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A monomeric complex of ammonia and cuprous chloride: $\text{H}_3\text{N} \cdots \text{CuCl}$ isolated and characterised by rotational spectroscopy and *ab initio* calculations

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The $\text{H}_3\text{N} \cdots \text{CuCl}$ monomer has been generated and isolated in the gas phase through laser vaporisation of a copper sample in the presence of low concentrations of NH_3 and CCl_4 in argon. The resulting complex cools to a rotational temperature approaching 2 K during supersonic expansion of the gas sample and is characterised by broadband rotational spectroscopy between 7 and 18.5 GHz. The spectra of six isotopologues are measured and analysed to determine rotational, B_0 ; centrifugal distortion, D_J , D_{JK} ; and nuclear quadrupole coupling constants of Cu, Cl, and ^{14}N nuclei, $\chi_{aa}(\text{X})$. The geometry of the complex is C_{3v} with the N, Cu, and Cl atoms located on the a inertial axis. Bond distances and the $\angle(\text{H}-\text{N} \cdots \text{Cu})$ bond angle within the complex are precisely evaluated through fitting of geometrical parameters to the experimentally determined moments of inertia and through *ab initio* calculations at the CCSD(T)(F12*)/AVQZ level. The $r(\text{Cu}-\text{Cl})$, $r(\text{Cu}-\text{N})$, and $\angle(\text{H}-\text{N} \cdots \text{Cu})$ parameters are, respectively, evaluated to be 2.0614(7) Å, 1.9182(13) Å, and 111.40(6)° in the r_0 geometry, in good agreement with the *ab initio* calculations. Geometrical parameters evaluated for the isolated complex are compared with those established crystallographically for a solid-state sample of $[\text{Cu}(\text{NH}_3)\text{Cl}]$. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4916391>]

I. INTRODUCTION

Aqueous copper (I) chloride reacts with a variety of simple Lewis bases to form products that each contain copper in a linear, two-coordinate geometry.¹ $[\text{Cu}(\text{NH}_3)\text{Cl}]$ is one of many examples of an extended structure where linear connecting links are supplied by a group 10 metal in its +1 coordination state.² The aim of the present work is the precise determination of the molecular geometry of the $\text{H}_3\text{N} \cdots \text{CuCl}$ monomer isolated in the gaseous phase. In the remainder of this work, $[\text{Cu}(\text{NH}_3)\text{Cl}]$ will denote the solid material, whilst $\text{H}_3\text{N} \cdots \text{CuCl}$ will represent the individual monomer unit containing N, Cu, and Cl atoms with the connectivity implied by the label. Pure rotational spectroscopy provides a uniquely powerful method by which both molecular geometry and intramolecular charge re-distribution can be explored in isolated, gas phase species. It thus becomes possible to distinguish the intrinsic features of a monomer unit from effects that may be induced by surrounding atoms within an extended array.

A crystallographic study³ of $[\text{Cu}(\text{NH}_3)\text{Cl}]$ revealed that the three dimensional structure of the material can be described through reference to the relative orientations of discrete $\text{H}_3\text{N} \cdots \text{CuCl}$ monomers. Each monomer has a C_{3v} geometry in which all heavy atoms lie on the local three-fold axis of symmetry. The unit cell of the crystal structure is chiral with the

linear arrangement of Cl, Cu, and N atoms within a single monomer conveniently defining a crystallographic three-fold axis. The axial monomer coordinates to three other monomer units to yield a structure resembling a propeller with the resulting coordination sphere of the axial copper atom being a trigonal bipyramid. The bond length separating copper atoms within this crystal structure is 2.979(1) Å. The optimised equilibrium geometry of $(\text{H}_3\text{N} \cdots \text{CuCl})_2$ was calculated by *ab initio* methods to be an eclipsed configuration containing $\text{Cu} \cdots \text{Cu}$ and $\text{H} \cdots \text{Cl}$ contacts of 3.174 Å and 2.209 Å, respectively.⁴ Evidently, the observed crystal structure results from a compromise between interactions internal to individual monomer units and others which exist between monomers. The coordination of NH_3 to a $\text{CuCl}(111)$ surface has been investigated by ultra-violet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and *ab initio* calculations.^{5,6} The nitrogen atom coordinates to an unsaturated copper site such that the C_{3v} axis of NH_3 is normal to the surface. The results of the present work will inform wider interpretations of structure in materials that contain linear, two-coordinate copper or group 10 metal atom linkages. In addition, they will bear upon understanding of the interaction of NH_3 with a copper chloride (111) surface.

The present work exploits the cold environment generated within a gas sample undergoing supersonic expansion to produce and isolate the $\text{H}_3\text{N} \cdots \text{CuCl}$ monomer for study. It is informed by recent experiments which have succeeded in generating a wide variety of complexes that contain metal halides coordinated to simple Lewis bases such as N_2 ,⁷ H_2 ,^{8,9} CO ,^{10–15} H_2O ,^{16–18} NH_3 ,¹⁹ H_2S ,^{17,20,21} C_2H_4 ,^{22,23} and C_2H_2 .^{22,24}

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Most pertinently, the spectra of five isotopologues of $\text{H}_3\text{N}\cdots\text{AgCl}$ were characterised and analysed to reveal aspects of the molecular geometry. It was shown that the $\text{H}_3\text{N}\cdots\text{AgCl}$ complex has C_{3v} symmetry with a bond between silver and nitrogen atoms with $r(\text{N}\cdots\text{Ag})$ and $r(\text{Ag}\text{---}\text{Cl})$ bond distances, respectively, determined as 2.15444(6) and 2.26333(6) Å in the r_0 geometry. The present work will precisely evaluate the bond distances separating heavy atoms within $\text{H}_3\text{N}\cdots\text{CuCl}$. It will provide information about the change in geometry of NH_3 on formation of the complex. Finally, precise measurements of the nuclear quadrupole coupling constants of N, Cu, and Cl within the complex will provide insight into the extent of charge redistribution within each of NH_3 and CuCl and between these sub-units upon formation of the complex.

II. EXPERIMENTAL

The chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer employed here has been described previously,^{25,26} so only a brief description will be provided. The instrument allows the measurement of broadband rotational spectra spanning a frequency range from 7 to 18.5 GHz in bandwidth. The spectrometer has an installed laser ablation source¹¹ that allows metal-containing molecules to be generated and studied.

