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Synthesis, characterization and spectroscopic properties of $[Cu^I(alkylisocyanide)_4]BF_4$ complexes. X-ray crystal structures of $[Cu(MIBI)_4]BF_4$ and $[Cu(CPI)_4]BF_4$

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Abstract—Alkylisocyanide complexes of copper(I) with formula $[Cu(CNR)_4]BF_4$ [where R = 2-methoxyisobutyl and 2-(carbomethoxy)-2-methylethyl] were synthesized by direct reaction of cuprous chloride with ligand. The stability of solid complexes and their aqueous solutions were tested by HPLC. Comparative studies were carried out on electronic, IR and ^{1}H NMR spectroscopy. Crystal structures of $[Cu(MIBI)_4]BF_4$ and $[Cu(CPI)_4]BF_4$ were determined from X-ray data and show a tetrahedral arrangement of ligands around the central copper atom in both compounds. © 1997 Elsevier Science Ltd

Keywords: copper(I) complexes; copper(I) alkylisocyanide complexes; structure of $[Cu(MIBI)_4]BF_4$; structure of $[Cu(CPI)_4]BF_4$.

Mononuclear copper(I) complexes are known with several types of neutral ligands. [1] These must be soft ones, to stabilize monovalent copper, and with no easily available lone electron pairs (except to coordinate the central atom), in order to preclude formation of polynuclear species. Many isocyanides meet these conditions, having thus the capability of forming mononuclear Cu^I complexes. Isocyanides are volatile liquids of unpleasant odor, highly unstable to polymerization and oxidation. [2] They can be stabilized by coordination, forming M—C bonds that hinder the reactivity of the functional group. Moreover, the volatility and odor of ligands is reduced. Thus, isocyanides can be adequately stored as isocyanide metal complexes. If the central atom is properly chosen, these complexes may serve as useful precursors for preparing other metal-isocyanide complexes, by substitution. For instance, some isocyanide copper complexes have been used as intermediates in the synthesis of ^{99m}Tc-isocyanide compounds. [3,4,5] The success of a ^{99m}Tc labeled molecule as a routine radiopharmaceutical agent depends on its biological properties, but also on the possibility of formulating a suitable stable kit for preparing it. This can be achieved by storing the isocyanide derivative as a copper complex. This complex is introduced in the kit formulation as a stable precursor for the ^{99m}Tc radiopharmaceutical. By reacting with Tc in a suitable oxidation state (Tc^I), the central atom is substituted and the desired Tc complex is formed.

Up to now, the X-ray structure only of $[Cu(CH_3CN)_4]BF_4$ has been reported [6] and no systematic study on these compounds has been performed. In the present work, copper(I) isocyanide complexes with CPI (2-(carbomethoxy)-2-methylethylisocyanide) and MIBI (2-methoxyisobutylisocyanide) were synthesized and chemical

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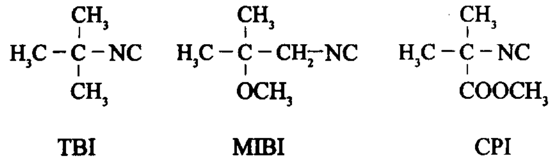

Fig. 1. Ligands used in the study.

characterization was performed, including solid-state and solution-stability testing. The X-ray structures of both complexes were determined, to check the existence of mononuclear cationic species, with the tetrahedral arrangement of ligands around the Cu^I central atom for these compounds. Comparison with analogous compounds $K_3[Cu^I(CN)_4]$, $[Cu(CH_3CN)_4]BF_4$ and $[Cu(TBI)_4]Br$ (TBI = terbutylisocyanide) was also performed. The ligands used in this work are shown in Fig. 1.

EXPERIMENTAL

Materials

All common laboratory chemicals were of analytical grade and used without further purification. CPI was a contribution of Dr James F. Kronauge (Department of Radiology, Harvard Medical School, Brigham and Women's Hospital, Boston, U.S.A.). [7] MIBI was synthesized by Dr Eduardo Manta *et al.*, Department of Pharmaceutical Chemistry, Faculty of Chemistry, Montevideo, Uruguay, by dehydration using the phosgene method. [8]

Synthesis

$[Cu^I(CNR)_4]BF_4$ (R = 2-*(carbomethoxy)*-2-*methylethyl* or 2-*methoxyisobutyl*). Cu^I complexes were synthesized by stirring for 15 min with 280 mg of cuprous chloride (2.8×10^{-3} mol) freshly recrystallized [9] and 1.23 g of MIBI or 1.27 g of CPI (11.2×10^{-3} mol) in 50 cm^3 anhydrous ethanol. After adding 0.31 g of NH_4BF_4 (3×10^{-3} mol) the mixture was stirred in a water bath at 60°C for 5 min and filtered through paper. The solution was rotavaporated (40°C) until a white solid began to appear. The complex was completely precipitated by adding 40 cm^3 of anhydrous ether (peroxide free). Purification was accomplished by dissolution in ethanol and reprecipitation with ether. The procedure yield was 50%. The white product obtained was stored protected from light under nitrogen and at low temperature.

