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# $N_2$–Cu–F: A Complex of Dinitrogen and Cuprous Fluoride Characterized by Rotational Spectroscopy**

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From the viewpoint of the fixation of atmospheric nitrogen, there is a long-term general interest in the identification and characterization of compounds that result from the reaction of transition metals with dinitrogen. In addition, the investigation of the interaction of $N_2$ with transition-metal compounds has intrinsic significance because of the isoelectronic, isolobal nature of dinitrogen and carbon monoxide. There is a voluminous amount of literature[1] on transition-metal carbonyl compounds, from which it is concluded that the nature of the generally strong bonding interaction of CO with the transition-metal center in such compounds is well-understood.

Recently, a series of simple linear transition-metal carbonyl complexes of the type OC–M–X (M = Cu,[2] Ag,[3] or Au[4]; X = F, Cl, or Br) were thoroughly investigated in the gas phase by means of their rotational spectra to give details of their geometry and electronic structure. Information about the electric-charge redistribution at the metal center is contained in the nuclear quadrupole coupling constants for M = Cu or Au. The interaction between CO and M was also found to be strong in these transient species. On the other hand, the hydrogen-bonded species OC···H–X, which may be envisaged, formally at least, as generated from OC–M–X by replacement of M by H, have been investigated extensively by rotational spectroscopy.[5–7] Such complexes are weakly bound (here depicted with ···) with intermolecular binding energies of only a few $\mathrm{kJ\,mol^{-1}}$. The dinitrogen complexes $N_2$···H–X have linear geometries similar to those of OC···H–X, but with slightly weaker hydrogen bonds.[8–10] The isostructural nature of OC···H–X and $N_2$···H–X can be understood by assuming that the electrophilic region of HX seeks the most nucleophilic region of CO or $N_2$ (namely, the axis of a nonbonding

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electron pair).[11] A quantitative scale of nucleophilicities $N$(B) of Lewis bases B, developed from intermolecular stretching force constants, confirms the order $N(\mathrm{CO}) > N(\mathrm{N_2})$.[12] The formal relationship between OC···H–X and OC–M–X and the similarity in the properties of OC···H–X and $N_2$···H–X raise interesting questions about $N_2$–M–X. Can these species be detected and identified? Are they isostructural with the corresponding carbonyl complexes? Are they less strongly bound than the carbonyl analogues? How does the electric-charge redistribution at the metal center upon formation of $N_2$–M–X compare with that when OC–M–X is formed? We report herein the experimental detection and characterization of an $N_2$–M–X analogue of OC–M–X, namely $N_2$–Cu–F, which has been observed in the gas phase through its rotational spectrum. The first report of an $N_2$–M–X species refers to $N_2$–Cu–Cl when isolated in a cryogenic matrix.[13]

The observed transitions of $^{15}N_2$–$^{63}$Cu–F and $^{15}N_2$–$^{65}$Cu–F exhibited a hyperfine structure that was attributed to coupling of the Cu nuclear spins (both the $^{63}$Cu and $^{65}$Cu nuclides have $I=\frac{3}{2}$) to the molecular rotation through the electric quadrupole and magnetic dipole (spin rotation) coupling mechanisms. A small additional splitting arising from the F ($I=\frac{1}{2}$) nuclear spin–rotation coupling and $^{n}$Cu,$^{19}$F spin–spin coupling was also partially resolved. The magnetic moment of the $^{15}$N nucleus ($I=\frac{3}{2}$) is too small to lead to additional hyperfine structure (see Figure 1). This fact was the reason for using $^{15}N_2$ in the initial search for the spectrum, for $^{14}N_2$ introduces two further quadrupole splittings from the $^{14}$N nuclei ($I=1$) and consequently a spread of intensity over more hyperfine components.

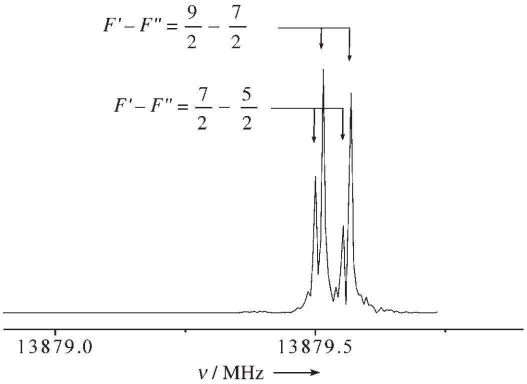

**Figure 1.** Two hyperfine components in the $J=3\leftarrow2$ transition of the isotopomer $^{15}N_2$–$^{63}$Cu–$^{19}$F (Note: Each component is a doublet as a result of a Doppler doubling effect. This is the larger of the two splittings shown.) The labels $F'$ and $F''$ are those appropriate to the coupling of the $^{63}$Cu nucleus only because the transitions shown are not split by the fluorine spin.