Experiments were performed using a gaseous sample containing ~4% NH_3 , ~1% CCl_4 , and 95% argon prepared to a total pressure of 6 bar. The described mixture of precursors is introduced into an evacuated chamber from a pulsed valve and allowed to pass over the surface of a copper rod from which material is ablated by the focussed pulse (~25 mJ pulse⁻¹) of radiation (532 nm) from a Nd:YAG laser. Components of the gas sample undergo fragmentation and subsequent chemical reactions within the plasma environment induced by the laser pulse.²⁶ Immediately subsequent to passing through the plasma, the sample undergoes supersonic expansion such that entrained molecules are rotationally cooled to temperatures of the order of 2 K. Generation of $\text{H}_3\text{N}\cdots\text{CuCl}$ results from the sequence of chemical reactions that occurs within the transient plasma and subsequent supersonic expansion. The naturally occurring ratios of isotopic abundances are 69:31 and 76:24 for (⁶³Cu : ⁶⁵Cu) and (³⁵Cl : ³⁷Cl), respectively. The spectra of $\text{H}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, $\text{H}_3^{14}\text{N}\cdots^{65}\text{Cu}^{35}\text{Cl}$, and $\text{H}_3^{14}\text{N}\cdots^{63}\text{Cu}^{37}\text{Cl}$ isotopologues were thus observed while using natural samples of copper and chlorine. The generation of isotopologues containing less abundant isotopes of nitrogen and hydrogen ($\text{H}_3^{15}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, and $\text{D}_2\text{H}^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$) required samples that were synthetically enriched in either ¹⁵NH₃ or ¹⁴ND₃. The $\text{D}_2\text{H}^{14}\text{N}$ present in $\text{D}_2\text{H}^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$ was generated through the natural process of isotopic exchange between ¹⁴ND₃ and hydrogen-containing contaminants within the sample manifold.

Complexes that form within the expanding jet and possess a permanent electric dipole moment can become polarised by an introduced microwave pulse on resonance with rotational transitions. An arbitrary waveform generator is used as the source of the chirped microwave pulse that sweeps from 0.5 to 12 GHz over a duration of 1 μs. This chirped pulse is passed through a 12.2 GHz low-pass filter and mixed against the

filtered output of a phase-locked dielectric resonant oscillator (PDRO) that supplies a 19.00 GHz signal. The AWG (arbitrary waveform generator) and PDRO are each phase-locked to a 10 MHz frequency accurate to 1 part in 10.¹¹ The output after mixing passes through a 7–18.5 GHz bandpass filter and is amplified prior to irradiation of the molecular sample. The data presented herein were acquired using a 300 W travelling wave tube amplifier. The microwave frequency sweep is introduced perpendicular to the propagation direction of the expanding gas via a microwave horn. The molecular emission signal (free induction decay, or FID, of the polarisation) is detected by a second horn antenna and amplified by a low noise amplifier. The FID is mixed down against the 19.00 GHz reference signal supplied by the PDRO and then passes through a 12.5 GHz low-pass filter before detection. Each FID is measured over a 20 μs period following each chirped polarisation pulse. A fast digital oscilloscope is phase-locked to the same 10 MHz external frequency reference used by the PDRO and AWG and used to digitise the molecular FID.

The sequence of microwave polarisation pulse and detection of FID is repeated eight times following each individual nozzle (i.e., gas sample introduction) pulse to maximise the duty cycle of the spectrometer. In order to record the spectrum of $\text{H}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$ during this study, 3.1 M FIDs (acquired from 382 500 valve pulses and requiring 102 h of real time) were co-added in the time domain. These were Fourier transformed using a Tektronix proprietary high-resolution window function (details provided as supplementary material²⁷) to yield the frequency domain spectrum spanning from 7 to 18.5 GHz. All observed transitions have a full width at half maximum (FWHM) of 65 kHz. This is compared to a FWHM of ~150 kHz for a traditionally applied Kaiser-Bessel window function.²⁸ The ability to shape the rotational spectrum line-shape is a special feature of CP-FTMW spectroscopy, and this was necessary to resolve out the hyperfine structure resulting from multiple quadrupolar nuclei.

III. AB INITIO CALCULATIONS

Except where stated otherwise, all *ab initio* calculations were performed with the MOLPRO package²⁹ using CCSD(T) (F12*),³⁰ a coupled-cluster method with single, double, and triple excitations, explicit correlation,³¹ and a perturbative treatment of triple excitations.³² Structure optimizations were calculated using the AVDZ, AVTZ, and AVQZ basis set combinations. These consist of the aug-cc-pVXZ (X = D,T,Q) basis sets on N and H atoms, aug-cc-pV(X+d)Z (X = D,T,Q) on the Cl atom, and aug-cc-pVXZ-PP (X = D,T,Q) on Cu atom with ECP-10-MDF effective core potential to account for scalar relativistic effects.^{33,34} The counterpoise-corrected dissociation energy was calculated using the AVQZ combination and the frequency analysis using the AVTZ combination.

IV. RESULTS

A. Determination of spectroscopic constants

The most intense signals observed when probing an expanding gas sample containing CCl_4 , NH_3 , Cu, and Ar assign

FIG. 1. The top panel displays the broadband spectrum measured when probing an expanding sample containing small percentages of NH_3 , CCl_4 , and Cu in a buffer gas of argon. The spectrum is averaged over 3.1 M FID's (acquired over 102 h of real time). The bottom panels present expanded sections of the spectrum in the top panel at levels of zoom implied by the labels on the respective y axes. From left to right, the bottom panels illustrate the signals obtained for (i) the $J'' \rightarrow J' = 1 \rightarrow 2$ transitions of $^{65}\text{Cu}^{37}\text{Cl}$, $^{63}\text{Cu}^{37}\text{Cl}$, $^{65}\text{Cu}^{35}\text{Cl}$, and $^{63}\text{Cu}^{35}\text{Cl}$, respectively, (ii) the $J'' \rightarrow J' = 1 \rightarrow 2$ transition in the Σ_{0a} state of $\text{NH}_3 \cdots \text{Ar}$, (iii) the $J'' \rightarrow J' = 0 \rightarrow 1$ transition of $^{35}\text{ClCN}$, and (iv) the $J'' \rightarrow J' = 2 \rightarrow 3$ transition of $\text{H}_3\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$.

to various isotopologues³⁵ of CuCl (Figure 1). This confirms that a fraction of the available CCl_4 molecules dissociate within the plasma to yield fragments that subsequently undergo chemical reactions. Two additional series of transitions are seen around 11 946 MHz and 11 711 MHz, respectively, and these are known to assign to isotopologues³⁶ of cyanogen chloride, $^{35}\text{ClCN}$, and $^{37}\text{ClCN}$, implying that NH_3 molecules can also undergo fragmentation within the plasma. Transitions of CCl_2 and ClCCH are not seen despite these having been observed in experiments employing similar expansion conditions but probing different gas samples.^{37,38} There is no evidence of the presence of CuCCH for which the $J'' \rightarrow J' = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions are known at ~ 8240 MHz and ~ 16481 MHz, respectively.³⁹ The fragmentation of NH_3 required for the generation of ClCN implies that three H atoms are released into the plasma for each ClCN product formed. It thus seems possible that hydrogen atoms act to buffer against the growth of unsaturated carbon chains within the plasma. This hypothesis might suggest that molecules such as CH_3Cl and HCN may be generated in high abundance. The rotational transitions of lowest frequency for these molecules are too high to measure using the present spectrometer. The measured spectrum does not contain evidence of the presence of CH_2Cl_2 , however, which is known to have transitions between 7 and 18.5 GHz. Transitions of $\text{Ar} \cdots \text{NH}_3$ ^{40,41} bound states are present.

