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An Extremly Bent Cyanide Bridge in Crystals of [(CN)$_3$Pt(μ-CN)Cu(NH$_3$)$_4$]. Influence of Electrostatic Forces on the Nature and Geometry of Bridging Cyanides in the Solid State†

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The dinuclear heterometallic complex [(CN)$_3$Pt(μ-CN)Cu(NH$_3$)$_4$] has been obtained in the solid state, and its structure has been determined by X-ray diffraction techniques at two temperatures (102 and 233 K). $C_4H_{12}CuN_8$-Pt crystallizes in the orthorhombic system, with $a = 14.554(3)$ Å, $b = 7.1901(12)$ Å, $c = 10.369(2)$ Å, and $V = 1085.1(3)$ Å^3 at 102 K ($a = 14.5091(10)$ Å, $b = 7.2739(4)$ Å, $c = 10.4570(7)$ Å, and $V = 1103.61(12)$ Å^3 at 233 K), in space group *Pnma*, with $Z = 4$. The Pt and Cu atoms are linked by a CN bridge that presents a very bent C≡N−Cu angle (120.1(6)° at 102 K). The C≡N and N−Cu distances at 102 K are 1.147(10) and 2.394(7) Å, respectively. [(CN)$_3$Pt(μ-CN)Cu(NH$_3$)$_4$] is embedded in an extensive electrostatic net formed by (N)H···N(C) interactions which, it is concluded, play an important role in the extreme deviation from linearity observed for the C≡N−Cu angle.

Introduction

Intermolecular interactions in molecular solids are not usually considered to exert an important influence on molecular shape, which is determined principally by the stronger covalent and ionic bonds. In the course of our studies on molecular solids with significant intermolecular interactions, we have prepared and characterized systems in which hydrogen bonding, other electrostatic interactions, and consequent long-range order have prevailed over the common coordination shapes observed for first-row transition elements. In aqua or ammine cyanurato-*N* ($C_3O_3N_3H_2^-$) complexes of first transition series elements, for example, the formation of a structurally dominant cyanurate ribbon persists throughout the series and in some cases obliges the metal center to adapt to unusual coordination shapes or bent bonding.[1] The cyanurate ribbon, which is held together by hydrogen bonds, is also present in the highly unusual molecular solid formed by *trans*-[Ni(cyan-κN)$_2$(NH$_3$)$_4$], which undergoes a second-order phase transformation through an easily accessible temperature range, giving rise to a continuous, tunable, reversible molecular shape change.[2]

Transition metal complexes of cyanide, CN$^-$, which have received a great deal of attention, mainly in the context of their physical properties,[3] are also candidates for study with respect to the balance between intra- and intermolecular forces. A terminal cyanide ligand is a potential hydrogen-bond acceptor, and since water molecules are present in many cyanide-containing complexes, the possibility exists for the formation of significant and structurally influential H-bonding networks. Still, the influence of the presence of water on the nature of the solids formed by cyanide complexes, and on their physical properties, has been suggested on only a few occasions.[4]

We recently reported the preferential formation of the discrete square Pt$_2$Cu$_2$ cyano complex [Pt(CN)$_4$Cu(bipy)(H$_2$O)]$_2$·2H$_2$O[5a] instead of the polymeric complex [Pt(CN)$_4$Cu(bipy)]$_\infty$,[5b] in the presence of water. The isolation of the discrete molecular compound is likely a result of the presence in the solid of an extensive network of hydrogen bonds between the H$_2$O moieties and the terminal CN ligands. The hydrogen bonding stabilizes the terminal cyanide moieties and also lowers the solubility of the square complex, thus favoring its precipitation to an extent that it becomes competitive with the formation of the naturally insoluble polymer.

In what follows, we report the preparation and solid-state characterization of the dinuclear compound [(CN)$_3$Pt(μ-CN)-Cu(NH$_3$)$_4$], in which NH$_3$ is the hydrogen-bond donor. This dinuclear PtCu complex is embedded in an extensive network of (C)N···H(NH$_2$) interactions and presents what is to our knowledge the most closed C≡N−M angle (120.1(6)°) reported to date for a cyanide ligand bridging two metal centers.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000−200 cm^{-1} for samples in Nujol mulls between polystyrene films on a Perkin-Elmer 883 spectrophotometer.

