

## The Bonding of Nitric Oxide in Transition-metal Nitrosyl Complexes

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IN monomeric transition-metal complexes the nitric oxide is currently considered<sup>1</sup> to be in the form  $\text{NO}^+$  when the stretching frequency,  $\nu(\text{N}-\text{O})$ , falls in the range 2300—1515  $\text{cm}^{-1}$ . The value of  $\nu(\text{N}-\text{O})$  is lower than that of the free ion  $\text{NO}^+$  according to the extent of back-donation of metal  $d$  electrons into the  $\pi^*\text{NO}$  antibonding orbitals. The stretching frequency of ionic  $\text{NO}^+$  is very similar to that of the isoelectronic molecule

nitrogen<sup>2</sup> [ $\nu(\text{N}-\text{N}) = 2331 \text{ cm}^{-1}$ ], but oxygen, which is isoelectronic with the ion  $\text{NO}^-$ , absorbs<sup>2</sup> at 1555  $\text{cm}^{-1}$ . I therefore suggest that, when  $\nu(\text{N}-\text{O})$  is found in the region 1500—1700  $\text{cm}^{-1}$ , the nitric oxide be assigned the structure  $\text{NO}^-$ , and that frequencies at the upper end of this scale arise formally by partial donation of an electron pair from  $\pi^*\text{NO}$  to the metal  $d$  orbital from which it originated.

<sup>1</sup> J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32; W. P. Griffith, *J. Chem. Soc.*, 1963, 3286.

<sup>2</sup> K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds", John Wiley and Sons Inc., New York, 1963.

Previously it has been assumed<sup>3</sup> that NO<sup>-</sup> absorbs at *ca.* 1200 cm.<sup>-1</sup> and this assignment is supported by a <sup>15</sup>N substitution experiment<sup>4</sup> on the black isomer of the compound [Co(NO)(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub>. Recent X-ray structural investigations<sup>5</sup> have shown that this compound contains linear Co-N-O or Co-O-N bonds. It is now suggested that its π\*NO orbital contains a time-average population of three electrons, by comparison with the stretching frequencies<sup>2</sup> of molecules with the (π\*)<sup>4</sup> configuration—878 cm.<sup>-1</sup> (hydrogen peroxide) and 892 cm.<sup>-1</sup> (fluorine). It is probable, but not required by the present model, that the oxygen atom is bonded to cobalt.

For ν(N-O) in the region 1700—1900 cm.<sup>-1</sup> each case should be treated on its own merit. For example, the compound (Et<sub>4</sub>N)<sub>2</sub>[Ru(NO)Cl<sub>5</sub>] absorbs at 1830 cm.<sup>-1</sup> and formally contains Ru(II) and NO<sup>+</sup>, but the compound K<sub>2</sub>[Pt(NO)Cl<sub>5</sub>] absorbs<sup>4</sup> at 1711 cm.<sup>-1</sup> and formally contains Pt(IV) and NO<sup>-</sup>. Moreover, care should be exercised in dealing with ν(N-O) obtained from solid-state spectra, since it may vary by as much as

100 cm.<sup>-1</sup> depending on the environment of the nitrosyl complex in the crystal lattice.

According to ν(N-O), NO<sup>-</sup> is present in the ions<sup>1,6</sup> [V(NO)(CN)<sub>5</sub>]<sup>6-</sup> (1575 cm.<sup>-1</sup>), [Cr(NO)(CN)<sub>5</sub>]<sup>4-</sup> (1515 cm.<sup>-1</sup>), [Cr(NO)(CN)<sub>5</sub>]<sup>3-</sup> (1630 cm.<sup>-1</sup>), and [Mn(NO)(CN)<sub>5</sub>]<sup>3-</sup> (1700 cm.<sup>-1</sup>). The order of molecular orbital energies<sup>7</sup> is therefore  $d'_{xz} < d_{yz} \leq d_{xy} < \dots \pi^* < \pi^{**}$ , where  $d'_{xz}$  now represents a molecular orbital derived from  $d_{xz}$  and π\*NO, the electrons of which are mainly localised on the nitric oxide; π\*\* represents the corresponding antibonding orbital, and the positions of the σ\* orbitals are undetermined. The degeneracy of e( $d_{xz}$ ,  $d_{yz}$ ) and e(π\*NO) is removed, usually by a Jahn-Teller distortion from linearity of the M-N-O skeleton.

In many cases the assignment of NO<sup>-</sup> results in a more realistic oxidation state for the metal. For example, K<sub>3</sub>[Mn(NO)(CN)<sub>5</sub>] is prepared from K<sub>3</sub>[Mn(CN)<sub>6</sub>] in hot aqueous solution but K<sub>5</sub>[Mn(CN)<sub>6</sub>] is rapidly oxidised by water, and even K<sub>4</sub>[Mn(CN)<sub>6</sub>] is easily oxidised by air.

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<sup>3</sup> W. P. Griffiths, J. Lewis, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, 7, 38.

<sup>4</sup> W. P. Griffiths, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1961, 775.

<sup>5</sup> D. Hall and A. A. Taggart, *J. Chem. Soc.*, 1965, 1359; D. Dale and D. Crowfoot-Hodgkin, *J. Chem. Soc.*, 1965, 1364.

<sup>6</sup> W. P. Griffiths, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1959, 1632.

<sup>7</sup> H. B. Gray, P. T. Manoharan, J. Pearlman, and R. F. Riley, *Chem. Comm.*, 1965, 62.