An expanded section of the measured broadband spectrum is shown in Figure 2. Additional to all of the above-mentioned species for which transition frequencies are known, the spectrum contains novel features. Many new transitions can tentatively be assigned to the spectra of naturally abundant isotopo-

logues of a novel complex of $\text{H}_3\text{N} \cdots \text{CuCl}$ on the initial basis that (i) the spectrum of each isotopologue displays the general features expected for a symmetric rotor and also extensive hyperfine splittings (see below for rationalisation of geometry and hyperfine structure) and (ii) observed shifts in the spectra on substitution of the Cu and Cl isotopes are broadly consistent with the basic geometry anticipated for $\text{H}_3\text{N} \cdots \text{CuCl}$. The Cu atom is expected to be closer to the center of mass of the complex than Cl, and indeed, substitution of ^{63}Cu by ^{65}Cu generates a smaller decrease in B_0 (~ 3.0 MHz) than substitution of ^{35}Cl by ^{37}Cl (~ 70 MHz). Isolated hydrogen- and

FIG. 2. Section of the broadband spectrum displayed in Figure 1 showing the $J'' \rightarrow J' = 2 \rightarrow 3$ transitions of $\text{H}_3\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ and $\text{H}_3\text{N} \cdots ^{65}\text{Cu}^{35}\text{Cl}$. The experimental data (black) are displayed above spectra of each isotopologue (respectively, blue and red) simulated from the model Hamiltonian.

halogen-bonded complexes of the form $\text{H}_3^{14}\text{N} \cdots \text{YX}$ (where Y is either H or a halogen atom, while X is a halogen atom) have consistently been observed to contain a $\text{N} \cdots \text{Y}$ bond and adopt a C_{3v} geometry. *Ab initio* calculations of the geometry of $\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ and the structure of $[\text{Cu}(\text{NH}_3)\text{Cl}]$ identified³ through crystallography are also consistent with a C_{3v} and symmetric rotor geometry for an isolated monomer of $\text{H}_3\text{N} \cdots \text{CuCl}$. Hyperfine structure is expected as a result of the presence of nuclei that have non-zero electric quadrupole moments. The abundant isotopes of nitrogen (^{14}N), copper (^{63}Cu and ^{65}Cu), and chlorine (^{35}Cl and ^{37}Cl), respectively, have nuclear spins (I) equal to 1, 3/2, and 3/2 and this will lead to extensive hyperfine structure. The spectrum tentatively assigned to $\text{H}_3^{14}\text{N} \cdots ^{65}\text{Cu}^{35}\text{Cl}$ is shifted in frequency from that of $\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ by only a relatively small increment, consistent with the expected geometry in which the copper atom is located very close to the centre of mass of the complex. Further evidence in support of the tentative assignment is available from relative intensities of the transitions assigned to the various isotopologues. These are consistent with the naturally occurring isotopic abundance ratios of Cu and Cl. The geometry of the complex will be re-examined later following a determination of spectroscopic parameters through assignment and fitting of measured transition frequencies using Western's PGOPHER program.⁴²

The Hamiltonian employed for isotopologues containing H_3^{14}N , H_3^{15}N , or D_3^{14}N is

$$H = H_R - \frac{1}{6}\mathbf{Q}(\text{Cu}) : \nabla\mathbf{E}(\text{Cu}) - \frac{1}{6}\mathbf{Q}(\text{Cl}) : \nabla\mathbf{E}(\text{Cl}) - \frac{1}{6}\mathbf{Q}(\text{N}) : \nabla\mathbf{E}(\text{N}). \quad (1)$$

The first term on the right hand side is the Hamiltonian of a semi-rigid symmetric rotor and contains terms representing the rotational constants of the ground vibrational state, A_0 and B_0 ; and the quartic centrifugal distortion constants, D_J , D_{JK} , and D_K . The Hamiltonian used for $\text{D}_2\text{H}^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ contains 2nd, 3rd, and 4th terms as shown in Eq. (1), but the first term is chosen as appropriate to an asymmetric semi-rigid rotor while using the Watson A reduction and I' representation. The second, third, and fourth terms of Eq. (1), each describes an

interaction between the nuclear electric quadrupole moment and the electric field gradient at a nucleus and, respectively, apply to the Cu, Cl, and N atoms. The projection of each nuclear quadrupole coupling tensor onto the a -inertial axis, denoted by $\chi_{aa}(\text{X})$ (where $\text{X} = \text{Cu}$, Cl , or N), is precisely determined through fits that determine nuclear quadrupole coupling constants for all axial nuclei of $\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$, $\text{H}_3^{14}\text{N} \cdots ^{65}\text{Cu}^{35}\text{Cl}$, $\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{37}\text{Cl}$, $\text{D}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$, and $\text{H}_3^{15}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ isotopologues. Hyperfine structure arising from nuclear quadrupole coupling of deuterium atoms was not resolved during the present experiments.

