Gas phase complexes of H$_3$N···CuF and H$_3$N···Cul studied by rotational spectroscopy and ab initio calculations: the effect of X (X = F, Cl, Br, I) in OC···CuX and H$_3$N···CuX†

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Complexes of H$_3$N···CuF and H$_3$N···Cul have been synthesised in the gas phase and characterized by microwave spectroscopy. The rotational spectra of 4 isotopologues of H$_3$N···CuF and 5 isotopologues of H$_3$N···Cul have been measured in the 6.5–18.5 GHz frequency range using a chirped-pulse Fourier transform microwave spectrometer. Each complex is generated from a gas sample containing NH$_3$ and a halogen-containing precursor diluted in Ar. Copper is introduced by laser ablation of a solid target prior to supersonic expansion of the sample into the vacuum chamber of the microwave spectrometer. The spectrum of each complex is characteristic of a symmetric rotor and a C$_3v$ geometry in which the N, Cu and X atoms (where X is F or I) lie on the C$_3$ axis. The rotational constant ($B_0$), centrifugal distortion constants ($D_J$ and $D_{30}$), nuclear spin-rotation (C$_{2g}$(Cu) = C$_{2g}$(Cu)) constant (for H$_3$N···CuF only) and nuclear quadrupole coupling constants ($\eta_{2S}$X) where (X = N, Cu, I) are fitted to the observed transition frequencies. Structural parameters are determined from the measured rotational constants and also calculated ab initio at the CCSD(T)(F12*)/AVQZ level of theory. Force constants describing the interaction between ammonia and each metal halide are determined from $D_J$ for each complex. Trends in the interaction strengths and geometries of B···CuX (B = NH$_3$, CO) (X = F, Cl, Br, I) are discussed.

1. Introduction

Gerry and co-workers demonstrated that B···MX complexes, where B is a Lewis base, M is a coinage metal, and X is a halogen atom, can be generated through laser vapourisation of a metal target in the presence of a gas sample undergoing supersonic expansion, then interrogated by microwave spectroscopy.¹ The pure rotational spectra of OC···MX (X = F, Cl, Br) were measured and interpreted to determine the geometries of the complexes. An extensive and systematic study of the rotational spectra of B···MX complexes, also generated by a combination of laser vapourisation and supersonic expansion, has since been performed. Complexes where the Lewis base is H$_2$O,² N$_2$,³ CO,⁴,⁵,⁶ H$_2$O$_2$,⁷ H$_2$S,⁸ NH$_3$,⁹,¹⁰ C$_2$H$_2$,¹¹,¹² C$_2$H$_4$,¹³,¹⁴ or c-C$_3$H$_6$¹⁵ have been reported. Metal-containing (B···MX) complexes have also been investigated by ab initio methods which have explored the nature of bonding interactions and the influence of the halide on the interaction between the metal and the Lewis base.¹⁶–¹⁹

This work presents analyses of the rotational spectra of H$_3$N···CuI and H$_3$N···CuF. The structures of the complexes as well as the strengths of interactions between NH$_3$ and the different CuX (X = F, I) molecules are determined from measured spectroscopic constants and through ab initio calculations. Unlike H$_3$N···CuCl, for which a crystal structure¹⁰ was known before its observation in the gas phase, H$_3$N···CuI and H$_3$N···CuF have not been structurally characterised in the condensed phase. The reaction of copper(n) fluoride and copper metal with ammonia has been observed both in gaseous and in anhydrous liquid ammonia.²⁰ Among the products obtained were copper(i) fluoride and copper(n) fluoride ammine complexes. It has been suggested that copper(i) fluoride ammine complexes may serve as intermediates that allow the isolation of binary copper(i) fluoride which has not yet been characterized in the solid phase. The results of the present work are compared with those of the previously published reports on H$_3$N···CuCl¹⁰ and OC···CuX (X = F, Cl, Br, I).¹¹,¹² Clear trends are identified and described. Legon and co-workers earlier performed systematic
studies of hydrogen- and halogen-bonded complexes, B·HX and B·XY (where Y is a halogen atom). The present work compares the properties of H3N·MX with selected H3N·HX and H3N·XY complexes that have been characterised previously.

