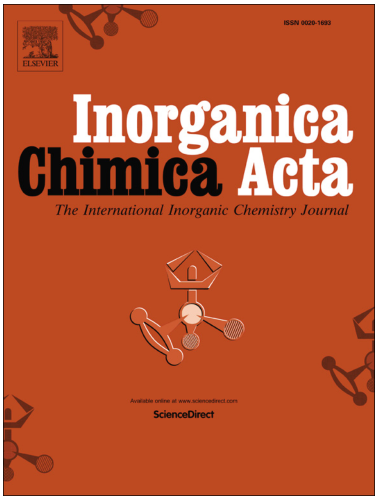

Research paper

Tris(3,5-dimethylpyralzoly)methane copper(I) complexes featuring one disubstituted cyanamide ligand

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Tris(3,5-dimethylpyralzoly)methane copper(I) complexes featuring one disubstituted cyanamide ligand

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Abstract. The complexes [Cu{HC(3,5-Me_2pz)$_3$}($NCNR_2$)][BF_4] (**1**–**8**; R_2 = Me_2 **1**, Et_2 **2**, C_5H_{10} **3**, C_4H_8O **4**, C_4H_8 **5**, $C_3H_6C_6H_4$ [$NC_3H_6C_6H_4$ is1,2,3,4-dihydroisoquinoline-2-yl] **6**, (CH_2Ph)$_2$ **7**, (Me)Ph **8**) were prepared by the reaction of [Cu(NCMe)$_4$][BF_4] with HC(3,5-Me_2pz)$_3$ and $NCNR_2$ (CH_2Cl_2, 20–25 °C) and these species were characterized by C, H, N analyses, high resolution mass-spectrometry with electrospray ionization, ^{1}H, ^{13}C{^{1}H} NMR and FTIR spectroscopic techniques, molar conductivity measurements, thermogravimetry/differential thermal analysis, and also by single-crystal X-ray diffraction for **3**. The theoretical topological analysis of the electron density distribution (QTAIM method) together with the NBO analysis were applied to study the nature of Cu–N and Cu–C coordination bonds in [Cu{HC(3,5-Me_2pz)$_3$}($NCNMe_2$)]$^+$, [Cu{HC(3,5-Me_2pz)$_3$}(NCMe)]$^+$, and [Cu{HC(3,5-Me_2pz)$_3$}(CNMe)]$^+$ model species. The nature of Cu–N coordination bonds in [Cu{HC(3,5-Me_2pz)$_3$}($NCNMe_2$)]$^+$ and [Cu{HC(3,5-Me_2pz)$_3$}(NCMe)]$^+$ is very similar, whereas Cu–C contact in [Cu({HC(3,5-Me_2pz)$_3$}(CNMe)]$^+$ is relatively more covalent. The calculated vertical total energies for the Cu–N and Cu–C coordination bonds cleavage increase in the following row: $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCMe)]^+$ (36 kcal/mol) < $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNMe_2)]^+$ (41 kcal/mol) < $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(CNMe)]^+$ (47 kcal/mol), and these theoretical data are coherent with the experimental observations.

Keywords:

Tris-pyrazolylmethane complexes, copper(I), dialkylcyanamide ligands, QTAIM method, NBO analysis

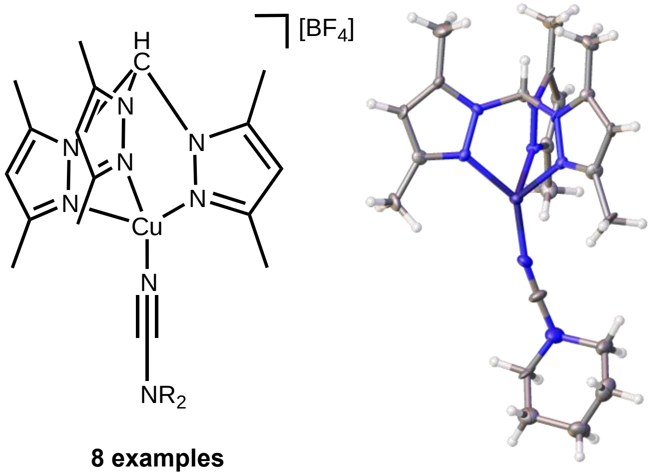
Highlights

Eight examples of mononuclear dialkylcyanamide complexes $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNR_2)][BF_4]$

X-ray diffraction Structure of $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNC_5H_{10})][BF_4]$

Comparison of the nature of metal-ligand bond in $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNR_2)][BF_4]$ and $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(CNR)][BF_4]$ using QTAIM method and NBO analysis

