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The First Precise Molecular Structure of a Monomeric Transition Metal Cyanide, Copper(I) Cyanide

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Abstract: Copper(I) cyanide is an important reagent in organic, organometallic, and supramolecular chemistry because of both the copper center and the versatile cyanide ligand. Solid-phase CuCN and many of its derivatives show oligomeric or polymeric structures, a trait shared by other metal cyanides. Often, it is difficult to specify the orientation of the cyano ligand in an X-ray structure. Here the first preparation and precise structure of a monomeric transition metal cyanide is reported. Gas-phase reaction between copper vapor and cyanogen (NCCN) clearly gives CuCN (not CuNC). The precise structure of CuCN so produced is determined by millimeter/submillimeter-wave spectroscopy. Because of the highly efficient synthesis and the presence of significant amounts of two copper isotopes, such strong signals were seen that natural-abundance materials allowed observation of transitions for the four isotopomers $^{63}\mathrm{Cu}^{12}\mathrm{C}^{14}\mathrm{N}$, $^{65}\mathrm{Cu}^{12}\mathrm{C}^{14}\mathrm{N}$, $^{63}\mathrm{Cu}^{13}\mathrm{C}^{14}\mathrm{N}$, and $^{63}\mathrm{Cu}^{12}\mathrm{C}^{15}\mathrm{N}$ and the determination of r_o, r_s, and $r_m^{(2)}$ structures. All data unequivocally show a linear geometry and that the carbon of cyanide is bound to copper with a Cu−C distance of 1.82962(4) Å in the $r_m^{(2)}$ structure, which is likely to be closest to the equilibrium geometry.

Introduction

The cyanide ion is the simplest species containing carbon and nitrogen, both elements essential in forming biologically important molecules such as amino acids, proteins, nucleotides, and alkaloids. Indeed, the abiotic formation of some of these biomolecules is thought to be a result of the interaction of cyanide ion derivatives with other simple molecules.[1] Cyanide salts and metal complexes[2−5] are important species in such diverse fields as organic synthesis (e.g., organocuprates[6−12]), mining (e.g., in metal extraction[13,14]), bioinorganic chemistry relative to enzyme active sites,[15] high-temperature superconductors,[16−20] and formation of zeolite-like inorganic structures capable of host−guest chemistry.[21−23] In particular, copper(I) cyanide, the subject of this report, is an important reagent[8] in the selective formation of organic compounds by construction of carbon−carbon and carbon−silicon bonds.[7,10,24] The structures of the resulting organocuprates, most of which are quite reactive, have been examined by a variety of methods, such as multinuclear NMR, X-ray diffraction, and computational methods, but even after this intense scrutiny, their structures are a matter of some debate.[11,12,25−27] In fact, the structure of solid copper(I) cyanide itself is under ongoing study.[28−30] Our

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intention is to provide precise bond length and angle data for comparison with theoretical predictions. Low-coordinate compounds are the simplest to calculate reliably and the most straightforward to analyze, because there are no multiple interactions between one metal and several ligands.

Simple cyanide compounds exhibit a variety of structures in both the solid state and the gas phase.[2] Even in the gas phase, where only a single metal−cyanide interaction is to be expected, so far three types of structures have been observed. In early metal species, the more electronegative nitrogen is bonded, giving rise to preferred isocyanide structures, several of which are known (CaNC, MgNC, SrNC, and AlNC[31−38]). Interestingly, the metastable MgCN and AlCN isomers have also been observed by rotational spectroscopy.[39] Meanwhile, among alkalis, whereas the favored bonding of lithium cation and cyanide anion is the linear isocyanide form, LiNC,[40] for sodium and potassium, fascinating quasitopic structures are found, in which the alkali metal cation orbits the cyanide anion in a plane bisecting the C−N vector.[41−43] Surprisingly, for neutral monomeric transition metal cyanides, the only data of which we are aware are very recent optical experiments on the *isocyanide* FeNC.[44] In contrast, from solid-phase structures of inorganic and organometallic cyanides it appears that bonding of a transition metal to the cyanide carbon is preferred.[2−4] Theoretical studies on monomeric neutral metal transition metal cyanides predict metal−carbon bonding,[45−48] but we note that for corresponding radical cations the picture is not so clear; for example, metal−nitrogen bonding is calculated to be favored in $[Cu-NC]^+$, whereas for the corresponding iron species, cyanide and isocyanide forms are predicted to have virtually equal energies.[49] As for experimental determination of metal−cyanide bonding, since carbon and nitrogen are neighbors in the Periodic Table, the certain assignment of the positions of carbon and nitrogen in a structure is often difficult,[50] and there are well-documented cases where mistakes have been made.[51]

Thus, it seemed especially important to unambiguously determine the first structure of a monomeric transition metal cyanide. Here we report the synthesis of CuCN in the gas phase and its characterization by submillimeter/millimeter-wave spectroscopy. Our high-precision structural data clearly verify that the cyanide form is favored over its isomer CuNC, and allow direct comparison of theoretical predictions with experimental bond lengths.

