Inorg. Chem. **1992**, *31*, 263-267 **263**

Contribution from the Department of Physics, College of Education, AlMustansiriyah University, Baghdad, Iraq,
Department of Chemistry, Eastern University of Sri Lanka, Vantharumoolai, Sri Lanka,
and School of Chemistry, University of Birmingham, Birmingham B15 2TT, U.K.

Redox-Responsive Molybdenum Mononitrosyl Complexes Incorporating Cyclic Polyether Cation Binding Sites and X-ray Crystal Structure of [Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}]

Najat J. AlObaidi,[1a] Sithy S. Salam,[1b] Paul D. Beer,[1c] Christopher D. Bush,[1d] Thomas A. Hamor,*,[1d]
Ferida S. McQuillan,[1d] Christopher J. Jones,*,[1d] and Jon A. McCleverty[1e]

Received November 14, 1989

The complexes [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_n$CH$_2$O}] (n = 2–5; HB(Me$_2$pz)$_3^-$ = hydrotris(3,5-dimethylpyrazolyl)borate) have been synthesized and characterized by spectroscopic methods. All contain the redox-active {Mo(NO)}$^{3+}$ moiety incorporated in an unusually large chelate ring which forms a cyclic polyether structure. Cyclic voltammetric studies of these compounds reveal a reduction process at ca. −1.3 V (SCE) which is shifted to more anodic potentials in the presence of an equimolar concentration of sodium ions. At higher concentrations, decomposition is associated with the reduction process. In the case where n = 3, 1:1 complexes with Li$^+$, Na$^+$, and K$^+$ have been isolated. The molecular structure of [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}] has been determined by X-ray diffraction methods. The compound crystallizes in the orthorhombic space group *Pbca* (No. 61) with eight molecules in a cell of dimensions a = 16.937 (3), b = 15.143 (4), and c = 22.034 (8) Å. Full-matrix least-squares refinement gives final R, R_w on F of 0.051, 0.079 for 3063 observed [$F > 5\sigma(F)$] data. This structure confirms the presence of a 14-membered chelate ring (Mo–O = 1.903 (4) and 1.910 (4) Å; O–Mo–O = 101.0 (2)°) and a linear nitric oxide ligand (Mo–N–O = 177.9 (5)°; N–O = 1.190 (6) Å). The cyclic polyether ring is extended away from the bulky HB(Me$_2$pz)$_3$ ligand.

Introduction

The production of compounds which may act as detectors for specific substrates at the molecular level presents a challenging long-term goal for synthetic chemists.[2] As a part of the development of such systems, it is important to demonstrate that simpler prototype compounds can exhibit a change in their physical properties in the presence of a substrate. Among other systems, interest has focused on cyclic polyether derivatives because of the ability of the polyether to bind cations and act as a receptor site. The linking of a cyclic polyether to a group which may change its spectroscopic, magnetic, or electrochemical properties in response to the binding of a cation at the polyether site then provides a simple prototype "molecular sensor". To this end, crown ether derivatives carrying pendant organic redox sites involving nitrophenyl or antraquinone substituents have been synthesized.[3-5] The reduction potentials of the pendant redox centers in these molecules have been shown to be sensitive to the binding of alkali-metal ions. A cyclic polyether incorporating a redox-active quinone incorporated in the polyether ring has also been described.[6] Again, the reduction potential of the quinone moiety was found to undergo an anodic shift in the presence of alkali-metal ions.

In addition to these purely organic molecules, compounds incorporating transition-metal redox centers in a cyclic polyether have also been described.[7-14] This work has almost entirely concentrated on metallocene redox centers which can undergo oxidation processes.[12-14] In our laboratory, we have developed an extensive derivative chemistry for the {Mo(NO)(HB(Me$_2$pz)$_3$)} (HB(Me$_2$pz)$_3^-$ = hydrotris(3,5-dimethylpyrazolyl)borate) moiety.[15,16] We have also demonstrated that the reduction potential of the {Mo(NO)}$^{3+}$ core in [Mo(NO)HB(Me$_2$pz)$_3$XY] (X and Y are halide, alkyl- or aryl–oxo, or alkyl- or aryl–amido) is very sensitive to the nature of X and Y.[17-19] This work provides a basis for the development of compounds containing both a reducible molybdenum mononitrosyl redox center and a cyclic polyether cation binding site. The first objective of the work described here was to demonstrate the synthesis of [Mo(NO)HB(Me$_2$pz)$_3$(CP)] in which CP represents a cyclic polyether receptor site bound via oxygen atoms to the {Mo(NO)HB(Me$_2$pz)$_3$}$^{2+}$ moiety. The second objective was to establish whether the electrochemical properties of the molecule would be affected by the presence or absence of a cationic substrate.[20] Our synthetic and structural results are described here along with some preliminary studies of the effect of sodium ions on the reduction potentials of the complexes.

Experimental Section

Materials. All reagents were used as supplied, and [Mo(NO){HB(Me$_2$pz)$_3$}I$_2$]·C$_6$H$_5$Me was prepared according to previously described methods.[21] Solvents used as reaction media were dried according to standard methods and freed of oxygen before use. All reactions were carried out under nitrogen, but purification procedures were carried out in air except in the case of the alkali-metal complexes, which were manipulated under a dry nitrogen atmosphere. Silica Gel 60 (70–230 mesh) was used as the stationary phase for column chromatography. Elemental analyses were carried out by the Microanalytical Laboratory, University of Birmingham.

Apparatus. Infrared spectra were recorded using a PE 297 spectrometer. The 270-MHz and 400-MHz ^{1}H NMR spectra were obtained from

---

(1) (a) AlMustansiriyah University. (b) Eastern University of SriLanka. (c) Present address: Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K. (d) University of Birmingham. (e) Present address: School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

(2) Dix, J. P.; Vogtle, F. *Chem. Ber.* **1980**, *113*, 457.