Graphical Abstract



8 examples

Introduction

Metal-activated cyanamide ligands $NCNR_2$ exhibit enhanced reactivity relatively to nitriles NCR (R = alkyl, aryl). Thus, disubstituted cyanamides are involved in various types of nucleophilic additions and 1,3-dipolar cycloadditions (see reviews [1, 2]) that are not feasible for NCR's. For example, we demonstrated that copper(I) complexes catalyze the 1,3-dipolar cycloaddition between ketonitrones and disubstituted cyanamides. Notably, this was the first example of a metal catalyzed cycloaddition reaction to afford 2,3-dihydro-1,2,4-oxadiazoles [3]. In continuation of that work, we studied plausible intermediates of the addition and synthesized homoleptic *tetrakis*-cyanamide copper(I) complexes $[Cu(NCNR_2)_4][BF_4]$ [4]. It is noteworthy that apart from these $[Cu(NCNR_2)_4]^+$ species, only one example of mononuclear copper complex featuring disubstituted cyanamide was known before this work, viz. $[Cu(NCNMe_2)_2(DPEphos)[BF_4]$ (DPEphos is bis[2-diphenylphosphino)phenyl]-ether) [5], and mononuclear $(NCNR_2)Cu$ complexes were not reported. Hence, information on structural types of copper(I/II) complexes with disubstituted cyanamides is quite scarce and insufficient for further development of their chemistry.

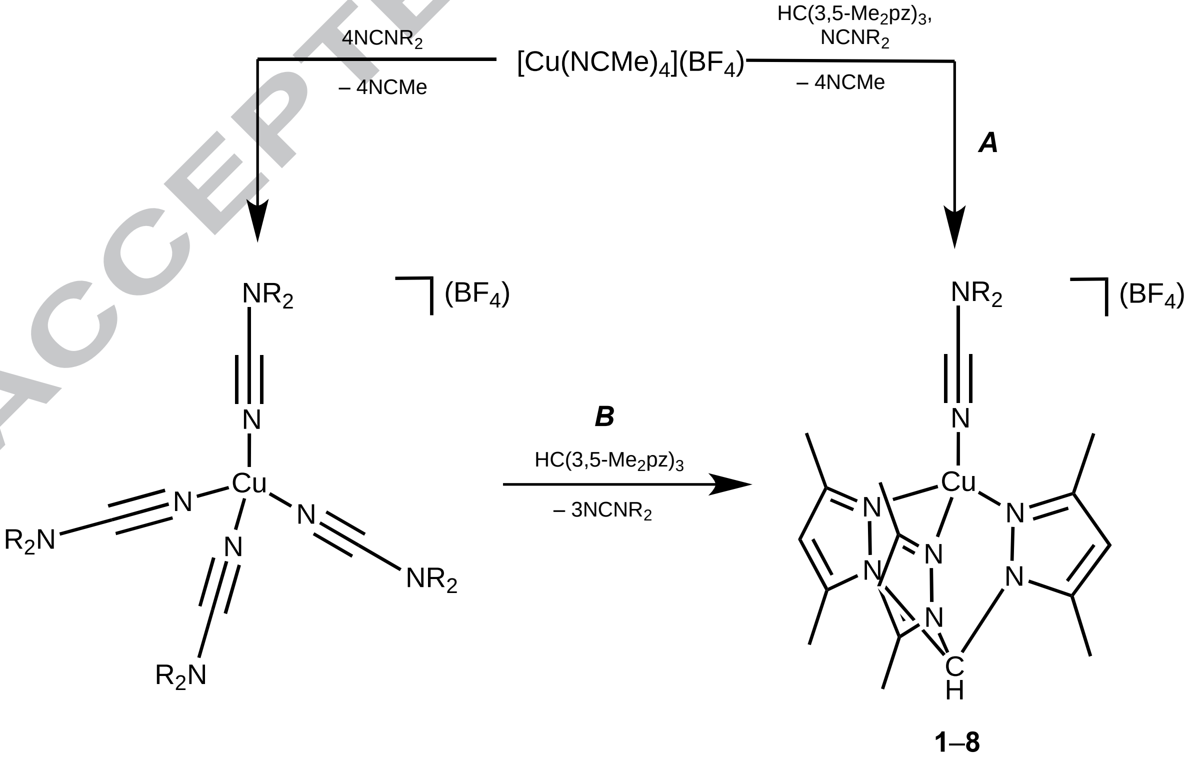
Recently, we reported on the synthesis and structural studies of copper(I) complexes with one isocyanide ligand CNR, *viz.* $[Cu\{HC(3,5-Me_2pz)_3\}(CNR)][BF_4]$ ($\{HC(3,5-Me_2pz)_3\}$ = tris(3,5-dimethylpyrazolyl)methane) and studied their structural features [6]. Species with the $\{[HC(3,5-Me_2pz)_3]Cu\}$ moiety can serve as a convenient model to prepare complexes bearing only one dialkylcyanamide ligand. It is noteworthy that some mononuclear 6–8 and 10 groups transition metal complexes bearing one cyanamide ligand $(NCNR_2)M$ were synthesized and characterized by X-ray diffraction study, viz. $[Cr(CO)_5(NCNEt_2)]$ [7], $[Mo\{N(3,5-Me_2C_6H_3)(^tBu)\}_3(\eta^2-NCNMe_2)]$ [8], $[Mo(Ph_2PC_2H_4PPh_2)_2(N_2)(NCNEt_2)]$ [9], $[W(CO)_3(P^iPr_3)_2(NCNMe_2)]$ [10], $[MnCp(CO)_2(NCNMe_2)]$ [11], $[Mn(CO)_2\{PPh(OEt)_2\}_3(NCNEt_2)][BPh_4]$ [12], $[ReCl_2(PPh_2Me)_3(NCNEt_2)]$ [13], $[Ru\{P(OEt)_3\}_4(NH_2{}^iPr)(NCNEt_2)][BPh_4]$ [14], $[RuCl_2(bpy)(CO)(NCNR_2)]$ (R_2 = Me_2, Et_2) [15], $[Os\{P(OEt)_3\}_4\{NH_2{}^iPr\}\{NCNEt_2\}][BPh_4]$ [14], $[PtCl_2(Me_2SO)(NCNR_2)]$ (R_2 = Me_2, C_5H_{10}) [16], $[Pt(Ph)(PPh_3)_2(NCNMe_2)](BPh_4)\bullet Et_2O$ [17], $[Pt(CF_3)(PPh_3)_2(NCNEt_2)][BF_4]$ [18], and $[Ph_3PCH_2Ph][PtCl_3(NCNMe_2)]$ [19]. It is important to note that not a single example of such monomeric copper complex, bearing one $NCNR_2$, was reported until our recent work.