Synthesis of [(CN)$_3$Pt(μ-CN)Cu(NH$_3$)$_4$] (1). CuSO$_4$·5H$_2$O (0.010 g, 0.040 mmol) was added to an aqueous solution of 0.020 g (0.039 mmol) of Ba[Pt(CN)$_4$]·4H$_2$O. The resulting green precipitate was filtered off and washed with H$_2$O. The solid, still in the same filter, was treated with a concentrated NH$_4$OH solution until only white solid BaSO$_4$ remained in the filter and the ammonia solution passing through the filter was colorless. The dark purple solution obtained was

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† Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

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transferred to test tubes and layered with 1-propanol. From those tubes were obtained dark purple crystals of $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ (**1**) after partial interdiffusion of the solvents. The crystals lost transparency and color upon being removed from solution. The infrared spectra obtained for Nujol mulls of compound **1** prepared under an atmosphere of ammonia showed the following absorptions: ν(NH) 3338 (s), 3266 (m), and 3186 (m) cm^{-1}; ν(CN) 2157 (m), 2139 (m), 2127 (s), 2121 (s) cm^{-1}. When the crystals and the emulsions were treated under normal laboratory conditions—that is to say, not in an atmosphere of ammonia—one extra absorption was observed at 2181 cm^{-1} while the absorption at 2157 cm^{-1} decreased in intensity. Elemental analysis was not performed because of the behavior of the product in the absence of ambient ammonia.

X-ray Structure Determination. X-ray data were collected for a single crystal of $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ (**1**), first at 233 K and then at 102 K. After the initial determination of the cell dimensions and crystal system, data collection parameters were determined independently at each temperature on the basis of two-dimensional ($\omega-\theta$) scans of several reflections.[6a] It was found that the peak shapes were different at the two temperatures, and the scan parameters were adjusted accordingly. During intensity data collection, the scan speed for each reflection was determined on the basis of a preliminary scan and the weakest reflections were measured at the slowest speed; that is, no reflection was skipped on the basis of a poor showing on the first scan. Experimental stability was followed by monitoring reflections after every 30 min of accumulated beam time. The unit cell parameters were determined independently at each temperature, using the same set of 25 scattering vectors for both. Measurements for absorption correction were also made independently at each of the two temperatures, using the same set of reflections for both.

After data reduction and the application of absorption corrections, the structure was solved by direct methods and refined in both cases by full-matrix least-squares calculations.[6b−d] For each of the two data sets, the hydrogen atoms—all of which belong to NH_3 groups—were located in difference Fourier maps; and some were found to behave acceptably well when refined as independent atoms. For the structure determination at 233 K, the NH_3 ligands were treated as rigid groups, with variable torsion angles about the Cu−N bonds. Each H atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent N atom. At 102 K, where the hydrogen atoms were found to behave even better, one of the ammine ligands was treated as a variable metric rigid group with free rotation about the Cu−N bond and with dependent displacement parameters for the hydrogen atoms and the other NH_3 group was refined freely. The hydrogen atoms were treated as freely as the data quality permitted because of the importance of hydrogen bonding in the interpretation of this structure. Also at 102 K, restraints to isotropic behavior were applied to two of the carbon atoms of the CN ligands and a small extinction parameter was applied. The refinements converged with the residuals given in Table 1.

Results and Discussion

The reaction of $Ba[Pt(CN)_4]$ with $CuSO_4{\cdot}5H_2O$ produces the rapid precipitation of a green solid, which upon treatment with a concentrated aqueous ammonia solution yields a white precipitate of $BaSO_4$ and a dark blue solution. A dark blue solid, $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ (**1**), can be isolated from the solution. Compound **1** loses NH_3 when it is not in an ammonia atmosphere and changes color when treated with solvents other than aqueous ammonia. To record the IR spectrum of **1**, it is necessary to prepare the Nujol mull in an ammonia-rich atmosphere. The IR spectrum of a sample thus prepared shows four absorptions in the cyanide region—2157 (m), 2139 (m), 2127 (s), and 2121 (s) cm^{-1}—corresponding to the four independent cyanide groups in the molecule. The IR spectrum of a mull prepared under normal laboratory conditions shows an extra absorption at 2181 cm^{-1}. The new absorption appears at higher frequency than those corresponding to compound **1** and is consistent with the formation of a bridging cyanide by coordination of a terminal CN group to the copper center at a coordination site vacated by loss of NH_3.