(3) Kaifer, A.; Echegoyen, L.; Gustowski, G. A.; Goli, D. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 7168.

(4) Gustowski, G. A.; Echegoyen, L.; Goli, D. M.; Kaifer, A.; Schultz, R. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 1633.

(5) Echegoyen, L.; Gustowski, G. A.; Gatto, V. J.; Gokel, G. W. *J. Chem. Soc., Chem. Commun.* **1986**, 220.

(6) Wolf, R. E., Jr.; Cooper, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 4646.

(7) Bell, A. P.; Hall, C. D. *J. Chem. Soc., Chem. Commun.* **1980**, 163.

(8) Akabori, S.; Habata, Y.; Sakamoto, Y.; Sato, M.; Ebine, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 537.

(9) Sato, M.; Kubo, M.; Ebine, S.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 421.

(10) Fu, E.; Green, M. L. H.; Lowe, V. J.; Marder, S. R. *J. Organomet. Chem.* **1988**, *341*, C39.

(11) Beer, P. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1115.

(12) Beer, P. D.; Sikanyika, H.; Blackburn, C.; McAleer, J. F.; Drew, M. G. B. *J. Organomet. Chem.* **1988**, *356*, C19.

(13) Andrews, M. P.; Blackburn, C.; McAleer, J. F.; Patel, V. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1122.

(14) Saji, T. *Chem. Lett.* **1986**, 275.

(15) McCleverty, J. A. *Chem. Soc. Rev.* **1983**, *12*, 331.

(16) AlObaidi, N.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Paxton, K. *J. Chem. Soc., Dalton Trans.* **1986**, 1525.

(17) AlObaidi, N.; Chaudhury, M.; Clague, D.; Jones, C. J.; Pearson, J. C.; McCleverty, J. A.; Salam, S. S. *J. Chem. Soc., Dalton Trans.* **1987**, 1733.

(18) AlObaidi, N.; Charsley, S. M.; Hussain, W.; Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; Reynolds, S. J. *Transition Met. Chem.* (*London*) **1987**, *12*, 143.

(19) Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; Reynolds, S. J.; Adams, H.; Bailey, N. A.; Denti, G. *J. Chem. Soc., Dalton Trans.* **1986**, 733.

(20) AlObaidi, N.; Beer, P. D.; Bright, J. P.; Jones, C. J.; McCleverty, J. A.; Salam, S. S. *J. Chem. Soc., Chem. Commun.* **1986**, 239.

(21) Reynolds, S. J.; Smith, C. F.; Jones, C. J.; McCleverty, J. A.; Bower, D. C.; Templeton, J. L. *Inorg. Synth.* **1985**, *23*, 4.

0020-1669/92/1331-0263$03.00/0 © 1992 American Chemical Society

solutions in CDCl$_3$ using a JEOL GX270 spectrometer at the University of Birmingham and a Bruker WH400 spectrometer of the SERC high-field NMR service at the University of Warwick. Mass spectra were recorded using a Kratos MS80 spectrometer. Cyclic voltammetric measurements were made using a PAR 174A polarograph.

Preparations. [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$O}] (1). A solution of [Mo(NO){HB(Me$_2$pz)$_3$}I$_2$]·C$_6$H$_5$Me (1.0 g, 1.3 mmol), 1.8-dihydroxy-3,6-dioxaoctane (C$_6$H$_{14}$O$_4$; 2 cm^3, 15 mmol), and triethylamine (2.0 cm^3) in dichloromethane (60 cm^3) was heated under reflux for 1 h. After this time, the solvent volume was reduced (to ca. 25 cm^3) by evaporation under reduced pressure and the red product precipitated by slow addition of *n*-hexane. This material could be purified by column chromatography on silica gel using 1% (v/v) tetrahydrofuran in dichloromethane as the eluant. The major red/pink band was collected. Further purification could be effected by recrystallization using dichloromethane to dissolve the material followed by the dropwise addition of *n*-hexane and slow evaporation of the solvent under ambient conditions; yield 0.4 g (48%). Anal. Calc for C$_{21}$H$_{34}$N$_7$BO$_5$Mo: C, 44.2; H, 6.0; N, 17.2. Found: C, 44.4; H, 6.0; N, 17.5.

[Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}] (2). A procedure similar to that described above for [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$O}] was employed using 1,11-dihydroxy-3,6,9-trioxaundecane (C$_9$H$_{18}$O$_5$; 2 cm^3, 11.6 mmol) in place of 1,8-dihydroxy-3,6-dioxaoctane; yield 0.62 g (68%). Anal. Calc for C$_{23}$H$_{38}$N$_7$BO$_6$Mo: C, 44.9; H, 6.2; N, 15.9. Found: C, 45.4; H, 6.4; N, 16.2.

[Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_4$CH$_2$O}] (3). A procedure similar to that described above for [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$O}] was employed using 1,14-dihydroxy-3,6,9,12-tetraoxatetradecane (C$_{10}$H$_{22}$O$_6$; 2.0 cm^3, 9.5 mmol) instead of 1,8-dihydroxy-3,6-dioxaoctane; yield 0.6 g (61%). Anal. Calc for C$_{26}$H$_{42}$N$_7$BO$_7$Mo: C, 45.5; H, 6.4; N, 14.9. Found: C, 45.3; H, 6.5; N, 15.1.

[Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_5$CH$_2$O}] (4). A procedure similar to that described above for [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$O}] was employed using [Mo(NO){HB(Me$_2$pz)$_3$}I$_2$]·C$_6$H$_5$Me (1.5 g, 2.0 mmol), 1.17-dihydroxy-3,6,9,12,15-pentaoxaheptadecane (C$_{12}$H$_{26}$O$_7$; 1.5 cm^3, 6.0 mmol) in place of 1,8-dihydroxy-3,6-dioxaoctane, and a reaction time of 3 h; yield 0.7 g (47%). Anal. Calc for C$_{27}$H$_{46}$N$_7$BO$_8$Mo: C, 46.1; H, 6.5; N, 13.9. Found: C, 46.0; H, 6.4; N, 14.1.

[Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}Na]PF$_6$. A solution of [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}] (123 mg, 0.2 mmol) and NaPF$_6$ (168 mg, 1.0 mmol) in acetonitrile (50 cm^3) was heated under reflux for 30 min. The mixture, after being allowed to cool, was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was redissolved in dichloromethane (30 cm^3), the mixture was filtered, and diethyl ether was added dropwise to the filtrate to precipitate the magenta product (40 mg, 26%), which was collected by filtration, washed with *n*-pentane, and dried in vacuo. Anal. Calc for C$_{23}$H$_{38}$N$_7$BO$_6$F$_6$PNaMo: C, 35.3.1; H, 4.9; N, 12.5. Found: C, 35.4; H, 5.0; N, 12.7. IR: ν_{NO} 1650, ν_{PF} 850 cm^{-1}.

[Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}Li]BF$_4$. This compound was prepared by following the procedure described above for [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}Na]PF$_6$ using LiBF$_4$ (94 mg, 1.0 mmol) instead of NaPF$_6$. Anal. Calc for C$_{23}$H$_{38}$N$_7$LiB$_2$O$_6$F$_4$Mo: C, 39.0; H, 5.4; N, 13.8. Found: C, 39.0; H, 5.3; N, 13.8. IR: ν_{NO} 1680, ν_{BF} 1075 cm^{-1}.

[Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}K]PF$_6$. This compound was prepared by following the procedure described above for [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}Na]PF$_6$ using [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}] (62 mg, 0.1 mmol) and KPF$_6$ (92 mg, 0.5 mmol) in acetonitrile (25 cm^3). The crude reaction product was redissolved in dichloromethane (25 cm^3). Anal. Calc for C$_{23}$H$_{38}$N$_7$BO$_6$F$_6$PKMo·$^1/_5$C$_5$H$_{12}$: C, 35.4; H, 5.0; N, 12.0. Found: C, 35.9; H, 4.7; N, 12.2. IR: ν_{NO} 1645, ν_{PF} 850 cm^{-1}.

X-ray Structural Studies of 2-Nitrosyl-2-(hydrotris(3,5-dimethylpyrazol-1-yl)borato)-2-molybdena-1,3,6,9,12-pentaoxacyclotetradecane, [Mo(NO){HB(Me$_2$pz)$_3$}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}]. A reddish, brick-shaped crystal (0.4 × 0.5 × 0.6 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer; cell dimensions and intensities were measured by $\omega/2\theta$ scans with graphite-monochromated Mo Kα radiation and scan range (ω) = (1.1 + 0.35 tan θ)°. A total of 4964 unique reflections were scanned within the octant 0–*h*, 0–*k*, 0–*l* up to θ = 25°. Two standard reflections measured every 2 h showed no significant variation in intensity. A total of 3063 structure amplitudes with $F > 5\sigma(F)$ were considered observed and used in the analysis. Crystallographic data are given in Table I. The structure was determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for the heavier atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atom with isotropic temperature factors U = 0.07 Å^2. Weights $w = 1/(\sigma^2(F) + 0.001F^2)$, which resulted in a satisfactory weighting analysis, were used in the least-squares refinement. The refinement converged to R = 0.051, R_w = 0.079, with a maximum shift:error ratio of 0.2. The residual electron density in a final difference map was within the range −0.99 to +0.76 e Å^{-3}. No corrections were made for absorption or extinction.

Table I. Crystallographic Data for the Complex [{Mo(NO){HB(Me$_2$pz)$_3$}}{OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$O}] (**2**)

formula C$_{23}$H$_{38}$BMoN$_7$O$_6$	fw 615.3
a = 16.937 (3) Å	space group *Pbca* (No. 61)
b = 15.143 (4) Å	T = 20 °C
c = 22.034 (8) Å	λ = 0.71069 Å
V = 5651.2 Å^3	μ = 4.98 cm^{-1}
Z = 8	$R(F_o)^a$ = 0.051
ρ_{calc} = 1.447 g cm^{-3}	$R_w(F_o)^b$ = 0.079

$^a R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Fractional Atomic Coordinates (Mo, ×10^5; Others, ×10^4) with Esd's in Parentheses