The relative intensities of $J'' \rightarrow J'$ transitions in the observed rotational spectra are generally consistent with a rotational temperature approaching 2 K. Given the expected energy increment between states with $K = 0$ and $K = 1$, rapid relaxation from the latter to the former state would be expected in the absence of effects inhibiting the process, and this would result in weak (or effectively zero) intensities for transitions having $K = 1$. Consistent with arguments presented during previous studies of $\text{H}_2\text{DN} \cdots \text{HX}$ and $\text{H}_2\text{DP} \cdots \text{HCl}$,⁴³ transitions having $K_{-1} = 1$ (which correlate with those having $K = 1$ in free ammonia) are completely absent from the observed spectrum of $\text{D}_2\text{H}^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$, where the symmetry of the H_3N sub-unit is broken with respect to the exchange of identical nuclei. Experimentally determined values of Δ_{JK} and $\chi_{bb}(\text{X}) - \chi_{cc}(\text{X})$ are thus not available for $\text{D}_2\text{H}^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$. However, it will be shown that the other isotopologues of $\text{H}_3\text{N} \cdots \text{CuCl}$ contain three equivalent ^1H nuclei which are exchanged by a C_3 rotation. This symmetry property leads to nuclear spin statistics, a consequence of which are collisional propensity rules that inhibit collisional relaxation from $K = 1$ to $K = 0$ states and thereby the retention of significant $K = 1$ population.⁴⁴ Thus, $K = 1$ transitions of observable intensity may be expected in the spectra of isotopologues containing NH_3 or ND_3 . A consequence of the extensive hyperfine splittings and small isotopic shifts on substitution of ^{63}Cu for ^{65}Cu in all isotopologues is that $K = 0$ and $K = 1$ transitions are predicted to be extensively overlapped. Therefore, transitions having $K = 1$ could not be assigned confidently for isotopologues containing $^{14}\text{NH}_3$ or $^{15}\text{NH}_3$, precluding the determination of D_{JK} for these species. The circumstances are different

TABLE I. Determined spectroscopic constants of isotopologues of $\text{H}_3\text{N} \cdots \text{CuCl}$ containing $^{14}\text{NH}_3$.

	$\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$	$\text{H}_3^{14}\text{N} \cdots ^{65}\text{Cu}^{35}\text{Cl}$	$\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{37}\text{Cl}$
B_0/MHz	2470.3345(16) ^a	2467.734 75(51)	2401.6357(117)
D_J/kHz	0.419(99)	(0.488) ^b	(0.464) ^b
D_{JK}/kHz	(45.96) ^b	(43.59) ^b	(43.77) ^b
$\chi_{aa}(\text{Cu})/\text{MHz}$	66.629(24)	61.282(94)	67.38(21)
$\chi_{aa}(\text{Cl})/\text{MHz}$	-23.041(34)	-23.030(47)	-18.147(42)
$\chi_{aa}(\text{N})/\text{MHz}$	-2.676(36)	-2.694(37)	-2.822(71)
N^c	52	29	9
σ^c	15.5	13.6	12.2

^aNumbers in parentheses are one standard deviation in units of the last significant figure. All fits assume a value for A_0 of 186 696 MHz, obtained from data in Ref. 49.

^bValues of D_J in square brackets calculated by scaling results of *ab initio* calculations according to the ratio of *ab initio* and experimental results for $\text{H}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ (see text). Values of D_{JK} in square brackets calculated using the same procedure but using $\text{D}_3^{14}\text{N} \cdots ^{63}\text{Cu}^{35}\text{Cl}$ as the reference isotopologue.

^c N is the number of fitted transitions. σ denotes the rms deviation of the fit.

TABLE II. Spectroscopic constants determined for $\text{H}_3^{15}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, and $\text{D}_2\text{H}^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$.

	$\text{H}_3^{15}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$	$\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$		$\text{D}_2\text{H}^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$
B_0/MHz	2411.365 69(69) ^a	2234.4711(18)	$((B_0 + C_0)/2)/\text{MHz}$	2306.6143(25)
D_J/kHz	(0.466) ^b	0.388(61)	Δ_J/kHz	0.293(83)
D_{JK}/kHz	(43.64) ^b	33.95(75)	...	...
$\chi_{aa}(\text{Cu})/\text{MHz}$	66.671(54)	66.57(20)	$\chi_{aa}(\text{Cu})/\text{MHz}$	66.16(24)
$\chi_{aa}(\text{Cl})/\text{MHz}$	-23.131(94)	-22.52(14)	$\chi_{aa}(\text{Cl})/\text{MHz}$	-22.87(22)
$\chi_{aa}(\text{N})/\text{MHz}$	...	-2.692(77)	$\chi_{aa}(\text{N})/\text{MHz}$	-2.504(80)
N^c	11	48	N^c	34
σ^c	11.8	14.5	σ^c	16.9

^aNumbers in parentheses are one standard deviation in units of the last significant figure. Fits assume values of A_0 of 186 711 MHz, 936 72 MHz, and 113 628 MHz for $\text{H}_3^{15}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, and $\text{D}_2\text{HN}\cdots^{63}\text{Cu}^{35}\text{Cl}$, respectively, obtained from data in Refs. 49 and 50.

^bCalculated as described in footnote (b) of Table I.

^c N is the number of fitted transitions. σ denotes the rms deviation of the fit.

for $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$, where intense $K = 1$ transitions were unambiguously distinguished and fitted to obtain a value of D_{JK} for this isotopologue.

It is possible to predict values of D_{JK} for isotopologues containing ^1H with reasonable confidence through a semi-empirical procedure that uses the value of D_{JK} established for $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$. First, the parameter is calculated at the MP2/aug-cc-pVTZ level for all isotopologues using the Gaussian 09 package.⁴⁵ The calculated result for $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$ is then divided by the experimentally determined value to obtain a ratio. This provides a scaling factor that can be used to obtain an expectation value for the experimental value of D_{JK} from values calculated *ab initio* for all other isotopologues. The other quartic centrifugal distortion constant, D_J , was precisely fitted only for the $\text{H}_3^{15}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$ and $\text{D}_3^{14}\text{N}\cdots^{63}\text{Cu}^{35}\text{Cl}$ isotopologues. The earlier-described semi-empirical approach was therefore adopted to obtain expectation values of D_J for other isotopologues. The data did not allow the determination of D_K for any isotopologue and no attempt was made to calculate this parameter. Assignments of measured transitions for all isotopologues studied and fits to determine the various spectroscopic constants are provided as supplementary material.²⁷ All evaluated spectroscopic parameters are presented in Tables I and II.

B. Molecular geometry

Qualitative aspects of the geometry of the complex can be inferred from evidence already presented. The described observation that the intensities of transitions having $K = 1$, relative to those of transitions having $K = 0$, vary according to the symmetry of the isotopologue under examination, and the involved nuclear spins imply that hydrogen atoms are exchanged by a C_3 rotation about the I_a inertial axis of the complex. The geometries of various hydrogen-,^{46,47} halogen-,⁴⁸ and metal-bonded¹⁹ complexes containing ammonia have previously been found to have C_{3v} symmetry and each is described by the general formula, $\text{H}_3\text{N}\cdots\text{YX}$. The geometry of each involves a bond between N and Y atoms such that the local C_3 axis of the NH_3 sub-unit aligns with the axis defined by the $\text{Y}-\text{X}$ bond. Given these previous observations and the evidence from crystallography that monomers in this basic

geometry exist within the solid-state structure of $[\text{Cu}(\text{NH}_3)\text{Cl}]$, it is reasonable to start from the assumption that $\text{H}_3\text{N}\cdots\text{CuCl}$ has the C_{3v} geometry shown in Figure 3. A quantitative analysis of the geometry of the complex will involve fitting structural parameters to the experimentally determined moments of inertia.