Experimental Section

The pure rotational spectra of CuCN and its isotopomers were measured with a millimeter/sub-millimeter-wave direct absorption spectrometer, which is described in detail elsewhere.[52] Briefly, the source of tunable millimeter-wave radiation is a phase-locked Gunn oscillator/Schottky diode multiplier combination. Several Gunn oscillators and a series of multipliers are necessary to cover the range 100−550 GHz. The radiation is launched from the source quasi-optically by using a scalar feedhorn and is passed through a wire grid and several focusing Teflon lenses into the reaction chamber. A rooftop reflector is located at the back of the cell, which rotates the polarization of the incoming radiation by 90° and reflects it back through the chamber and optics and into the detector. The detector is a helium-cooled InSb hot electron bolometer. The molecules of interest are created in the reaction cell, which contains a Broida-type oven for metal vaporization. The chamber is continuously evacuated during molecule synthesis with a Roots-type blower. Phase-sensitive detection is carried out by modulation of the source, and all signals are recorded at twice the modulation frequency of 25 kHz, such that second-derivative spectra are obtained.

CuCN was synthesized in the gas phase by the reaction of copper vapor and cyanogen. Approximately 5−8 mTorr of $(CN)_2$ was mixed with 20−25 mTorr of argon carrier gas and flowed into the chamber from beneath the oven, thus entraining the copper vapor. CuCN formed spontaneously in the hot gas mixture without use of a d.c. discharge, and was continuously synthesized for several hours. The main isotopomer, $^{63}Cu^{12}C^{14}N$, was observed with such strong signals that the other isotopomers ($^{65}Cu^{12}C^{14}N$, $^{63}Cu^{13}C^{14}N$, and $^{63}Cu^{12}C^{15}N$) could be observed in their natural abundances. The elemental abundances are ^{63}Cu:^{65}Cu = 69.1:30.9, ^{12}C:^{13}C = 98.9:1.1, and ^{14}N:^{15}N = 99.6:0.4, respectively.[53] The source of the isotopic masses used was NIST.[54]

No previous spectroscopic work had been done for monomeric, gas-phase CuCN. Hence, an in-depth search had to be carried out to identify its spectrum. A trial rotational constant B_0 for CuCN was initially estimated from that of ZnCN, which in concurrent preliminary studies was found to be approximately 4 GHz.[55] About $4B_0$ was then initially searched in frequency space (∼18 GHz) using scans 100 MHz in frequency converge. The CuCN signals found were so strong that the main line and the vibrational satellite signals were readily identified in

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Table 1. Observed Transition Frequencies for the Most-Abundant Isotopomer $^{63}Cu^{12}C^{14}N$ ($\tilde{X}^1\Sigma^+$)[a]