	x	y	z
Mo	−219 (3)	17864 (3)	15889 (2)
N(1)	−419 (3)	2651 (3)	2038 (2)
N(2)	496 (3)	720 (3)	1001 (2)
N(3)	1055 (3)	924 (4)	576 (2)
N(4)	1214 (3)	2260 (3)	1642 (2)
N(5)	1714 (3)	2146 (3)	1151 (2)
N(6)	80 (3)	2621 (4)	762 (3)
N(7)	696 (3)	2502 (4)	372 (2)
C(1)	−222 (5)	−630 (5)	1337 (4)
C(2)	339 (4)	−155 (4)	942 (3)
C(3)	787 (4)	−494 (4)	483 (3)
C(4)	1241 (4)	181 (5)	257 (3)
C(5)	1844 (6)	174 (6)	−233 (4)
C(6)	1339 (4)	2794 (4)	2701 (3)
C(7)	1660 (3)	2569 (4)	2101 (3)
C(8)	2431 (4)	2646 (4)	1909 (3)
C(9)	2461 (3)	2370 (4)	1314 (3)
C(10)	3147 (4)	2346 (5)	887 (4)
C(11)	−1114 (5)	3555 (6)	799 (4)
C(12)	−395 (5)	3242 (5)	505 (4)
C(13)	−60 (5)	3520 (5)	−26 (4)
C(14)	616 (5)	3040 (5)	−114 (3)
C(15)	1226 (6)	3110 (7)	−609 (4)
C(16)	−57 (4)	1056 (4)	2855 (3)
C(17)	−429 (4)	193 (5)	3052 (3)
C(18)	−1225 (5)	−387 (5)	3844 (3)
C(19)	−2076 (5)	−190 (5)	3711 (4)
C(20)	−2997 (5)	1 (5)	2937 (5)
C(21)	−3112 (5)	−28 (5)	2269 (5)
C(22)	−2048 (4)	743 (7)	1867 (4)
C(23)	−1781 (4)	1505 (5)	1485 (4)
O(1)	−698 (3)	3212 (3)	2350 (2)
O(2)	175 (2)	989 (3)	2239 (2)
O(3)	−706 (3)	307 (3)	3655 (2)
O(4)	−2206 (3)	−193 (3)	3079 (3)
O(5)	−2845 (3)	737 (4)	1957 (3)
O(6)	−1007 (2)	1349 (3)	1293 (2)
B	1376 (5)	1861 (5)	533 (4)

Complex neutral-atom scattering factors were taken from ref 22. Computations were carried out on the University of Birmingham Honeywell computer and at the University of Manchester Regional Computer Centre with the SHELX76[23a] and ORTEP[23b] programs. Fractional atomic coordinates are presented in Table II.

Discussion

Synthetic Studies. Previous attempts to produce chelating dialkoxo derivatives of the {Mo(NO)(Me$_2$pz)$_3$}$^{2+}$ moiety using α,ω-diols have been unsuccessful.[24] However, when larger sulfur

---

(22) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. 4.

(23) (a) Sheldrick, G. M. SHELX: Program for Crystal Structure Determination, University of Cambridge, 1978. (b) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

donor atoms are used, it is possible to synthesize the chelating dithiolate complex $[Mo(NO)\{HB(Me_2pz)_3\}(MeC_6H_3\text{-}3,4\text{-}S_2)]$.[25] This finding suggested that, if sufficiently large chelate rings were involved, chelating dialkoxo complexes should also be isolable under the appropriate reaction conditions. It has already been established that the reaction between $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ and alcohols, ROH, in the presence of NEt_3 offers a convenient route to the dialkoxide complexes $[Mo(NO)\{HB(Me_2pz)_3\}(OR)_2]$.[24] Accordingly, we have investigated the reactions between the polyethylene glycols $HOCH_2(CH_2OCH_2)_nCH_2OH$ (n = 2–5) and $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ in the presence of NEt_3. When a large excess of the glycol is present, the new chelate complexes $[Mo(NO)\{HB(Me_2pz)_3\}\{OCH_2(CH_2OCH_2)_nCH_2O\}]$ (**1**–**4**, respectively, with n = 2–5) can be conveniently prepared using this reaction. There is no need to use high-dilution techniques to avoid polymer or dialkoxide formation.

Attempts to isolate complexes of **1**–**4** with alkali-metal ions were only partially successful. Although complexes did appear to form, these were not usually stable and rapidly reacted with moisture to produce oily materials. Only in the case of **2** were tractable solids obtained. Elemental analyses of these are consistent with 1:1 rather than 2:1 complexes being formed with Li, Na, and K. The solid-state (KBr disk) infrared spectra of $[(\mathbf{2})M]^+$ contained ν_{NO} at 1680 (M = Li), 1650 (M = Na), and 1645 cm^{-1} (M = K) compared with the value of 1635 cm^{-1} observed when no alkali-metal ion is present. Unfortunately, even these materials are of limited stability in air, and further attempts at NMR spectroscopic characterization in solution appeared to result in opening of the chelate ring and other degradation reactions. The low stability of these species may be associated with the sensitivity of the Mo–alkoxide bond to acid hydrolysis.[15] In this case, the alkali-metal ion may serve as a Lewis acid to promote solvolysis or hydrolysis reactions.

Spectroscopic Studies. The new complexes all exhibited ν_{BH} at ca. 2550 cm^{-1} in their infrared spectra along with other bands associated with the $HB(Me_2pz)_3$ ligand. In addition, the ν_{NO} was observed in the region 1635–1640 cm^{-1}, in accord with previous observations for dialkoxides of this type.[15] The 400-MHz ^1H NMR spectral data for the polyether complexes are presented in Table III. These are consistent with the presence of a plane of symmetry in the molecule as required by the chelate formulation. All exhibit two signals of relative area 2:1 in the region δ 5.7–5.9 (relative to $SiMe_4$) attributable to the pyrazolyl 4-H protons, while the pyrazolyl 3- and 5-methyl protons appear in the range δ 2.2–2.6. The presence of a plane of symmetry requires an area ratio of 3:3:6:6 for these signals, but as result of overlap, these resonances appear as two or three signals of relative area 6:12 or 3:6:9, respectively. The protons associated with the cyclic polyether ring gave rise to three basic groups of signals. The methylene protons separated from the molybdenum by at least two oxygen atoms give rise to a complex group of overlapping multiplets in the region of δ 3.7. The protons on the β-carbon of the alkoxide moiety appear as a complex multiplet at slightly lower field in the region δ 3.8–3.9. It has been observed previously that protons on the α-carbon of alkoxide ligands bound to the $\{Mo(NO)HB(Me_2pz)_3\}^{2+}$ moiety appear at unusually low field as AB pairs.[15] Similarly, the α-methylene protons of these chelate complexes appear as two multiplets in the region of δ 5.5. The splitting patterns of these signals arise from a geminal coupling of 11 Hz within the AB pair and couplings of 5–6 Hz to the two β-methylene protons. This gives rise to a quintet in some cases, but in others higher multiplicity is resolved.

