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Reaction of Free and Co-ordinated 5-Nitro-1,10-phenanthroline with Sodium Methoxide in Dimethylsulphoxide

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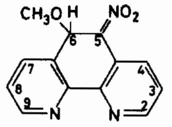
Reactions of low-spin iron(II) complexes of 1,10-phenanthroline(phen) and related α,α′-diimines in aqueous solution have been extensively studied. The mechanism of acid aquation of species such as $Fe(phen)_3^{2+}$ appears well understood: rate laws [1], conventional activation parameters [2], and volumes of activation [3] are all in accord with a dissociative process. Reactions with strong nucleophiles, such as hydroxide and cyanide ions, proceed *via* second order kinetics [4]. Unlike the situation with cobalt(III) ammine and amine complexes, no acidic hydrogen atoms are present in 1,10-phenanthroline and related molecules, so it is not possible to explain second order kinetics with hydroxide ion in terms of a normal conjugate base mechanism [5]. Possible mechanisms for these reactions include direct nucleophilic attack at the metal centre [6a], formation of reactive ion-pairs [6b] or, as has recently been proposed [6c], initial attack by the nucleophile on the co-ordinated ligand followed by facile rearrangement to give the observed products.

It has been suggested that attack on co-ordinated 1,10-phenanthroline and its derivatives takes place at the 2- or 9-positions. Most of the evidence for this has been obtained with complexes of 5-nitro-1,10-phenanthroline [7–13]. For example, hydroxide, methoxide, ethoxide and cyanide ions have been shown to reversibly form adducts with $Ru(NO_2\text{-}phen)_3^{2+}$ and the analogous iron(II) complex [7–12]. The ^1H nmr spectrum of the ruthenium species formed was interpreted [12] in terms of nucleophile addition to the 2- or 9-positions of the ligand. This study was however handicapped by poor solubility and poorly resolved broad spectra. We are, therefore, prompted to report some results of a high-field ^1H nmr (220 MHz) examination of the reaction of 5-nitro-1,10-phenanthroline {and the *tris* iron(II) and ruthenium(II) complexes} with methoxide ion in dimethylsulphoxide which is part of a larger study that will be described in detail elsewhere.

In this system there are no solubility problems, and well resolved spectra were obtained that permitted unambiguous assignments to be made allowing the adduct to be characterised. Assignments of protons in either ring of the free ligand were based on established chemical shifts and coupling constants [14], consideration of possible canonical forms, and ^{13}C nmr spectra.

A rapid reaction followed addition of sodium methoxide to a solution of 5-nitro-1,10-phenanthroline in dimethylsulphoxide to give a deep red solution [15]. There was however no reaction between 1,10-phenanthroline and sodium methoxide.

The reaction of 5-nitro-1,10-phenanthroline was associated with changes in the ^1H nmr spectrum, the most important being the loss of the H(6) singlet resonance from the aromatic region, and the appearance of a singlet of equal intensity at 6.03 δ. This spectrum is consistent with the adduct being the Meisenheimer complex (1). These spectra are shown in Fig. 1, and the assignments listed in Table I. With



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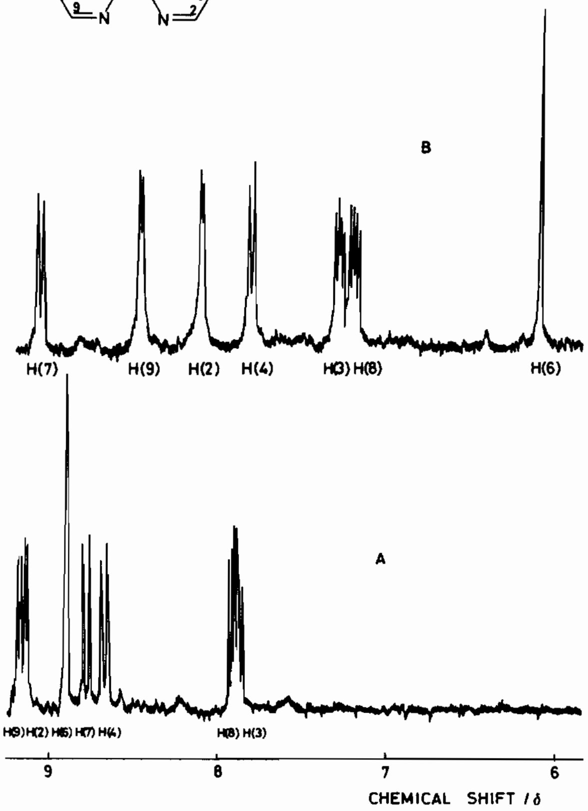

Fig. 1. Nmr spectra (220 MHz) of 5-nitro-1,10-phenanthroline in d_6 dimethylsulphoxide before (A) and after addition of sodium methoxide (B).