2. Experimental and theoretical methods

Broadband microwave spectra were measured using a chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer fitted with a laser ablation source. Detailed descriptions of the spectrometer and laser ablation source are provided in ref. 25 and 26. A gas sample containing ~4.0% NH₃ and ~1.5% SF₆ (when generating H₃N·CuF) or CF₃I (when generating H₃N·CuI) is diluted in argon and prepared at a total pressure of 6 bar. The sample is pulsed (from a Parker-Hannifin Series 9 solenoid valve, using pulse length of 960 μs set using Parker-Hannifin Iota One Valve Driver) into the vacuum chamber of the spectrometer and passes over the surface of a copper rod that is ablated by a Nd:YAG laser pulse (λ = 532 nm, pulse duration of 10 ns, pulse energy of 20 mJ) before undergoing supersonic expansion. A repetition rate of ~1.05 Hz is employed. The copper rod is continually translated and rotated in order to expose a fresh surface to each laser pulse and to ensure shot-to-shot reproducibility of signal intensities. Isotopically-enriched samples of ¹⁵NH₃ (Sigma-Aldrich, 98% ¹⁵N) and ND₃ (Sigma-Aldrich, 99% D) were used to detect ¹⁵NH₃ and ND₃-containing complexes respectively.

The sequence employed to record broadband microwave spectra involves (i) polarization of the sample by a microwave chirp that sweeps from 6.5 to 18.5 GHz within 1 μs and (ii) recording of the free induction decay of the molecular emission over a subsequent period of 20 μs. The sequence of (i) and (ii) is repeated eight times following each gas sample introduction pulse. The free induction decay (FID) of the polarization is digitized using a 25 Gs s⁻¹ digital oscilloscope after down-mixing against a 19 GHz local oscillator. Frequency domain spectra are obtained through a Fourier transform that uses the high resolution window function (full width at half maximum (FWHM) ~ 65 Hz) described by Tektronix (details provided as ESI†). The spectra of H₃N·CuF, H₃¹⁵N·CuF and D₃N·CuF were averaged for 1500k, 540k and 2520k free induction decays (FIDs) respectively prior to being Fourier transformed. The spectra of H₃N·CuI, H₃¹⁵N·CuI and D₃N·CuI were averaged for 660k, 180k and 540k FIDs respectively prior to being Fourier transformed.

Structure optimizations and counter-poise corrected dissociation energies were calculated using the molpro package at the CCSD[T](F12*) level of theory, a coupled-cluster method with single and double excitations, explicit correlation, and a perturbative treatment of triple excitations. Only valence electrons are included in the correlation treatment. A basis set combination consisting of aug-cc-pVQZ on H, N and F atoms and aug-cc-pVQZ-PP on Cu and I atoms was used and will be referred to by AVQZ. ECP-10-MDF and ECP-28-MDF were used on Cu and I respectively to account for scalar relativistic effects. For the density fitting approximation used to accelerate the CCSD[T](F12*) calculation, the respective def2-QZVPP basis sets were employed for the MP2 and Fock terms. For the complementary auxiliary basis required for the F12 treatment, the def2-TZVPP MP2 density fitting basis sets were used. Force constants were calculated from the second derivative of the energy with respect to the internal coordinates using the GAUSSIAN 09 package at the MP2 level of theory. A basis set combination consisting of aug-cc-pVTZ on H, N and F atoms, aug-cc-pVTZ-PP on Cu and I atoms was used.

3. Results

3.1 Spectral analysis and assignment

Fig. 1 displays sections of the broadband spectrum measured when probing a gas sample containing CF₃I, NH₃ and argon that interacts with the plasma plume produced by ablation of the copper rod. The most intense transitions are observed for CF₃I while those of NH₃·Ar, CF₃I·NH₃ and IF₄ are also strong. The spectrum of H₃N·CuI was identified through the analysis of groups of transitions, significantly weaker in intensity than those of the species listed above, which are separated by frequency increments of ~2.2 GHz. Distinctive and extensive hyperfine splittings are present in each J′→J′ state as expected for a complex that contains copper and iodine nuclei (which have I = 3/2 and 5/2 respectively). A different range of chemical products was observed, including NH₃·SF₆.
NH$_3$ \cdot \cdot Ar$^{41}$ and (NH$_3$)$_2$$^{46}$ after exchanging the gas sample for another that contains SF$_6$, NH$_3$, and argon. The frequency of the $J' \rightarrow J'' = 1 \rightarrow 0$ transition of CuF lies above the upper limit of the spectrometer. Consecutive $J' \rightarrow J''$ transitions of H$_3$N \cdot \cdot CuF, which have lower intensities than those of NH$_3$ \cdot \cdot SF$_6$, NH$_3$ \cdot Ar and (NH$_3$)$_2$, were observed at intervals of $\sim$ 8.0 GHz and display hyperfine structure arising from the presence of the copper nucleus (I = 3/2). The $J' \rightarrow J'' = 1 \rightarrow 0$ and $2 \rightarrow 1$ transitions of H$_3$N \cdot \cdot CuF are shown in Fig. 2. The spectra observed for each of H$_3$N \cdot \cdot CuF and H$_3$N \cdot \cdot Cu contain only $a$-type transitions, consistent with the $C_{nv}$ geometries (Fig. 3) anticipated for each of these complexes and previously observed for each of H$_3$N \cdot \cdot AgCl$^9$ and H$_3$N \cdot \cdot CuCl$^{10}$. Western’s PGOPHER$^{47}$ was used to fit parameters in the Hamiltonian shown below to the observed transitions of each complex;

