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Solid State Spectroscopic Studies of Molybdenum Oxo Species with Coordinated ONR Groups

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A re-investigation of some complexes of molybdenum claimed to contain coordinated C-nitroso compounds has demonstrated that these solids are complex and that π-coordination of RNO cannot be the sole structural component.

Middleton and Wilkinson[1] reported the formation of coloured solids $MoO_2(ONR)$ (R = Me, Ph) when molybdenum hexacarbonyl was refluxed in the corresponding nitro compound for 16 h under nitrogen. Crystalline specimens could not be isolated but it was suggested on the basis of IR spectroscopic data that these solids contained π-coordinated C-nitroso compounds. In view of our interest in the coordination chemistry of C-nitrosco compounds[2] we decided to investigate these solids using a much wider range of spectroscopic techniques than was employed in the original study. It was also decided to widen the investigation to include R = Pr^n and Pr^i. For ease of reference we designate the materials studied of approximate stoichiometry $MoO_2(ONR)$ as **I**, **II**, **III** and **IV**, where R = Ph, Me, Pr^n and Pr^i, respectively. Our IR spectra for **I** and **II** are in good agreement with those of Middleton and Wilkinson[1] and confirm the absence of carbonyl ligands. These authors identified the band at 950 cm^{-1} with that of η^2-coordinated nitroso compounds but this is ambiguous because the Mo=O stretching frequency values lie within the range[7,8] 930–960 cm^{-1}. It was also apparent that the previously reported[1] solubility of **I** and **II** in DMSO could not be repeated: DMSO-d_6 solution NMR measurements of these insoluble materials showed only extremely minute quantities of the starting nitro compounds, presumably occluded within the solid materials which themselves were insoluble. Repeated preparations over many years have never resulted in DMSO soluble products.

Extension of the spectroscopic study of these solids was obviously desirable in order to obtain further evidence for the organic component RNO. Table 1 presents the CP MAS ^{13}C and ^{15}N NMR spectral data for complexes **I**–**IV**.

Table 1 ^{13}C and ^{15}N CP MAS NMR spectra of the complexes $MoO_2(ONR)$, (δ/ppm)

R	^{13}C	^{15}N
Ph	135.9(q), 129.2(nq)	−256.2
Me	157.4(nq), 43.6(q), 34.7(q), 28.5(q), 19.2(q)	−354.0, −339.9, −267.1, −204.8
Pr^n	169.9(q), 141.8(nq), 138.8(q), 63.1(nq), 44.9(nq), 21.9(nq), 18.4(q), 11.7(q)	−354.5, −342.8, −273.4, −252.9, −164.8
Pr^i	55.4(q), 46.0(nq), 45.9(q), 42.3(nq), 23.6(nq), 21.5(q), 11.6(q)	−326.4, −189.1

Complex **I** has a quaternary ^{13}C resonance at δ 135.9: this is much lower (10–14 ppm,[8] 24 ppm[9]) than those observed for other π-bonded nitrosobenzene complexes of molybdenum. The ^{15}N signal at δ −256.2 is close to those shown by >N−CO– groups. It appears that complex **II** contains four different N-containing groups, with signals at δ −354 and −339.9 probably due to amino nitrogens whereas those at δ −267.1 and −204.8 ppm can be associated with >N−CO– and –C=N– groups respectively. The ^{13}C signal at δ 158 is also compatible with the >N−CO– group. The other carbon signals are probably associated with methyl-containing functions: π-coordinated nitrosomethane could account for the signals of δ 34 and 43 whereas the presence of $COCH_3$ and $NCOCH_3$ could account for those at δ 28 and 19, respectively.

The ^{15}N spectrum of complex **III** has some similar features to that of complex **II** with the presence of amino groups, >N−CO– and >C=N– suggested by the first four signals and complex **IV** also has a signal indicative of an amino group. The well known[2,17] insertion reactions of carbon monoxide with π-coordinated nitroso compounds leading to >N−CO– and RNCO formation may be responsible for some of our reaction products. It is clear that the reaction products from molybdenum hexacarbonyl and organic nitro compounds exhibit a far greater degree of complexity than originally proposed.[1]