Data were obtained exclusively from the vibrational ground state of the complex precluding experimental determination of the r_e geometry within the present work. Rotational constants measured for the vibrational ground state of the complex can, however, be used to calculate an r_0 molecular geometry. The method involves fitting values of geometrical parameters to the experimentally determined moments of inertia without correcting for the slightly varying zero-point vibrational effects in different isotopologues. Under the initial assumption that the molecular geometry has the C_{3v} symmetry shown in Figure 3, the geometry of the complex can be defined with reference to four geometrical parameters. The bond length between the copper and chlorine atoms is denoted by $r(\text{Cu}-\text{Cl})$ with other bond lengths represented using a similar convention. The only angle required is that defining the pyramidal structure internal to the NH_3 sub-unit and represented by $\angle(\text{H}-\text{N}\cdots\text{Cu})$. Isotopic substitutions are available at the Cu, Cl, N, and H atoms allowing the $r(\text{Cu}-\text{Cl})$ and $r(\text{N}-\text{Cu})$ distances to be fitted directly to the experimentally determined moments of inertia. The data available through isotopic substitutions of hydrogen atoms do not allow changes in $r(\text{N}-\text{H})$ and $\angle(\text{H}-\text{N}\cdots\text{Cu})$ to be unambiguously distinguished. The value assumed for $r(\text{N}-\text{H})$ in the complex was therefore established by (i) fitting $r(\text{N}-\text{H})$ to the ground state rotational

FIG. 3. The C_{3v} geometry of $\text{H}_3\text{N}\cdots\text{CuCl}$ with nitrogen, copper, and chlorine atoms coloured blue, dark grey, and green, respectively. The a , b , and c inertial axes are mutually perpendicular with the a and b inertial axes oriented as shown.

TABLE III. Results of *ab initio* calculations of molecular geometries of $\text{H}_3\text{N}\cdots\text{CuCl}$ and each of the isolated sub-units, NH_3 and CuCl .

	$r_e(\text{CCSD(T)}(\text{F12}^*))$					
	AVDZ		AVTZ		AVQZ	
	$\text{NH}_3 + \text{CuCl}$	$\text{H}_3\text{N}\cdots\text{CuCl}$	$\text{NH}_3 + \text{CuCl}$	$\text{H}_3\text{N}\cdots\text{CuCl}$	$\text{NH}_3 + \text{CuCl}$	$\text{H}_3\text{N}\cdots\text{CuCl}$
$r(\text{Cu—Cl})/\text{\AA}$	2.056	2.058	2.050	2.054	2.048	2.053
$r(\text{Cu—N})/\text{\AA}$	...	1.908	...	1.905	...	1.904
$r(\text{N—H})/\text{\AA}$	1.012	1.015	1.012	1.015	1.012	1.014
$\angle(\text{H—N}\cdots\text{Cu}/^{\circ})$	112.1 ^a	111.7	112.2 ^a	111.8	112.2 ^a	111.8

^aThe angle internal to free NH_3 is defined as $\angle(\text{H—N}\cdots^*)$ to allow ready comparison with values of $\angle(\text{H—N}\cdots\text{Cu})$ identified for the complex. The asterisk represents a dummy atom of zero mass placed on the C_3 axis of NH_3 on the opposite side of the nitrogen atom to the three hydrogen atoms.

constants⁴⁹ of free NH_3 to determine the r_0 value appropriate to the isolated sub-unit, (ii) calculating *ab initio* the change in the r_e value of $r(\text{N—H})$ when NH_3 coordinates to CuCl to form $\text{H}_3\text{N}\cdots\text{CuCl}$, and then (iii) assuming the r_0 value of this parameter changes to the same extent on complex formation. The results of the *ab initio* calculations necessary for this procedure are available in Table III.

Finally, the contraction⁵⁰ of 0.0011 Å observed in $r(\text{N—H})$ on substitution of H for D in the r_0 geometry of free NH_3 is assumed to occur also within the $\text{H}_3\text{N}\cdots\text{CuCl}$ complex. The final results of the fit of the r_0 geometry of the complex are shown in Table IV.

An alternative approach to determination of the molecular geometry involves using observed changes in rotational constants on isotopic substitution to generate coordinates for the substituted atoms. This analysis has the advantage of yielding values for parameters that are closer to r_e results and more internally consistent when over-determined (i.e., in the limit where extensive data are acquired from many isotopologues).⁵¹ The r_s coordinates of atoms on the a -inertial axis, a_{Cu} , a_{Cl} , and a_{N} , are determined using the equation⁵²

$$|a| = \sqrt{\frac{\Delta I_b}{\mu_s}}, \quad (2)$$

where $\mu_s = \frac{\Delta m M}{\Delta m + M}$ is the reduced mass calculated, M is the mass of the parent isotopologue, and Δm is the change in mass resulting from the isotopic substitution. The change in the moment of inertia about the b -inertial axis upon isotopic substitution is denoted by ΔI_b . Only the magnitudes of r_s coordinates are determined with the signs reported in Table I being those which are most physically reasonable. Uncertainties are calculated using $\delta a = 0.0015/|a|$ as recommended by Costain.⁵³ The hydrogen atoms cannot be unambiguously located by the r_s method alone and calculation by the first moment condition is known to yield inaccurate results for hydrogen. If the $r(\text{N—H})$ distance is held constant at the value estimated as described above, a value for $\angle(\text{H—N}\cdots\text{Cu})$ can be determined by the r_s method using the expression provided in Ref. 54. The results for all coordinates are consistent with those obtained earlier through the r_0 fit. The r_0 and r_s molecular geometries are compared with the r_e geometry calculated *ab initio* in Table III.

Before exploring differences between the *ab initio* calculated (r_e) and experimentally determined (r_0 and r_s) results, it is important to assess whether any effects excluded by the present *ab initio* calculations might introduce significant errors. Post basis set limit contributions to the geometry of NH_3 were examined in detail in Ref. 55, where it was shown that core correlation reduces the calculated $r(\text{N—H})$ distance by

TABLE IV. Geometrical parameters and nuclear co-ordinates of $\text{H}_3\text{N}\cdots\text{CuCl}$.