$$H = H_R - \frac{1}{2} eQ(Cu) \cdot \nabla E(Cu) - \frac{1}{2} eQ(I) \cdot \nabla E(I) - \frac{1}{2} eQ(N) \cdot \nabla E(N) + I_{Cu} C_{Cu} a \cdot J$$

where $H_R$ is the Hamiltonian of a semi-rigid, prolate symmetric rotor. The second, third, and fourth terms on the right hand side describe the coupling of the nuclear electric quadrupole moment with the electric field gradient at each of the Cu, I and N nuclei (respectively). The interaction is given by the scalar (or inner product of the nuclear quadrupole moment dyadic, $Q$, and the dyadic of the electric field gradient arising from extra nuclear charges, $\nabla E$. The nuclear quadrupole coupling constants are denoted by $Q_{a}^{Cu}(X)$ [where $X$ is Cu, N or I] and can be determined from the nuclear quadrupole hyperfine structure. The last term describes the magnetic hyperfine interaction between the nuclear magnetic moment of Cu and the effective magnetic field generated by the rotation of the molecular framework. An attempt to fit $C_{Cu}(Cu) = C_{Cu}(Cu)$ for H$_3$N$^{14}$N, $^{63}$Cu and $^{65}$Cu yielded a result with uncertainty similar to the value of the parameter. It was therefore not included in the parameter set used in the final fits. The coupling scheme used for H$_3$N$^{14}$N, $^{63}$Cu and $^{65}$Cu is $F_1 = I + I_{Cu}$, $F_1 = I + I_{Cu}$ and $F_2 = F_2 + I_{N}$. For H$_3$N$^{14}$N, $^{63}$Cu and $^{65}$Cu, the coupling scheme is $F_1 = I + I_{Cu}$ and $F_2 = F_2 + I_{N}$. Given that $I_{Cu} = 1/2$ for $^{15}$N and that the described experiments do not resolve any hyperfine splittings introduced by the $^{15}$N nucleus, the term of eqn (1) that applies to the nitrogen atom is omitted when fitting the spectra of isotopologues containing $^{15}$N. Hyperfine splittings introduced by the hydrogen and fluorine nuclei were also not resolved by the present experiments. In every case, the $A_0$ rotational constant is fixed to the value of $C_0$ for free ammonia for the purpose of simulating intensities. The results of spectroscopic fits are provided in Tables 1 and 2 for H$_3$N \cdot \cdot CuF and H$_3$N \cdot \cdot Cu respectively.