Table 1. Crystallographic Data for Compound **1**

	T = 102 K	T = 233 K
empirical formula	$C_4H_{12}CuN_8Pt$	$C_4H_{12}CuN_8Pt$
fw	430.85	430.85
λ(Mo Kα) (Å)	0.710 73	0.710 73
space group	*Pnma* (No. 62)	*Pnma* (No. 62)
Z	4	4
temp (K)	102	233
a (Å)	14.554(3)	14.5091(10)
b (Å)	7.1901(12)	7.2739(4)
c (Å)	10.369(2)	10.4570(7)
V (Å^3)	1085.1(3)	1103.61(12)
ρ_{calcd} (g cm^{-3})	2.637	2.593
μ (cm^{-1})	148.2	145.7
R1^a [$I > 2\sigma(I)$]	0.0287	0.0319
wR2^b (all data)	0.0719	0.0849

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$; $P = (F_o^2 + 2F_c^2)/3$; weight parameters a and b are given in the Supporting Information.

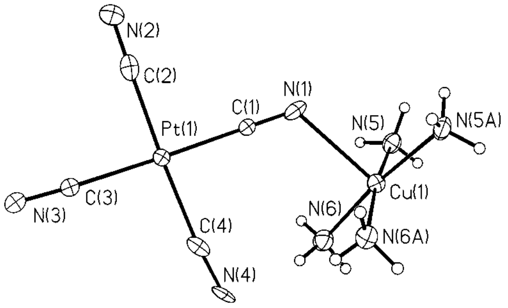

Figure 1. Perspective drawing of compound **1** at 102 K. Non-hydrogen atoms are represented by their 70% probability ellipsoids.

The structure of compound **1** was determined at two different temperatures, 102 and 233 K. Figure 1 is a drawing of one molecule of **1**, and Table 2 lists the principal bond distances and angles.

The compound $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ is formed by $[Pt(CN)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$ units held together by a bridging CN group. In the solid state, the $[Pt(CN)_4]$ group is located on a crystallographic symmetry plane and the $[Cu(NH_3)_4]$ group is bisected by the same plane. All of the atoms except those of the NH_3 ligands reside on special positions. The Pt atom is coordinated by four cyanide ligands, as in the starting material, and the Cu atom is coordinated by four NH_3 groups and the CN bridge, giving a total of five nitrogen atoms forming a square-based pyramid about copper. For the purposes of this discussion, we shall use the bond distances and angles from the structure determination at 102 K; but as can be verified by reference to Table 2, all of the important points apply equally well to the determination at 233 K. Although the Pt−C(bridge) distance is formally smaller than the Pt−C distances corresponding to the terminal cyanide ligands, the difference is within experimental error (102 K: 1.973(7)−2.002(9) Å). The C≡N distance in the bridging cyanide, 1.147(10) Å, is the second

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(6) (a) Diffractometer control program: *CAD4/PC*, Version 2.0; Nonius bv: Delft, The Netherlands, 1996. (b) Data were processed on an AlphaStation 200 4/166 (OpenVMS/Alpha V6.2), with the program XCAD4B (K. Harms, 1996) and with the commercial package: *SHELXTL*, Release 5.05/VMS; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996. (c) Direct methods: Sheldrick, G. M. *SHELXS-97: Fortran program for crystal structure solution*; University of Göttingen: Göttingen, Germany, 1997. (d) Refinement: Sheldrick, G. M. *SHELXL-97: Fortran program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$[a]

