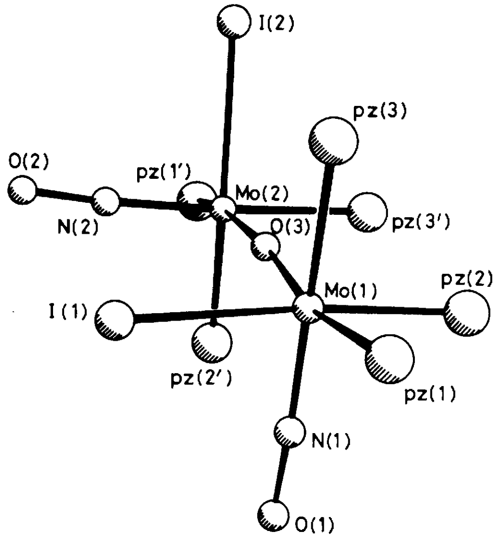


Figure 4. The geometry of the bimetallic skeleton showing the eclipsed arrangement of the co-ordination polyhedra and the slightly bent μ-oxo bridge (pz = pyrazolyl ring). Rings pz(1) and pz(1′) *etc.* occupy equivalent sites in the co-ordination polyhedra of Mo(1) and Mo(2)

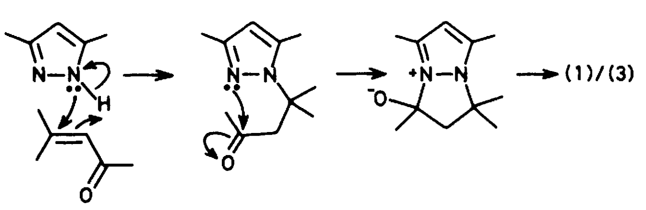
The i.r. spectrum of (2) exhibits two ν(NO) in the solid state and in solution. This may be due to coupling between the two Mo(NO) centres through the O atom, although the OMo(NO) planes are almost orthogonal, giving rise to symmetric and asymmetric stretching modes of the Mo(NO)-OMo(NO) entity. Alternatively, the occurrence of these two bands may be related to the two somewhat different overall site symmetries of the NO groups, if one takes into account that N(1)O(1) is adjacent to a pyrazolyl group in the other half of the molecule, whereas N(2)O(2) is adjacent to I(1). The latter explanation seems more reasonable.

The ^{1}H n.m.r. spectrum of (2) shows ten methyl resonances, two of which are of twice the intensity of the other eight, and six C^4 proton signals. Thus all six 3,5-dimethylpyrazolyl groups are magnetically inequivalent, revealing that (2) has the same structure in solution as it does in the solid state. Usually, the methyl resonances in this type of complex occur in the range δ 7—8 p.p.m., and the appearance of two signals at 9.03 and 9.01 p.p.m., and two at 6.82 and 6.77 p.p.m., is unusual. However, as we mentioned above, two of the pyrazolyl rings are virtually face to face, and it is quite possible that ring currents arising from this intermolecular interaction may be responsible for these shielding and deshielding effects.

The Origin of Compounds (1)/(3), (2), *and* [Mo{HB(Me$_2$pz)$_3$}(NO)I(OEt)].—First, it must be noted that all the species isolated, and characterised, were obtained in relatively low yield. That other species are produced is obvious since approximately 70% of the Mo in the reaction mixtures is unaccounted for. However, despite repeated attempts at separation and spectral characterisation, we were unable to identify other products, although significant decomposition seems to occur.

The formation of (1)/(3), while unexpected because of the presumed stability of the $HB(Me_2pz)_3$ group, presumably arises by initial attack of diacetone alcohol, or less likely mesityl oxide, leading to the release of 3,5-dimethylpyrazole. Such an attack by a potentially chelating di-oxygen-containing ligand is not without precedent. Thus, addition of *o*-catechol to $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ in refluxing benzene afforded, not $[Mo\{HB(Me_2pz)_3\}(NO)(O_2C_6H_4)]$, but the deboronated species $[Mo(Me_2Hpz)_3(NO)(O_2C_6H_4)]I_3$, whose structure has been established crystallographically.[14] This deboronation reaction proceeded in good yield and we presume that a by-product is the stable catecholate ion, $[B(O_2C_6H_4)_2]^-$, although we have not confirmed this. We may therefore imagine that diacetone alcohol can behave similarly, extracting the boron atom as the ions $[B(OCMe_2CH_2COMe)_2]^+$ or $[B(OCMe_2CHCOMe)_2]^-$.

The pyrazole so released could then add to mesityl oxide, affording the bicyclic cation as shown in the Scheme. Addition of pyrazoles to α,β-unsaturated carbonyl compounds is known,[15] but so far as we are aware, 1,4-cycloaddition of this particular type is new. So far, we have not been able to achieve this cyclisation using the pyrazole, mesityl oxide, and traces of HI, although our attempts have not been exhaustive.



Scheme.

The binuclear complex $[\{Mo[HB(Me_2pz)_3](NO)I\}_2O]$, may be produced in several ways. Firstly, water is generated during the dehydration of diacetone alcohol, present in both reaction systems studied. This dehydration may be acid catalysed (by HI possibly) or base catalysed (by pyrazole or some other unidentified base). Attack by H_2O on $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ could give $[Mo\{HB(Me_2pz)_3\}(NO)I(OH)]$, and this hydroxide could further react with the di-iodide, eliminating HI and affording the μ-oxo-species. We have made the hydroxide by another route,[1] but so far have been unable to demonstrate unambiguously formation of the μ-oxo-species as outlined above. Secondly, we have noted that in recrystallisation of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ in dry toluene in the air, small but significant amounts of (2) are formed. Indeed, if dry air is passed slowly through a suspension of pure $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ in refluxing heptane (refluxing temperature quite similar to that of the acetone–diacetone alcohol–mesityl oxide mixture) olive-green solids apparently identical to (2) are produced. This implies that there is a reaction between $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ and O_2 giving the μ-oxo-species (2), but this has so far been difficult to prove. Thus it appears that the source of the bridging O atom could be H_2O or oxygen and further work is necessary to clarify this situation.

The mechanism of formation of $[Mo\{HB(Me_2pz)_3\}(NO)I(OEt)]$ must be even more speculative than the foregoing suggestions. We have shown[6] that $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ can be reduced by basic solvents, giving $[Mo\{HB(Me_2pz)_3\}(NO)I_2]^-$. However, although acetone is sufficiently ' basic ' to achieve this reduction, its concomitant oxidation to an ethoxide radical seems unlikely. One-electron oxidation of acetone usually leads to the production of methyl or acetyl radicals, although occasionally $CH_2COMe^{\bullet}$ can be formed.[16] It is possible that enolisation of the acetone, followed by elimination of HI from the di-iodide precursor, could give the transient $[Mo\{HB(Me_2pz)_3\}(NO)I\{OC(=CH_2)Me\}]$ which might then undergo hydrolysis of the methylene group affording the ethoxide complex and formaldehyde. We have been unable, however, to detect C(1)-derived reaction products and, given the low yield of the ethoxide, this is not surprising. We are confident, however, that ethanol is *not* present in the reaction or crystallisation solvents, so that $[Mo\{HB(Me_2pz)_3\}(NO)I(OEt)]$ is not produced by adventitious ethanol, but must be formed *via* a relatively mild cleavage of a C–C bond in acetone.

Acknowledgements

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