Is nickel dibromide bent in a nitrogen matrix? A combined simultaneous Fourier-transform infrared and X-ray absorption fine structure matrix isolation study [*]

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Combined Fourier-transform (FT) IR and X-ray absorption fine structure (XAFS) studies of $NiBr_2$ isolated in a nitrogen matrix have shown that it is non-linear (125° FTIR, 145° XAFS), with the shortest $Ni-N_{matrix}$ interaction at 2.61 Å, compared to a linear geometry in a methane matrix.

Matrix isolation is a widely used technique for the generation and stabilisation of many species and allows for the detailed study of the interaction of co-ordinatively unsaturated centres with potential ligand molecules. Whilst the most common matrix material is probably argon, nitrogen is also widely used as it often gives excellent spectral quality. Although it has been known for a long time that metal atoms can form dinitrogen complexes when isolated in nitrogen matrices,[1] for other systems, the nature and form of any interaction between the isolated species and the nitrogen host is less clear-cut, but it has been shown to be different from argon, oxygen, neon, *etc.*, but similar to carbon monoxide,[2] and adduct formation has been invoked in the cases of $AlCl_3$ [3] and $CrCl_3$.[4] We have shown previously from the isotope pattern on ν_3 in the infrared spectrum that $NiCl_2$ is non-linear (*ca.* 130°) in a nitrogen matrix but linear in an argon matrix,[5] and that the anomalous bond length obtained from the Ni K-edge X-ray absorption fine structure (XAFS) spectra[6] is in accordance with this finding, but we were unable to obtain *direct* structural evidence for non-linearity as the Cl K-edge was not accessible.

In this paper we describe our findings for $NiBr_2$ isolated in nitrogen and several other matrices.[†] Fourier-transform IR spectra[‡] show that when $NiBr_2$ is trapped in an argon matrix the ν_3 asymmetric stretching mode occurs at 419.2 cm^{-1} with the well resolved nickel isotope pattern giving a bond angle of *ca.* 180° in reasonable agreement with earlier observations.[7] If neon (423.5 cm^{-1}), methane (410.6 cm^{-1}) or oxygen (409.1 cm^{-1}) matrices are used then small shifts are observed, and the nickel isotope pattern gives approximately linear geometries in all cases. A much more radical change is observed when a nitrogen matrix is used, where the ν_3 mode shifts to 331.9 cm^{-1} and the Ni isotope pattern yields a bond angle of *ca.* 125°. In addition, no features assignable to ν_{NN} modes were detected in the FTIR spectra. Although bond angles derived from infrared isotope patterns are usually considered to be reliable, the *difference* in isotopic shift between a bond angle of 180 and 130° is only of the order of 0.2–0.3 cm^{-1} in this case. Therefore we wanted to confirm whether this apparent severe structural perturbation was genuine using both Ni and Br K-edge XAFS to obtain interatomic distances and bond angles. In addition we also wanted to use the Ni K-edge XAFS to identify any Ni–N interactions and the Ni K-edge X-ray absorption near-edge structure (XANES) to establish the local geometry.

In order to improve the reliability of the structural information derived from XAFS studies of matrix-isolated species we have developed a new experimental set-up that enables the *simultaneous* collection of both FTIR and XAFS data, and as far as we are aware, there is no other report of such a facility in the literature, although we have reported a sequential combined XAFS–FTIR experiment previously.[11] The experimental configuration will be described in detail elsewhere and consists of an APD Cryogenics DE204SL cryostat mounted in a purpose built aluminium vacuum chamber capable of being used for transmission and fluorescence XAFS, transmission and reflectance FTIR, and with ports for sample deposition, gas inlet, observation and photolysis. Fourier-transform IR spectra were collected using focusing external optics with a Bruker IFS66 spectrometer, the vacuum chamber and optical transfer path were enclosed in a dry-air purged box. The XAFS spectra were measured at the Daresbury Laboratory SRS, data reduction was carried out using PAXAS,[12] and fitting of the experimental data utilised the single and multiple scattering curved wave theory in EXCURV92.[§,13]