	233 K	102 K
Pt(1)−C(1)	1.965(9)	1.973(7)
Pt(1)−C(2)	2.004(11)	1.983(9)
Pt(1)−C(3)	2.002(10)	1.991(8)
Pt(1)−C(4)	2.021(12)	2.002(9)
Pt(1)$\cdots$Pt(1)#1	3.6751(2)	3.6235(6)
Pt(1)$\cdots$Pt(1)#2	3.6752(2)	3.6236(6)
Cu(1)−N(5)	2.009(6)	2.016(5)
Cu(1)−N(6)	2.026(6)	2.018(5)
Cu(1)−N(1)	2.413(9)	2.394(7)
C(1)−N(1)	1.156(12)	1.147(10)
C(2)−N(2)	1.134(14)	1.148(11)
C(3)−N(3)	1.126(13)	1.136(11)
C(4)−N(4)	1.127(15)	1.131(12)
Pt(1)#1$\cdots$Pt(1)$\cdots$Pt(1)#2	163.47(2)	165.620(18)
N(5)#3−Cu(1)−N(5)	90.5(3)	90.9(3)
N(5)−Cu(1)−N(6)#3	172.9(2)	173.2(2)
N(6)#3−Cu(1)−N(6)	89.3(3)	89.8(3)
N(5)#3−Cu(1)−N(6)	172.9(2)	173.2(2)
N(5)−Cu(1)−N(6)	89.6(2)	89.3(2)
N(5)#3−Cu(1)−N(1)	90.9(2)	91.42(18)
N(5)−Cu(1)−N(1)	90.9(2)	91.42(18)
N(6)#3−Cu(1)−N(1)	96.3(2)	95.40(19)
N(6)−Cu(1)−N(1)	96.3(2)	95.40(19)
N(1)−C(1)−Pt(1)	178.5(8)	179.6(7)
C(1)−N(1)−Cu(1)	120.7(7)	120.1(6)
N(2)−C(2)−Pt(1)	179.6(9)	179.3(7)
N(3)−C(3)−Pt(1)	177.4(8)	177.6(7)
N(4)−C(4)−Pt(1)	175.1(8)	174.6(7)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y + 1, -z$. (#2) $-x, -y, -z$. (#3) $x, -y + {}^1/_2, z$.

longest of the four CN distances, but again the differences are within experimental error and all of the CN bond lengths lie within the range expected for a triple bond (102 K: 1.131(12)−1.148(11) Å). The equatorial Cu−N(ammonia) distances are equal within experimental error (102 K: 2.016(5), 2.018(5) Å). The distance Cu−N(1), from copper to the nitrogen atom of the bridging cyanide, has a value of 2.394(7) Å at 102 K, in keeping with the fact that copper coordinates weakly to a fifth nitrogen-bound ligand. Still, this distance is larger than what could have been expected (2.19, 2.21 Å);[7] but there is no doubt that it represents a covalent bond. The apical Cu−N(1) bond can be compared, for example, to the Cu−O(apical) distances of 2.41 Å found in $[Cu(dien)(H_2O)M(CN)_6]$ (M = Fe,[8a] Cr[8b]). The Cu−N(1) bond is essentially perpendicular to the CuN_4(ammine) plane, as expected for a fifth covalently bonded ligand in a square-based pyramidal coordination environment. The presence of a C≡N bridge is also in accord with the IR spectrum of **1**, in which the highest absorption in the ν(C≡N) region appears at 2157 cm^{-1}, which is higher than ν(C≡N) for the starting material ($(NBu_4)_2[Pt(CN)_4]$, 2121 cm^{-1}). At the same time, the shift to higher frequency is not as pronounced as those observed for other, more linear, Pt(μ-CN)Cu bridges.[5]

The molecules are packed in such a way that the $[Pt(CN)_4]$ groups are stacked, with the Pt atoms forming an unbounded, nearly linear chain with a Pt$\cdots$Pt distance of 3.6236(6) Å at 102 K or 3.6751(2) Å at 233 K and a Pt$\cdots$Pt$\cdots$Pt angle of 165.62(2)° (102 K) or 163.47(2)° (233 K). The variation of the Pt$\cdots$Pt distance with temperature accords with the variations observed in other linear Pt(II)$\cdots$Pt(II) chains.[9] Figure 2 shows the packing of compound **1** in the crystal. The Pt$\cdots$Pt distance in **1** is greater than those observed in the red form of $[PtCl_2(bipy)_2]$ (3.370(2)−3.449(1) Å); this is because the atoms of the NH_3 groups in **1** shim the layers of the planar $[Pt(CN)_4]$ units, while for $[PtCl_2(bipy)_2]$ all the atoms of a given molecule lie in the same plane. However, it is worth noting that the presence of the NH_3 groups augments the Pt(II)$\cdots$Pt(II) distance by less than 0.25 Å.

