Synthetic, Electrochemical and Spectroelectrochemical Studies of Oxygen-bridged Bimetallic Molybdenum Species

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The species $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1** $[L = HB(3,5\text{-}Me_2C_3HN_2)_3]$ has been synthesised. In a separate procedure two diastereomers of both $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1,1′** and $[\{Mo(NO)L(Cl)\}(\mu\text{-}O)\{Mo(NO)L(I)\}]$ **2,2′** were isolated. Electrochemical studies of **1** have shown that the species undergoes a fully reversible, fast one-electron reduction. Spectroelectrochemistry shows that two weak near-infrared bands develop as **1** is reduced but that these bands show little or no solvent dependence. Measurements suggest that $\mathbf{1}^-$ is delocalised and is best described as a class III species.

The compound $[\{Mo(NO)L(I)\}_2(\mu\text{-}O)]$ $[L = HB(3,5\text{-}Me_2C_3HN_2)_3]$ has been previously synthesised and characterised by X-ray crystallography.[1] It was found that the bridging system was slightly asymmetric, with Mo–O bond lengths of 186 and 193 pm respectively. These bond lengths are shorter than would be expected for a single-bonded system and, hence, a degree of $d_\pi \leftarrow p_\pi$ donation was proposed. The interactions are also increased by the near eclipsing of the two octahedral units. The Mo–O–Mo system is slightly but significantly bent (171.0°). The great majority of molybdenum compounds containing a single μ-oxo group have a linear array of three atoms,[2] although exceptions have been reported.[3]

The present study reports the synthesis and characterisation of $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1** as well as the isolation of a diastereomer **1′**. The isolation of two diastereomers of $[\{Mo(NO)L(Cl)\}(\mu\text{-}O)\{Mo(NO)L(I)\}]$ is also achieved.

Experimental

All reactions were carried out under dry nitrogen and toluene was distilled from sodium and benzophenone prior to use. The complexes $[Mo(NO)LX_2]$ (X = Cl or I) were prepared as described in the literature,[4,5] and $[Mo(NO)LCl(NH_2)]$ as described elsewhere.[6] Column chromatography was carried out using silica gel as support (Merck 60, 70–230 mesh).

Infrared, electronic, mass and 400 MHz NMR spectra were recorded respectively on Perkin Elmer 297, Perkin Elmer Lambda 9, Kratos MS 90 and Bruker WH400 instruments. Elemental analysis for $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1** was performed by the Microanalytical Laboratory, University of Birmingham.

Cyclic voltammetry studies were carried out in dichloromethane containing 0.2 mol dm^{-3} NBu_4BF_4, in a three-electrode cell encompassing a platinum bead working electrode, a platinum wire secondary electrode, and a calomel reference electrode. Ferrocene was added as an internal reference. Initial studies were carried out using a PAR 174A potentiostat with built-in waveform generator with a Philips *x–y* pen recorder. Data were also acquired using a PAR 360 potentiostat interfaced with an Amstrad PC1512 computer *via* an EG&G analogue-digital convertor and processed using Condecon™ 300 software which is available from EG&G.[‡]

Spectroelectrochemistry was carried out using a Perkin Elmer Lambda 9 spectrometer whilst samples were electrolysed in an optically transparent thin layer electrochemistry (OTTLE) cell using a Metrohm potentiostat. The temperature was held at −20 °C. Samples were dissolved in the requisite solvent containing 0.4 mol dm^{-3} NBu_4BF_4 and an Ag–AgCl reference electrode was employed. During electrolysis potentials were varied in order to obtain the best plots.