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[*] *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

[†] To our knowledge there are only two previous reports of infrared studies of matrix isolated 3d transition-metal bromides, one involving $NiBr_2$,[7] the other dealing with the vaporisation of $CrBr_3$ to give $CrBr_4$, $CrBr_3$ and $CrBr_2$,[8] both of which only discussed argon matrices. Electron diffraction studies of $NiBr_2$[9] indicate that the vapour phase geometry is linear, and there was no evidence of dimer formation in the electron diffraction,[9] matrix infrared[7] or mass spectrometric experiments.[10]

[‡] Bruker IFS66 spectrometer, 0.5 cm^{-1} resolution, 2.0–2.5 cm^{-1} full width at half maximum (fwhm); Br isotopic splitting was observed at 0.25 cm^{-1} resolution, but we were unable to resolve this satisfactorily in order to obtain bond angle information.

[§] Nickel K-edge and Br K-edge XAFS spectra were collected in fluorescence mode (Ar–He ion chamber for I_0, NaI–Tl scintillator detector for I_f) using a Si220 double-crystal monochromator detuned to give 50% harmonic rejection on station 9.2 of the Daresbury Laboratory SRS operating at 2 GeV with average circulating currents of 150–300 mA. Eight to twelve spectra were collected for each sample at each edge and averaged. Spectra were calibrated using the first maximum in the first derivative of the K-edge of Ni foil (8332 eV) and the L_2 edge of Au foil (13 731 eV) for the Ni and Br edges respectively. Bromine K-edge data had to be truncated at *ca.* 12.5 $Å^{-1}$ due to a large glitch. Data reduction was carried out by fitting the pre-edge region to a quadratic polynomial, subtracting this from the data and approximating the atomic component of the post-edge region by high (typically sixth) order polynomials or splines. Low r features in the Fourier transforms were removed as described previously.[14] The XAFS spectral simulations were carried out using curved wave single and multiple scattering theory employing a von Barth ground state and a Hedin–Lundqvist exchange potential. Amplitude reduction factor AFAC (due to shake up and shake off processes) was set to 0.75 for Ni and 0.82 for Br. The number of refined independent parameters were kept below $2\Delta k \Delta r/\pi$. Phases and amplitudes were checked against model compounds and found to be satisfactory. Errors in interatomic distances arising from data collection and analysis have been estimated to be ± 1.5% for well defined co-ordination shells,[15] and this is usually an order of magnitude greater than the statistical errors reported by EXCURV92.[13] Accuracy of co-ordination numbers is generally considered to be ± 1.

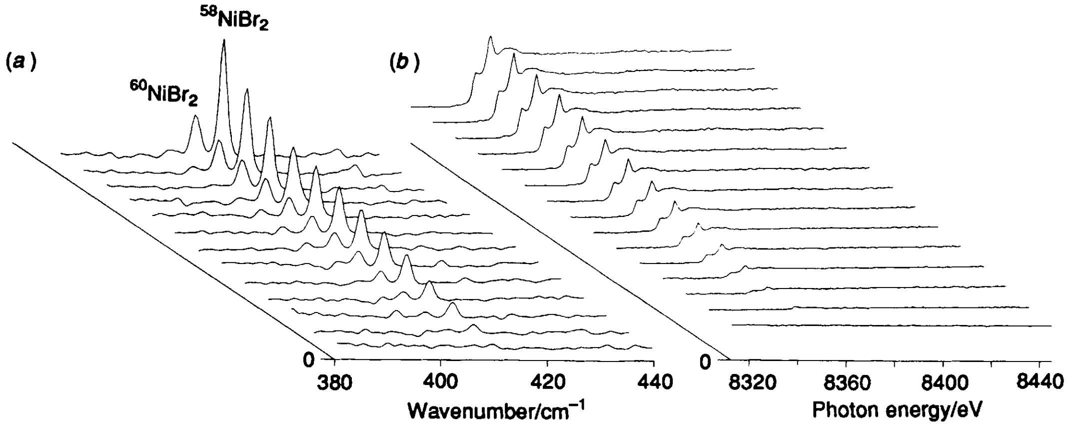

Fig. 1 Simultaneous FTIR (*a*) and Ni K-edge XANES (*b*) spectra obtained during the deposition of $NiBr_2$ into a methane matrix