The goal of this work was at least two-fold. First, we aimed to synthesize and characterize mononuclear cationic copper(I) complexes $[Cu(L)(NCNR_2)][BF_4]$ (L = tridentate ligand, e.g. tris(3,5-dimethylpyrazolyl)methane abbreviated as $\{HC(3,5-Me_2pz)_3\}$) featuring one disubstituted cyanamide. These copper species could be interesting for the study of stoichiometric reactions involving copper(I) center-bound cyanamides. Secondly, we planned to compare the structural features and chemical properties of these types of complexes with the relevant nitrile $[Cu\{HC(3,5-Me_2pz)_3\}(NCMe)]^+$ [20] and isocyanide analogues $[Cu\{HC(3,5-Me_2pz)_3\}(CNR)]^+$ [6].

In this work, we compare the reactivity of conventional nitrile NCR and disubstituted cyanamide ligands $NCNR_2$. Both disubstituted cyanamides and nitriles coordinate to a metal center in their neutral form. In contrast, unsubsituted cyanamide $NCNH_2$ and monosubstituted NCNHR tend to be deprotonated upon coordination to a metal centers and form anionic heterocumulene ligands, e.g. $NCNR^{-}$,[21] which structure are different from coordinated $NCNR_2$'s.

Results and discussion

The mixed-ligand $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNR_2)][BF_4]$ species (**1**–**8**; $R_2 = Me_2$ **1**, Et_2 **2**, C_5H_{10} **3**, C_4H_8O **4**, C_4H_8 **5**, $C_3H_6C_6H_4$ [$NC_3H_6C_6H_4$ is 1,2,3,4-dihydroisoquinoline-2-yl] **6**, $(CH_2Ph)_2$ **7**, (Me)Ph **8**) were synthesized by two methods (**Scheme 1**). In the first synthetic route, CH_2Cl_2 solutions of $HC(3,5\text{-}Me_2pz)_3$ and $[Cu(NCMe)_4][BF_4]$ were combined in a 1:1 ratio, followed by addition of 1 equivalent of $NCNR_2$ ($R_2 = Me_2$, Et_2, C_5H_{10}, C_4H_8O, C_4H_8, $C_3H_6C_6H_4$, $(CH_2Ph)_2$, (Me)Ph). Compounds **1**–**8** were isolated in good to excellent yields (93–96%; **Scheme 1**, ***A***). An alternative method consists of addition of CH_2Cl_2 solutions of $HC(3,5\text{-}Me_2pz)_3$ to CH_2Cl_2 solutions of $[Cu(NCNR_2)_4][BF_4]$[4] in a 1 : 1 molar ratio (**Scheme 1**, ***B***) at room temperature. The former high-yielding method is easier and it is recommended for synthesis of **1**–**8**.



1–**8**

Scheme 1. Synthesis of (dialkylcyanamide)copper(I) complexes **1**–**8**.