The mass spectra of **1**–**4** contained polyisotopic ion clusters at m/z values corresponding to the molecular ion (M^+) (m/z = 573, 617, 661, and 705 for **1**–**4**, respectively) in addition to prominent ions corresponding to $\{M - (NO)\}^+$ and $\{Mo(NO)HB(Me_2pz)_3\}^+$.

Electrochemical Studies. The effect of added Na^+ ions on the electrochemical properties of the polyether complexes is a topic of particular interest. This has been investigated by recording the cyclic voltammograms of the polyether complexes and then adding first one and then a second molar equivalent of $NaBPh_4$. Attempts to study this interaction in CH_2Cl_2 or tetrahydrofuran solutions were unsuccessful. Only poorly defined waves were observed after $NaBPh_4$ was added to these solutions. Better results were obtained using MeCN, although some of the complexes were of limited stability in the presence of Na^+ in this solvent also. The results of the electrochemical experiments are summarized in Table IV. All of the complexes exhibit an essentially reversible one-electron reduction process at ca. −1.3 V (SCE) in MeCN. Plots of scan rate, v, against $i_pv^{-1/2}$ (i_p = peak current) for this wave were linear over the scan rate range v = 100–500 mV s^{-1}. An irreversible oxidation process was also observed at ca. +1.6 V.

Table III. Infrared and ^1H NMR Spectra Data for $[Mo(NO)L\{OCH_2(CH_2OCH_2)_nCH_2O\}]$

compd	n	ν_{NO},[a] cm^{-1}	shift,[b] ppm	area[c]	assgnt
1	2	1635	5.803	2 s	$Me_2C_3N_2\mathit{H}$
			5.709	1 s	
			5.655	2 qi	$MoOC\mathit{H}_2$–
			5.421	2 qi	
			3.790	4 m	$MoOCH_2C\mathit{H}_2O$–
			3.685	4 m	$CH_2OC\mathit{H}_2C\mathit{H}_2OCH_2$
			2.524	6 s	$\mathit{Me}_2C_3N_2H$
			2.303	9 s	
			2.275	3 s	
2	3	1640	5.797	2 s	$Me_2C_3H_2\mathit{H}$
			5.709	1 s	
			5.854	2 oc	$MoOC\mathit{H}_2$–
			5.302	2 qi	
			3.905	4 m	$MoOCH_2C\mathit{H}_2O$–
			3.684	8 m	$CH_2OC\mathit{H}_2C\mathit{H}_2OCH_2$
			2.551	6 s	$\mathit{Me}_2C_3H_2H$
			2.333	3 s	
			2.299	9 s	
3	4	1635	5.802	2 s	$Me_2C_3H_2\mathit{H}$
			5.714	1 s	
			5.756	2 qi	$MoOC\mathit{H}_2$–
			5.392	2 qi	
			3.858	4 t	$MoOCH_2C\mathit{H}_2O$–
			3.746	12 m	$CH_2OC\mathit{H}_2C\mathit{H}_2OCH_2$
			2.535	6 s	$\mathit{Me}_2C_3H_2H_3$
			2.340	3 s	
			2.304	9 s	
4	5	1640	5.801	2 s	$Me_2C_3H_2\mathit{H}$
			5.711	1 s	
			5.703	2 qi	$MoOC\mathit{H}_2$–
			5.421	2 qi	
			3.815	4 m	$MoOCH_2C\mathit{H}_2O$–
			3.725	16 m	$CH_2OC\mathit{H}_2C\mathit{H}_2OCH_2$
			2.529	6 s	$\mathit{Me}_2C_3N_2H$
			2.304	12 s	

[a] Obtained from samples as KBr discs. [b] Obtained at 400 MHz in $CDCl_3$ solution. [c] Relative signal areas and multiplicities are given with s = singlet, d = doublet, t = triplet, qi = quintet, oc = octet, m = multiplet (with complex couplings not fully resolved), and b = broad.

As a blank experiment, similar measurements were carried out on $[\{Mo(NO)\{HB(Me_2pz)_3\}\}(OEt)_2]$. The addition of 1 equiv of $NaBPh_4$ to the solution of $[\{Mo(NO)\{HB(Me_2pz)_3\}\}(OEt)_2]$ produced no significant change in the position of the reduction wave. However, the reduction process became irreversible, as indicated by the value of i_{pc}/i_{pa}, and an anodic shift in the return oxidation wave from −1.22 to −1.04 V occurred over a period of 3 min. Addition of a second molar equivalent of $NaBPh_4$ led to a substantial decrease in i_{pc}. Thus, although the presence of Na^+ does not appear to shift the reduction potential of $[\{Mo(NO)\{HB(Me_2pz)_3\}\}(OEt)_2]$, it does appear to promote decomposition of the complex.

The addition of 1 equiv of $NaBPh_4$ to the solution of **1** initially produced little change in the position of the reduction wave as did the addition of a second equivalent. However, the wave became irreversible, as judged by the increase in i_{pc}/i_{pa}, and an anodic shift was apparent in E_{pa}. The complex was rapidly de-

---

(24) Denti, G.; McCleverty, J. A.; Wlodarczyk, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2021.

(25) AlObaidi, N.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1989**, *8*, 1033.