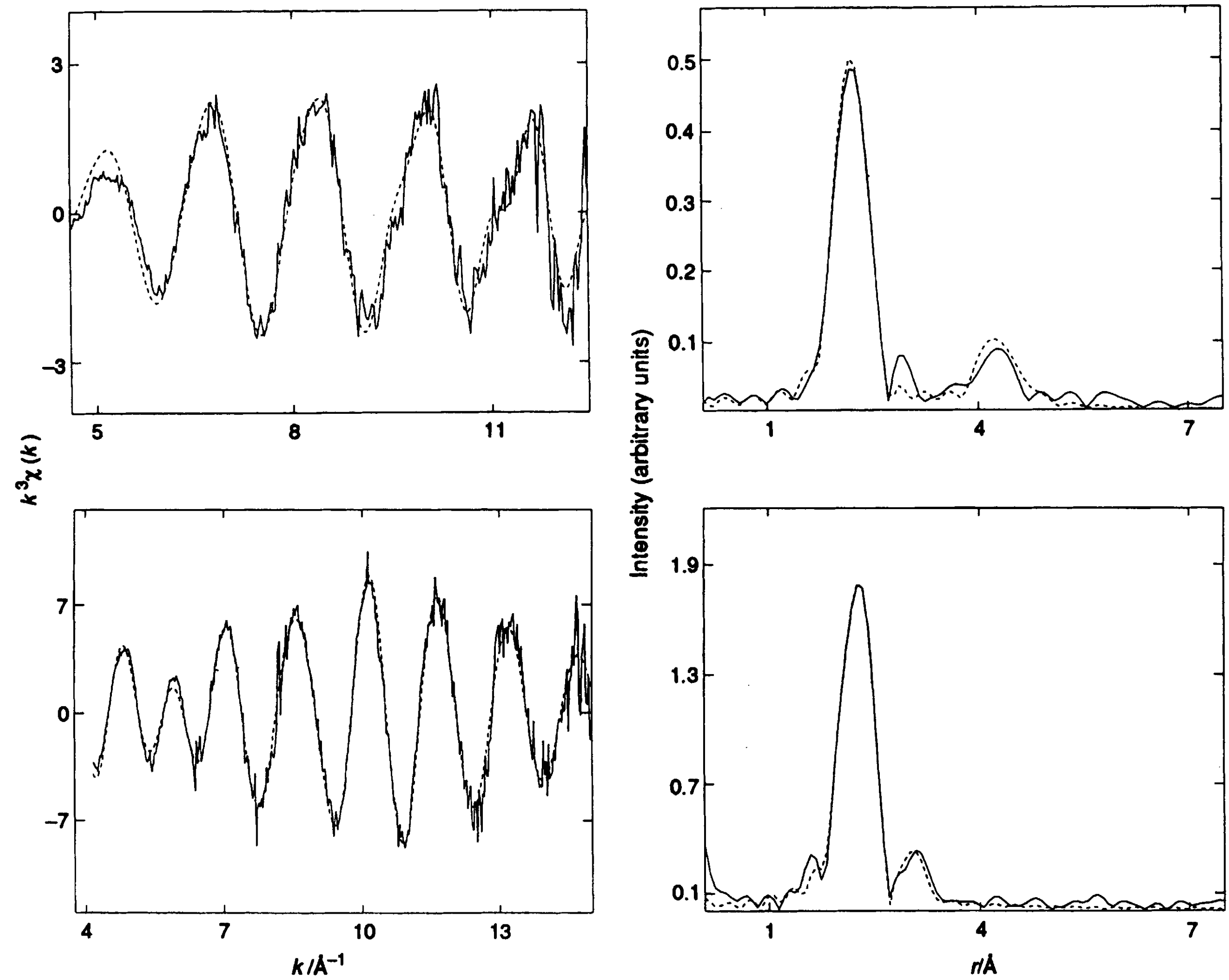

Fig. 2 Bromine K-edge (top) and Ni K-edge (bottom) XAFS and Fourier transforms for $NiBr_2$ isolated in a nitrogen matrix (—— experimental data, – – – curved wave theory)

Fig. 1 shows the *simultaneous* collection of FTIR (2 cm^{-1} resolution, 2.0–2.5 cm^{-1} fwhm) and Ni K-edge XANES data obtained during the deposition of $NiBr_2$ into a methane matrix. Methane is used as the 'inert' matrix gas as the cryostat has a base temperature of *ca.* 10 K, which is unsatisfactory for neon matrices, and in the case of argon matrices, the argon backscattering was found to mask all but the first co-ordination shell in the Br K-edge data. It is clear from the FTIR and XAFS spectra that the sample composition is remaining constant during deposition, and that the deposition process is giving rise to well isolated $NiBr_2$ molecules because of the quality of the isotope pattern. Similar sets of FTIR and Ni K-edge XANES spectra were also obtained during the deposition of $NiBr_2$ into a nitrogen matrix. In this case the Ni K-edge XANES were very different from those for a methane matrix, with no intense pre-edge feature, but with a small feature at the foot of the edge. These radical changes in the XANES features are still under investigation, but do demonstrate that there is a significant change in geometry of $NiBr_2$ between methane and nitrogen matrices.

The Br K-edge XAFS were expected to be most informative in terms of determining the linearity or otherwise of the $NiBr_2$ unit because of the multiple scattering enhancement in linear or near-linear systems. Indeed this was the case, and for $NiBr_2$ in a methane matrix two features in the Fourier transform were observed that gave a Br–Ni distance of 2.19(3) Å and a Br $\cdots$ Br interaction of 4.36(6) Å that could only be modelled satisfactorily using