J'	J''	v_2	ν	$\nu_{obs} - \nu_{calc}$	J'	J''	v_2	ν	$\nu_{obs} - \nu_{calc}$	J'	J''	v_2	ν	$\nu_{obs} - \nu_{calc}$	J'	J''	v_2	ν	$\nu_{obs} - \nu_{calc}$
44	43	0	371297.666	−0.035	61	60	1c	516412.331	−0.010	64	63	2c	544810.504	−0.007	60	59	3d	513651.438	0.019
45	44	0	379712.724	−0.041	62	61	1c	524831.475	−0.007	45	44	2d	383680.498	−0.027	61	60	3c	522162.181	0.004
46	45	0	388126.235	−0.009	63	62	1c	533248.346	−0.002	46	45	2d	392179.737	−0.007	61	60	3d	522162.181	0.004
47	46	0	396538.091	−0.010	64	63	1c	541662.899	−0.004	47	46	2d	400677.176	−0.007	62	61	3c	530670.441	−0.009
48	47	0	404948.287	−0.016	52	51	1d	441123.387	0.015	52	51	2d	443136.326	−0.004	62	61	3d	530670.441	−0.009
49	48	0	413356.821	0.008	54	53	1d	458018.764	0.001	54	53	2d	460106.187	0.006	63	62	3c	539176.171	−0.028
51	50	0	430168.631	0.012	55	54	1d	466463.466	−0.002	55	54	2d	468587.998	0.004	63	62	3d	539176.171	−0.028
52	51	0	438571.862	0.018	56	55	1d	474906.122	−0.007	56	55	2d	477067.663	−0.017	51	50	4c	439296.297	0.008
53	52	0	446973.255	0.019	59	58	1d	500221.470	−0.009	59	58	2d	502493.597	0.001	51	50	4d	439296.297	0.008
54	53	0	455372.786	0.024	60	59	1d	508655.582	−0.012	60	59	2d	510964.392	−0.001	52	51	4c	447871.884	0.016
55	54	0	463770.410	0.026	61	60	1d	517087.486	0.006	61	60	2d	519432.873	0.003	52	51	4d	447871.884	0.016
56	55	0	472166.088	0.019	62	61	1d	525517.091	−0.008	62	61	2d	527898.986	−0.005	54	53	4c	465016.333	0.004
57	56	0	480559.800	0.020	63	62	1d	533944.422	0.007	64	63	2d	544824.022	0.015	54	53	4d	465016.333	0.004
58	57	0	488951.501	0.018	64	63	1d	542369.400	0.010	51	50	3c	436949.506	−0.023	55	54	4c	473585.118	−0.008
59	58	0	497341.152	0.010	45	44	2c	383678.236	0.029	51	50	3d	436949.506	−0.023	55	54	4d	473585.118	−0.008
60	59	0	505728.731	0.009	46	45	2c	392177.158	0.002	52	51	3c	445480.802	−0.011	56	55	4c	482151.540	−0.037
61	60	0	514114.186	−0.002	47	46	2c	400674.306	0.005	52	51	3d	445480.802	−0.011	56	55	4d	482151.540	−0.037
62	61	0	522497.491	−0.014	52	51	2c	443131.560	0.008	54	53	3c	462536.987	0.002	59	58	4c	507836.440	0.011
63	62	0	530878.610	−0.027	54	53	2c	460100.409	−0.002	54	53	3d	462536.987	0.002	59	58	4d	507836.440	0.011
64	63	0	539257.511	−0.038	55	54	2c	468581.682	0.013	55	54	3c	471061.806	0.013	60	59	4c	516393.073	0.002
51	50	1c	432103.883	0.001	56	55	2c	477060.753	−0.006	55	54	3d	471061.806	0.013	60	59	4d	516393.073	0.002
52	51	1c	440543.753	−0.001	59	58	2c	502484.612	0.001	56	55	3c	479584.373	0.012	61	60	4c	524947.159	0.006
54	53	1c	457417.734	−0.004	60	59	2c	510954.623	0.004	56	55	3d	479584.373	0.012	61	60	4d	524947.159	0.006
55	54	1c	465851.771	−0.005	61	60	2c	519422.256	0.001	59	58	3c	505138.239	0.021	62	61	4c	533498.609	−0.024
56	55	1c	474283.793	−0.003	62	61	2c	527887.469	−0.007	59	58	3d	505138.239	0.021	62	61	4d	533498.609	−0.024
60	59	1c	507990.995	0.034	63	62	2c	536350.239	−0.003	60	59	3c	513651.438	0.019	63	62	4c	542047.491	0.022
															63	62	4d	542047.491	0.022

[a] In MHz.

two transitions. The frequencies of additional transitions could then be adequately predicted. Final transition frequencies were measured from scans with 5 MHz in frequency coverage. Except for the $^{63}Cu^{12}C^{15}N$ isotopomer, only two scans had to be averaged to determine the frequencies: one scan in increasing frequency and the other in decreasing frequency. For the ^{15}N isotopomer, two to three such scan pairs were averaged to improve the signal strength. All line profiles were fit to Gaussian shapes to determine the line center. Line widths varied from 800 to 1200 kHz over the 365−545 GHz frequency range used for the measurements.

Results and Discussion

Synthesis. To make monomeric CuCN, an efficient synthesis in the gas phase had to be developed. Monomerization of solid-phase CuCN appeared to be impractical. In one study, only small amounts of $Cu_n(CN)_n$ species were formed by sublimation of solid CuCN, and extensive decomposition into copper and cyanogen was observed.[56] In another study, solid CuCN was subjected to laser ablation and the products analyzed by mass spectrometry. From detailed analysis of the ions generated, there was no evidence of $Cu_n(CN)_n^{\pm}$ ions and hence of neutral electron-precise species $Cu_n(CN)_n$.[28] This difficulty in generating monomer from the solid-phase sample is similar to that encountered in making CH_3Li or $LiNH_2$.[57,58] Fortunately, as described in detail in the Experimental Section, monomeric CuCN could be made very efficiently in a continuous flow process for several hours at a time by passing cyanogen vapor into a reaction cell containing copper vapor produced by heating a sample of the metal. The copper(I) cyanide was formed without use of a d.c. discharge. Although the mechanism of this reaction was not investigated, it involves oxidation of elemental copper and reduction of the cyanogen carbon−carbon bond. Interestingly, our synthesis of CuCN is the reverse of its high-temperature decomposition.[56] Remarkably, as was the case in our synthesis of LiCCH,[59] such strong signals for CuCN were observed that several isotopomers were characterized with use of only natural abundance (as opposed to isotopically enriched) precursors.