Table IV. Electrochemical Data for [Mo(NO){HB($Me_2pz)_3$}{$OCH_2(CH_2OCH_2)_nCH_2O$}] in the Absence and Presence of Sodium Ions[a]

	[Mo(NO){HB($Me_2pz)_3$}{$OCH_2(CH_2OCH_2)_nCH_2O$}][b]				[Mo(NO){HB($Me_2pz)_3$}{OCH_2-($CH_2OCH_2)_nCH_2O$}] with 1 equiv of $NaBPh_4$ added[f]		
	n	E_{pc},[c] V	E_{pa},[d] V	i_{pc}/i_{pa}[e]	E_{pc},[c] V	E_{pa},[d] V	i_{pc}/i_{pa}[e]
1	2	−1.34	−1.14	0.93	−1.34	−1.04	1.32
2	3	−1.36	−1.28	1.01	−1.04	−0.96	1.03
3	4	−1.32	−1.23	0.90	−1.08	−0.96	1.30
4	5	−1.30	−1.16	1.03	−1.18	−1.04	1.22
[Mo(NO){HB($Me_2pz)_3$}$(OEt)_2$]		−1.40	−1.28	0.98	−1.42	−1.22	1.63

[a] Solutions in MeCN were ca. 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in [$Bu^nN]BF_4$ as base electrolyte. A Pt-bead test electrode was used with an SCE reference electrode and a scan rate of 0.2 s^{-1}. Potentials are quoted relative to the SCE, and under these conditions, E_f for the oxidation of ferrocene was found to be 0.41 V with ΔE_p in the range 80–100 mV. No compensation for internal cell resistance was made. [b] Linear plots of scan rate (v) against $i_{pc}v^{-1/2}C$ (i_p = peak current and C = molar concentration) were obtained over the range v = 0.05–0.5 V s^{-1} for the reduction wave. The reductions were judged to be one-electron processes on the basis of comparisons with [Mo(NO){HB($Me_2pz)_3$}Cl_2] and from previous measurements.[16] All of the chelate complexes also exhibited an irreversible one-electron oxidation process in the range +1.4 to +1.6 V. [c] Cathodic peak potential. [d] Anodic peak potential. [e] Ratio of cathodic to anodic peak currents. [f] One molar equivalent of $NaBPh_4$ dissolved in Me_2CO (1 cm^3) was added to the solution in the electrochemical cell. Blank experiments involving the addition of only Me_2CO in these proportions produced no detectable change in the cyclic voltammogram.

graded in the presence of Na^+ ions, and the wave disappeared over a period of minutes.

In contrast, **2** was found to be stable in the electrochemical cell for at least 1 h in the presence of excess Na^+ ions. The addition of 1 equiv of $NaBPh_4$ to the solution produced anodic shifts of 320 mV in both E_{pc} and E_{pa}, while the value of i_{pc}/i_{pa} remained unchanged. The addition of a second equivalent of $NaBPh_4$ produced no further detectable change in the wave.

In the case of **3**, the addition of the first equivalent of $NaBPh_4$ resulted in anodic shifts of 240 mV in E_{pc} and 270 mV in E_{pa}. The wave became irreversible, as indicated by the increased i_{pc}/i_{pa} value, and after the addition of a second equivalent of $NaBPh_4$, no further change took place except that the wave disappeared over a period of minutes.

Similar behavior was found for **4**, with anodic shifts of 120 mV in E_{pc} and E_{pa} occurring after addition of the first equivalent of $NaBPh_4$. No further significant change occurred on adding a further 0.5 equiv of $NaBPh_4$, but again the complex was degraded and the wave disappeared over a period of minutes.

Attempts to assess the effects of other alkali-metal ions on the reduction potentials of these complexes were unsuccessful. The addition of Li^+ ions to the electrochemical cell induced immediate degradation of the reduction wave. The addition of K^+ ions to a solution of **2** led to the production of two reduction waves of similar height at a 1:1 molar ratio. The second of these corresponded to the free cyclic polyether complex, while the first had E_{pc} = −1.10 V and E_{pa} = −1.02 V. This appears to indicate incomplete complexation of K^+ by the polyether. Again, degradation occurred over a period of minutes, so that more definitive results could not be obtained.

The electrochemical data establish that the reduction potentials of these chelating polyether complexes are sensitive to the presence of Na^+ ions, provided the molecule contains a cyclic polyether moiety with a ring size of at least 14 atoms, including Mo. In accord with the results of the synthetic studies described earlier, **2** appears to be the complex most stable toward degradation in the presence of Na^+ ions.

The benzo-crown ether derivative [{Mo(NO){HB($Me_2pz)_3$}}-Cl{NHC_6H_3-3,4-$(OCH_2CH_2OCH_2CH_2)_2O$}], in which the cyclic polyether is separated from the molybdenum atom by an arylamido group, has been synthesized.[19] This complex has been found to exhibit an anodic shift in reduction potential of only 60 mV in the presence of Na^+ ions. This finding suggests that Coulombic effects on the reduction potentials of complexes of this type amount to less than 60 mV. Thus, the binding of Na^+ ions to **2**–**4** cannot be affecting the reduction potential of the molybdenum mononitrosyl redox center through Coulombic effects alone.