multiple scattering techniques, clearly indicating a linear or near-linear geometry. The Br K-edge XAFS and Fourier transform of the $NiBr_2$–N_2 system (Fig. 2) were very different from those from a methane matrix and in particular the intensity of the second shell in the Fourier transform was much reduced in the nitrogen matrix data, clearly indicating a change in geometry. These data yielded a Br–Ni distance of 2.27(3) Å, with a Br ··· Br distance of 4.34(6) Å, giving a bond angle of *ca.* 145°. The Br ··· Br shell was fitted using multiple scattering to maintain consistency of data analysis, and it was found that the multiple scattering effect at these angles causes an effective decrease in the intensity of the Fourier transform. Whilst the Br–Ni–Br bond angle from the XAFS analysis is larger than that derived from the FTIR Ni isotope pattern, it should be noted that the isotope pattern is not very sensitive in this case (the calculated difference in isotope shift between 125 and 145° is only 0.17 cm^{-1}), and that the value determined from the central atom isotope pattern gives the lower estimate of the bond angle.

The Ni K-edge XAFS and Fourier transform of the methane matrix data contained two features, one at 2.19(3) Å from the Ni–Br shell and a second one at *ca.* 4.3–4.4 Å, that is at approximately twice the Ni–Br distance. We believe that this second feature is due to a Ni–Br–Ni–Br–Ni multiple scattering pathway in the linear $NiBr_2$ unit which we have also observed in the low-temperature Fourier transforms of the Fe K-edge XAFS of *trans*-$[FeL_2Br_2]\cdot 2Me_2CO$[14] [L = *cis*-1,2-bis(diphenylphosphino)ethylene] and the Ni K-edge XAFS of *cis* and *trans* square-planar nickel phosphine halides, but which was absent in the analogous tetrahedral systems.[16] Unfortunately, this cannot be modelled properly within EXCURV92.