All complexes were characterized by C, H, N analyses, high resolution mass-spectrometry with electrospray ionization, ^{1}H, ^{13}C{^{1}H} NMR and FTIR spectroscopic techniques, molar conductivity measurements, thermogravimetry/differential thermal analysis, and also by single-crystal X-ray diffraction (for **3**). Microanalytical data for **1**–**8** are in good agreement with the calculated values. High-resolution mass-spectra of **1**–**8** exhibit sets of peaks corresponding to the molecular ions $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNR_2)]^+$ with characteristic isotopic pattern. The FTIR spectra of **1**–**8** in KBr display two C≡N absorption bands in the range 2240–2250 cm^{-1} and 2210–2225 cm^{-1}, which is apparently due to the decomposition of the complexes in KBr pellet. In Nujol oil, **1**–**3** display one broad band of υ(C≡N) in the region 2240–2250 cm^{-1}, **5**–**8** demonstrate one broad bond with a shoulder at 2240–2260 cm^{-1}, and **4** displays two bands 2250 and 2240 cm^{-1}. All these bands are moderately high-frequency shifted (20–30 cm^{-1}) from those in the corresponding uncomplexed dialkylcyanamide (2210–2225 cm^{-1}).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**–**8** exhibit signals from one $HC(3,5\text{-}Me_2pz)_3$ and from two R groups in the $NCNR_2$ ligands. The values of molar conductivities in nitromethane (73–90 Ohm^{-1} cm^{-1} mol^{-1}) for **1**–**8** agree well with the typical range for 1:1 electrolytes (75–95 Ohm^{-1}cm^{-1}mol^{-1}) in this solvent [22]. The thermogravimetry/differential thermal analysis data (**Figures S42–S49** and **Table S1**) demonstrate that mass loss starts in the interval ca. 130–150 °C due to the extrusion of $NCNR_2$. The mass of the final product (610 °C) corresponds to CuF_2 (**2**–**5**) or Cu (**1**), or does not correspond to any stoichiometry of the proposed final products (**6**–**8**).

Single-crystal X-ray diffraction studies were performed for **3** (**Figure 1**). This species is the first example of a crystallographically characterized monomeric copper(I) complex of the type $[Cu(L)(NCNR_2)][BF_4]$ (L = *tris*-pyrazolylmethane or *tris*-pyrazolylborate-based ligand) bearing one metal center-bound cyanamide. The coordination polyhedron, distorted tetrahedron, of **3** is formed by one dialkylcyanamide ligand and one $\{HC(3,5\text{-}Me_2pz)_3\}$. The τ_4 parameter 0.69 indicates a significant deviation from the ideal (τ_4 1.0) [23] tetrahedral geometry. The N–Cu–N angles are restrained by the chelate rings to *ca*. 88° (from 86.9(3) to 88.9(3)°) and the N–Cu–N angles from the N atoms of {HC(3,5-$Me_2pz)_3$} to the N atom of a dialkylcyanamide span the interval from 116.2(3) to 139.6(3)°. The Cu–N distances (N of {HC(3,5-$Me_2pz)_3$} ligand), that range from 2.046(8) to 2.138(7) Å, are close to the Cu–N bond values in [Cu{HC(3,5-$Me_2pz)_3$}(NCMe)][BF_4] (2.080(4)–2.0893 Å).[24] The Cu–N(1) bond length (1.883(8) Å) is equal within 3σ to those in [Cu{HC(3,5-$Me_2pz)_3$}(NCMe)][BF_4] (1.865(4) Å) [24]. The nitrile C≡N bond length (1.147(13) Å) in the $NCNC_5H_{10}$ ligand exhibits a value comparable with those in [Cu{HC(3,5-$Me_2pz)_3$}(NCMe)][BF_4] (1.137(7)Å) [24], the Cu–N–C angle (167.0(9)°) is non-linear and N–C–N (177.0(12)°) is close to the linear.