In order to obtain a more definitive view of the structural arrangements in these cyclic polyether complexes, a single-crystal X-ray diffraction study was undertaken. Unfortunately, suitable crystals of one of the cyclic polyether complexes bound to an alkali-metal cation could not be obtained. However, a structural study of **2** has been possible and confirms the formulation of this compound as a chelate complex incorporating a cyclic polyether moiety.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses and Torsion Angles (Esd's ca. 1°)

Mo–N(1)	1.775 (5)	C(16)–C(17)	1.515 (9)
Mo–N(2)	2.248 (5)	C(17)–O(3)	1.419 (8)
Mo–N(4)	2.215 (5)	C(18)–O(3)	1.432 (8)
Mo–N(6)	2.224 (6)	C(18)–C(19)	1.500 (10)
Mo–O(2)	1.903 (4)	C(19)–O(4)	1.411 (9)
Mo–O(6)	1.910 (4)	C(20)–O(4)	1.405 (9)
N(1)–O(1)	1.190 (6)	C(20)–C(21)	1.485 (12)
N(3)–B(1)	1.522 (9)	C(21)–O(5)	1.421 (9)
N(5)–B(1)	1.537 (9)	C(22)–O(5)	1.365 (8)
N(7)–B(1)	1.548 (10)	C(22)–C(23)	1.498 (11)
C(16)–O(2)	1.416 (8)	C(23)–O(6)	1.397 (8)
N(1)–Mo–N(2)	178.3 (2)	N(4)–Mo–O(6)	162.8 (2)
N(1)–Mo–N(4)	95.2 (2)	N(6)–Mo–O(6)	89.1 (2)
N(2)–Mo–N(4)	83.9 (2)	O(2)–Mo–O(6)	101.0 (2)
N(1)–Mo–N(6)	93.8 (2)	Mo–N(1)–O(1)	177.9 (5)
N(2)–Mo–N(6)	84.6 (2)	Mo–O(2)–C(16)	128.8 (4)
N(4)–Mo–N(6)	77.6 (2)	C(17)–O(3)–C(18)	112.8 (5)
N(1)–Mo–O(2)	96.6 (2)	C(19)–O(4)–C(20)	111.6 (6)
N(2)–Mo–O(2)	84.8 (2)	C(21)–O(5)–C(22)	113.0 (6)
N(4)–Mo–O(2)	90.0 (2)	Mo–O(6)–C(23)	131.1 (4)
N(6)–Mo–O(2)	164.5 (2)	N(3)–B(1)–N(5)	109.9 (5)
N(1)–Mo–O(6)	96.6 (2)	N(3)–B(1)–N(7)	109.5 (6)
N(2)–Mo–O(6)	84.0 (2)	N(5)–B(1)–N(7)	107.7 (6)
O(6)–Mo–O(2)–C(16)	−89.3		
Mo–O(2)–C(16)–C(17)	131.2		
O(2)–C(16)–C(17)–O(3)	−175.7		
C(16)–C(17)–O(3)–C(18)	166.6		
C(17)–O(3)–C(18)–C(19)	−90.7		
O(3)–C(18)–C(19)–O(4)	68.1		
C(18)–C(19)–O(4)–C(20)	−179.2		
C(19)–O(4)–C(20)–C(21)	−178.7		
O(4)–C(20)–C(21)–O(5)	−78.8		
C(20)–C(21)–O(5)–C(22)	79.7		
C(21)–O(5)–C(22)–C(23)	174.4		
O(5)–C(22)–C(23)–O(6)	−165.7		
C(22)–C(23)–O(6)–Mo	−100.1		
C(23)–O(6)–Mo–O(2)	83.6		

Structural Studies. Atomic coordinates of the complex [{Mo(NO){HB($Me_2pz)_3$}}{$OCH_2(CH_2OCH_2)_3CH_2O$}] are listed in Table II, and selected geometric parameters are given in Table V. The numbering scheme used is that illustrated in Figure 1. The coordination geometry about molybdenum is essentially octahedral (maximum angular deviation from ideal octahedral 17.2°, N(4)–Mo–O(6) = 162.8 (2)°, mean deviation 6.9°, with deviations which show a consistent pattern when compared with analogous structures based on the {Mo(NO)HB($Me_2pz)_3$} moiety. These are due to the steric rigidity of the tridentate ligand, when complexed to a metal, and the relatively small bulk of the nitrosyl group. For example, comparison with [Mo(NO)HB($Me_2pz)_3$-(2-$NHC_5H_4N)_2$][26] shows that corresponding angles differ by a

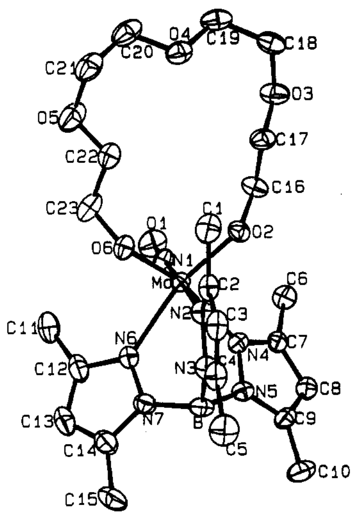

Figure 1. ORTEP[23b] diagram of complex **2** showing the atom-labeling scheme used. H atoms have been omitted for clarity.

maximum of only 1.8°, with a mean difference of 0.8°. Thus, the N–Mo–N angles between the nitrogen atoms of the $HB(Me_2pz)_3$ ligand are always less than 90°. A further common feature is that the trans angle involving the nitrosyl nitrogen atom is close to 180°, whereas the other two trans angles are generally in the range 160–165°.

No crystal structure of any other metal–tetraethylene glycolate ring system has so far been reported in the literature. Our ring system may, however, be compared with that of benzo-15-crown-5, wherein an aromatic C–C bond replaces the molybdenum atom. Cross-ring distances of O(3)- - -O(5) = 5.249 (7) and C(17)- - -C(22) = 3.877 (9) Å compare with corresponding distances in benzo-15-crown-5[28] of 4.791 (5) and 5.954 (5) Å, respectively. The molybdenum–tetraethylene glycolate ring thus shows a constriction, C(17)- - -C(22), not found in the more open ring of benzo-15-crown-5. The ring is, however, sufficiently flexible to act as host to metal ions in a manner similar to that of benzo-15-crown-5[29] or the 15-crown-5 cyclic polyether[30] with the five coordinating oxygens all pointing into the center of the ring and O–C–C–O conformations synperiplanar–synclinal.