Found: Cu, 10.4; C, 47.9; H, 7.4; N, 9.7. Calc. for Cu-MIBI ($C_{24}H_{44}BCuF_4N_4O_4$): Cu, 10.5; C, 47.8; H, 7.4; N, 9.3%. Found: Cu, 9.5; C, 41.6; H, 5.3. Calc. for Cu-CPI ($C_{24}H_{36}BCuF_4N_4O_8$): Cu, 9.6; C, 43.7; H, 5.5%. M.p (°C): Cu-MIBI, 96–97; Cu-CPI, 92–94.

$K_3[Cu(CN)_4]$ was synthesized from KCN and CuCN [10]. $[Cu(TBI)_4]Br$ was a contribution of Dr J. A. Kronauge. Both compounds were used for comparative purposes.

Elemental analysis

Elemental analysis were accomplished on an elemental analyzer Carlo Erba EA 1108. Copper content was determined iodimetrically after oxidation to Cu^{II}.

Physical measurements

Conductivity measurements were performed at 25°C in MeOH in the concentration range 10^{-3}–10^{-4} M in order to apply Feltham and Hayter's method to determine electrolyte type [11].

IR spectra were recorded in the range 4000–600 cm^{-1} on a Perkin–Elmer 1310 spectrometer in KBr pellets. The IR spectrum of the liquid MIBI ligand was obtained between NaCl plates.

Electronic UV spectra in aqueous solution were measured with a Shimadzu 210 UV spectrophotometer.

^1H NMR spectra were obtained from a Varian FTX-L-100 spectrometer with Me_4Si as internal standard and D_2O or $CDCl_3$ as solvent.

HPLC analysis

HPLC analyses of the copper complexes were carried out on a reverse-phase mode with a Varian 500 equipment with UV detector (Varian Micropack MCH-10 column, isocratic mode, 1 cm^3 min^{-1} flow, detection wavelength 230 nm). The mobile phase was aqueous 0.05 M $(NH_4)_2SO_4$: MeOH (5 : 95).

X-ray diffraction

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of an ethanolic solution into ether.

Diffraction intensities of $[Cu^I(MIBI)_4]BF_4$ and $[Cu^I(CPI)_4]BF_4$ were collected with a Rigaku AFCS 7 four-circle diffractometer, at room temperature. In the case of $[Cu^I(MIBI)_4]BF_4$, a crystal of approximate dimensions $0.35 \times 0.20 \times 0.10$ mm, carefully cut from a larger block was used for data collection.

Crystal data for $[Cu^I(MIBI)_4]BF_4 \cdot C_{24}H_{44}O_4N_4Cu \cdot BF_4$, $M = 602.98$, orthorhombic, $a = 15.198(2)$, $b = 21.478(4)$, $c = 10.095(3)$ Å, $U = 3295.3(12)$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.215$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 0.717$ mm^{-1}, $F(000) = 1272$, crystal size $0.35 \times 0.20 \times 0.10$ mm.

Data for Cu-MIBI were collected in the range $2.23 \leqslant \theta \leqslant 27.50°$. 4841 reflections were collected in the 2θ–ω scan mode. All appropriate corrections to the data were applied. 4608 reflections were unique ($R_{int} = 3.53\%$) and 2626 [$I > 2\sigma(I)$] were used in the full-matrix least-squares refinement with the SHELXL-93 program [12]. The structure was solved using direct methods with the SHELXS-86 program. [13] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions (C—H 0.97 Å for secondary C atoms and 0.96 Å for primary C atoms) and refined isotropically with equivalent H atoms with equal U_{iso} factors. Final residuals were $R = 0.0644$ for a weighting scheme of $w-1 = [\sigma^2(F_0^2)+(0.1441P)^2+0.9548P]$, where $P = (F_0^2+2F_c^2)/3$. The goodness-of-fit (GoF) finished at 1.043. The mean final shift/esd was 0.065. The maximum and minimum residual densities were 0.649 and -0.639 e Å^{-3}, respectively. Selected bond distances and angles are given in Table 1. Tables of coordinates, anisotropic temperature factors, hydrogen atom coordinates and a full listing of geometric data are available as supplementary data. The asymmetric unit is shown in Fig. 2, along with the labelling scheme used.