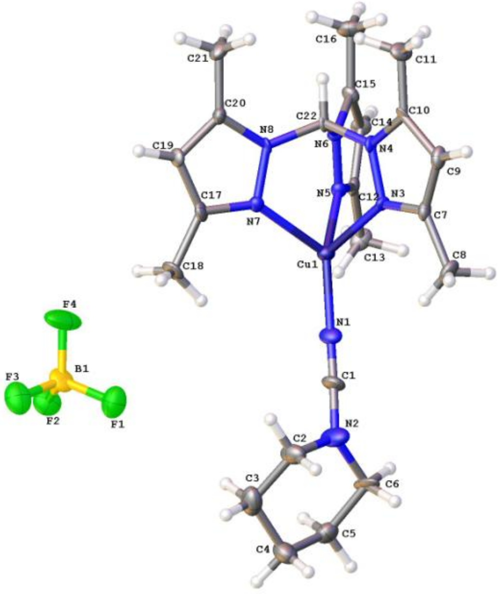


Figure 1. Molecular structure of **3** at 100 K with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Nitrile complexes of the type [CuL(NCMe)][X]$_n$ (L = *tris*-pyrazolylmethane, n = 1, or *tris*-pyrazolylborate-based ligands, n = 0; X = BF_4, PF_6) are known. These species were synthesized by (i) the addition of L (L = *tris*-pyrazolylmethane or *tris*-pyrazolylborate-based species) to a solution of [Cu(NCMe)$_4$]X (X = BF_4 or PF_6) either at room temperature in CH_2Cl_2, acetone, or CH_2Cl_2/MeCN for 1–24 h under argon or (ii) in MeOH upon reflux for 2 h [25-29]. Typically complexes of this type are relatively stable in air, and, in particular, the complexes

$[Cu\{HC(Rpz)_3\}(NCMe)](PF_6)$ (Rpz = 3-Butpz, 3-Phpz, 3,5-Me_2pz; pz - pyrazolyl) are moderately air stable even in solutions [26]. Bubbling dioxygen into CH_2Cl_2 solutions of the complexes at –78 °C provides no color change although a faint green solution results upon warming to room temperature [26]. At the same time, some other authors [29] reported that $[Cu\{HC(Rpz)_3\}(NCMe)][PF_6]$ (Rpz = 3,5-Me_2pz, 3,5-Me_2-4-Brpz) are rapidly (within a few min) oxidized by O_2 at 7 °C in a CH_2Cl_2 solution. The complexes [Cu(L)(NCMe)]X (L= tris(3,5-diisopropyl-1-pyrazolyl)methane; X = ClO_4, PF_6) are relatively stable toward O_2 [27], and $[Cu(HCpz_3)(NCMe)][BF_4]$ is a shelf-stable monomeric species [25]. Some works [27, 28] describe low to moderate stability of these complexes, e.g. $[CuL(NCMe)][BF_4]$ (L = tris(3-isopropyl-4,5-trimethylenepyrazolyl)methane [28] or hydrotris(3,5-diisopropyl-1-pyrazolyl)borate [27]) are very air-sensitive species.

Complexes **1**–**8** demonstrated air instability both in solution and in the solid state. For example, these species start to decompose after 15–30 minutes at room temperature in $CDCl_3$ or CD_2Cl_2 to give the known *bis*-ligated complex, $[Cu\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$ [30] (identified by X-ray diffraction study, see Supplementary Materials), free $NCNR_2$ (identified by ^{1}H NMR) and an unidentified copper species. Moreover, our attempts to crystallize **4** from a CH_2Cl_2 solution in air for 1 day led to formation of the crystalline copper(II) dimer $[Cu_2(\mu\text{-}OH)_2\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2\bullet 2CH_2Cl_2$ (**9**$\bullet 2CH_2Cl_2$), whose structure was determined by X-ray diffraction study (see **Figure 2** and **ESI** for the details).

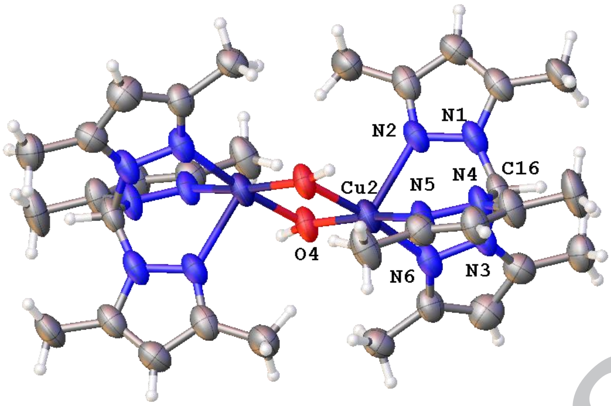


Figure 2. Molecular structure of **9**•2CH_2Cl_2 at 100 K with the atomic numbering scheme; BF_4^- and the two CH_2Cl_2 molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

The facile oxidation of the acetonitrile analog [Cu{HC(3,5-Me_2pz)$_3$}(NCMe)][PF_6] by O_2 to yield the dimeric [Cu_2(μ-OH)$_2${HC(3,5-Me_2pz)$_3$}$_2$][PF_6]$_2$ is known [29]. In the solid state, **6**–**8** gradually turn from colorless to green at room temperature for 1–2 days in air, whereas **1**–**5** demonstrate less stability and become greenish-beige color immediately after preparation. Therefore, we can propose that our complexes **1**–**8**, due to the weakness of Cu–N(cyanamide) bond and kinetic lability, undergo fast $NCNR_2$ ligand dissociation/substitution with formation of some intermediate complexes that can be easily oxidized in air forming the copper(II) species [Cu{HC(3,5-Me_2pz)$_3$}$_2$][BF_4]$_2$ and [Cu_2(μ-OH)$_2${HC(3,5-Me_2pz)$_3$}$_2$][BF_4]$_2$. Notably, the isocyanide analogues [Cu{HC(3,5-Me_2pz)$_3$}(CNR)][BF_4] demonstrate greater stability and exhibit relatively strong Cu–C bonds (*ca*. 50 kcal•mol^{-1} based on DFT calculations) [6].