Observed frequencies of individual components (estimated accuracy 1 kHz) in the $J=2\leftarrow1$ and $J=3\leftarrow2$ transitions were fitted by using the program SPFIT[14] to give the rotational constant $B_0$, the centrifugal distortion constant $D_J$, the $^{n}$Cu nuclear quadrupole $\chi_{aa}(^{n}\mathrm{Cu})$ and spin–rotation $M_{bb}(^{n}\mathrm{Cu})$ coupling constants, and the $^{19}$F spin–rotation coupling constant $M_{bb}(^{19}\mathrm{F})$ for each of the isotopomers $^{15}N_2$–$^{63}$Cu–F and $^{15}N_2$–$^{65}$Cu–F. The $^{n}$Cu,$^{19}$F spin–spin coupling constant $D_{aa}(^{n}\mathrm{Cu},^{19}\mathrm{F})$ was held fixed at its value for $^{n}$Cu$^{19}$F[15] because this quantity depends only on the distance $r$(Cu–F), and we show below that this distance differs little from that in free CuF. The results are recorded in Table 1, which also includes the standard deviation $\sigma$ and the number of hyperfine components $N$ included in each fit. We note that the ratios $\{\chi_{aa}(^{63}\mathrm{Cu})/\chi_{aa}(^{65}\mathrm{Cu})\} = 1.0806(3)$ and $\{M_{bb}(^{63}\mathrm{Cu})/M_{bb}(^{65}\mathrm{Cu})\} = 0.94(2)$ agree within experimental error with the ratios 1.08(2)and 0.935 of the electric quadrupole and magnetic dipole moments of the two Cu nuclides.[16] Moreover, the value of $M_{bb}(^{19}\mathrm{F})$ is identical within experimental error for the two isotopomers.

**Table 1:** Spectroscopic constants of three isotopomers of $N_2$–Cu–F.

| Spectroscopic constant | $^{15}N_2$–$^{63}$Cu–$^{19}$F | $^{15}N_2$–$^{65}$Cu–$^{19}$F | $^{14}N_2$–$^{63}$Cu–$^{19}$F |
|---|---|---|---|
| $B_0$ [MHz] | 2313.3839(2) | 2311.0884(2) | 2410.35(10)[a] |
| $D_J$ [kHz] | 0.351(8) | 0.349(7) | – |
| $\chi_{aa}$(Cu) [MHz] | 61.8838(70) | 57.2686(76) | – |
| $M_{bb}$(Cu) [kHz] | 9.85(10) | 10.51(10) | – |
| $M_{bb}$(F) [kHz] | −2.3(5) | −2.1(5) | – |
| $D_{aa}$(Cu,F) [kHz] | −10.3[b] | −10.3[b] | – |
| $\sigma$ [kHz] | 0.9 | 1.0 | – |
| $N$ | 13 | 13 | – |

[a] Estimated by finding the center of the $^{14}$N substructure in some of the $^{63}$Cu hyperfine components of the $J=2\leftarrow1$ and $3\leftarrow2$ transitions and assuming $\chi_{aa}$(Cu) and $D_J$ to be unchanged from $^{15}N_2$–$^{63}$Cu–$^{19}$F. [b] This quantity was fixed at the value for free CuF from reference [15] (see text).

Rotational transitions of $^{14}N_2$–$^{63}$Cu–F were also observed but were weak. They carry a complex hyperfine structure arising from the presence of three quadrupolar nuclei ($^{14}$N, $^{14}$N, and $^{63}$Cu) and one $I=\frac{1}{2}$ nucleus, which is yet to be fully resolved and assigned. It is possible to estimate the unperturbed frequency of transitions with reasonable accuracy (as described in footnote [a] of Table 1), and this estimation leads to the approximate rotational constant for this species given in Table 1.