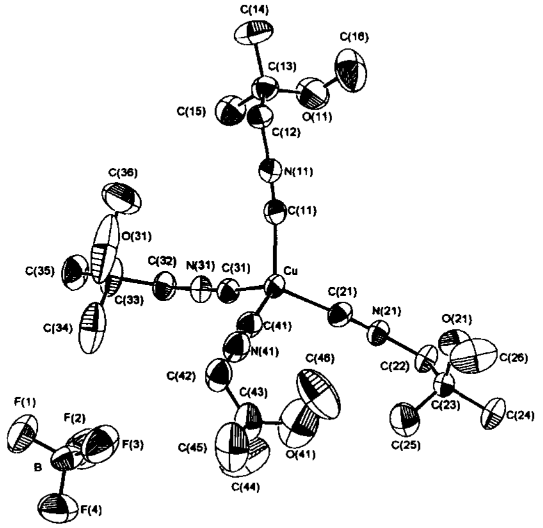

Fig. 2. The asymmetric unit of compound $[Cu(MIBI)_4]BF_4$, showing the atomic labeling used in the text and tables. Thermal ellipsoids are at the 40% level.

Crystal data for $[Cu^I(CPI)_4]BF_4 \cdot C_{24}H_{36}O_8N_4Cu \cdot BF_4$, $M = 658.92$, monoclinic, $a = 25.158(4)$, $b = 11.6553(7)$, $c = 25.200(4)$ Å, $\beta = 113.854(9)°$, $U = 6758.1(15)$ Å^3, space group Cc, $Z = 8$, $D_c = 1.295$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 1.516$ mm^{-1}, $F(000) = 2736$, crystal size $0.50 \times 0.30 \times 0.20$ mm.

Data for Cu-CPI were collected in the range $1.92 \leqslant \theta \leqslant 30.09°$. 14193 reflections were collected in the 2θ–ω scan mode. All appropriate corrections to the data were applied. 10,068 reflections were unique ($R_{int} = 12.26\%$) and 5049 [$I > 2\sigma(I)$] were used in the full-matrix least-squares refinement with the SHELXL-93 program. The structure was solved using direct methods with the SHELXS-86 program. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions (C—H 0.96 Å) and refined isotropically with the same U_{iso} factor. Final residuals were $R = 0.1236$ for a weighting scheme of $w-1 = [\sigma^2(F_0^2)+(0.2383P)^2+33.09P]$, where $P = (F_0^2+2F_0^2)/3$. The goodness-of-fit (GoF) finished at 1.228. Mean final shift/esd was 0.089. The maximum and minimum residual densities were 1.93 and -1.04 e/Å^{-3}, respectively. Selected bond distances and angles are given in Table 2. Tables of coordinates, anisotropic temperature factors, hydrogen atom coordinates and a full listing of geometric data are available as supplementary data. A molecule is shown in Fig. 3, along with the labelling scheme used. This compound showed instability upon exposure to X-rays. This explains the high R_{int} value and also the high residuals obtained.

Counterions BF_4^- for both compounds were

Table 1. Selected bond distances (Å) and angles (°) for the compound $[Cu(MIBI)_4]BF_4$

Cu—C(41)	1.952(9)	N(31)—C(32)	1.421(11)
Cu—C(21)	1.957(9)	C(41)—N(41)	1.128(11)
Cu—C(31)	1.959(9)	N(41)—C(42)	1.477(12)
Cu—C(11)	1.971(8)	B—F(3)	1.347(4)
C(11)—N(11)	1.127(9)	B—F(2)	1.347(4)
N(11)—C(12)	1.455(10)	B—F(4)	1.347(4)
C(21)—N(21)	1.142(10)	B—F(1)	1.347(4)
N(21)—C(22)	1.450(10)		
C(31)—N(31)	1.151(10)		