All spectra were measured using a copper sample containing $^{63}$Cu and $^{65}$Cu isotopes in their natural abundances. The intensities of the spectra of all isotopologues are consistent with the natural fractional abundances of $^{63}$Cu and $^{65}$Cu which are 69% and 31% respectively. Isotopically-enriched samples were used to allow measurement and assignment of the spectra of D$_3$N $\cdot \cdot ^{63}$CuI, H$_3$N$^{15}$N $\cdot \cdot ^{63}$CuI, D$_3$N $\cdot \cdot ^{65}$CuF and H$_3$N$^{15}$N $\cdot \cdot ^{65}$CuF. Given that only one isotope of each of fluorine and iodine is available, isotopic substitution was not possible at the halogen atom. Confirmation that the molecular carriers of the observed spectra contain copper was obtained through comparison of the nuclear quadrupole coupling constants, $Q_{a}^{Cu}(Cu) = eQ_{a}^{Cu}(Cu)$, for the various isotopologues. This nuclear quadrupole coupling constant provides a measure of the strength of the coupling of the electric field gradient ($\eta_a$) at the Cu nucleus along the axis $a$ with the ‘conventional’ nuclear electric quadrupole moment $eQ$, defined as $eQ = I_{Cu} c_{Cu} a \cdot J$. Note that both the dyadic $Q$ and its element $Q_{aa}$ contain the nuclear charge density while the constant $Q$ does not; hence multiplication by the charge of a proton $e$ on the left-hand side of the definition. For any given isotopologue, the electric field gradient is invariant to isotopic exchange (to a very good first approximation) even in the zero-point state so the ratio of the values of $\eta_{a}^{(65)Cu}$ in B \cdot \cdot $^{63}$CuX and $\eta_{a}^{(65)Cu}$ in $^{63}$CuX is equal to the ratio of the nuclear electric quadrupole moments of $^{63}$Cu and $^{65}$Cu. This condition is satisfied with the required level of precision for each pair of isotopologues for which the ratio can be calculated. The fitted rotational constant of H$_3$N $\cdot \cdot ^{63}$CuF is slightly smaller than that of H$_3$N $\cdot \cdot ^{65}$CuF. This implies that the Cu atom is sufficiently close to the centre of mass of this complex that any decrease in rotational constant (which would be required under the assumption of a rigid molecular framework, if Cu is not exactly at the centre of mass) is compensated by zero point effects. The rotational constant of H$_3$N $\cdot \cdot ^{65}$Cu is greater than that of H$_3$N $\cdot \cdot ^{63}$Cu by about 10 MHz. For H$_3$N $\cdot \cdot ^{65}$Cu,
B interconnecting in the geometry shown in Fig. 3. This assumption is consistent with the observations of a-type transitions and of a copper atom positioned close to the centre of mass in each of H$_3$N$'$C and H$_3$N$'$Cu. From this starting point, effective ground state ($r_0$) and substitution ($r_s$) geometries will be determined by fitting parameters in the model geometry (Fig. 3) to the experimentally-measured rotational constants. *Ab initio* calculations have been performed to establish equilibrium ($r_0$) geometries and other molecular properties.

The STRFIT* program is used to fit the $r_0$ geometries. The experimental results do not allow independent determination of the N-H bond length, $r$(N-H), and the angle defining the positions of the hydrogen atoms, $\angle$(H-N-Cu). For this reason, $r$(N-H) is held fixed while the $r$(Cu-X), $r$(Cu-N) and $\angle$(H-N-Cu) structural parameters are fitted. The assumed values of $r$(N-H) in the $r_0$ geometries of H$_3$N$'$CuF and H$_3$N$'$Cu are established by: (1) calculating the difference between the $r_0$ value of $r$(N-H) in isolated NH$_3$ and the $r_0$ value of the same parameter calculated at the CCSD(T)(F12$^*$)/AVQZ level; (2) adding the result of (1) to the $r_0$ value calculated for $r$(N-H) in each of H$_3$N$'$CuF and H$_3$N$'$Cu respectively. Large zero point changes occur in isolated NH$_3$ upon substitution of hydrogen atoms for deuterium. A shrinkage of 0.0011 Å in $r$(N-H) and an enlargement of 0.04 degrees in $\angle$(H-N-Cu) are observed. These changes are assumed to occur in H$_3$N$'$CuF and H$_3$N$'$Cu and are accounted for when fitting structural parameters. Fixing the $r$(N-H) distance as described above allows $r$(Cu-X), $r$(Cu-N) and $\angle$(H-N-Cu) to be determined with reasonable accuracy. Given that no isotopic substitution is available at either halogen atom, the uncertainties listed in Table 3 will be underestimated but the results agree satisfactorily with the results of the *ab initio* calculations.

3.2 Molecular geometry

By analogy with the geometries previously determined for the H$_3$N$'$AgCl$^0$ and H$_3$N$'$CuCl$^0$ complexes, it will initially be assumed that H$_3$N$'$CuX ($X = F, I$) adopt a $C_{2v}$ symmetry in which N, Cu and X are located on the inertial a axis while interconnected in the geometry shown in Fig. 3. This assumption is consistent with the observations of a-type transitions and of a copper atom positioned close to the centre of mass in each of H$_3$N$'$CuF and H$_3$N$'$Cu. From this starting point, the effective ground state ($r_0$) and substitution ($r_s$) geometries will be determined by fitting parameters in the model geometry (Fig. 3) to the experimentally-measured rotational constants. *Ab initio*