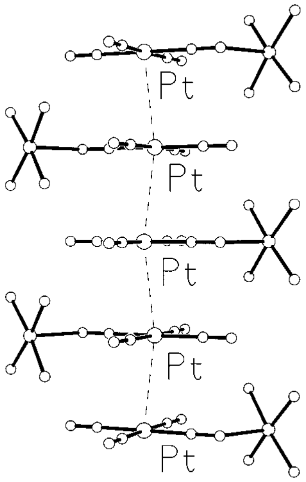

Figure 2. Packing of compound **1** showing the nearly linear Pt$\cdots$Pt$\cdots$Pt chain.

It is interesting, moreover, that in **1** only one of the four cyanide groups acts as a bridge and that the compound is discrete despite the presence of three terminal CN ligands that could also have served as bridges, thus forming a structure with the commoner polymeric nature. The reaction between $[Pt(CN)_4]^{2-}$ and Cu^{2+} in an ammonia−ammonium chloride solution has long been known to produce $[Pt(CN)_4Cu(NH_3)_2]_n{\cdot}2nG$ (G = guest molecule), one of the Hoffmann clathrates.[10] The difference between the well-known PtCu Hoffman type compound and compound **1** is the number of NH_3 moieties per Cu atom. While compound **1** has four NH_3 groups per Cu atom, the PtCu Hoffman type compound presents only two NH_3 units bonded to the Cu atom; and all of the CN groups of the Pt-containing fragment of the Hoffman clathrate are involved in strong, linear, covalent bonds, producing a two-dimensional net.

The most striking, as well as surprising, feature of compound **1** is the severely bent C≡N−Cu angle, which has values of 120.1(6)° at 102 K and 120.8(8)° at 233 K. Both the valence bond and molecular orbital descriptions of the C≡N−M′ system indicate that the N−M′ bond should be collinear with the triple bond. This situation holds for most of the CN bridges observed to date, although a few compounds with angles of about 140° have been reported. For example, one of the C≡N−Cu angles in $[\{Cu(dien)\}_2Fe(CN)_6]_n{\cdot}6nH_2O$ is 136.2(8)°, with a Cu−N distance of 2.21(1) Å,[4b] and $[\{Cu(dien)_2Fe(CN)_6\}_n][Cu(H_2O)(dien)Fe(CN)_6]_n{\cdot}4nH_2O$ has C≡N−Cu angles of 139 and 140°, with corresponding Cu−N distances of 2.32(1) and 2.31(1) Å.[8a] In a recently reported structure determination of a cyanide-bridged dinuclear (MnTl) complex, C≡N−Tl angles of 139.7(12) and 126.4(12)° were observed. However, crystals of that material

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Table 3. Shortest $H_2NH\cdots NC$ Contacts for Compound **1** at 102 K[a]

D−H···A	H···A (Å)	D···A (Å)	D−H···A (deg)	acceptor coordinates
N(5)−H(5A)···N(2)	2.25	3.126(8)	170.3	$x - {}^1/_2, y, -z + {}^1/_2$
N(5)−H(5B)···N(3)	2.36	3.219(7)	164.4	$-x, -y, -z$
N(5)−H(5C)···N(4)	2.57	3.142(8)	123.0	$x - {}^1/_2, y, -z - {}^1/_2$
N(5)−H(5C)···N(2)	2.59	3.351(7)	144.2	$-x - {}^1/_2, -y, z - {}^1/_2$
N(6)−H(6A)···N(1)	2.55(8)	3.279(8)	140(6)	$-x - {}^1/_2, -y, z - {}^1/_2$
N(6)−H(6A)···N(3)	2.56(8)	3.162(8)	125(6)	$x - {}^1/_2, y, -z - {}^1/_2$
N(6)−H(6B)···N(3)	2.49(8)	3.269(7)	160(6)	$-x, -y, -z$
N(6)−H(6C)···N(4)	2.51(9)	3.243(8)	156(8)	x, y, z

[a] Estimated standard deviations are not given for quantities involving hydrogen atoms that were refined as riders.

