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Correlation of NO stretching frequencies with coordination modes in metal complexes of *C*-nitroso compounds

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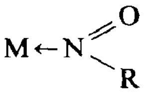
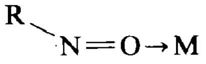
Abstract

It is shown that the previous use of IR spectroscopy for determination of the co-ordination mode of *p*-nitrosodimethylaniline (NODMA) is generally unreliable owing to a faulty assignment of the NO stretching frequency for NODMA itself.

The mode of coordination to a metal of any *C*-nitroso compound may be determined unambiguously by X-ray crystallography, and consequently attempts have been made to establish a simple empirical correlation of a physical parameter with the X-ray structural data. The most frequently employed technique is infra-red spectroscopy and changes in the NO stretching frequency have been correlated with the coordination mode revealed by the crystal structure. Both separately [1,2] and together [3] we have made use of a supposed relationship which has been used by other workers, namely that σ-N coordination (I) results in a small drop of ν(NO) on passing from the free ligand to the co-ordination compound, σ-O coordination (II) in a small rise in ν(NO), and π-NO coordination (III) by a large drop in ν(NO). In this communication we draw attention to a major difficulty in accepting the second of these correlations because of a long established confusion in infra-red spectroscopic interpretation.


(I)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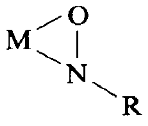
(III)

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There are only two cases in which σ-O coordination has been established by X-ray crystallography [4,5] and in both of these the ligand is *p*-nitrosodimethylaniline (NODMA). Consequently any correlation with ν(NO) depends upon the detailed assignment of the infra-red spectrum of NODMA itself. NODMA forms several σ-N coordination compounds for which the infra-red spectra have been recorded and the value given for ν(NO) in both the complex and the free ligand [6–11], the most frequently cited value for NODMA being 1527 cm^{-1}. There was a significant implied variation from this value, in a case in which ^{15}N labelling was used to demonstrate that in a $[Ru(bpy)_2(NODMA)Cl][PF_6]$ complex ν(NO) is 1286 cm^{-1} [12]. This could imply a lower value for ν(NO) in NODMA itself, but does demonstrate the importance of ^{15}N labelling in identifying the NO stretching frequency.

Although the NO stretching frequency in most monomeric *p*-substituted nitrosobenzenes falls within the range 1488–1513 cm^{-1} [13,14] it should be noted that this group of nitrosobenzenes does not include NODMA itself. Lüttke [15] reported a value ν(NO) of 1372 cm^{-1} on the basis of data derived by ^{15}N-substitution in the NO group, but unfortunately this has been totally ignored in the coordination chemistry literature. This value has been updated in a comprehensive study by Knieriem [16] in which both ^{15}N and deuterium substitutions were employed, the final value of ν(NO) in NODMA being given as 1363 cm^{-1}. This

