



Review

A structure-based analysis of the vibrational spectra of nitrosyl ligands in transition-metal coordination complexes and clusters

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ABSTRACT

The vibrational spectra of nitrogen monoxide or nitric oxide (NO) bonded to one or to several transition-metal (M) atom(s) in coordination and cluster compounds are analyzed in relation to the various types of such structures identified by diffraction methods. These structures are classified in: (a) terminal (linear and bent) nitrosyls, $[M(\sigma\text{-NO})]$ or $[M(\text{NO})]$; (b) twofold nitrosyl bridges, $[M_2(\mu_2\text{-NO})]$; (c) threefold nitrosyl bridges, $[M_3(\mu_3\text{-NO})]$; (d) σ/π -dihaptonitrosyls or “side-on” nitrosyls; and (e) isonitrosyls (oxygen-bonded nitrosyls).

Typical ranges for the values of internuclear N–O and M–N bond-distances and M–N–O bond-angles for linear nitrosyls are: 1.14–1.20 Å/1.60–1.90 Å/180–160° and for bent nitrosyls are 1.16–1.22 Å/1.80–2.00 Å/140–110°. The $[M_2(\mu_2\text{-NO})]$ bridges have been divided into those that contain one or several metal–metal bonds and those without a formal metal/metal bond ($M \cdots M$). Typical ranges for the M–M, N–O, M–N bond distances and M–N–M bond angles for the normal twofold NO bridges are: 2.30–3.00 Å/1.18–1.22 Å/1.80–2.00 Å/90–70°, whereas for the analogous ranges of the long twofold NO bridges these are 3.10–3.40 Å/1.20–1.24 Å/1.90–2.10 Å/130–110°. In both situations the N–O vector is approximately at right angle to the M–M (or $M \cdots M$) vector within the experimental error; i.e. the NO group is symmetrical bonded to the two metal atoms. In contrast the threefold NO bridges can be symmetrically or unsymmetrically bonded to an M_3 -plane of a cluster compound. Characteristic values for the N–O and M–N bond-distances of these NO bridges are: 1.24–1.28 Å/1.80–1.90 Å, respectively. As few dihaptonitrosyl and isonitrosyl complexes are known, the structural features of these are discussed on an individual basis.

The very extensive vibrational spectroscopy literature considered gives emphasis to the data from linearly bonded NO ligands in stable closed-shell metal complexes; i.e. those which are consistent with the “effective atomic number (EAN)” or “18-electron” rule. In the paucity of enough vibrational spectroscopic data from complexes with only nitrosyl ligands, it turned out to be very advantageous to use wavenumbers from the spectra of uncharged and saturated nitrosyl/carbonyl metal complexes as references, because the presence of a carbonyl ligand was found to be neutral in its effect on the $\nu(\text{NO})$ -values. The wide wavenumber range found for the $\nu(\text{NO})$ values of linear MNO complexes are then presented in terms of the estimated effects of net ionic charges, or of electron-withdrawing or electron-donating ligands bonded to the same metal atom. Using this approach we have found that: (a) the effect for a unit positive charge is [plus 100 cm^{-1}] whereas for a unit negative charge it is [minus 145 cm^{-1}]. (b) For electron-withdrawing co-ligands the estimated effects are: terminal CN [plus 50 cm^{-1}]; terminal halogens [plus 30 cm^{-1}]; bridging or quasi-bridging halogens [plus 15 cm^{-1}]. (c) For electro donating co-ligands they are: PF_3 [plus 10 cm^{-1}]; P(OPh)_3 [–30 cm^{-1}]; P(OR)_3 (R = alkyl group) [–40 cm^{-1}]; PPh_3 [–55 cm^{-1}]; PR_3 (R = alkyl group) [–70 cm^{-1}]; and $\eta^5\text{-C}_5\text{H}_5$ [–60 cm^{-1}]; $\eta^5\text{-C}_5\text{H}_4\text{Me}$ [–70 cm^{-1}]; $\eta^5\text{-C}_5\text{Me}_5$ [–80 cm^{-1}]. These values were mostly derived from the spectra of nitrosyl complexes that have been corrected for the presence of only a single electronically-active co-ligand. After making allowance for ionic charges or strongly-perturbing ligands on the same metal atom, the adjusted ‘neutral-co-ligand’ $\nu(\text{NO})^*$ -values (in cm^{-1}) are for linear nitrosyl complexes with transition metals of Period 4 of the Periodic Table, i.e. those