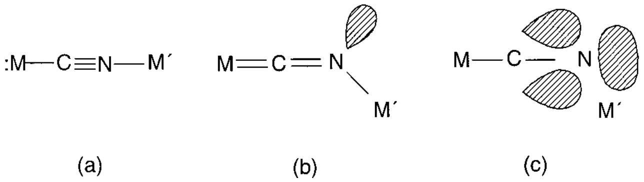

Figure 3. Models for bonding in the M−C≡N−M′ system: (a,b) valence bond models; (c) molecular orbital theory model.

suffered from disorder of the Tl atom, and the authors warned against using the quantitative aspects of the determination in drawing conclusions.[11]

By way of explaining the unusual shape presented by the C≡N−Cu system in compound **1**, we shall consider first its properties as an isolated system; after that, the crystalline surroundings will be taken into account. Angularity in the −C≡O−M′ fragment has been explained on the basis of two valence bond structures,[12] and since −C≡N−M′ is an isoelectronic system, a similar explanation can be applied to it in the first instance (Figure 3).

Figure 3a shows the situation for a linear bond, and Figure 3b corresponds to a C≡N−M′ angle of about 120°. The C≡N−Cu angle in compound **1** is 120.1(6)° at 102 K; so, as regards the angle, the situation described by Figure 3b should hold. However, the C≡N and Pt−C distances indicate that the principal contribution is from the structure shown in Figure 3a. Figure 3c, which represents the molecular orbital description of the electron density in the nitrogen region of the C≡N group, points again to the expected relationship between bent C≡N−M′ angles and longer C≡N distances. It has been demonstrated that there is less π electron density distal to the N atom of the CN group than exists in the analogous vicinity of the O atom of CO,[12a] so that the CN ligand should have less tendency to form bent bridges than CO; this is borne out by experiment, since CN bridges are usually linear. In short, none of these considerations offer an acceptable explanation of the observed shape of compound **1**. The Cu−N(1) distance (2.394(7) Å at 102 K) does not admit the possibility that this bond is largely electrostatic, given the large number of copper-centered complexes whose structural and spectroscopic properties have been explained in terms of covalent bonds, sometimes with significantly longer distances than what is observed here.

A surer explanation for the unusual structure of $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ (**1**) is revealed by the extensive network of intermolecular interactions in which the complex participates.

Although the compound is relatively small in terms of its number of atoms and bonds, it participates in a very complete set of electrostatic interactions. Table 3 lists the shortest

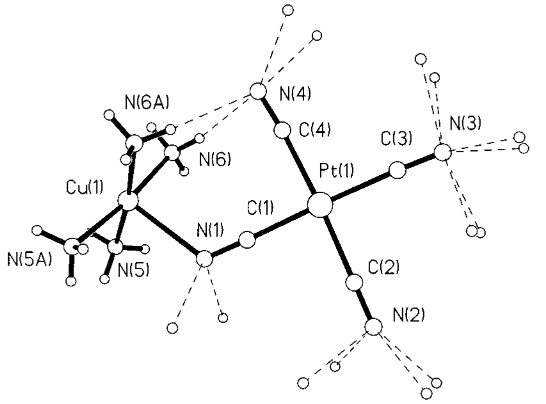

Figure 4. Drawing of compound **1** showing the locations of the hydrogen atoms closest to each of the N atoms of the CN groups.

C≡*N*···*H*−NH_2 distances. There are two crystallographically independent ammonia groups, centered at atoms N(5) and N(6), both with qualitatively similar intermolecular interactions. Two of the three hydrogen atoms of each NH_3 group are involved in interactions with N atoms of CN groups of adjacent molecules; these interactions have N−H···N angles greater than 150°. The third hydrogen atom of each ammonia group takes part in a bifurcated interaction in which the acceptors are two distinct cyanide nitrogen atoms; in this case, the N−H···N angles are smaller than those observed for the other hydrogen atoms, as is characteristic of bifurcated hydrogen donors.

