Solution Structure and Reactivity of $M^+[Fe(CO)_3(NO)]^-$, $M = Na$, K, or PPN [$PPN = (Ph_3P)_2N$]

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Summary The i.r. spectral data from the title complexes illustrate the phenomena of ion pairing involving a cation–nitrosyl interaction while the chemical reactivity of the anion is shown to be dependent upon the cation.

THE solution i.r. spectrum of $Na^+[Fe(CO)_3(NO)]^-$ reported by Manning in dimethyl sulphoxide (DMSO),[1] and by Beck in diglyme,[2] indicated the presence of a single C_{3v} species, ν_{CO} 1983 (A_1), 1881 (E), and ν_{NO} 1651 cm^{-1}. In tetrahydrofuran (THF) we have observed a spectrum that is essentially doubled compared to that above, ν_{CO} 1989 and 1978 (A_1), 1880 and 1869 (E); ν_{NO} 1615 and 1646 cm^{-1}. The gradual addition of the cyclic polyether, 18-crown-6, diminishes the high-frequency carbonyl and low-frequency nitrosyl bands with corresponding increases in the low CO and high NO bands, until finally a single pattern is obtained similar to that reported by Manning and Beck. Since the 18-crown-6 removes the cation from a tight ion pairing situation the data illustrate the presence of two species, tight ion pair A, ν_{CO} 1989 and 1880; ν_{NO} 1615 cm^{-1}, and solvent (or crown) separated ion pair B, ν_{CO} 1978 and 1869; ν_{NO} 1646 cm^{-1}, $A/B = 0{\cdot}9$ from intensity measurements. That A involves a cation nitrosyl interaction is apparent since removal of the cation from this environment will decrease the metal to nitrosyl π back-bonding and cause an increase in ν_{NO} for B. This reduction in $M \rightarrow NO$ π bonding results in an increase of electron density on the metal thereby increasing $M \rightarrow CO$ π bonding with a resulting decrease in ν_{CO} for species B.

Thus, while tight ion pairing between alkali metal cations and an oxygen atom of a terminal, or ketonic, carbonyl group has been observed for $[Co(CO)_4]^-$,[3] $[Mn(CO)_5]^-$,[4] $[Fe(CO)_3(COR)]^-$,[5] and $[Fe(CO)_3(PPh_3)(COR)]^-$,[6] and direct iron–sodium bonding observed for $Na^+[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$,[7] this is the first report of cation–nitrosyl ion pairing. This finding contradicts a recent assumption of cation–carbonyl ion pairing for this system based upon interpretation of Mössbauer data,[8] although the result is still compatible with the data themselves. The result also contradicts the implications of the formulation $[Fe(KOC)(CO)_2(NO)]$ originally designated for the salt by Hogsed.[9]

The K^+ salt exhibits similar behaviour but with a greater amount of tight ion pairing compared to the Na^+ salt, A/B (K^+) $= 1{\cdot}2$, reflecting the larger size of the K^+ ion which reduces the extent of solvation.[3] In diethyl ether both Na^+ and K^+ salts exhibit only tight ion pairing, while in dimethoxyethane predominantly separated ion pairing is observed. Such observations are in accord with the respective co-ordinating abilities of the solvents and therefore in the excellent co-ordinating solvents DMSO and diglyme only separated species would be expected, *cf.* refs. 1 and 2.

The nitrosyl bands of the various Na^+ and K^+ species A and B, and the PPN^+ [bistriphenylphosphinimminium, $(Ph_3P)_2N^+$] salt (ν_{CO} 1974, 1875, and ν_{NO} 1646 cm^{-1}) exhibit pronounced shoulders, whose cause is not clear; however, the absence of a fundamental band in the 800—820 cm^{-1} region of the spectra, coupled with the presence of the shoulders for the isotopically labelled salt $Na^+[Fe(CO)_3(^{15}NO)]^-$ [ν_{NO} 1615 (B) and 1578 cm^{-1} (A)], rules out Fermi resonance. We are investigating this aspect of the spectra which may be related to the considerable aggregation of species A and B we have observed by dilution techniques, or rotamer formation *via* restricted rotation about an iron–nitrogen bond of a non-linear nitrosyl ligand.

We have confirmed a recent report of the reaction of $PPN^+[Fe(CO)_3(NO)]^-$ with iodine to form the paramagnetic salt $PPN^+[Fe(NO)_2I_2]^-$.[10] However, we find that use of the K^+ salt results in the formation of $[Fe(NO)_2I]_2$. An intermediate situation is found when using the 18-crown-6 complexed K^+ salt where initial formation of the paramagnetic anion is observed, followed by a slow decomposition. In the absence of an intrinsically stabilized cation, PPN^+, or alkali metal cations stabilized *via* complexation, it seems that iodide extraction by the cation occurs from $[Fe(NO)_2I_2]^-$ to yield $[Fe(NO)_2I]$ which then dimerizes to a more stable 18-electron configuration. Finally, in the reaction of a large excess of I_2 with $K^+[Fe(CO)_3(NO)]^-$, we observe spectroscopic evidence for the sole formation of $K^+[Fe(NO)I_3]^-$, [ν_{NO}(THF) 1782 cm^{-1}], a species not observed when using the PPN^+ salt, probably for steric reasons.[10]

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