$[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1**.—The complex $[Mo(NO)LCl_2]$ (0.50 g, 1.01 mmol) together with water (0.5 cm^3) and NEt_3 (0.5 cm^3) in toluene (80 cm^3) was refluxed in air for 24 h. The resulting dark green mixture was cooled, filtered and the filtrate was evaporated to dryness *in vacuo*. The solid obtained was purified by column chromatography using dichloromethane as eluent. The main green fraction was collected. Recrystallisation from dichloromethane–pentane gave $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1** as a dark green powder. Yield 0.14 g (28%). IR (KBr): 2545 ν(BH), 1690 and 1660 cm^{-1} ν(NO). ^1H NMR ($CDCl_3$): δ 5.98 (1 H, s), 5.80 (1 H, s), 5.74 (1 H, s), 5.72 (1 H, s), 5.53 (1 H, s), 5.32 (1 H, s) (C–H, pyrazole ring), 3.06 (3 H, s), 2.98 (3 H, s), 2.52 (3 H, s), 2.48 (3 H, s), 2.38 (6 H, s), 2.32 (6 H, s), 2.28 (6 H, s), 1.00 (3 H, s) and 0.90 (3 H, s) ($C\text{–}CH_3$, pyrazole ring) (Found: C, 38.8; H, 5.1; N, 20.6. $C_{30}H_{44}B_2Cl_2Mo_2N_{14}O_3$ requires C, 38.6; H, 4.8; N, 21.0%).

Diastereomers $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1,1′** *and* $[\{Mo(NO)L(Cl)\}(\mu\text{-}O)\{Mo(NO)L(I)\}]$ **2,2′**.—The complex $[Mo(NO)LCl(NH_2)]$ (50 mg, 0.10 mmol) and $[Mo(NO)LI_2]$ (75 mg, 0.11 mmol) were refluxed together in toluene (50 cm^3) with NEt_3 (0.2 cm^3) for 24 h. The solution was cooled and filtered and the filtrate was evaporated to dryness *in vacuo*. The solid was purified by column chromatography (60 × 2 cm glass column, 60:40 dichloromethane–hexane as eluent) and four dark green fractions were collected. These were evaporated to dryness *in vacuo* and redissolved in dichlomethane to which hexane was added. The products were filtered and the collected solids were washed with pentane. Fraction I, $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1′**. Yield 1.3 mg (5%). IR (KBr): 2545 ν(BH), 1700 and 1660 cm^{-1} ν(NO). ^1H NMR ($CDCl_3$): δ 5.96 (1 H, s), 5.87 (1 H, s), 5.74 (1 H, s), 5.69 (1 H, s), 5.51 (1 H, s), 5.37 (1 H, s) (C–H, pyrazole

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[‡] The Condecon software uses convolution and deconvolutions in the treatment of digitalised data from cyclic voltammetric experiments.[7] An iterative approach is used to enable modelling of experimental data and, hence, mechanistic details can be gleaned.

ring), 3.18 (3 H, s), 3.12 (3 H, s), 2.50 (3 H, s), 2.46 (3 H, s), 2.36 (9 H, s), 2.34 (3 H, s), 2.24 (3 H, s), 2.23 (3 H, s), 0.98 (3 H, s) and 0.97 (3 H, s) (C–CH_3, pyrazole ring). Fraction II, [{Mo(NO)L(Cl)}(μ-O){Mo(NO)L(I)}] **2**. Yield 2.5 mg (5%). IR (KBr): 2545 ν(BH), 1690 and 1660 cm^{-1} ν(NO). ^1H NMR ($CDCl_3$): δ 6.01 (1 H, s), 5.90 (1 H, s), 5.75 (1 H, s), 5.70 (1 H, s), 5.48 (1 H, s), 5.29 (1 H, s) (C–H, pyrazole ring), 3.15 (3 H, s), 3.13 (3 H, s), 2.50 (3 H, s), 2.48 (3 H, s), 2.36 (6 H, s), 2.34 (3 H, s), 2.30 (3 H, s), 2.26 (3 H, s), 2.25 (3 H, s), 0.98 (3 H, s) and 0.87 (3 H, s) (C–CH_3, pyrazole ring). Fraction III, [{Mo(NO)L(Cl)}(μ-O){Mo(NO)L(I)}] **2′**. Yield 5.5 mg (11%). IR (KBr): 2545 ν(BH), 1690 and 1660 cm^{-1} ν(NO). ^1H NMR ($CDCl_3$): δ 5.94 (1 H, s), 5.78 (1 H, s), 5.73 (1 H, s), 5.72 (1 H, s), 5.57 (1 H, s), 5.40 (1 H, s) (C–H, pyrazole ring), 3.02 (3 H, s), 2.99 (3 H, s), 2.53 (3 H, s), 2.46 (3 H, s), 2.37 (6 H, s), 2.34 (3 H, s), 2.31 (3 H, s), 2.24 (6 H, s), 1.00 (3 H, s) and 0.98 (3 H, s) (C–CH_3, pyrazole ring). Fraction IV, [{Mo(NO)L(Cl)}$_2$(μ-O)] **1**. Yield 8.7 mg (20%). Yields are based upon [Mo(NO)LCl(NH_2)].