C(41)—Cu—C(21)	106.5(4)	N(21)—C(21)—Cu	178.0(8)
C(41)—Cu—C(31)	109.6(4)	C(21)—N(21)—C(22)	174.2(9)
C(21)—Cu—C(31)	110.9(3)	N(31)—C(31)—Cu	173.9(7)
C(41)—Cu—C(11)	111.7(4)	C(31)—N(31)—C(32)	176.3(8)
C(21)—Cu—C(11)	115.4(4)	N(41)—C(41)—Cu	176.1(10)
C(31)—Cu—C(11)	102.7(3)	C(41)—N(41)—C(42)	178.0(11)
N(11)—C(11)—Cu	172.0(7)		
C(11)—N(11)—C(12)	175.3(8)		

Table 2. Selected bond distances (Å) and angles (°) for the compound $[\mathrm{Cu(CPI)_4}]\mathrm{BF_4}$

Cu(1)—C(21)	1.939(12)	N(51)—C(52)	1.451(13)
Cu(1)—C(11)	1.950(11)	C(61)—N(61)	1.143(12)
Cu(1)—C(31)	1.947(12)	N(61)—C(62)	1.429(13)
Cu(1)—C(41)	1.956(11)	C(71)—N(71)	1.143(13)
C(11)—N(11)	1.143(12)	N(71)—C(72)	1.431(13)
N(11)—C(12)	1.444(12)	C(81)—N(81)	1.164(13)
C(21)—N(21)	1.146(13)	N(81)—C(82)	1.440(14)
N(21)—C(22)	1.438(14)	B(1)—F(13)	1.350(5)
C(31)—N(31)	1.161(13)	B(1)—F(11)	1.350(5)
N(31)—C(32)	1.437(13)	B(1)—F(14)	1.350(5)
C(41)—N(41)	1.137(12)	B(1)—F(12)	1.350(5)
N(41)—C(42)	1.424(13)	B(2)—F(24)	1.352(5)
Cu(2)—C(81)	1.928(12)	B(2)—F(22)	1.352(5)
Cu(2)—C(71)	1.962(12)	B(2)—F(21)	1.352(5)
Cu(2)—C(51)	1.942(12)	B(2)—F(23)	1.352(5)
Cu(2)—C(61)	1.970(11)		
C(51)—N(51)	1.141(13)		
C(21)—Cu(1)—C(11)	114.4(8)	C(81)—Cu(2)—C(51)	108.7(9)
C(21)—Cu(1)—C(31)	108.1(9)	C(71)—Cu(2)—C(51)	110.7(5)
C(11)—Cu(1)—C(31)	109.8(5)	C(81)—Cu(2)—C(61)	110.4(5)
C(21)—Cu(1)—C(41)	110.4(5)	C(71)—Cu(2)—C(61)	106.8(9)
C(11)—Cu(1)—C(41)	105.6(8)	C(51)—Cu(2)—C(61)	108.8(9)
C(31)—Cu(1)—C(41)	108.5(8)	N(51)—C(51)—Cu(2)	174.1(19)
N(11)—C(11)—Cu(1)	172.6(18)	C(51)—N(51)—C(52)	172.8(19)
C(11)—N(11)—C(12)	177.6(18)	N(61)—C(61)—Cu(2)	176.6(19)
N(21)—C(21)—Cu(1)	169.0(21)	C(61)—N(61)—C(62)	176.9(16)
C(21)—N(21)—C(22)	178.1(20)	N(71)—C(71)—Cu(2)	175.0(17)
N(31)—C(31)—Cu(1)	173.6(17)	C(71)—N(71)—C(72)	173.6(17)
C(31)—N(31)—C(32)	175.1(16)	N(81)—C(81)—Cu(2)	173.7(19)
N(41)—C(41)—Cu(1)	175.8(16)	C(81)—N(81)—C(82)	174.0(19)
C(41)—N(41)—C(42)	175.1(16)		
C(81)—Cu(2)—C(71)	111.3(9)		

refined as a rigid group of variable size with F—B—F angles of 109.5°.

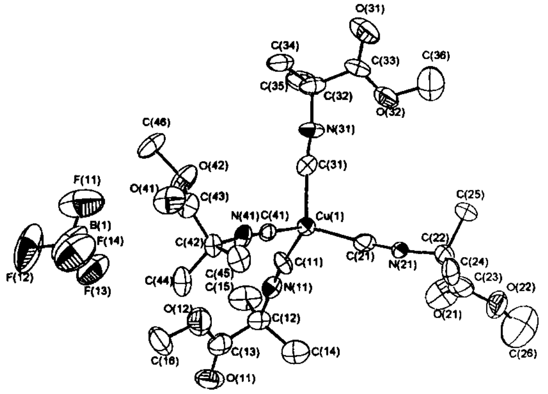

Fig. 3. Compound $[\mathrm{Cu(CPI)_4}]\mathrm{BF_4}$, showing the atomic labeling used in the text and tables. Thermal ellipsoids are at the 40% level.