Analysis of the Data. Table 1 lists the observed transition frequencies for major isotopomer $^{63}Cu^{12}C^{14}N$, while Table 2 gives those of $^{65}Cu^{12}C^{14}N$, $^{63}Cu^{13}C^{14}N$, and $^{63}Cu^{12}C^{15}N$. Observation of these four chemical species allows for an unambiguous identification of the structure of copper cyanide, namely, that the molecule is linear and copper is bonded to the carbon, *not* the nitrogen. Importantly, CuCN contrasts with the other known monomeric metal cyanides, since for Li, Ca, Mg, Sr, Al,[31−38,40] and (most recently) Fe,[44] the linear isocyanide form M−NC is the favored structure, whereas for NaCN and KCN a bent, T-shaped arrangement is the most stable.[41−43]

Because CuCN is a linear, triatomic molecule, it has a low-frequency vibrational mode that entails bending along the linear "backbone" of the molecule. This property was not used to assign the bond lengths in CuCN, but the effect of a low-energy bending mode is to complicate assignment of the observed transitions. The CuCN excited vibrational state is sufficiently low in energy such that rotational transitions are easily excited in several quanta of this mode, which is indicated by quantum number v_2. The bending vibration is also, to a first approximation, doubly degenerate in energy. (There are two identical, orthogonal planes in which the molecule can bend.) The bending motion in two planes couples together to generate an additional angular momentum ℓ, which in turn couples with the rotation

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Table 2. Observed Transition Frequencies of Other CuCN Isotopomers[a]

J'	J''	v_2	$^{65}Cu^{12}C^{14}N$ ν	$\nu_{obs} - \nu_{calc}$	$^{63}Cu^{13}C^{14}N$ ν	$\nu_{obs} - \nu_{calc}$	$^{63}Cu^{12}C^{15}N$ ν	$\nu_{obs} - \nu_{calc}$
44	43	0	368205.657	−0.052				
45	44	0	376550.845	−0.025	375832.916	−0.066	-	-
46	45	0	384894.441	−0.029	384160.485	−0.044	372307.267	−0.047
47	46	0	393236.475	0.000	392486.449	−0.025	380377.559	−0.029
48	47	0	401576.834	−0.016			388446.387	0.033
49	48	0	409915.574	0.014	409133.430	0.012	396513.498	−0.082
50	49	0					404579.198	−0.038
51	50	0	426587.866	0.019	425773.545	0.008		
52	51	0	434921.374	0.019				
53	52	0	443253.081	0.022	442406.568	0.017		
54	53	0	451582.944	0.019	450720.325	0.018	436825.535	0.035
55	54	0	459910.934	0.016	459032.224	0.042	444882.873	0.056
56	55	0	468237.037	0.034	467342.172	0.030	452938.382	0.013
57	56	0	476561.168	0.021	475650.178	0.027	460992.161	0.035
58	57	0	484883.331	0.018	483956.199	0.023	469044.083	0.028
59	58	0	493203.483	0.015	492260.197	0.017	477094.141	0.017
60	59	0	501521.581	0.005	500562.156	0.026	485142.342	0.042
61	60	0	509837.597	−0.007	508862.014	0.024	493188.519	−0.033
62	61	0	518151.496	−0.020	517159.705	−0.021	501232.908	0.060
63	62	0	526463.260	−0.018			509275.179	0.024
64	63	0	534772.811	−0.043	533748.652	−0.033	517315.431	−0.011
65	64				542039.775	−0.064		
66	65						533389.775	−0.052
67	66						541423.799	−0.061
51	50	1c	428508.471	0.006				
52	51	1c	436878.349	−0.003				
55	54	1c	461976.595	−0.006				
56	55	1c	470338.755	−0.004				
57	56	1c	478698.899	0.004				
60	59	1c	503766.813	0.007				
61	60	1c	512118.491	0.001				
62	61	1c	520467.968	−0.004				
63	62	1c	528815.211	−0.003				
64	63	1c	537160.182	0.001				
51	50	1d	429068.296	0.029				
52	51	1d	437448.729	0.003				
55	54	1d	462578.547	0.000				
56	55	1d	470951.170	−0.010				
57	56	1d	479321.736	−0.029				
60	59	1d	504420.857	−0.011				
61	60	1d	512782.886	−0.010				
62	61	1d	521142.690	−0.003				
63	62	1d	529500.232	0.009				
64	63	1d	537855.473	0.023				