Results and Discussion

Synthetic Studies.—The complex [{Mo(NO)L(Cl)}$_2$(μ-O)] **1** was initially synthesised by the addition of water to a refluxing solution of [Mo(NO)LCl_2] in toluene. Triethylamine was present to act as a base and remove any liberated HCl. It was found that a high boiling solvent such as toluene was necessary in order to achieve a reasonable yield.

A reaction between [Mo(NO)LCl(NH_2)] and [Mo(NO)LI_2] designed to synthesise a NH^- bridged species, yielded four dark green species. Although three of the fractions were isolated in quantities too small for elemental analysis, mass spectra showed two species with molecular ions at *m*/*z* 936 and two at *m*/*z* 1028. These masses correspond to the species [{Mo(NO)L(Cl)}$_2$(μ-O)] and [{Mo(NO)L(Cl)}(μ-O){Mo(NO)L(I)}] respectively, but are close to the NH^- bridged species. Lower mass peaks were also observed corresponding to fragments from these species but conclusive evidence as to their identity could not be found in the mass spectra.

The NMR data confirmed that the most prevalent species was [{Mo(NO)L(Cl)}$_2$(μ-O)] **1**, as isolated previously. No evidence was found for the presence of an NH resonance in any of the NMR spectra. It is possible that the NH proton signal could not be observed due to the relaxation rate of nitrogen-14. However, it has been noted that NH protons in the systems [Mo(NO)LX(NHR)] (X = Cl or I, R = alkyloraryl)[8] are always observed as broad signals, whereas in the systems [Mo(NO)LX(NHNRR′)] (X = I; R = Me, R′ = Me or Ph)[9] they appear as sharp singlets. In addition, the NH signals in [Mo(NO)LI(NH_2)], [Mo(NO)LCl(NH_2)] and [W(NO)LCl(NH_2)][10] are visible as two broad singlets at room temperature. It would therefore seem unlikely that in this case the relevant proton would be too broad to observe, leading to the conclusion that the species isolated were pairs of oxygen-bridged diastereomers, *viz.* [{Mo(NO)L(Cl)}$_2$(μ-O)] **1**,**1′** and [{Mo(NO)L(Cl)}(μ-O){Mo(NO)L(I)}] **2**,**2′**.

During further reactions of [Mo(NO)LCl(NH_2)] with a variety of reagents, but often in the presence of NEt_3, two dark green fractions were isolated in small and varying yields. The two fractions were demonstrated to be [{Mo(NO)L(Cl)}$_2$(μ-O)] **1**,**1′** as evidenced by mass spectral and infrared data. Once again the source of the O^{2-} is almost certainly water which would be present in the NEt_3 and may be present in the [Mo(NO)LCl(NH_2)] starting material.

It appears that the mechanisms for the production of oxygen-bridged species vary depending upon the starting materials. The reaction between [Mo(NO)LCl_2] and water produces only one diastereomer **1**, presumably the thermodynamic species, whereas a mixture of [Mo(NO)LCl(NH_2)] and [Mo(NO)LCl_2] or just [Mo(NO)LCl(NH_2)] alone produces a mixture of diastereomers **1**, **1′** despite both reactions being carried out in toluene. This implies that the NH_2 group plays an important role in the mechanism additionally evidenced by the isolation of the two diastereomers of [{Mo(NO)L(Cl)}(μ-O){Mo(NO)L(I)}] **2**,**2′**.