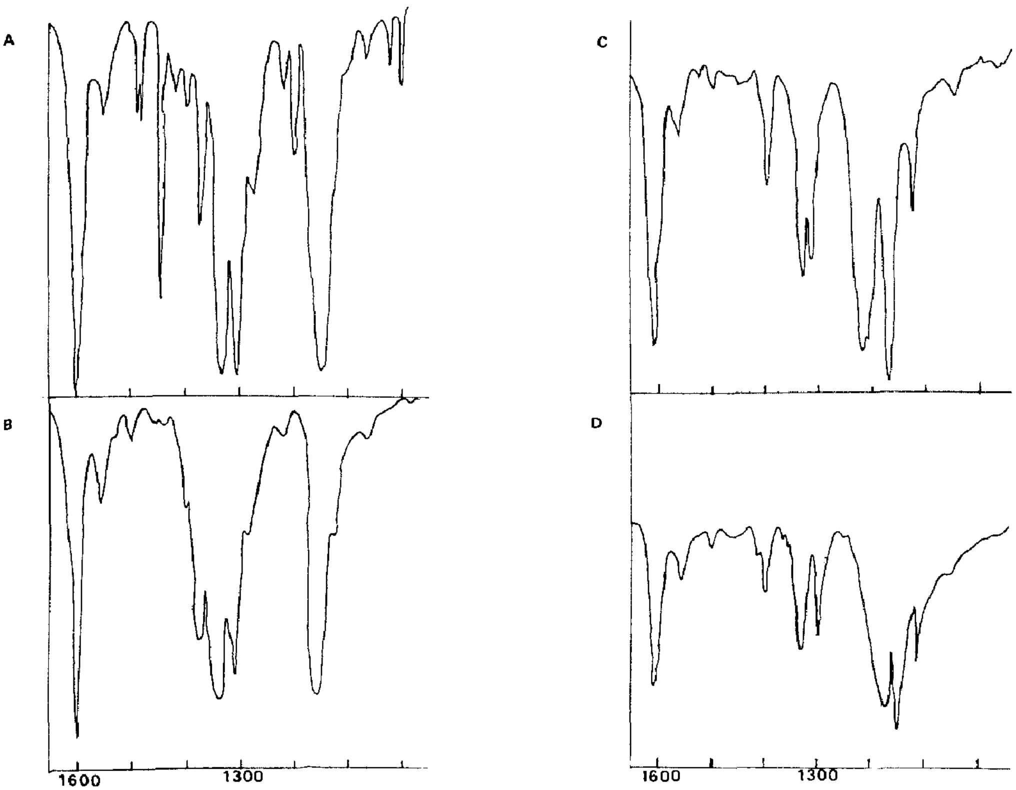

Fig. 1. Infra-red spectra of four NODMA complexes recorded with KBr discs: A = $PtCl_2(NODMA)_2$; B = $PdCl_2(NODMA)_2$; C = $NiCl_2(NODMA)_2$; D = $Me_2SnCl_2(NODMA)_2$.

Table 1

IR data for NODMA complexes

Complex	Bands in 1300–1600 cm^{-1} range	Previously chosen ν(NO) (cm^{-1})	Ref.
(A) $PtCl_2(NODMA)_2$	1307,1337,1374,1397,1423,1447,1483,1490,1554	1490	[a]
(B) $PdCl_2(NODMA)_2$	1312,1340,1377,1403,1435,1501,1530,1556	1501	[a]
(C) $NiCl_2$(NODMA0$_2$	1318,1331,1400,1455,1500,1525,1565	1500	[a]
(D) $Me_2SnCl_2(NODMA)_2$	1305,1337,1372,1399,1417,1505,1563	1563	[a]
NODMA	1302,1337,1363,1397,1441,1527,1551	1363	16
NODMA	1303,1341,1367,1398,1460,1530,1555	1530	18
NODMA	1305,1341,1367,1400,1447,1531,1555		[a]

[a] This work.

study, though remaining in thesis form, has been available for ten years in the literature on *C*-nitroso compounds through its citation by Talberg [17].

The spectra both of NODMA and of the various coordination compounds exhibit many bands in the 1000–1600 cm^{-1} range, but authors can be highly selective in the listing of bands in this range. In only one instance [9] was there a spectrum of both NODMA and a coordination compound, namely $[PdCl_2(NODMA)_2]$. In some cases [6,10,11] only two bands are reported for halide complexes, and in two other cases only one such band [4,8]. There appears to have been an unfortunate prejudgement in relating the infra-red evidence in terms of the mode of coordination of NODMA.

The accompanying figures and table demonstrate the complexity of the infra-red spectra of four NODMA complexes and of NODMA itself. In the absence of ^{15}N-substitution studies, unambiguous identification of the NO stretching frequency is difficult. We therefore suggest that the previously employed simple correlations of $\Delta\nu$(NO) with σ-N or σ-O coordination mode are incomplete, and should be employed with caution. Such a conclusion adds further point to the endeavour to find bases for correlation with other spectroscopic data, such as ^{13}C NMR [1] and XPS spectra [3], or with bond lengths derived from X-ray crystal structures of nitroso-compounds and resulting coordination compounds. Evidence for such correlations will be published in the near future.

Experimental

The complexes were prepared by published methods [3–9] involving mixing of solutions of the metal salt and NODMA with appropriate concentration of the mixed solutions at which immediate precipitation does not occur.

Acknowledgements

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