[a] In MHz.

of the molecule, labeled by quantum number J. (CuCN has no unpaired electrons; hence, the total angular momentum J is the rotational angular momentum, i.e., $S = 0$ and $L = 0$). The coupling of ℓ and J results in effects on pure rotational spectra called ℓ-type doubling and ℓ-type resonance.[60] The net result is that additional rotational levels are generated in the v_2 levels. For example, in the $v_2 = 1$ state, all rotational levels are split into two, labeled as 1c and 1d, or ($01^{1c}0$) and ($01^{1d}0$), where the notation is ($v_1v_2^{\ell}v_3$). In $v_2 = 2$, three levels are generated corresponding to the (02^00), ($02^{2c}0$), and ($02^{2d}0$) states, and so forth. Rotational transitions originating from within these excited levels were identified in the spectra and were measured. Hence, in Table 1, transitions from the $v_2 = 1$, 2, 3, and 4 states are listed for $^{63}Cu^{12}C^{14}N$, and those from the $v_2 = 1$ level for the ^{65}Cu isotopomer are given in Table 2, as well as those recorded for the ground vibrational state (000). Therefore, in addition to the $J'' \rightarrow J'$ quantum numbers labeling the rotational energy levels, the v_2 bending mode quantum number is also given. As shown in Table 1, the effects of ℓ-type splittings are too small to be observed in the $v_2 = 3$ and 4 levels.

In Figure 1, the frequency progression of these so-called "satellite" lines relative to the ground state is shown for the $J = 44 \rightarrow 45$ transition, as well as positions of the isotopomers, and experimental relative intensities. The ground-state transition of $^{63}Cu^{12}C^{14}N$ is clearly the strongest, followed by that of the $^{65}Cu^{12}C^{14}N$ species. The $v_2 = 1$, 2, 3, and 4 satellite lines are higher in frequency relative to the (000) feature of the ^{63}Cu isotopomer and follow the expected progression for a rigid, linear species. The ℓ-type splittings collapse at higher v_2 levels, as well. The $v_2 = 1$ satellite lines of $^{65}Cu^{12}C^{14}N$ are also prominent in the spectrum. In contrast, the $^{63}Cu^{13}C^{14}N$ and $^{63}Cu^{12}C^{15}N$ features originating in the ground state are much weaker. Moreover, while this frequency range includes the $J = 44 \rightarrow 45$ transition of the ^{13}C isotopomer, it includes a different transition of the ^{15}N isotopomer ($J = 46 \rightarrow 47$), because the nitrogen substitution substantially changes the moment of inertia. It is important to note that the excited vibrational data were not used to establish the bond lengths in CuCN, although

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(60) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Wiley: New York, 1984.

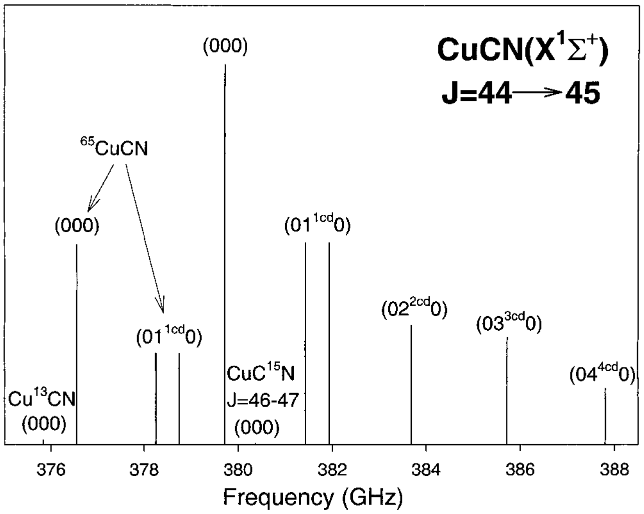

Figure 1. A stick diagram illustrating the prominent spectral lines and their relative intensities observed for the J = 44−45 rotational transition of ^{63}Cu^{12}C^{14}N. The main isotopomer ^{63}Cu^{12}C^{14}N in its (000) ground vibrational state is the strongest feature. Vibrational satellite lines arising from the v_2 = 1, 2, 3, and 4 states of this species are also present, which exhibit effects of ℓ-type doubling. Visible in the data as well are lines arising from the less abundant isotopomers, ^{65}Cu^{12}C^{14}N and ^{63}Cu^{13}C^{14}N, and the J = 46−47 transition of ^{63}Cu^{12}C^{15}N, all observed in natural abundance. The vibrational progression indicates that CuCN is a linear molecule.