### Table 1 Determined spectroscopic constants of 4 isotopologues of H$_3$N$'$Cu

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>H$_3$N$'$-$^{63}$CuF</th>
<th>H$_3$N$'$-$^{65}$CuF</th>
<th>D$_3$N$'$-$^{63}$CuF</th>
<th>D$_3$N$'$-$^{65}$CuF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$/MHz</td>
<td>4037.4554(19)$^a$</td>
<td>4037.513(10)</td>
<td>3570.3874(16)</td>
<td>3926.6944(36)</td>
</tr>
<tr>
<td>$D_0$/kHz</td>
<td>1.30(25)</td>
<td>2.9(13)</td>
<td>[1.20]$^b$</td>
<td>1.04(48)</td>
</tr>
<tr>
<td>$\Delta w$(Cu)/MHz</td>
<td>-2.717(15)</td>
<td>-2.787(90)</td>
<td>-2.776(41)</td>
<td>—</td>
</tr>
<tr>
<td>$N^d$</td>
<td>18</td>
<td>8</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>$\sigma_{\text{rms}}$/kHz</td>
<td>7.4</td>
<td>23.8</td>
<td>15.8</td>
<td>9.1</td>
</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are one standard deviation in units of the last significant figure. $^b$ Value in square brackets is fixed. $^c$ For $H_3N'$$^{63}$CuF and $H_3N'$$^{65}$Cu. $^d$ N is the number of fitted transitions, $\sigma_{\text{rms}}$ denotes the r.m.s. deviation of the fit.

### Table 2 Determined spectroscopic constants of 5 isotopologues of H$_3$N$'$Cu

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>H$_3$N$'$-$^{63}$CuF</th>
<th>H$_3$N$'$-$^{65}$CuF</th>
<th>D$_3$N$'$-$^{63}$CuF</th>
<th>D$_3$N$'$-$^{65}$CuF</th>
<th>H$_3$N$'$-$^{15}$N$'$-$^{63}$CuF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$/MHz</td>
<td>1162.03613(67)$^a$</td>
<td>1153.4533(19)</td>
<td>1064.91348(73)</td>
<td>1058.27044(50)</td>
<td>1135.26715(70)</td>
</tr>
<tr>
<td>$D_0$/kHz</td>
<td>0.1289(73)</td>
<td>0.09(17)</td>
<td>0.0907(72)</td>
<td>0.097$^b$</td>
<td>0.1048(63)</td>
</tr>
<tr>
<td>$\Delta w$(Cu)/MHz</td>
<td>12.96(26)</td>
<td>9.73(30)</td>
<td>9.66(54)</td>
<td>10.91(95)</td>
<td>14.15(47)</td>
</tr>
<tr>
<td>$\Delta w$(Cu)/MHz</td>
<td>62.94(93)</td>
<td>58.70(44)</td>
<td>63.75(17)</td>
<td>58.99(41)</td>
<td>65.25(29)</td>
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<tr>
<td>$\Delta w$(N)/MHz</td>
<td>-2.28(11)</td>
<td>-2.18(41)</td>
<td>-2.59(19)</td>
<td>-2.83(18)</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta w$(I)/MHz</td>
<td>-613.99(28)</td>
<td>-613.62(77)</td>
<td>-612.86(49)</td>
<td>-614.32(77)</td>
<td>-614.25(43)</td>
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<tr>
<td>$N^d$</td>
<td>71</td>
<td>35</td>
<td>46</td>
<td>14</td>
<td>32</td>
</tr>
<tr>
<td>$\sigma_{\text{rms}}$/kHz</td>
<td>13.2</td>
<td>20.3</td>
<td>21.0</td>
<td>14.6</td>
<td>12.2</td>
</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are one standard deviation in units of the last significant figure. $^b$ Numbers in square brackets have been fixed. $^c$ N is the number of fitted transitions, $\sigma_{\text{rms}}$ denotes the r.m.s. deviation of the fit.
ΔIb is the change in the moment of inertia about the b inertial axis upon substitution, μ is the reduced mass for the isotopic substitution and is given by \( \frac{Δm \cdot M}{Δm + M} \) where M is the mass of the isotope of the halogen atom selected as parent and Δm is the change in mass upon substitution. The signs assigned to coordinates are those yielding bond lengths consistent with the \( \text{ab initio} \) calculations within acceptable precision limits.