The observed spectra of $N_2$–Cu–F are consistent with a linear geometry (although a slightly bent arrangement with a low energy barrier to the linear conformation cannot be ruled out on the basis of ground-state spectroscopic constants alone). On the assumption of a linear geometry and an $r_0$(N–N) value (1.1000 Å) that is unchanged from free $N_2$,[17] the two bond lengths $r$(N–Cu) = 1.790(2) Å and $r$(Cu–F) = 1.739(3) Å were obtained by a least-squares fit to the rotational constants of the three isotopomers given in Table 1. We note that $r$(Cu–F) is close to the value $r_0$(Cu–F) = 1.74865 Å of free CuF. This agreement provides an a posteriori justification of the assumption that the $r_0$ bond length of $N_2$ is unchanged from the free $N_2$ molecule because the strong N–N triple bond is less likely to change than the CuF single bond when $N_2$–Cu–F is formed. We performed electronic-structure calculations at the QCISD/6-311G* level of theory with Gaussian 98,[18] with the results $r_e$(N–N) = 1.113 Å, $r_e$(N–Cu) = 1.761 Å, and $r_e$(Cu–F) = 1.743 Å, while for free $N_2$ and CuF calculations at the same level of theory gave 1.104 Å and 1.767 Å, respectively. This geometry leads to $B_e = 2434$ MHz, which is in good agreement with the observed quantity $B_0$ (Table 1).

The Cu nuclear quadrupole coupling constant $\chi_{aa}(^{63}\mathrm{Cu})$ carries information about the change in the electric-charge distribution near the Cu nucleus when $N_2$–Cu–F is formed from CuF. This quantity is proportional to the electric field gradient at the Cu nucleus along the internuclear axis $a$. The series Cu–F, Ar–Cu–F, $N_2$–Cu–F, and OC–Cu–F is of interest in this context. The values of $\chi_{aa}(^{63}\mathrm{Cu})$ are 21.9562(24),[15] 38.0556(15),[15] 61.8825(8), and 75.406(19) MHz,[2] respectively. These values show that the electric field gradient along the internuclear axis at the Cu nucleus increases smoothly along the series. The QCISD/6-311G* calculation predicts $\chi_{aa}(^{63}\mathrm{Cu}) = 49.5$ and 21.3 MHz for $N_2$–Cu–F and Cu–F, respectively, thus indicating that this quantity is quite well accounted for at this level of theory. The calculation also indicates that the electric-charge redistribution on formation of $N_2$–Cu–F from the component molecules is small. Relative to the free molecules $N_2$ and Cu–F, the changes in the natural atomic charges on the atoms[19] $N_{\mathrm{inner}}$, $N_{\mathrm{outer}}$, Cu, and F are $\Delta q(N_i) = 0.142\,e$, $\Delta q(N_o) = -0.147\,e$, $\Delta q(\mathrm{Cu}) = +0.014\,e$, and $\Delta q(\mathrm{F}) = -0.009\,e$, respectively, which correspond to an intermolecular charge transfer $\Delta q(\mathrm{int})$ of only 0.005 e from $N_2$ to Cu–F. The binding energy relative to $N_2$ and Cu–F is 139 kJ mol$^{-1}$ from these calculations. At the same level of theory, the corresponding results for OC–Cu–F are $\Delta q(\mathrm{Cu}) = +0.023\,e$, $\Delta q(\mathrm{F}) = -0.014\,e$, $\Delta q(\mathrm{int}) = 0.009\,e$, and 203 kJ mol$^{-1}$ for the binding energy. Evidently, there is a weaker interaction between $N_2$ and Cu–F than between CO and Cu–F. It is interesting to note that the ratio of the binding energies of $N_2$–Cu–F and OC–Cu–F is 0.68 while the ratio of the intermolecular stretching force constants for the corresponding hydrogen-bonded complexes $N_2\cdots$HF and OC⋯HF is 0.65.[12] Given that the hydrogen-bonding interactions have a substantial electrostatic component and given the relatively small electric-charge redistribution that accompanies formation of the compounds of CO and $N_2$ with Cu–F, it is apparent that electrostatic interactions may also be significant in these metal complexes.

## Experimental Section

$^{15}N_2$–Cu–F was synthesized by laser ablation of a copper rod over which a pulse of a gas mixture Ar/$SF_6$/$^{15}N_2$ (partial pressure ratio ≈100:0.5:2) was expanded into a vacuum. The pulse was formed with a solenoid valve from a stagnation pressure of 7 bar. A pulse of light (ca. 25 mJ) from a Nd–YAG laser operating at 532 nm was focused onto the rod to yield Cu vapor. The plume of ablated metal was immediately entrained by the supersonically expanded gas pulse, thereby producing CuF, which then combined with $^{15}N_2$ to form the desired product. The laser-ablation assembly has been described in detail elsewhere.[20] Its output feeds into a hole at the center of one of two mirrors that constitute the evacuated Fabry–Perot cavity of a Fourier-transform microwave spectrometer. Molecules of $^{15}N_2$–$^{63}$Cu–F and $^{15}N_2$–$^{65}$Cu–F were delivered thereby into the cavity, where they were polarized by pulses of microwave radiation and their $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ ground-state rotational transitions recorded in the usual way.[21]

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