Spectroscopic Studies.—Proton NMR spectra were obtained for all four species. In common with [{Mo(NO)L(I)}$_2$(μ-O)] the spectra showed that the molecules do not possess a plane or an axis of symmetry. Additionally the methyl resonances spread over a range of about 2.2 ppm, as a consequence of ring currents due to the interleaving of pyrazole rings.

The infrared spectra showed similar patterns for all species. Most noticeable was the universal appearance of two nitrosyl resonances, a feature shared with [{Mo(NO)L(I)}$_2$(μ-O)].

Electrochemical Studies.—Cyclic voltammetry was carried out on complex **1** in dichloromethane, using 0.2 mol dm^{-3} NBu_4BF_4 as base electrolyte, and one reduction process was observed with a half wave potential of −0.560 ± 0.005 V. Additionally, cyclic voltammetric studies of the minor isomer of [{Mo(NO)L(Cl)}$_2$(μ-O)] **1′** showed a reversible reduction process with a half-wave potential of −0.315 ± 0.005 V. Reasons for the difference between the two potentials are not known.

Attempts at coulometry on complex **1** failed to give a satisfactory result since plots of current against charge passed gave various intercept values, all of which were less than one electron equivalent. Hence, analysis of the cyclic voltammogram using the Condecon software was attempted. Analysis of the reduction process for [{Mo(NO)L(Cl)}$_2$(μ-O)] **1** proved it to involve a single electron in a fully reversible diffusion controlled process with $E_{\frac{1}{2}} = -0.560 \pm 0.010$ V. The failure to observe a second reduction process suggests that the mixed-valence state is stable with respect to disproportionation. However, attempts at chemical reduction by cobaltocene ($E_{\frac{1}{2}} = -0.90$ V) in bulk and in an EPR tube produced only starting material, **1**, in the former case and a very weak signal, presumably due to $\mathbf{1}^-$, in the latter.*

Spectroelectrochemical Studies.—Reductive electrolysis of complex **1** was carried out in various solvents at −20 °C while monitoring the UV/VIS/near-IR spectrum. The results are shown in Table 1

Plots showing the electronic spectra for **1** and $\mathbf{1}^-$ in $CHCl_3$ are shown in Fig. 1. In each solvent the reduced species was reoxidised electrolytically to test the chemical reversibility. In all four solvents reversible behaviour was demonstrated.

Reductive electrolysis of **1** leads to the loss of two charge-transfer bands at *ca.* 17 500 and 21 500 cm^{-1} and the appearance of two new bands at about 22 000 and 26 000 cm^{-1}. All bands show some solvatochromism, however, attempts to correlate the band energies with solvent parameters (*e.g.* optical and static dielectric constants) have not shown any pattern.

Near-infrared bands in $\mathbf{1}^-$. Whereas many models describing class II mixed-valence behaviour are currently vying for acceptance, that developed by Hush remains the easiest to apply. This model relates the energy of any intervalence charge transfer (i.v.c.t.) band, E_{op}, to spectroscopically measurable properties of the molecule under consideration and to solvent properties. The relevant expression is given by equation (1), where

$$E_{outer} = \frac{(me)^2}{4\pi\varepsilon_0}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad (1)$$

E_{outer} is the outer-sphere contribution to the energy, d_1 and d_2 are the metal–ligand distances, a_1 and a_2 are the

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* Some other systems containing the $\{Mo(NO)L\}^{2+}$ core have also displayed very slow kinetics upon attempted chemical reduction with cobaltocene as well as with other chemical reductants.