The complexity of the reaction products is confirmed by XPS studies of **I** and **II**. Fig. 1, which shows the wide scan spectra, shows features characteristic of Mo, C and O, but the 3p photoemission peaks from Mo overlap severely with the region where we expect N 1s features making it impossible to obtain information about the chemical state or concentration of the nitrogen component. The Mo 3d peaks exhibit interesting differences between the two samples (Fig. 2, see full text). Complex **I** has two bands corresponding to spin–orbit splitting, the relative intensities of the two components being in good agreement with the theoretical value. Complex **II** provides clear evidence in the shape of the 3d peaks for Mo in two different oxidation states. Subtracting the spectrum of **I** from that of **II** gives the difference spectrum shown in Fig. 2, shifted by *ca.* 1.5 eV to higher binding energy compared with the Mo $3d_{5/2}$ peak from the phenyl compound. The Mo $3d_{5/2}$ binding energy for the phenyl derivative is consistent with Mo in a 6+ oxidation state.

Differential sample charging, which can give rise to multiple peaks, does not appear to be a significant problem, as shown by the near equivalence of the kinetic energies and shapes of the C 1s photoemission peaks from the

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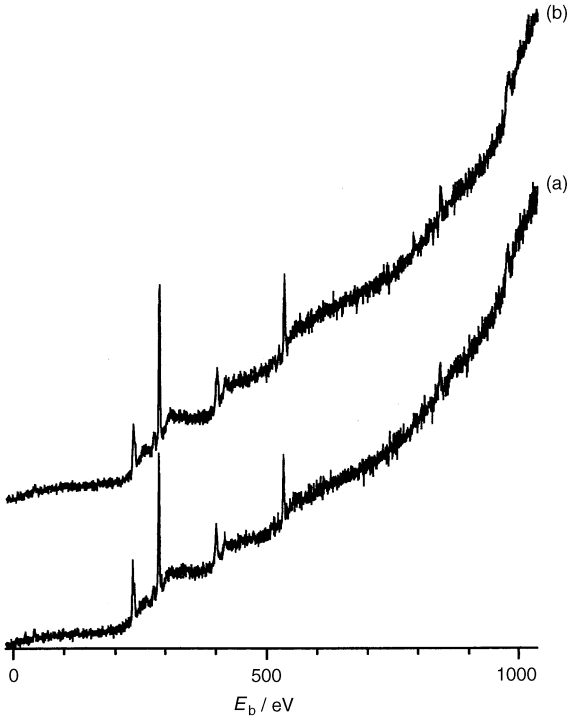

Fig 1 X-Ray photoelectron survey spectra for (a) $MoO_2(ONPh)$ and (b) $MoO_2(ONMe)$.

two samples (Fig. 3, see full text). The two O 1s spectra, by contrast, show a significant difference in binding energies (Fig. 3). Complex **I** has a predominant component at 531.5 eV with a weak shoulder at *ca.* 533.5 eV, whereas the O 1s spectrum from **II** consists almost exclusively of a peak at 533.4 eV.

All of our investigations demonstrate that the nature of the solids **I** and **II** are of a greater complexity than the approximate formula[1] suggests, solid **II** being the most complex. The materials, though of undoubted structural interest, should not be classified as complexes of C-nitroso compounds with molybdenum dioxide.

Techniques used: IR, ^{1}H and ^{13}C solution NMR, ^{13}C, ^{15}N and ^{95}Mo CP MAS NMR, XPS, elemental analysis

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Table 2: CHN analyses

Table 3: Surface layer compositions derived from XPS measurements

Fig. 2: Mo 3d XP spectra for (a) $MoO_2(ONPh)$ and (b) $MoO_2(ONMe)$. Curve (c) shows the difference spectrum (b) – (a).

Fig. 3: C 1s and O 1s XP spectra for (a) $MoO_2(ONPh)$ and (b) $MoO_2(ONMe)$.

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References cited in this synopsis

1 A. R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1981, 1898.
2 M. Cameron, B. G. Gowenlock and G. Vasapollo, *Chem. Soc. Rev.*, 1990, **19**, 355.
7 L. S. Liebeskind, K. B. Sharpless, R. D. Wilson and J. A. Ibers, *J. Am. Chem. Soc.*, 1978. **100**, 7061.
8 D. A. Muccigrosso, S. E. Jacobson. P. A. Apgar and F. Mares, *J. Am. Chem. Soc.*, 1978, **100**, 7063.
17 S. Cenini, M. Pizzotti and C. Crotti, *Aspects of Homogeneous Catalysis*, ed. R. Ugo, Reidel, Dordrecht, 1988, vol. 6, pp. 97–198.