Theoretical study of the nature and energies of Cu–N and Cu–C coordination bonds in [Cu{HC(3,5-Me_2pz)$_3$}L]$^+$ (L = $NCNMe_2$, NCMe, CNMe) model species. Additional information on the binding in metal complexes can be obtained by the theoretical topological analysis of the electron density distribution (QTAIM method) [31] together with the Natural Bond Orbital (NBO) analysis [32, 33]. This integrated approach has already been successfully used by us [4, 6, 34, 35], and in the present work we applied these methods to study the nature of Cu–N and Cu–C coordination bonds in $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNMe_2)]^+$, $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCMe)]^+$, and $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(CNMe)]^+$ model species.

The main results of the topological analysis of the electron density distribution and values of the Wiberg bond indices (bond orders) [36] was computed using the NBO partitioning scheme for the Cu–N and Cu–C coordination bonds in optimized equilibrium geometries of $[Cu(\{HC(3,5\text{-}Me_2pz)_3\}L]^+$ (L = $NCNMe_2$, NCMe, CNMe) model species are presented in **Table 1**. The Poincare-Hopf relationship (criterion that show that all critical points were determined) was satisfied in all cases.

Table 1. Results of the topological analysis of the electron density distribution and values of the Wiberg bond indices for the Cu–N and Cu–C coordination bonds in optimized equilibrium geometries of $[Cu\{HC(3,5\text{-}Me_2pz)_3\}L]^+$ (L = $NCNMe_2$, NCMe, CNMe) model species.*

Model species	$\rho(\mathbf{r})$, e/Å^3	$\nabla^2\rho(\mathbf{r})$, e/Å^5	H_b, Hartree/Å^3	ε	WI
$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNMe_2)]^+$	0.611	15.232	-0.067	0.007	0.39
$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCMe)]^+$	0.611	15.352	-0.067	0.000	0.39
$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(CNMe)]^+$	0.719	13.773	-0.161	0.001	0.69

***** $\rho(\mathbf{r})$ – density of all electrons, $\nabla^2\rho(\mathbf{r})$ – Laplacian of electron density, H_b – energy density, ε – ellipticity of electron density, WI – Wiberg bond indices. Results in this table refer to zero Kelvin temperature.

In all cases, we found the suitable bond critical points (3, –1) for the Cu–N and Cu–C contacts, where the electron density falls down in two perpendicular directions of space and rises in the third direction. The values of $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, and H_b parameters in these bond critical points (3, –1) are typical for closed-shell interactions. The ellipticity of electron density (parameter provides a quantitative measurement of the anisotropy of the electron density and associated to the π character of bonds) in these bond critical points (3, –1) is low (not exceeding 0.007) confirming the single bond character of these contacts. It can be concluded that the nature of Cu–N coordination bonds in $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNMe_2)]^+$ and $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCMe)]^+$ is very similar, whereas Cu–C contact in $[Cu\{HC(3,5\text{-}Me_2pz)_3\}$ $(CNMe)]^+$ is relatively more covalent. The calculated vertical total energies for the Cu–N and Cu–C coordination bonds cleavage, computed as difference between the total electronic energies of optimized structures of complexes M–L and total electronic energies of frozen geometries of parts M and L, increase in the following order: $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCMe)]^+$ (36.10(1) kcal/mol) < $[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNMe_2)]^+$ (41.39(1) kcal/mol) <

[Cu{HC(3,5-Me_2pz)$_3$}(CNMe)]$^+$ (47.05(1) kcal/mol), and these theoretical data are coherent with the experimental observations, viz. greater stability of isocyanide complexes [Cu{HC(3,5-Me_2pz)$_3$}(CNR)][BF_4][6] both in solution and in the solid state compared to the acetonitrile and dialkylcyanamide analogues [Cu{HC(3,5-Me_2pz)$_3$}(NCR)][BF_4] (R = Me, NR'$_2$).