When using eqn (2) the a coordinate is defined with respect to the principal axis system of the parent isotopologue and \( \angle (\text{H–N–Cu}) \) and \( r(\text{N–H}) \) cannot be independently determined for either H3N–CuF or H3N–CuCl. The scaling procedure applied earlier to fix \( r(\text{N–H}) \) when fitting an \( r_s \) geometry is now used to fix an \( r_a \) value. In this case, the difference between the \( r_a \) and \( r_s \) values of \( r(\text{N–H}) \) in free NH3 is added to the \( r_a \) value calculated for \( r(\text{N–H}) \) in H3N–CuCl to establish the value of \( r(\text{N–H}) \) in the \( r_s \) geometry. Thus, a value of \( \angle (\text{H–N–Cu}) \) is determined using the equation provided in ref. 50. The uncertainties of \( r_a \) coordinates are calculated using \( δa = 0.0015/|a| \) as recommended by Costain. All structural parameters and nuclear coordinates are provided in Table 3 alongside those of H3N–CuCl. The lack of an isotopic substitution at the halogen atom prevents the determination of an \( r_s \) coordinate for the halogen atom. \( r_s \) coordinates determined from Kraitchman’s equations \(^{32} \) are typically closer to \( r_a \) structural parameters than \( r_a \) values owing to partial cancellation of zero point effects when \( r_s \) coordinates are calculated. From Table 3 it can be seen that \( r(\text{N–Cu}) \) increases with increasing mass of the halogen atom of H3N–CuX. The value of \( \angle (\text{H–N–Cu}) \) is essentially independent of the halogen atom.

### 3.3 Interaction strength and ionicity

The strength of the interaction between NH3 and CuX can be assessed with reference to the dissociation energy for the H3N–CuX → NH3 + CuX reaction and also the force constant of the N•••Cu bond. \( \text{ab initio} \) calculations of both these quantities have been performed. As shown in Table 4, the dissociation energy of H3N–CuX decreases with increasing mass of the halogen atom with the highest result being 197 kJ mol\(^{-1} \) for the H3N–CuF complex.

| Table 3 | \( r_a \) and \( r_s \) and \( \text{ab initio} \) \( r_a \) structures and the corresponding principal axis coordinates of H3N–CuF and H3N–CuCl |
|--------------------------------|----------------------------------|----------------------------------|----------------------------------|
| \( r_a \) | H3N–CuF | H3N–CuCl | H3N–CuF | H3N–CuCl |
| \( r(\text{Cu–X}) \)/Å | 1.74919(55)\(^a\) | 2.35525(46) | — | — |
| \( r(\text{Cu–N}) \)/Å | 1.89276(61) | 1.9357(13) | 1.89(5) | 1.9361(13) |
| \( \angle (\text{H–N–Cu}) \)/° | 1.0187\(^a\) | 1.0185 | [1.0180] | [1.0178] |
| \( a(\text{Cu}) \)/Å | 0.94180(72) | 0.94170 | 0.94230 | 0.94230 |
| \( b(\text{Cu}) \)/Å | 0.94180(72) | 0.94170 | 0.94230 | 0.94230 |

\( a, b \) Numbers in parentheses are one standard deviation in units of the last significant figure. \( a \) Numbers in square brackets have been fixed at values determined as described under "Molecular Geometry". \( a \) An imaginary number was obtained as the Kraitchman coordinate.

The results of the \( \text{ab initio} \) calculations of the force constants, \( k_{ab} \), follow the same trend with \( k_{ab}(\text{N–Cu}) \) of H3N–CuF found to be 242 N m\(^{-1} \). The \( \text{ab initio} \) results for the \( k_{ab}(\text{N–Cu}) \) can be compared with others determined from the experimental data as shown in Table 4. The experimentally-determined force constants are calculated by applying a model\(^{24} \) which accounts for contributions to the centrifugal distortion constants from both the Cu–X and N•••Cu bonds. The force constants appropriate to the Cu–X and N•••Cu bonds are denoted by \( F_{11} \) and \( F_{22} \) respectively in eqn (3);

\[
hD_J = \frac{1}{2} \left[ \frac{h^4}{I_{ab}} \right] \left\{ (m_1a_1)^2 (F^{-1})_{11} + (m_1a_1 + m_2a_2)^2 (F^{-1})_{22} \right\}
\]

where \( m_1 \) and \( m_2 \) are the masses of the halogen and copper atoms respectively. The principal axis coordinates of the halogen and copper atoms are \( a_1 \) and \( a_2 \) respectively. This model allows the calculation of either \( F_{11} \) or \( F_{22} \) provided the other is known. Even where neither parameter is accurately known, a good estimate of one will allow an approximate value and uncertainty limits to be assigned to the other.