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with atomic orbitals ($\dots 4s3d4p$): [ca. 1750, Cr(NO)]; [1775, Mn(NO)]; [1796, Fe(NO)]; [1817, Co(NO)]; [ca. 1840, Ni(NO)]. Period 5 ($\dots 5s4d5p$): [1730 Mo(NO)]; [—, Tc(NO)]; [1745, Ru(NO)]; [1790, Rh(NO)]; [ca. 1845, Pd(NO)]. Period 6 ($\dots 6s4f5d6p$): [1720, W(NO)]; [1730, Re(NO)]; [1738, Os(NO)]; [1760, Ir(NO)]; [—, Pt] respectively. Environmental differences to these values, e.g. data taken in polar solutions or in the crystalline state, can cause $\nu(\text{NO})^*$ variations (mostly reductions) of up to ca. 30 cm^{-1} .

Three spectroscopic criteria are used to distinguish between linear and bent NO groups. These are: (i) the values of $\nu(^{14}\text{NO})$ themselves, and (ii) the isotopic band shift – (IBS) – parameter which is defined as $[\nu(^{14}\text{NO}) - \nu(^{15}\text{NO})]$, and, (iii) the isotopic band ratio – (IBR) – given by $[\nu(^{15}\text{NO})/\nu(^{14}\text{NO})]$. The former is illustrated with the $\nu(^{14}\text{NO})$ -data from trigonal bipyramidal (TBP) and tetragonal pyramidal (TP) structures of $[\text{M}(\text{NO}(\text{L})_4)]$ complexes (where M = Fe, Co, Ru, Rh, Os, Ir and L = ligand). These values indicate that linear (180°) and strongly bent (130° – 120°) NO groups in these compounds absorb over the 1862 – 1690 cm^{-1} and 1720 – 1525 cm^{-1} -regions, respectively. As was explicitly demonstrated for the linear nitrosyls, these extensive regions reflect the presence in different complexes of a very wide range of co-ligands or ionic charges associated with the metal atom of the nitrosyl group. A plot of the IBS parameter against M–N–O bond-angle for compounds with general formulae $[\text{M}(\text{NO})(\text{L})_y]$ ($y = 4, 5, 6$) reveals that the IBS-values are clustered between 45 and 30 cm^{-1} or between 37 and 25 cm^{-1} for linear or bent NO groups, respectively. A plot of IBR shows a less well defined pattern. Overall it is suggested that bent nitrosyls absorb ca. 60 – 100 cm^{-1} below, and have smaller co-ligand band-shifts, than their linear counterparts.

Spectroscopic $\nu(\text{NO})$ data of the bridging or other types of NO ligands are comparatively few and therefore it has not been possible to give other than general ranges for 'neutral co-ligand' values. Moreover the bridging species data often depend on corrections for the effects of electronically-active co-ligands such as cyclopentadienyl-like groups. The derived neutral co-ligand estimates, $\nu(\text{NO})^*$, are: (a) twofold bridged nitrosyls with a metal–metal bond order of one, or greater than one, absorb at ca. 1610 – 1490 cm^{-1} ; (b) twofold bridged nitrosyl ligands with a longer non-bonding M–M distance, ca. 1520 – 1490 cm^{-1} ; (c) threefold bridged nitrosyls, ca. 1470 – 1410 cm^{-1} ; (d) σ/π dihaptonitrosyl, $[\text{M}(\eta^2\text{-NO})]$, where M = Cr, Mn and Ni; ca. 1490 – 1440 cm^{-1} . Isonitrosyls, from few examples, appear to absorb below ca. 1100 cm^{-1} .

To be published DFT calculations of the infrared and Raman spectra of complexes with formulae $[\text{M}(\text{NO})_{4-n}(\text{CO})_n]$ (M = Cr, Mn, Fe, Co, Ni, and $n = 0, 1, 2, 3, 4$, respectively) are used as models for the assignments of the $\nu(\text{MN})$ and $\delta(\text{MNO})$ bands from more complex metal nitrosyls.

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