NH_3	r_0	r_s	$r_e(\text{CCSD(T)}(\text{F12}^*))/\text{AVQZ}^a$	
$r(\text{N—H})/\text{\AA}$	1.0162	1.0154	1.012	
$\angle(\text{H—N}\cdots^*)/\text{deg}$	111.38	111.67	112.2	
$\text{H}_3\text{N}\cdots\text{CuCl}$	r_0	r_s	$r_e(\text{CCSD(T)}(\text{F12}^*))/\text{AVQZ}$	
$r(\text{Cu—Cl})/\text{\AA}$	2.0614(7)	2.058(4)	2.053	2.105(1)
$r(\text{Cu—N})/\text{\AA}$	1.9182(13)	1.918(4)	1.904	1.894(3)
$r(\text{N—H})/\text{\AA}$	(1.0186) ^c	(1.0179) ^c	1.014	0.89(4)
$\angle(\text{H—N}\cdots\text{Cu})/\text{deg}$	111.40(6)	111.5(1)	111.8	118(3)
$a_{\text{Cu}}/\text{\AA}$	0.3333(4)	0.331(4)	0.333	0.349
$a_{\text{Cl}}/\text{\AA}$	−1.7282(4)	−1.7266(9)	−1.720	−1.756
$a_{\text{N}}/\text{\AA}$	2.2515(9)	2.2497(7)	2.237	2.243
$a_{\text{H}}/\text{\AA}$	2.6232(3)	2.6232(6)	2.614	2.66
$b_{\text{H}}/\text{\AA}$	0.9483(4)	0.947(1)	0.942	0.79

^aGas phase geometry of the $\text{H}_3\text{N}\cdots\text{CuCl}$ monomer.

^bGeometrical parameters of monomer units of $\text{H}_3\text{N}\cdots\text{CuCl}$ within $[\text{Cu}(\text{NH}_3)\text{Cl}]$ as determined by X-ray crystallography (Ref. 3).

^c $r(\text{N—H})$ fixed at value determined as described under “Molecular Geometry”.

0.0013 Å. Full treatment of triple and a perturbative treatment of quadruple excitations induces changes that are much smaller in magnitude. Our own calculations for CuCl show that extrapolation to the basis set limit and post fc-CCSD(T) contributions including core-valence correlation, full treatment of triple, and a perturbative treatment of quadruple excitations⁵⁶ yield an r_e bond length that is effectively unchanged from the value of 2.048 Å calculated at the CCSD(T)(F12^{*})/AVQZ level (Table III). Remaining errors arising from the low-level relativistic treatment employed are of the order of 0.003 Å. Consistent with a previous study of H₃N···AgCl,¹⁹ an anharmonic correction to the calculated $r(\text{Cu—N})$ distance was computed by solving the 1d Schrödinger equation exactly on a 1d potential computed from a fc-CCSD(T) (F12^{*})/AVTZ relaxed scan. The effect of such a correction, omitted when calculating the value of the parameter shown in Tables III and IV, is to increase the $r(\text{Cu—N})$ distance by 0.003 Å. Similarly, accounting for core-valence correlation increases the value of this parameter by a further 0.002 Å. Noting these adjustments, the level of agreement between the *ab initio* calculated (r_e) geometry, and the r_0 and r_s geometries determined from the experimental data is excellent. Exact agreement is not expected given that the calculations yield an equilibrium geometry while experimental data are available only for the zero-point vibrational level.

C. Force constant and ionicity

The force constant of the bond between NH₃ and CuCl can be estimated from the measured rotational and centrifugal distortion constants through a calculation requiring several assumptions. The simplest treatment represents each of NH₃ and CuCl as a point mass that is located on the centre of mass of the sub-unit. The internal geometries of each of the sub-units are neglected, and all stretching modes of Σ symmetry are assumed to be much higher in energy than the intermolecular mode. The relationship between the spectroscopic constants and the vibrational frequency, ω_σ , of the stretching mode of the pseudo-diatomic is then given by⁵⁷

$$\frac{\omega_\sigma}{c} \cong \left(\frac{4B_0^3}{c^2 D_J} \right)^{\frac{1}{2}}, \quad (3)$$

where c is the speed of light. Experimentally determined values of both B_0 and D_J are available only for H₃¹⁴N···⁶³Cu³⁵Cl and D₃¹⁴N···⁶³Cu³⁵Cl isotopologues. Equation (3) yields a result of 400(48) cm^{−1} for ω_σ/c where the corresponding force constant, k_σ , is 137(32) N m^{−1}. The large uncertainties in these quantities are a result of the poorly determined values of D_J . An alternative model provided by Millen⁵⁸ takes some account of the internal geometry of sub-units, while retaining the assumption that other stretching modes of Σ symmetry do not significantly affect the measured distortion constant. The model assumes that the geometries of the isolated sub-units do not change significantly on formation of the complex and are strictly appropriate only for equilibrium values of rotational and centrifugal distortion constants. Zero-point quantities are often used given that equilibrium values are rarely available. The expression provided by Millen as appropriate to a sym-

metric top is

$$\frac{\omega_\sigma}{c} \approx (4B_0^3/c^2 D_J)^{\frac{1}{2}} \left[1 - \frac{B_0}{C_{\text{NH}_3}} - \frac{B_0}{B_{\text{CuCl}}} \right]^{\frac{1}{2}}, \quad (4)$$

where C_{NH_3} and B_{CuCl} are the rotational constants of isolated NH₃ and CuCl, respectively. Results are calculated for the two isotopologues of H₃N···CuCl for which B_0 and D_J are determined such that $k_\sigma = 72(17)$ N m^{−1} and 72(11) N m^{−1} for H₃N···⁶³Cu³⁵Cl and D₃N···⁶³Cu³⁵Cl, respectively. These correspond with values of ω_σ/c of 291(35) and 271(21) cm^{−1}, respectively. The result for ω_σ/c is 384 cm^{−1} when calculated at the CCSD(T) (F12^{*})/AVTZ level, in reasonable agreement with the experimentally derived result, given the approximations involved. The value of k_σ for H₃N···⁶³Cu³⁵Cl is thus somewhat higher than the result of 44 N m^{−1} obtained for H₃N···AgCl, consistent with the change on substitution of the metal atom in other B···MX complexes.