For each of H3N–CuF, H3N–CuCl and H3N–CuI, it can initially be assumed that \( F_{11} \) is equal to \( k_{ab} \) of the appropriate, isolated metal halide diatomic.\(^{44,55,56} \) The \( r_a \) coordinates and moments of inertia (\( I_{ab} \)) calculated from the ground state rotational constants (\( B_0 \)) of the various complexes are then used to determine the \( F_{22} \) values. In the limit of a rigid Cu–X bond, \( F_{11} \) tends to infinity and \( F_{22} \) approaches an asymptotic value. Where \( F_{11} \gg F_{22} \), any change in the assumed value of \( F_{11} \) induces only
a very small change in the determined value of $F_{22}$. As shown in Fig. 4, the assumption that the various $F_{11}$ are reasonably approximated by $k_r$ for the isolated metal halides ($k_r$(Cu–F) = 333 N m$^{-1}$; $k_r$(Cu–I) = 172 N m$^{-1}$) implies that the bond between the metal and halogen atoms is significantly more rigid than that between the metal and the nitrogen atoms, in each of H$_2$N···CuF and H$_2$N···CuI. After propagating the uncertainty in the measured value of $D_r$ the assumption that $F_{11}$ of H$_2$N···CuCl = 172 ± 5 N m$^{-1}$ implies $F_{22}$ = 111(33) N m$^{-1}$ for H$_2$N···Cu where the dominant contribution is the uncertainty in $D_r$. An assumed value of $F_{11}$ for H$_2$N···CuF of 333 ± 10 N m$^{-1}$ would imply that $F_{22}$ falls within a narrow range between 202 and 213 N m$^{-1}$. However, the uncertainty in the measured value of $D_r$ again makes the dominant contribution and $F_{22}$ = 210(70) N m$^{-1}$ after propagation of the uncertainty in $D_r$. The level of agreement between the experimentally-determined results and those calculated ab initio is closest for H$_3$N···CuF and CuI. After propagating the uncertainty in the measured value of $D_r$ the assumption that the various $F_{11}$ of H$_3$N···CuI are consistent with expectations following the earlier study of H$_2$N···CuCl and also with the trend established for OC···CuX. $r$(Cu–N) lengths on substituting a lighter by a heavier halogen atom and is longer in H$_2$N···CuBr than in H$_2$N···CuF by 0.043(2) Å. A very similar difference is observed between $r$(Cu–N) in OC···CuF and the same parameter in OC···CuI. The trend observed earlier for the Ar···CuX series involved greater incremental changes on substitution of the halogen atom. $r$(Cu–Ar) in Ar···CuF is 0.077(3) Å shorter than the same parameter in Ar···CuBr. The attachment of an isolated

![Image](https://via.placeholder.com/150)

**Fig. 4** Plot to illustrate the variation of $F_{22}$ as a function of the assumed value of $F_{11}$ for each of H$_2$N···CuF and H$_2$N···CuI. The values of $k_r$ for the isolated CuF and CuI molecules, assumed equal to $F_{11}$ in the respective H$_2$N···CuF and H$_2$N···CuI complexes, are marked with a cross (X).

<table>
<thead>
<tr>
<th>$F_{11}$(Cu–I) = 172 N m$^{-1}$</th>
<th>$F_{22}$(H$_2$N···Cu) = 111(33) N m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{11}$(Cu–F) = 333 N m$^{-1}$</td>
<td>$F_{22}$(H$_3$N···Cu) = 210(70) N m$^{-1}$</td>
</tr>
</tbody>
</table>

Table 5: $Z_{aa}$(Cu), $Z_{aa}$(X), $r$(Cu–N/O) and $\Delta r$ for OC···CuX, H$_2$N···CuX and CuX