The donor···acceptor (N···N) distances in these interactions are larger than the sum of the van der Waals radii of the donor and acceptor atoms (3.0 Å for N···N[13]); they are within the range sometimes considered to represent weak hydrogen bonds. Whether or not some or all of these contacts could usefully be called hydrogen bonds, it is clear that compound **1** in the solid state is enveloped by stabilizing electrostatic interactions.

As regards the acceptor side of these interactions, it can be seen from Figure 4 that the N atoms of the CN groups are fairly symmetrically surrounded by electrostatic contacts.

Each N atom of the terminal cyanide groups is involved in at least two crystallographically unique interactions, one with an N−H···N angle greater than 150° and the other corresponding to the bifurcated hydrogen. Moreover, since the CN groups reside on mirror planes and the donor atoms do not, the total number of interactions in which the CN ligand acts as an acceptor is at least 4 for each nonbridging cyanide. The N atom of the bridging CN ligand acts as acceptor in one unique bifurcated contact—or a total of two when the mirror-related equivalent contact is taken into account; together with the bonds to the Cu and C atoms, these interactions complete a distorted tetrahedral environment around atom N(1). Thus, the N atom of the bridging cyanide ligand is the one that is least involved

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in electrostatic interactions with neighboring hydrogen atoms, a feature that is consistent with the fact that N(1) is already involved in a bond to the Cu center.

In sum total, compound **1**, which contains 26 atoms including hydrogen, is involved in the solid state in 24 intermolecular electrostatic interactions. N.b.: Here each bifurcated interaction is counted once on the donor side and twice on the acceptor side, once for each acceptor atom involved. Two further electrostatic interactions are present, namely, N(6)−H(6C)···N(4) and its symmetry equivalent contact, which are intramolecular and would not be possible if the CN bridge were linear or nearly so. We conclude that this three-dimensional electrostatic net plays a decisive role in establishing the deformation observed in the C≡N−Cu angle. The influence of crystal packing forces has been invoked previously as a causal factor for deformations of approximately 30° (that is, for C≡N−M′ angles between 151.1 and 154.2°).[14] In the absence of an explanation based on properties intrinsic to the complex, compound **1**, with a modification of approximately twice that (59.9(6)° at 102 K), establishes the influence that this kind of noncovalent force can exert on the bridging cyanides in the solid state. We note, in passing, that the previously mentioned heteronuclear compounds $[\{Cu(dien)\}_2Fe(CN)_6]_n\cdot 6nH_2O$ and $[\{Cu(dien)_2Fe(CN)_6\}_n][Cu(H_2O)(dien)Fe(CN)_6]_n\cdot 4nH_2O$, which have bent C≡N−Cu angles, also participate in extensive hydrogen bonding or electrostatic networks in the solid state. They are, however, more complicated structures—polymers with 12-atom rings—so that other structural constraints may also enter into play in establishing the bent angles in these systems.

Conclusions

The structure of compound **1** demonstrates that the cyanide group can act as a severely bent bridge, forming C≡N−M′ angles with as much as a 60° deformation from linearity, while maintaining the C≡N triple bond. A more general conclusion about the nature of the N−M′ bond in such a situation is not as clearly established by the present results, given the covalent plasticity of Cu(II);[15] there is little doubt that the (C)N−Cu bond in the present case is significantly covalent, although we are not able to estimate the extent of any electrostatic contribution. The extensive collection of noncovalent interactions formed upon crystallization must exert a heavy influence on the very nature of $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ (**1**). It appears that the formation of the N−Cu bond involving the bridging cyanide is a consequence not only of the enthalpy of this bond but also of the extra stability gained through the formation of the very complete set of electrostatic contacts that are thus enabled. The entire set of characteristics observed—formation of the N−Cu bond, severe bending of the C≡N−Cu angle, and formation of the enveloping electrostatic net—is a *gestalt* phenomenon, by which we mean that none of these characteristics can be fully understood without considering the others. This type of occurrence, unique to the solid state, is enabled when intermolecular space is dominated by moderate to strong interactions.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ at 102 and 233 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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