While the force constant calculated by the above method provides some indication of the strength of the interaction between the two sub-units, the measured nuclear quadrupole coupling constants provide a measure of charge rearrangement on complex formation. One perspective is provided by analysis of the measured value of $\chi_{aa}(\text{Cl})$. The Townes-Dailey model^{59,60} allows this quantity to be connected with the ionicity of the Cu—Cl bond

$$i_c = 1 + \frac{\chi_{aa}(\text{Cl})}{eQq(n,l,0)(\text{Cl})}, \quad (5)$$

where $eQq(n,l,0)(\text{Cl})$ is the coupling constant that would result from a single np_{*z*} electron in the isolated chlorine atom and is 109.74 MHz.⁵⁷ The result for H₃N···CuCl is 0.79 representing a significant change from the ionicity of free CuCl which is 0.71. The value of $\chi_{aa}(\text{Cu})$ in free CuCl is 16.2 MHz, and this quantity increases to 66.2 MHz on attachment of NH₃. Given that valence electrons are supplied by d-orbitals on the copper atom, no simple expression connects the ionicity of the Cu—Cl bond with $\chi_{aa}(\text{Cu})$. The magnitude of the increase in $\chi_{aa}(\text{Cu})$ indicates that significant charge re-arrangement occurs on complex formation. The value of $\chi_{aa}(\text{N})$ decreases from −4.0842(3) MHz in free NH₃ to −2.676(36) MHz and −2.64(2) MHz in H₃N···CuCl and H₃N···AgCl, respectively. The measured quantities are the projections of the nuclear quadrupole coupling tensors onto the *a*-axis in each case. It is thus possible that a difference between $\chi_{aa}(\text{N})$ in the complex and that in the free molecule arises because of large-amplitude oscillations in the zero-point vibrational state of the complex. However, the force constants of the respective intermolecular bonds in H₃N···CuCl and H₃N···AgCl are comparatively high. Various hydrogen- and halogen-bonded complexes display smaller differences between $\chi_{aa}(\text{N})$ and $\chi_0(\text{N})$ despite having intermolecular force constants that are significantly smaller. For this reason, it is likely that the observed decrease in $\chi_{aa}(\text{N})$ on formation of each of H₃N···CuCl and H₃N···AgCl arises principally because of charge re-distribution. Trends in force constant and ionicity will be examined across a broad range of complexes within the Conclusions.

TABLE V. Nuclear quadrupole coupling constants, force constants and ionicities for B...MCl complexes.

	M = Cu				M = Ag		
	$\chi_{aa}(^{63}\text{Cu})/\text{MHz}$	$\chi_{aa}(^{35}\text{Cl})/\text{MHz}$	i_c	$k_o/(\text{N m}^{-1})$	$\chi_{aa}(^{35}\text{Cl})/\text{MHz}$	i_c	$k_o/(\text{N m}^{-1})$
MCl ^a	16.2	−32.1	0.71	...	−36.4	0.67	...
Ar...MCl ^a	33.2	−28.0	0.74	47	−34.5	0.69	23
Kr...MCl ^a	36.5	−27.3	0.75	57	−33.8	0.69	34
Xe...MCl ^a	41.8	−26.1	0.76	69	−32.3	0.71	49
H ₂ O...MCl ^b	50.3	−25.5	0.77	58(2) ^c	−32.3	0.71	37
H ₂ ...MCl ^b	54.1	−24.4	0.78	5.5	−32.2	0.71	5.3
H ₃ N...MCl ^b	66.6	−23.0	0.79	72(17)	−29.8	0.73	44(2)
H ₂ S...MCl ^b	61.8	−23.0	0.79	87	−29.4	0.73	63
C ₂ H ₂ ...MCl ^d	65.3	−21.8	0.80	94(12)	−28.9	0.74	51(2)
OC...MCl ^d	70.8	−21.5	0.80	115	−28.1	0.74	75
C ₂ H ₄ ...MCl ^d	63.8	−21.0	0.80	77(11)	−27.9	0.75	56

^aReferences 35, 61, and 65–70.^bReferences 9, 16, 19, 20, and 63.^cNumbers in parentheses are one standard deviation in units of the last significant figure. Standard deviation not stated where significantly smaller than the final significant figure quoted.^dReferences 13, 14, and 22–24.

V. CONCLUSIONS

It has been shown that the symmetry of the isolated H₃N...CuCl monomer is the same as that adopted by the building blocks of the solid-state structure of [Cu(NH₃)Cl]. Bond lengths and angles have been precisely measured for the isolated species. The $r(\text{Cu}—\text{Cl})$ parameter of 2.0614(9) Å for H₃N...CuCl is slightly shorter than the value of 2.105(1) Å identified in [Cu(NH₃)Cl] (Table IV) through crystallography. The $r(\text{N}—\text{Cu})$ parameter is found to be 1.9182(16) Å in H₃N...CuCl and thus longer than the distance of 1.894(3) Å found for [Cu(NH₃)Cl].

Along with all other B...MCl complexes studied to date, the angular geometry of H₃N...CuCl is predicted by rules originally proposed to rationalise the geometries of hydrogen- and halogen-bonded complexes.⁴⁷ These rules state that, in the equilibrium geometry of a complex, the axis of HX or XY or MCl lies along the axis of a non-bonding electron pair carried by the acceptor atom of B, or in the absence of n-pairs, along the local symmetry axis of a π -electron pair. The force constants, nuclear quadrupole coupling constants, and ionicities in Table V are presented such that $\chi_{aa}(^{35}\text{Cl})$ for B...CuCl decreases on descending the table. This mode of presentation carries the advantage that trends in $\chi_{aa}(^{63}\text{Cu})$ for B...CuCl and in $\chi_{aa}(^{35}\text{Cl})$ for B...AgCl are easily visualised and allow easier comparisons between works. It is first important to note that the experimental method described within this work is appropriate for the generation of complexes containing a very wide range of Lewis bases. The earlier-described combination of laser vapourisation with supersonic expansion yields signal intensities that have proven high enough to allow the measurement of a wide range of transitions for every complex featured in Table V. Experiments suggest that, for any given choice of metal and halogen precursors, the highest signal intensity levels can be achieved for complexes containing C₂H₂, C₂H₄, CO, and H₂S. However, signal intensity is somewhat dependent upon instrument design and tuning characteristics in Balle-Flygare FTMW spectrometers.