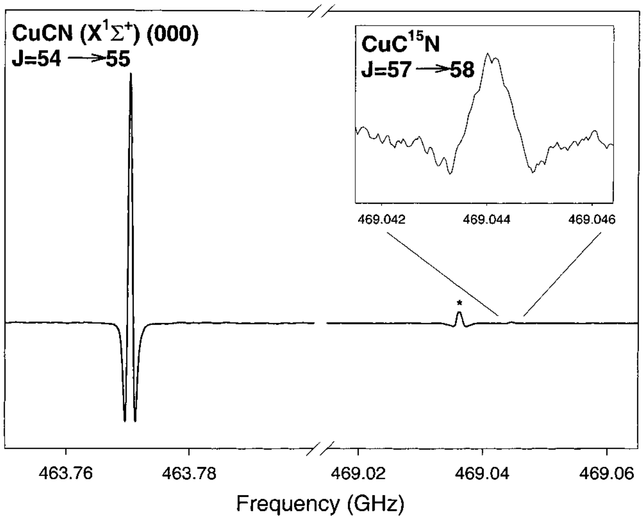

Figure 2. A sample spectrum of CuCN showing the J = 54−55 transition of the main isotopomer ^{63}Cu^{12}C^{14}N in its ground vibrational state near 463.8 GHz. Also included in these data is the J = 57−58 transition of the ^{15}N isotopomer near 469 GHz, additionally shown as an insert in the figure. The feature marked by an asterisk is an unidentified line. Both species were observed in their natural isotopic abundances, indicating the high signal strength obtained for CuCN. These data are a composite of two 100 MHz scans, each lasting about 50 s in duration.

the pattern itself confirms a linear structure. However, the observations illustrate the complexity of the spectroscopic assignments.

Figure 2 shows a sample spectrum of $J = 54 \rightarrow 55$ transition of ^{63}Cu^{12}C^{14}N in its ground vibrational state (000) and the $J = 57 \rightarrow 58$ line of ^{63}Cu^{12}C^{15}N, observed in the natural nitrogen abundance. The signal-to-noise ratio is better than 400:1 for the main line, and the ^{15}N isotopomer transition is clearly visible in the spectrum, as shown in the insert. The other feature in the data, marked by an asterisk, is an unidentified line. This spectrum is a composite of 2 single 100 MHz scans, each recorded in about 50 s. They have been truncated to fit into a single figure.

The data were analyzed with the appropriate $^1\Sigma$ Hamiltonian which includes ℓ-type effects. The rotational constant B and centrifugal distortion constant D have been determined for all four isotopomers in their ground (000) vibrational state, as shown in Table 3. These parameters have also been established for the vibrationally excited states; in the $v_2 = 1$ level, the ℓ-type doubling constant q and its centrifugal distortion constant q_D have been additionally determined, whereas for the $v_2 = 2$ level, q_{eff} was determined. The rms values of the global fits are 16, 19, 33, and 34 kHz respectively, for ^{63}Cu^{12}C^{14}N, ^{65}Cu^{12}C^{14}N, ^{63}Cu^{13}C^{14}N, and ^{63}Cu^{12}C^{15}N.

From the data in Table 3, two vibrational frequencies of CuCN can be estimated: the copper−carbon stretch (ω_1) and the bending vibration (ω_2). The heavy-atom stretch can be approximately determined by treating the CN moiety as a unit and using the relationship for diatomic molecules, $\omega_1 \approx (4B_o\text{-}(3)/D_o)^{1/2}$.[53] Using this equation, the stretching frequency was found to be $\omega_1 \approx 478$ cm^{-1}. Similarly, the bending energy can be estimated from the ℓ-type doubling constant of the (010) state by using the approximate expression $\omega_2 \approx 2.6B_e(2)/q$.[53] Assuming $B_e = B_o$, it is found that $\omega_2 \approx 270$ cm^{-1}. These values are in reasonable agreement with those calculated by Boldyrev et al.,[48] who found $\omega_1 = 453$ cm^{-1} and $\omega_2 = 225$ cm^{-1}, using a CCSD(T)/6-311+G* level of theory.