Conclusions

In this study, we succeeded in synthesizing a new type of mononuclear (cyanamide)Cu^I complex, viz. the cationic monocyanamide [Cu{HC(3,5-Me_2pz)$_3$}(NCNR_2)] BF_4] species. These complexes demonstrate air instability both in solution and in the solid state and undergo spontaneous oxidation in air giving [Cu{HC(3,5-Me_2pz)$_3$}$_2$][BF_4]$_2$ and [Cu_2(μ-OH)$_2${HC(3,5-Me_2pz)$_3$}$_2$][BF_4]$_2$. Similar behavior is demonstrated as with some nitrile complexes of the type [CuL(NCMe)]X, which can be easily oxidized by O_2 [20]. By contrast, results of our previous work [6] revealed that isocyanide complexes of the same type, [Cu{HC(3,5-Me_2pz)$_3$}(CNR)][BF_4], are more stable in solutions and also as solids.

As can be inferred from inspection of the theoretical data, the Cu–N bond in [Cu{HC(3,5-Me_2pz)$_3$}(NCNMe_2)]$^+$ and [Cu{HC(3,5-Me_2pz)$_3$}(CNMe)]$^+$ demonstrate relatively less covalent character than the Cu–C bond in [Cu{HC(3,5-Me_2pz)$_3$}(CNMe)]$^+$. The calculated vertical total energies for the Cu–N and Cu–C coordination bonds cleavage increase in the following row: [Cu{HC(3,5-Me_2pz)$_3$}(NCMe)]$^+$ < [Cu{HC(3,5-Me_2pz)$_3$}(NCNMe_2)]$^+$ < [Cu{HC(3,5-Me_2pz)$_3$}(CNMe)]$^+$, suggesting greater stability of the isocyanide complexes [Cu{HC(3,5-Me_2pz)$_3$}(CNR)][BF_4] [6] compared to the acetonitrile and dialkylcyanamide analogues [Cu{HC(3,5-Me_2pz)$_3$}(NCR)][BF_4] (R = Me, NR'$_2$), which is in accord with the experimental observations.

Experimental Section

Materials and Instrumentations. The diakylcyanamides NCNR$_2$ (R$_2$ = Me$_2$, Et$_2$, C$_5$H$_{10}$, C$_4$H$_8$O, C$_4$H$_8$; Aldrich) and solvents were obtained from commercial source and used as received. The cyanamides NCN(CH$_2$Ph)$_2$, NCN(Me)Ph, NCNC$_3$H$_6$C$_6$H$_4$ [1,2,3,4-dihydroisoquinoline-2-ylcarboxamide]],[37] the copper(I) complex [Cu(NCMe)$_4$][BF$_4$],[38] and HC(3,5-Me$_2$pz)$_3$ [39] were synthesized in accord with the published procedures. The high resolution mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization source (HRESI$^+$ MS) and MeOH was employed as the solvent. The instrument was operated in positive ion mode using an *m/z* range of 50–3000. The capillary voltage of the ion source was set at –4500 V (positive mode mass-spectrometry) and the capillary exit ±(70–150) V. In the isotopic pattern, the most intense peak is reported. Infrared spectra were recorded using a Bruker FTIR TENSOR 27 instrument in KBr pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Bruker Avance III 400 spectrometer at ambient temperature. Residual solvent signals were used as the internal standard. Microanalyses (C, H, N) were carried out on a Euro EA3028-HT instrument. Molar conductivities were measured with a Mettler Toledo meter FE30/FG3 in a solution of nitromethane (molar concentrations were 2.0–5.5•10^{-4} mol/L) at room temperature. The thermogravimetry/differential thermal analysis (**Figures S42–S49**) were performed with a NETZSCH TG 209 F1 Libra thermoanalyzer and MnO$_2$ powder was used as a standard. The initial weights of the samples were in the range 1.1–2.3 mg. The experiments were run in an open aluminum crucible in a stream of argon at a heating rate of 10 K/min. The final temperature was 610 °C. Processing of the thermal data was performed with Proteus analysis software [40].