Trends in the measured nuclear quadrupole coupling constants and force constants provide some insight into the strengths of interactions between the sub-units of these complexes. The magnitudes of $\chi_{aa}(^{35}\text{Cl})$ for B...CuCl and B...AgCl, respectively, decrease along the sequence where B is Ar > Kr > Xe > H₂O > NH₃ > H₂S > C₂H₂ > CO > C₂H₄. The fractional change in $\chi_{aa}(^{35}\text{Cl})$ on formation of B...MCl from the isolated B and MCl sub-units is greatest where M = Cu. Values of $\chi_{aa}(^{63}\text{Cu})$ for B...CuCl are in the reverse sequence with an exception being the result for H₂S...CuCl. The value of k_σ for any given B...CuCl is greater than the same quantity for B...AgCl, by a factor that varies between 1.25 and 2.0. The quantity is consistently higher than that in a hydrogen or halogen-bonded complex of similar geometry. The trend in k_σ of B...MCl is less consistent than that seen in $\chi_{aa}(^{35}\text{Cl})$, possibly because calculation of the parameter from the available data set involves various assumptions that will not be universally reliable. The general pattern is toward increasing k_σ with decreasing $\chi_{aa}(^{35}\text{Cl})$ for both B...CuCl and B...AgCl. Important exceptions to this rule are the values for k_σ of H₂...AgCl and H₂...CuCl which are significantly lower than those found in Ar...AgCl and Ar...CuCl. The nature of the bonding between rare gas atoms and metal halides has already been explored at length⁶¹ and it would be of considerable interest to compare k_σ for H₂...AgCl with results for Ne...AgCl and He...AgCl, for example, if these can be measured in future.

The counterpoise-corrected dissociation energy of H₃N...CuCl is calculated as 183 kJ mol^{−1} at the CCSD(T)(F12*)/AVTZ level. It is thus more strongly bound than H₃N...AgCl for which the dissociation energy was calculated to be 126 kJ mol^{−1} at the same level of theory.¹⁹ It is possible to establish the complete trend in dissociation energy with respect to Cu, Ag, and Au only for OC...MCl¹² and H₂...MCl where experimental data are available for all three noble metal atoms. Antes *et al.*⁶² performed a detailed *ab initio* study of OC...MCl complexes at HF, MP2, and CCSD(T) levels and demonstrated that $D_e(\text{OC} \cdots \text{AuCl}) > D_e(\text{OC} \cdots \text{CuCl}) > D_e(\text{OC} \cdots \text{AgCl})$

across this series. This trend was supported by force constants established through experimental studies of $\text{OC}\cdots\text{MCl}$. The same trend was later identified in $\text{H}_2\cdots\text{MCl}$ through calculations and experiments on complexes where $\text{M} = \text{Cu}, \text{Ag},$ or Au .^{9,63,64} Comparisons of force constants and calculated dissociation energies for all other $\text{B}\cdots\text{MCl}$ complexes are consistent with the proposal that $D_e(\text{B}\cdots\text{CuCl}) > D_e(\text{B}\cdots\text{AgCl})$ for all Lewis bases studied. Experimental data on $\text{B}\cdots\text{AuCl}$ complexes are currently very limited.

The dissociation energy of 183 kJ mol^{-1} calculated for $\text{H}_3\text{N}\cdots\text{CuCl}$ is the highest for any $\text{B}\cdots\text{CuCl}$ complex to date, with $\text{C}_2\text{H}_4\cdots\text{CuCl}$ and $\text{C}_2\text{H}_2\cdots\text{CuCl}$ next in the series having $D_e = 155\text{ kJ mol}^{-1}$ and $D_e = 148\text{ kJ mol}^{-1}$, respectively. Each of $\text{H}_2\text{S}\cdots\text{CuCl}$ and $\text{H}_2\text{O}\cdots\text{CuCl}$ is calculated to be more weakly bound with $D_e = 135\text{ kJ mol}^{-1}$ and $D_e = 116\text{ kJ mol}^{-1}$, respectively. In light of these results, it is interesting to re-visit the assumption made in earlier works^{16,20} that monomer sub-units do not experience any internal structural change when binding together to form a complex. A very small and barely measurable reduction of $\sim 0.5^\circ$ in $\angle(\text{H}-\text{N}\cdots\text{Cu})$, relative to the $\angle(\text{H}-\text{N}\cdots*)$ angle (where $*$ indicates that the Cu atom has been replaced by a dummy atom of zero mass) defined for isolated NH_3 , is identified in the present work through both experiment and *ab initio* calculations. Earlier studies of $\text{H}_2\text{O}\cdots\text{CuCl}$ and $\text{H}_2\text{S}\cdots\text{CuCl}$ did not explore changes in the geometries of H_2O and H_2S , respectively. Given the very small change in $\angle(\text{H}-\text{N}\cdots\text{Cu})$ on formation of $\text{H}_3\text{N}\cdots\text{CuCl}$, the similarity between the mechanisms binding each of H_2O , H_2S , and NH_3 to CuCl , each involving interaction of a lone pair on the Lewis base with the metal atom, and that the interactions between each of H_2O or H_2S and CuCl are calculated to be significantly weaker than that between NH_3 and CuCl ; the assumption of rigid H_2O and H_2S sub-units in the earlier studies can be expected to be reliable.

Experiments performed on $\text{C}_2\text{H}_4\cdots\text{MCl}$ and $\text{C}_2\text{H}_2\cdots\text{MCl}$ each detected significant changes in the monomer sub-units on complex formation. The bond separating the carbon atoms in each hydrocarbon was observed to extend (by $\sim 0.03\text{ \AA}$), while the $\angle(*-\text{C}-\text{H})$ angle (where $*$ is positioned on the midpoint of the $\text{C}\equiv\text{C}$ bond) in ethyne distorts by 12° from the linear geometry of the isolated molecule on attachment to CuCl . In these cases, the interaction between B and the metal atom results from donation of π electrons from the CC bond to the metal atom, removing electrons from bonding orbitals, and causing the observed lengthening of the CC bond. Interestingly, an even more substantial extension was observed in the H—H bond length of H_2 on attachment to AgCl ,⁹ amounting to a fractional increase in the H—H distance of 7.9% with respect to the same parameter in isolated H_2 . This change was rationalised through calculation of Mulliken charges that showed electron density being transferred from bonding orbitals of H_2 into unoccupied *d*-orbitals on the metal atom. Geometrical changes in CO and MX monomers were also observed to accompany the formation of $\text{OC}\cdots\text{MX}$ complexes which are amongst the most strongly bound of the complexes featured in Table V. However, consistent with binding of CO to MX via a lone pair on the carbon atom, geometrical changes in the monomers on formation of these complexes are small compared with those accompanying the formation

of $\text{C}_2\text{H}_4\cdots\text{MCl}$, $\text{C}_2\text{H}_2\cdots\text{MCl}$, and $\text{H}_2\cdots\text{AgCl}$. The measured change in $\text{C}\equiv\text{O}$ distance on formation of $\text{OC}\cdots\text{MX}$ is less than $0.01\text{ \AA}$ for every combination of M and X studied.

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