<table>
<thead>
<tr>
<th>H$_2$N···MX</th>
<th>OC···MX</th>
<th>H$_3$N···MX</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_{aa}$(M)/MHz</td>
<td>$Z_{aa}$(X)/MHz</td>
<td>$Z_{aa}$(M)/MHz</td>
</tr>
<tr>
<td>CuF</td>
<td>66.196(12)</td>
<td>75.406(19)</td>
</tr>
<tr>
<td>CuCl</td>
<td>66.629(24)</td>
<td>70.823(210)</td>
</tr>
<tr>
<td>CuBr</td>
<td>—</td>
<td>67.534(12)</td>
</tr>
<tr>
<td>CuI</td>
<td>62.943(95)</td>
<td>64.504(3)</td>
</tr>
<tr>
<td>HCl</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HI</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ICl</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>BrCl</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$r$(Cu–N)/Å</td>
<td>$\Delta r$/Å</td>
<td>$r$(Cu–C)/Å</td>
</tr>
<tr>
<td>CuF</td>
<td>1.89282(63)</td>
<td>0.0071(6)</td>
</tr>
<tr>
<td>CuCl</td>
<td>1.9183(16)</td>
<td>0.0073(7)</td>
</tr>
<tr>
<td>CuBr</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CuI</td>
<td>1.9357(13)</td>
<td>0.0147(5)</td>
</tr>
</tbody>
</table>

$^a$ Ref. 44, 55, 56 and 61–64. $^b$ Ref. 24 and references therein. $^c$ $\Delta r$ denotes the change in $r$(Cu–X) when B···MX form from isolated B and MX units.

### 4. Conclusions

The spectra of H$_2$N···CuF and H$_2$N···CuI are each consistent with the $C_{nv}$ geometry illustrated in Fig. 3. Quantitative details of the geometries and measured nuclear quadrupole coupling constants of the H$_2$N···CuX series are compared with results from other B···CuX in Table 5. The $r$(Cu–N) distances determined for H$_2$N···CuF and H$_2$N···CuI are consistent with expectations following the earlier study of H$_2$N···CuCl and also with the trend established for OC···CuX. $r$(Cu–N) lengthens on substituting a lighter by a heavier halogen atom and is longer in H$_2$N···CuBr than in H$_2$N···CuF by 0.043(2) Å. A very similar difference is observed between $r$(Cu–N) in OC···CuF and the same parameter in OC···CuI. The trend observed earlier for the Ar···CuX series involved greater incremental changes on substitution of the halogen atom. $r$(Cu–Ar) in Ar···CuF is 0.077(3) Å shorter than the same parameter in Ar···CuBr. The attachment of an isolated
CuX species to either CO or NH\textsubscript{3} to form B···CuX causes a change in r(Cu–X). The Cu–F bonds of H\textsubscript{3}N···CuF and OC···CuF shrink slightly on formation of these complexes from the isolated NH\textsubscript{3}/CO and CuX sub-units. In contrast, r(Cu–X) in the analogous B···CuCl, B···CuBr and B···CuI species extend slightly on complex formation. The difference between r(Cu–X) in B···CuX and in the corresponding CuX diatomic is denoted by ∆r in Table 5 for H\textsubscript{3}N···CuX and OC···CuX. For both B = CO and B = NH\textsubscript{3}, ∆r is greatest for the iodide. Recent works have described significant changes in the bond length of carbon monoxide were identified where OC···CuX and OC···AgX form from their constituent sub-units. At the level of precision of the present experiments and a previous work, the bond angle within NH\textsubscript{3} does not change significantly when the molecule attaches to MX to form either H\textsubscript{3}N···CuX or H\textsubscript{3}N···AgX.

Trends in the OC···CuX and H\textsubscript{3}N···CuX series can also be examined from the perspective of the measured nuclear quadrupole coupling constants. Changes in \(Z_{aa}\) for the metal and halogen atoms provide insight into the extent of electric charge redistribution when a complex forms from its component units. The determined \(Z_{aa}\) of OC···CuX and H\textsubscript{3}N···CuX are compared with those for isolated MX species and for selected hydrogen- and halogen-bonded complexes in Table 5. The fractional changes in \(Z_{aa}(M)\) and \(Z_{aa}(X)\) on formation of the complex from the isolated sub-units, B and MX, are greater for OC···CuX than for H\textsubscript{3}N···CuX or Ar···CuX. The opposite trend is observed for the hydrogen-bonded complexes, OC···HX and H\textsubscript{3}N···HX. The described differences between the B···MX, B···HX\textsuperscript{23} and B···X\textsuperscript{21} series arise because the properties of hydrogen- and halogen-bonded complexes are governed mainly by electrostatic interactions whereas the binding between OC or NH\textsubscript{3} and CuX has a significant covalent component. It has been shown that the ionicity of the Cu–X bond of OC···CuX decreases with increasing mass of the halogen atom. An ionicity of 0.73 is determined for H\textsubscript{3}N···CuCl and therefore consistent with the trend identified earlier for the OC···CuX series.

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