Table 1 Spectroelectrochemical data for $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1**

Solvent	Species	ν_{max}/cm^{-1} ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)				
$CHCl_3$	**1**	—	—	17 730 (2 220)	23 350 (26 290)	31 650 (10 250)
	$\mathbf{1}^-$	6 800 ± 750 (20 ± 5)	11 900 ± 400 (50 ± 5)	21 900 (2 150)	26 150 (8 660)	31 650 (10 250)
CH_2Cl_2	**1**	—	—	17 800 (3 350)	21 700 (26 900)	31 000 (10 250)
	$\mathbf{1}^-$	8 700 ± 500 (300)	—	23 000 (7 350)	26 200 (7 300)	—
Acetone	**1**	—	—	17 820 (2 160)	23 320 (27 100)	—
	$\mathbf{1}^-$	8 950 ± 500 (25 ± 5)	11 600 ± 250 (65 ± 5)	21 780 (2 160)	25 930 (7670)	—
MeCN	**1**	—	—	17 640 (1 760)	23 320 (20 000)	31 530 (8 450)
	$\mathbf{1}^-$	7 600 ± 1 000 (15 ± 5)	11 750 ± 500 (35)	21 700 (1 840)	26 040 (7210)	—

Table 2 Near-IR data for $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]^-$ $\mathbf{1}^-$

	Solvent	$(1/D_s - 1/D_{op})$	ν_{max}/cm^{-1}	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$	$\Delta\nu_{\frac{1}{2}}/cm^{-1}$	$\Delta\nu_{\frac{1}{2}}$(calc.)*$/cm^{-1}$
Band 1	$CHCl_3$	0.267	6 800 ± 750	20	4 600 ± 1 000	3 960
	CH_2Cl_2	0.381	8 700 ± 500	300	5 000 ± 500	3 399
	Acetone	0.495	8 950 ± 500	25	3 300 ± 500	4 547
	MeCN	0.526	7 600 ± 750	20	3 950 ± 500	4 190
Band 2	$CHCl_3$	0.267	11 900 ± 400	45	2 300 ± 500	5 243
	Acetone	0.495	11 750 ± 300	65	2 300 ± 500	5 176
	MeCN	0.526	11 750 ± 500	35	3 300 ± 500	5 210

* Values for $\Delta\nu_{\frac{1}{2}}$(calc.) were obtained from: $\Delta\nu_{\frac{1}{2}} = (2\,310\nu_{max})^{\frac{1}{2}}$.

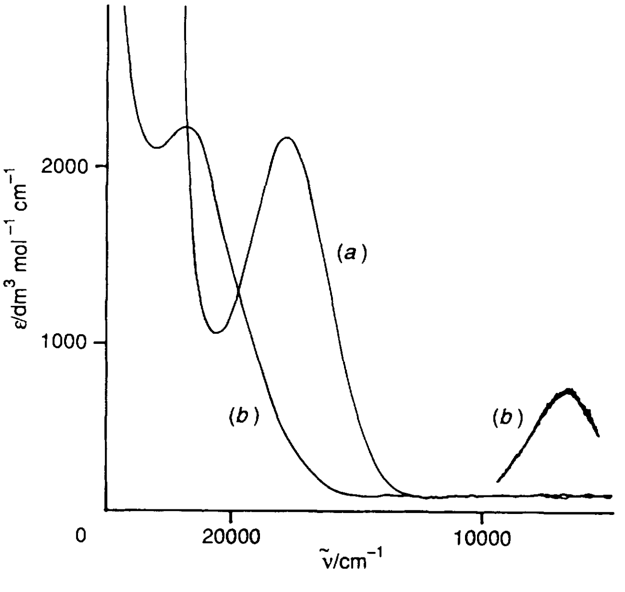

Fig. 1 Plots showing electronic spectra of (*a*) **1** and (*b*) $\mathbf{1}^-$ in $CHCl_3$ at −20 °C

molecular radii at the electron donor and acceptor sites, *r* is the separation between the metal centres, D_{op} and D_s are the optical and static dielectric constants of the solvents, *m* is the extent of charge transfer and ε_0 is the permittivity of free space. This equation predicts a solvent dependence for the i.v.c.t. band of a class II mixed-valence species.

In the near-IR region complex **1** is transparent, but two absorption bands appear for the reduced product. The properties of the near-IR bands are summarised in Table 2, including values of $\Delta\nu_{\frac{1}{2}}$ and $\Delta\nu_{\frac{1}{2}}$(calc.), the spectral band width at half-height. The $\Delta\nu_{\frac{1}{2}}$(calc.) values were obtained from the ν_{max} data.