Bond Lengths and Structure. Because every single atom was isotopically substituted in CuCN, a complete substitution, or r_s structure, could be calculated. This structure is thought to be better than a simple r_0 geometry because it takes into account some of the effects of zero-point vibration. To solve for the geometry, Kraitchman's equations were used which account for the differences in the center of mass with isotopic substitution. For a complete explanation, see ref 60. The resulting bond lengths are given in Table 4.

r_o and r_s bond lengths represent structures determined by the usual least-squares fit to the moments of inertia for the various isotopes (r_o), and by solving Kraitchman's equations (r_s).[60] However, as discussed by Watson et al.,[61] a better structure can be determined by taking into account the appropriate mass dependence in the experimentally determined moments of inertia for the various isotopomers. This method of calculation usually results in bond lengths, called $r_m^{(2)}$ bond lengths, that are very close to the equilibrium values. All three types of bond lengths have been computed for CuCN and are given in Table 4.

As mentioned above, the linear cyanide structure of transition metal species CuCN contrasts with the other known structures of metal cyanides, where electropositive elements Li, Al, Mg, Ca, and Sr bond through nitrogen,[31−38,40] and Na and K orbit the cyanide π cloud.[41−43] Previously, the Ziurys group was able to observe very weak signals from small amounts of metastable MgCN produced along with larger amounts of MgNC, thus the structure of the minor component could be determined.[37] In the experiments described here, we can say that because the signal intensities for CuCN were so strong, the cyanide form must be the most stable. Even the ^{15}N isotopomer of CuCN could be observed by using natural-abundance materials (in which the ^{15}N concentration is about 0.4%). Therefore, we estimate that

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(61) Watson, J. K. G.; Roytburg, A.; Ulrich, W. *J. Mol. Spectrosc.* **1999**, *196*, 102−119.

Table 3. Spectroscopic Constants for CuCN ($\tilde{X}^1\Sigma^+$)[a]

parameter	^{63}Cu^{12}C^{14}N	^{65}Cu^{12}C^{14}N	^{63}Cu^{13}C^{14}N	^{63}Cu^{12}C^{15}N
$v_2 = 0$				
B	4224.9768(15)	4189.7512(15)	4181.7989(17)	4052.4738(15)
D	0.00146816(24)	0.00144511(24)	0.00145109(25)	0.00133630(22)
$v_2 = 1$				
B	4247.1012(21)	4211.6818(20)		
D	0.00153848(30)	0.00151428(29)		
q	−5.6778(43)	−5.5865(41)		
q_D	0.00001933(61)	0.00001888(59)		
$v_2 = 2$				
B	4269.6420(65)			
D	0.0016152(22)			
H	$-7.7(2.3) \times 10^{-10}$			
q_{eff}	$-2.096(15) \times 10^{-9}$			
$v_2 = 3$				
B	4292.6157(22)			
D	0.00169691(32)			
$v_2 = 4$				
B	4316.0143(22)			
D	0.00177716(32)			
rms of fit	0.016	0.019	0.033	0.043

[a] In MHz, errors are 3σ and apply to the last quoted decimal places(s).

Table 4. Structures for CuCN and Some Related Molecules

molecule	r(Cu–C) (Å)[a]	r(C–N) (Å)[a]	method	ref
CuCN	1.83231(7)	1.1576(1)	mm-wave (r_0)	this work
	1.83284(4)	1.15669(3)	mm-wave (r_s)	this work
	1.82962(4)	1.16213(3)	mm-wave ($r_m^{(2)}$)	this work
	1.853	1.161	B3LYP	48
	1.826	1.182	MP2	48
	1.863	1.177	CCSD(T)	48
	1.94	1.15	SCF	47
	1.93	1.19	CIPSI	47
	1.96	1.16[b]	MCSCF	62
	1.98	1.172[b]	CASSCF	66
	1.97	1.172[b]	CCI	66
	1.96	*c*	SCF	66
	1.90	1.17	CI	66
	2.49	1.15	SCF	45,46
CuCN solid	1.85 or 1.86	*c*	EXAFS	29
CuCN solid	1.85(4)	*c*	NMR	30
$[Cu_3(CN)_3(H_2O)]_8$	1.83(2)−1.86(2)	1.12(2)−1.19(2)	X-ray	68
$[(Me_2PhSi)_3C-Cu-CN-Li(THF)_2]_2$	1.851(4)	1.151(5)	X-ray	69
$[(Me_2PhSi)_3C-Cu-CN-K]_4$	1.853(12), 1.856(12), 1.883(13), 1.866(12)	1.129(13), 1.132(13), 1.140(12), 1.168(13)	X-ray	69
$[(Me_2PhSi)_3C-Cu-CN-Li(THF)_3]_2$	1.85(2), 1.79(2)	1.15(2), 1.20(2)	X-ray	69
$[(t\text{-}Bu)Cu(CN)Li(OEt_2)_2]_8$	1.878(8)	1.159(9)	X-ray	70
$[(Trip)Cu-CN-Li(OEt_2)_2]_2$	1.858(5)	1.144(6)	X-ray	71