Stability studies

Stability was tested by HPLC analysis of 1.5 mg $\mathrm{cm^{-3}}$ solutions, as described above. Stability in aqueous, ethanolic and ethanol: water (1 : 1 and 1 : 3) media was tested after 24, 48 and 72 h storage at room temperature.

RESULTS AND DISCUSSION

It was expected that $\mathrm{Cu^{I}}$ would form stable complexes with isocyanides. On the contrary, if $\mathrm{Cu^{II}}$ complexes were prepared, they should show fast decomposition, accompanied by metal reduction. [1] CuCl was chosen as the copper(I) source and ethanol as solvent for synthesis, where ligands and complexes are soluble. The reported procedure, using CuCl as the starting compound, was useful to synthesize both isocyanide complexes in good yields. By maintaining the stoichiometric ratio $\mathrm{Cu^{I}}$: ligand (1 : 4), purification was easy to accomplish. The purity of the products was very high, as was tested by HPLC analysis. Cationic complexes can be identified by a characteristic peak in each case (retention times: Cu-MIBI 4.9 min; Cu-CPI 3.5 min; Cu-TBI 4.3 min). This synthetic route could be used as a general procedure for obtaining new $\mathrm{Cu^{I}}$-isocyanide complexes. Stability of the solid compounds was very good, when appropriately stored. If they are stored under nitrogen at −20°C, no decomposition was observed up to 12 months.

Solutions of the complexes were also stable. After a storage period of 24 h at room temperature, aqueous, alcoholic and hydroalcoholic solutions, remained unchanged. Only when solutions were stored for longer periods (more than 48 h) a very small amount of degradation product was detected (HPLC retention time 3.4–3.5 min).

It is concluded that complexing Cu^I with alkyl isocyanides gives stable complexes with the formula $[Cu^I(alkylisocyanide)_4]BF_4$ and these complexes may be used as stable precursors for obtaining new isocyanide coordination compounds, by substitution of central atom. The soft character of these ligands make them suitable for obtaining complexes with metals in low oxidation states, as showed by $^{99m}Tc^I$ radiopharmaceuticals formed by metal substitution.

Conductivity measurements showed that the three complexes are uni-univalent electrolytes. The slopes of the λ_e ($S\ cm^2\ eq^{-1}$) vs $\sqrt{C_e}$ ($eq\ dm^{-3}\ 10^2$) plot were within the range 250–260, previously reported for 1 : 1 electrolytes in methanol. [8,14] Cu-MIBI, 251; Cu-CPI, 252; Cu-TBI, 257.

Table 3 shows selected spectroscopic data for the complexes.

The intense UV absorption in the electronic spectra can be assigned to charge-transfer transitions. The $[Ar]3d^{10}$ configuration of copper(I) rules out the occurrence of *d–d* electronic transitions. The isolated isocyano group is not a chromophore [15] and only weak absorptions in the UV region could be expected from ligands. $K_3[Cu(CN)_4]$ also showed similar absorptivity for the main band in the 210–230 nm region (Table 3).

IR spectra of the complexes confirmed that, except for the CN band, all other ligand characteristic peaks remained unchanged after complexation. The presence of the ester functional group in the Cu-CPI complex was revealed by the $C{=}O$ stretching frequency at 1740 cm^{-1}, which is consistent with the absorption at 1752 cm^{-1} previously reported for the free ligand. [16] In the 1050–1300 cm^{-1} region, bands assigned to symmetrical and asymmetrical $C{-}O{-}C$ stretching and $R{-}COOCH_3$ bending ($CH_3{-}O$) were also observed. Cu-MIBI showed $-OCH_3$ typical bands [17] and its IR spectrum agrees with the one performed in this work for the free MIBI ligand. Cu-TBI complex showed *tert*-butyl group characteristic bands, especially four bands in the region 1400–1200 cm^{-1}.