The bonds to the pyrazolyl rings [2.215 (5)–2.248 (5) Å] are similar in length to those found previously in this type of complex. As had been observed before, the bond trans to the nitrosyl group tends to be long and is, in fact, the longest of the three in the present structure. This has been attributed[27] to the trans effect of the strongly π-accepting nitrosyl ligand. The Mo–nitrosyl length, 1.775 (5) Å, is also in good agreement with previous results and is consistent with a strongly bonding interaction. The Mo–O lengths, 1.903 (4) and 1.910 (4) Å, compare well with lengths of 1.900 (4)–1.908 (4) Å found[31] in $[Mo(NO)HB(Me_2pz)_3(OEt)(O^iPr)]$ and in the corresponding diisopropoxo complex. The Mo–O–C angles, 128.8 (4) and 131.1 (4)°, are also similar to those of 129.5 (4)–133.4 (4)° found previously in these two complexes.[31] The large angles at oxygen and the short Mo–O bond distances have been attributed[31] to $p\pi \rightarrow d\pi$ donation from oxygen to molybdenum. The alkoxy to Mo π-donation is enhanced by the near-coplanarity of the two C–O–Mo–NO moieties (torsion angles N(1)–Mo–O(2)–C(16) and N(1)–Mo–O(6)–O(23) are 8.8 (8) and −14.4 (8)°, respectively, in the present structure), which allows the alkoxy in-plane π-donation to share a common molybdenum orbital with the π-accepting nitrosyl ligand.[31]

The 14-membered molybdenum–tetraethylene glycolate ring has its atoms alternately above and below the mean ring plane by amounts ranging from 0.15 to 0.45 Å, rms deviation 0.31 Å. Inspection of the endocyclic torsion angles (Table V) shows that, to a rather rough first approximation, it possesses mirror (C_s) symmetry, the putative plane passing through the molybdenum atom and O(4).

The pyrazolyl rings are planar to within the limits of experimental error. The methyl groups lie close to their respective ring planes [maximum deviation 0.07 (1) Å]; however, the molybdenum and boron atoms deviate by somewhat greater amounts, up to 0.27 and 0.11 Å, respectively. The interplanar angles, 121.6 (6), 122.5 (6), and 115.5 (6)°, show the pattern previously noted,[16,27,31] whereby the small angle occurs between the two rings encompassing the less bulky nitrosyl group. The pyrazolyl rings are oriented nearly symmetrically with respect to the 14-membered ring. The pyrazolyl ring comprising atoms N2, N3, and C2–C4, trans to the nitrosyl group, is almost perpendicular to the least-squares ring plane (interplanar angle 85.2 (5)°), and the other two pyrazolyl rings are inclined to it at angles of 138.1 (5) and 134.8 (5)°.

Conclusion

The results described here demonstrate that complexes containing unusually large chelate rings, up to 20-membered in one case, can be obtained by linking the ends of α,ω-dihydroxy polyethers through a $\{Mo(NO)\{HB(Me_2pz)_3\}\}^{2+}$ moiety. The electrochemical findings establish that incorporating the Mo-based redox couple in the cyclic polyether ring results in significantly larger shifts in the reduction potential of the complex when equimolar concentrations of Na^+ ions are present than in systems where the redox center is separated from the cyclic polyether by an arylamido moiety.[20,32] However, the penalty for obtaining this increased shift is a reduction in the stability of the complex in the presence of Na^+ ions. Despite this limitation, the chelate complexes described here constitute a new type of redox-responsive host in which a reducible metal constitutes a component atom in the cyclic polyether ring.

Acknowledgment. We are grateful to Mr. T. Green for experimental assistance and to the SERC for support (to C.D.B). The X-ray structural studies were a contribution from the Crystallography Unit, Universities of Aston and Birmingham.

Registry No. **1**, 137917-00-1; **1**$^-$, 137917-06-7; **2**, 104626-20-2; **2**$^-$, 137917-07-8; **3**, 104602-26-8; **3**$^-$, 137917-08-9; **4**, 104580-11-2; **4**$^-$, 137917-09-0; $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$, 60106-46-9; $[Mo(NO)\{HB(Me_2pz)_3\}\{OCH_2(CH_2OCH_2)_3CH_2O\}Na]PF_6$, 137917-01-2; $[Mo(NO)\{HB(Me_2pz)_3\}\{OCH_2(CH_2OCH_2)_3CH_2O\}Li]BF_4$, 137917-03-4; $[Mo(NO)\{HB(Me_2pz)_3\}\{OCH_2(CH_2OCH_2)_3CH_2O\}K]PF_6$, 137917-05-6; $[Mo(NO)\{HB(Me_2pz)_3\}(OEt)_2]$, 60106-33-4; $[Mo(NO)\{HB(Me_2pz)_3\}(OEt)_2]^-$, 137917-10-3.

Supplementary Material Available: Listings of crystallographic details, hydrogen atom positions, anisotropic temperature factors, and bond distances and angles and an alternative view of the complex (8 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

---

(26) AlObaidi, N.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Paxton, K. *J. Chem. Soc., Dalton Trans.* **1987**, 1063.

(27) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 429.

(28) Hanson, I. R. *Acta Crystallogr.* **1978**, *B34*, 1026.

(29) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796.

(30) Bünzli, J.-C. G.; Klein, B.; Chapuis, G.; Schenk, K. J. *Inorg. Chem.* **1982**, *21*, 88.

(31) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 951.

(32) Beer, P. D.; Jones, C. J.; McCleverty, J. A.; Salam, S. S. *J. Inclusion Phenom.* **1987**, *5*, 521.