[a] Errors are 3σ and apply to the last quoted decimal places(s). [b] Assumed value. [c] Not determined.

if the isocyanide form of CuNC was present, it must be a very minor component of the reaction product. For comparison, theoretical calculations which include relative energies of cyanide and isocyanide isomers CuCN and CuNC, respectively, have indicated that CuCN is more stable by 1.8 to 2.6 kcal mol^{-1} [46,47,62] or 11 kcal mol^{-1}.[48] In contrast, in another estimate, CuCN has been predicted to be 0.7 kcal mol^{-1} *less* stable.[46] On the basis of our experimental results, if we assume that (1) an equilibrium mixture of CuCN and CuNC was formed under our conditions, (2) the reaction temperature is approximately 500 K, and (3) our limit of detection of a minor component is about 0.4%, then our results would be consistent with CuCN being at least 5 kcal mol^{-1} more stable than CuNC.

The copper(I) center has a d^{10} electronic configuration and is capable of back-bonding to appropriate π-acid ligands, including cyanide, carbon monoxide, and alkenes.[63,64] Meanwhile, the cyanide ligand is not only a good σ-donor, but a reasonable π-acid.[2−4,65] In the specific case of CuCN, Nelin et al. claimed on the basis of theoretical results that there is essentially no back-bonding from Cu(I) to cyanide, but from their results it seems that there is slightly more back-bonding in CuCN than in CuNC,[62] and that there is more covalent character in CuCN than in CuNC. Both these workers and Bauschlicher[66] suggest that the bonding in CuCN/CuNC is to a large degree ionic. Our data do not directly indicate the degree

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(62) Nelin, C. J.; Bagus, P. S.; Philpott, M. R. *J. Chem. Phys.* **1987**, *87*, 2170−2176.

(63) Hathaway, B. J. Copper. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 5, pp 533−774.

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(65) Vinogradov, A. S.; Preobrajenski, A. B.; Knop-Gericke, A.; Molodtsov, S. L.; Krasnikov, S. A.; Nekipelov, S. V.; Szargan, R.; Hävecker, M.; Schlögl, R. *J. Electron Spectrosc. Relat. Phenom.* **2001**, *114−116*, 813−818.

(66) Bauschlicher, C. W., Jr. *Surf. Sci.* **1985**, *154*, 70−78.

of covalent bonding or back-bonding. However, as seen in Table 4, our experimental copper−carbon bond length is most accurately predicted in recent work by Boldyrev et al.[48] Interestingly, in solid-phase samples of CuCN, where the copper(I) center is two-coordinate because of bridging of the cyanide ligand, the Cu−C distance is only slightly greater. The structures of other two-coordinate complexes are listed near the bottom of Table 4. As for higher coordination numbers, Stemmler et al.[29] searched the Cambridge Structural Database and found 15 structures having three-coordinate Cu(I) and unambiguous distinction between the C and N of the cyanide ligand. Here, the Cu−C distance averaged 1.92 ± 0.03 Å.

From our data and those of solid-state samples, clearly the Cu−C distance is relatively insensitive to changes in coordination number, increasing by only about 5% on going from gas-phase CuCN to the three-coordinate compounds just mentioned. This small change may be a reflection of the sterically undemanding profile of the cyanide ligand. A comparison was sought with alkali metal acetylides such as M−CCR (R = H, M = Li, Na, K), which we made in monomeric form in the gas phase[57,59] and whose bonding is certainly ionic, without back-bonding from the metal to the alkyne π-system. Among solid-phase structures only four-coordinate, oligomeric complexes are known,[59,67,69,70] and in these the M−C bond lengths range from 12 to 17% longer than those in the monomers.

Conclusions

The first precise structure of a monomeric, neutral transition metal complex to the cyanide ion has been determined. Reaction of copper metal vapor and cyanogen gives CuCN. Millimeter-wave spectroscopy clearly shows that the cyanide CuCN is the most stable form. Signal intensities using precursors of natural isotopic abundance were so strong that even transitions for the ^{15}N isotopomer could be assigned with certainty, and transitions due to several excited vibrational states were also identified. Our results show that the experimentally determined copper−carbon distance was accurately predicted by recent calculations. Efforts continue in our lab to make and characterize fundamentally important low-coordinate organometallics in the gas phase.

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(67) See Table 1 of Goldfuss et al. (Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *J. Am. Chem. Soc.* **1997**, *119*, 1072−1080) for a list of oligomeric structures.

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(69) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *Organometallics* **2000**, *19*, 5780−5783.

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