All complexes showed a single strong absorption in the 2000–2200 cm^{-1} region, distinctive of the $C{\equiv}N$ stretching mode, proving the high symmetry of these

Table 3. Selected spectroscopic data for the complexes

Species	[a]UV spectra λ(nm)	^1H NMR (ppm)	ν_{CN} (cm^{-1})
Cu-CPI	$220(1.4\times10^4)$ 240(sh) 272(sh)	[b]1.78 (s, 6H) 3.90 (s, 3H)	2175
Cu-MIBI	$219(1.4\times10^4)$ 242(sh) 273(sh)	[b]1.13 (s, 6H) 3.11 (s, 3H) 3.58 (s, 2H)	2190
Cu-TBI	$215(2.2\times10^4)$ 239(sh) 276(sh)	[b]1.50 (s)	2170
$K_3[Cu(CN)_4]$	$209(1.4\times10^4)$ 223(sh) 235 257(sh) 284 309		2080
CPI		[c,e]1.68 (s, 6H) 3.83 (s, 3H)	2141
MIBI		[c]1.28 (s, 6H) 3.28 (s, 3H) 3.40 (s, 2H)	2140
TBI		[d,f]1.17 (t)	2131

[a] UV absorption bands measured in aqueous solution; ε values are presented in parentheses in $dm^3\ mol^{-1}\ cm^{-1}$.

[b] D_2O as solvent.

[c] $CDCl_3$ as solvent.

[d] Neat liquid.

[e] [8].

[f] [7].

molecules. Isocyanides form quite strong M—C bonds when acting as ligands, but show a very variable capacity for accepting metal electrons *via* pi bonding. Extensive metal to ligand π-back donation is shown by a decrease of the C≡N stretching frequency with respect to the free ligand. The slight frequency increase detected for the studied compounds (Table 3), is consistent with a negligible π retrodonation from the Cu^I core to the isocyanide ligands. Similar compounds, with Ag^I as the central atom, show the same behavior [18]. In fact, isocyanides act as pure donor ligands in these cases.

Likewise, $K_3[Cu(CN)_4]$ also showed a ν_{CN} shift to higher frequencies compared with free CN^- ion. This would suggest that Cu—CN and C—N bonds in this complex are very similar to those found with isocyanide as ligands.

The ^1H NMR spectra of the complexes showed the same general pattern as the ligands (Table 3). Chemical shifts downfield when complexation happens were consistent with a essentially donor character of the ligand, as was previously discussed [19]. All the signals exhibited no spin–spin coupling, which is also consistent with a symmetrical coordination allowing free rotation of the ligands. Moreover, the $^{14}N—^1H$ coupling in the methylene group in MIBI was absent in the complex, probably due to an electric-field gradient about the N nucleus.

The crystal structure for both compounds consist of monomeric units of $[Cu(alkylisocyanide)_4]^+$. The polyhedron of coordination around the Cu ion is tetrahedral for both compounds. The ligands connect the central metal atom through the isonitrilic carbon atoms with bond lengths range from 1.952(9) to 1.971(8) Å for compound Cu-MIBI and from 1.928(12) to 1.970(11) Å for Cu-CPI. Bond distances data were compared with those found in the literature for tetrahedral $K_3[Cu(CN)_4]$ [20] and $[Cu(CH_3NC)_4]BF_4$ [6]. Found Cu—C distances are very near to 2.00 Å and similar values have been reported for copper-methylisocyanide and copper-cyanide complexes.

As to the C-N distances, they are around 1.14 Å, again very similar to reference compounds. They are very close to 1.16 Å (bond length for free cyanide ligand), thus suggesting C—N bond order of three in all complexes.

The metal–ligand atom angles are typical for a tetrahedron [from 106.5(4)° to 115.4(4)° for Cu-MIBI and from 105.63(81) to 114.36(84)° for Cu-CPI]. As a consequence, both reported structures are open packaged. The copper ions are somewhat screened in Cu-CPI, by the tertiary carbon character of Cα in CPI in contrast to the primary carbon character in MIBI.

The Cu-MIBI shows a linear ligand structure along the Cu—C(1)—N(1)—C(2) chains with angles between 172.0(7)° for N(11)—C(11)—Cu to 178.0(11)° for C(41)—N(41)—C(42). This linear structure is again present in the other compound, showing angles between 168.95(2.08)° for Cu(1)—C(21)—N(21) to 178.13(1.85)° for C(21)—N(21)—C(22). This linear sequence of atoms is in accordance with a C—N bond order of three and a single $\sigma_{Cu—CN}$ bond, with no π back-bonding [21].

All intra-ligand bond angles are very near to expected values for free MIBI and CPI ligands, with no indication of steric strain to accommodate ligands around the coordination center.

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