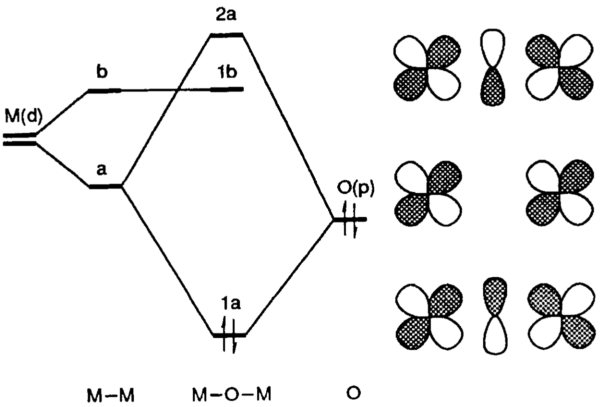

Fig. 2 Qualitative molecular orbital description of an M–O–M bridge

Plots of E_{op} against $(1/D_{op} - 1/D_s)$ were made for the two bands in $\mathbf{1}^-$ measured in a variety of solvents. Band 1 shows slight variation with solvent and the best-fit line has a slope of 3.2×10^3 cm^{-1}, and a *y* intercept value of 6.8×10^3 cm^{-1}. However, the correlation coefficient of these data is only 0.46. Band 2, in contrast, shows very little variation with solvent.

The band-width data reported in Table 2 reveal that for band 1 the widths are close to the predicted values, however, for band 2 the widths are about half of those calculated. Narrow bands tend to be indicative of delocalised bonding descriptions. For example, the Creutz–Taube ion $[(H_3N)_5Ru(NC_4H_4N)\text{-}Ru(NH_3)_5]^{5+}$ has near-IR band-widths about one third of those predicted.[11]

The spectroscopic data collected suggest that $\mathbf{1}^-$ is a delocalised species. Fig. 2 shows a qualitative molecular orbital diagram for the Mo–O–Mo bridge. The bridge has been treated as linear with C_2 symmetry, although the bonding description does not change for C_s or C_i symmetry. The true description would probably have non-degenerate d orbitals because of the asymmetric nature of the bridge. Additionally a second set of molecular orbitals, perpendicular to those shown, may be present if the symmetry allows. However, if this was the case then the p orbitals involved would donate a total of four electrons to the scheme. A similar qualitative diagram to that shown has been used in ref. 2 to explain the properties of a Ru–O–Ru array, albeit including two sets of Ru(d) and O(p) orbitals.

Although qualitative, Fig. 2 provides an explanation for the electronic observations. The absorption spectrum of the neutral species **1** is dominated by a strong band in the visible region. This band is lost upon reduction. Fig. 2 shows that this band is due to an electronic transition between the highest-occupied and lowest-unoccupied molecular orbitals 1a and 1b. Upon reduction the 1b level is partially filled and the 1a to 1b transition is reduced in intensity and shifted. The low-energy bands observed in the near-IR region then are due to transitions between the 1b and 2a levels.

Conclusion

Synthesis of $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1** has been achieved by the reaction of $[Mo(NO)LCl_2]$ with water in the presence of NEt_3. In a separate procedure diastereomeric pairs of $[\{Mo(NO)L(Cl)\}_2(\mu\text{-}O)]$ **1,1′** and $[\{Mo(NO)L(Cl)\}(\mu\text{-}O)\{Mo(NO)L(I)\}]$ **2,2′** were isolated by the reaction of $[Mo(NO)LCl(NH_2)]$ and $[Mo(NO)LI_2]$.

Cyclic voltammetric and spectroelectrochemical investigations show that complex **1** undergoes a one-electron reduction process and that the resulting mixed-valence species is delocalised. Complex $\mathbf{1}^-$ is thus a class III species.

Acknowledgements

We thank Mr. Terry Green for technical assistance and the SERC NMR service based at Warwick University for 400 MHz NMR spectra.

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Received 1*st October* 1992; *Paper* 2/05280F