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TABLE I. ^1H Nmr Spectra of 5-Nitro-1,10-phenanthroline and Derived Species in d_6 Dimethylsulphoxide[a].

Proton	Chemical Shift δ/ppm (multiplicity) ^3J/Hz			
	NO_2-phen	NO_2-phen + MeO^-	$Fe(NO_2\text{-phen})_3^{2+}$	$Ru(NO_2\text{-phen})_3^{2+}$
2	9.15(d) $J_{2,3}$ 4.5	8.18(d) $J_{2,3}$ 4.5	7.80[b]	8.20[b]
3	7.84(dd) $J_{2,3}$ 4.5 $J_{3,4}$ 8.0	7.34(dd) $J_{2,3}$ 4.5 $J_{3,4}$ 7.5	7.80[b]	7.78[b]
4	8.69(d) $J_{3,4}$ 8.0	7.87(d) $J_{3,4}$ 7.5	8.96(d) $J_{3,4}$ 8.0	8.91(d) $J_{3,4}$ 8.0
6	8.89(S)	6.03(S)	9.36(S)	9.32(S)
7	8.78(d) $J_{7,8}$ 8.0	9.16(d) $J_{7,8}$ 8.5	9.03(d) $J_{7,8}$ 7.5	8.90(d) $J_{7,8}$ 9.0
8	7.87(dd) $J_{7,8}$ 8.0 $J_{8,9}$ 4.5	7.24(dd) $J_{7,8}$ 8.5 $J_{8,9}$ 4.5	7.80[b]	7.78[b]
9	9.15(d) $J_{8,9}$ 4.5	8.56(d) $J_{8,9}$ 4.5	7.80[b]	8.20[b]

[a]Recorded at 15 °C on a Varian HR 220 instrument operating at 220 MHz using tetramethylsilane as standard. [b]Overlapping resonances prevented accurate measurement of coupling constants.

the exception of H(7), which interacts with the methoxy group, the other ring protons are moved up-field as expected with an increase in electron density of the ring systems. The long range proton couplings to the C(5) and C(6) resonances in the ^{13}C nmr spectrum of the adduct reinforces the interpretation that the methoxy group is bound to C(6) rather than C(5).

Dimethylsulphoxide solutions of the methoxy adduct in sealed nmr tubes are relatively stable (days) but considerably less stable when open to the air. These solutions, after a period of a few hours gave very broad ^1H nmr spectra, and displayed strong esr signals due to free-radical species [16].

The 220 MHz ^1H nmr spectra of the *tris* Ru(II) and Fe(II) complexes of 5-nitro-1,10-phenanthroline in dimethylsulphoxide were assigned using arguments referred to above. As expected H(2) and H(9) show marked up-field shifts on complexation; H(4) and H(8) are little affected while H(3), H(6) and H(7) are deshielded (see Table). Addition of excess sodium methoxide to dimethylsulphoxide solutions of $M(NO_2\text{-phen})_3^{2+}$ (M = Fe, Ru) brought about a general broadening of their ^1H nmr spectra which was caused by the presence of free radicals (esr). Facilitated by the use of a high-field spectrometer, useful information could be obtained from the broadened spectra. For instance the singlet at 6.38 δ in the spectrum obtained from the ruthenium complex is close to that predicted for H(6) in the co-ordinated Meisenheimer species (anology with Meisenheimer complex formation from the free ligand, and changes induced by complexation). The aromatic region resonances were too broad for assignments to be made with confidence. However, the general change in appearance is also in keeping with attack of methoxide at the 6-position of the co-ordinated ligand. Subsequent reactions take place, but these are relatively slow.

In conclusion, the reaction of 5-nitro-1,10-phenanthroline with sodium methoxide in dimethylsulphoxide leads to the formation of a Meisenheimer complex in which the methoxy group is bound at the 6-position. The same process appears to take place when the ligand is bound to iron(II) or ruthenium(II). In this solvent formation of radicals can broaden the nmr spectra of these species. Similarly, broad spectra have been reported when other solvents are used, and it may be that the presence of radicals is also responsible for this. In the light of these results some conclusions made from earlier work may require reappraisal.

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14 See for example 'High Resolution Nuclear Magnetic Resonance Spectroscopy', by J. W. Emsley, J. Feeny and L. H. Stucliffe, Pegamon Press (1965).

15 This colour is typical of a Meisenheimer complex. Full details of its electronic spectrum and other properties will be given in a subsequent publication.

16 The formation of radical anions from nitroaromatics in basic solutions is well known, *e.g.* see G. A. Russell E. G. Janzen, *J. Am. Chem. Soc.*, *84*, 4153 (1962); subsequent papers, and E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.*, *22*, 123 (1968).