The Ni K-edge data from $NiBr_2$ in a nitrogen matrix (Fig. 2) are radically different from those of the $NiBr_2$–CH_4 system in as much as the feature at *ca.* 4.35 Å is not present in the Fourier transform, implying non-linearity, and that the Ni K-edge XAFS clearly contains a contribution at low k, from a low z backscatterer, which was not evident in the $NiBr_2$–CH_4 system. Simulating the data gave a Ni–Br distance of 2.25(3) Å. Initially, attempts were made to fit the Ni–N interaction to a short distance, but whilst this gave a plausible fit with k^3 weighted data, a longer interaction of 2.61(4) Å gave a substantially better fit and once k^1 and k^2 weighted data were employed a short Ni–N interaction was ruled out. In addition, the Ni–Br distance derived from the data including a short Ni–N was in poor agreement with that from the Br K-edge data. The best fit obtained for the Ni–N interaction was for four nitrogen atoms at 2.61(4) Å and 12 nitrogen atoms at 3.21(5) Å. Therefore, there appears to be no *convincing* evidence for a short Ni–N interaction.*

The sum of the van der Waals radii[17] for Ni and N is 3.18 Å, and therefore a Ni–N bond length of 2.61 Å implies that there is only a small amount of bonding interaction present. Whilst the van der Waals radius of N (1.55 Å) is probably a good estimate, that for Ni (1.63 Å) may not be applicable as it was derived from Ni ··· Ni contact distances in stacked Ni^{II} dioxime square planar complexes.[18] There only appears to be a couple of examples in the literature for Ni–N bonded interactions of the order of 2.5–3.0 Å for Ni^{II} complexes,† and in both cases involve the co-ordination of solvents or bases such as aniline[19] and acetonitrile[20] to otherwise square-planar systems. Therefore it appears that there is no *substantial* bonding interaction between the nickel and the nitrogen host.

The Ni–Br bond length of 2.19(3) Å from the $NiBr_2$–CH_4 system is in good agreement with the electron diffraction values of 2.201(4) (r_g) and 2.177(5) Å (r_e),[9] although as pointed out previously,[6] it is not clear what level of comparison should be made between vapour-phase electron diffraction bond lengths and those obtained from XAFS for species isolated in cryogenic matrices.

Therefore, a combination of FTIR and XAFS has shown that, when $NiBr_2$ is isolated in a nitrogen matrix, the Br–Ni–Br unit is non-linear, with a bond angle of *ca.* 125° from the FTIR nickel isotope pattern and *ca.* 145° from the XAFS Br ··· Br distance, with an increase in the Ni–Br bond length of *ca.* 0.07 Å compared to a linear $NiBr_2$ unit in a methane matrix. There is no convincing evidence of a short Ni–N interaction, with the closest contact at 2.61 Å being best fit to a small occupation number, and this in conjunction with the lack of any detectable ν_{NN} modes in the FTIR spectra, indicates that there is no significant Ni–N bonding interaction between the nickel and the nitrogen matrix. The XANES spectra also clearly indicate a change of geometry, and the detailed implications of this are still being studied. Whether the bending of the $NiBr_2$ unit in a nitrogen matrix is due to electronic effects (*e.g.* ion-induced dipoles, *etc.*) or geometric effects (*e.g.* packing of the nitrogen lattice) is not resolved by these experiments, but further experimental and theoretical work are planned to try to unravel this intriguing problem.

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* In the $NiCl_2$–N_2 system studied previously[6] a similar situation was observed with no convincing evidence of a short Ni–N, the shortest [2.84(4) Å] being best fit by a small occupation number of two, and a longer distance [3.34(5) Å] best fit by six nitrogen atoms, but the analysis was complicated by the similarity of the Cl and N backscattering phases and amplitudes.

† Data obtained from 'CCDC QUEST' program of the Chemical DataBase Service at Daresbury.