X-ray structure determinations. Suitable crystals of **3** and **9** were measured at Agilent Technologies SuperNova and Xcalibur Eos diffractometers at a temperature of 100K using monochromated CuKα radiation. All structures have been solved by the direct methods by means of the SHELX program [41] incorporated in the OLEX2 program package [42]. For crystallographic data and refinement parameters see **ESI**. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the ‘riding’ model approximation, with U_{iso}(H) set to 1.5U_{eq}(C) and C–H 0.98 Å for CH_3 groups, with U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.97 Å for CH_2 groups, with U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.95 Å for CH groups and with U_{iso}(H) set to 1.5U_{eq}(O) and O–H 0.98 Å for OH-groups. Empirical absorption correction was applied in CrysAlisPro [43] program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The crystal structure of **9** contained disordered molecules of solvent that have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON program [44]. The high values of the some refinement parameters of structures (large *R*-values for all structures; large values of anisotropic displacement parameters for **9**) and relatively low bonds precision in the structural model (for **3**) are because of insufficient quality of the studied crystals. Although some refinement parameters are not perfect, the structural models in their principal features are correct. The following refinement restraints were used: for **3** Uanis(N7) = Uanis(N5); for **9** restrained some distances (O1_$1–H1_$1, O1A–H1A, Cu1–H1 Cu1A–H1A, Cu1A_$2–H1A, where 1 is 1-X,1-Y,2-Z and 2 is 2-X,2-Y,1-Z). Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (1442806 for **3**, 1817364 for **9**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Computational details. The full geometry optimization of $[Cu(\{HC(3,5\text{-}Me_2pz)_3\}L]^+$ (L = $NCNMe_2$, NCMe, CNMe) model species has been carried out at the M06/LanL2DZ level of theory with the help of *Gaussian-09* program package [45]. No symmetry restrictions have been applied during the geometry optimization procedure. In all cases the Hessian matrix was calculated analytically in order to prove the location of correct minima (no imaginary frequencies). The topological analysis of the electron density distribution with the help of the atoms in molecules method (QTAIM) has been carried out by using the Multiwfn program [46]. The Cartesian atomic coordinates for optimized equilibrium geometries of all model species are presented in **Table S5** (**ESI**).

Synthesis of [Cu{HC(3,5-Me$_2$pz)$_3$}(NCNR$_2$)][BF$_4$] (**1**–**8**). *Method A*: A solution of HC(3,5-Me$_2$pz)$_3$ (47.4 mg, 0.159 mmol) in CH$_2$Cl$_2$ (1 mL) was added under vigorous stirring to a solution of [Cu(NCMe)$_4$][BF$_4$] (50 mg, 0.159 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting transparent yellow reaction mixture was stirred for 30 min at room temperature, whereupon any one of NCNR$_2$ (R$_2$ = Me$_2$, Et$_2$, C$_5$H$_{10}$, C$_4$H$_8$O, C$_4$H$_8$, C$_3$H$_6$C$_6$H$_4$, (CH$_2$Ph)$_2$, (Me)Ph; 0.159 mmol) was added to the solution, stirred for 30 min and then the solvent was evaporated at room temperature in vacuum to dryness and washed with Et$_2$O (2 mL) to give in each case a pale greenish-beige crystalline solid. *Method B*: A solution of HC(3,5-Me$_2$pz)$_3$ (15 mg, 0.051 mmol) in CH$_2$Cl$_2$ (1 mL) was added to a solution of [Cu(NCNMe$_2$)$_4$][BF$_4$] (30 mg, 0.051 mmol) in CH$_2$Cl$_2$ (5 mL) under vigorous stirring. The resulting transparent reaction mixture was stirred for 1 h at room temperature and then the solvent was evaporated at room temperature in vacuum to dryness, washed with diethyl ether (2 mL) to give a pale beige crystalline solid.

[Cu{HC(3,5-Me$_2$pz)$_3$}(NCNMe$_2$)][BF$_4$] (**1**). Yield 79 mg, 96%. Anal. Calcd for C$_{19}$H$_{28}$N$_8$BCuF$_4$: C, 43.98; H, 5.44; N, 21.60%. Found: C, 43.85; H, 5.23; N, 21.56%. HRESI$^+$-MS, *m/z*: 431.1711 ([M]$^+$, calcd 431.1722). IR spectrum in KBr, selected bands, cm^{-1}: 2215, 2252 s *v*(N≡C). ^{1}H NMR in CD$_2$Cl$_2$, δ: 2.32 (s, 9H, Me), 2.54 (s, 9H, Me), 3.04 (s, 6H, NMe$_2$), 6.01 (s, 3H, CH$_{pyrazolyl}$), 7.74 (s, 1H, CH). ^{13}C{^{1}H} NMR in CD$_2$Cl$_2$, δ: 10.7 (Me), 13.3 (Me), 40.09 (NMe$_2$), 67.6 (CH), 106.6 (CH$_{pyrazolyl}$), 139.8, 150.7 (C$_{pyrazolyl}$), NCN was not detected. Λ_m = 82 Ohm^{-1} cm^{-1} mol^{-1}.

[Cu{HC(3,5-Me$_2$pz)$_3$}(NCNEt$_2$)][BF$_4$] (**2**). Yield 82 mg, 94%. Anal. Calcd for C$_{21}$H$_{32}$N$_8$BCuF$_4$: C, 46.12; H, 5.90; N, 20.49%. Found: C, 45.95; H, 5.72; N, 20.20 %. HRESI$^+$-MS, *m/z*: 459.2036 ([M]$^+$, calcd 459.2035). IR spectrum in KBr, selected bands, cm^{-1}: 2209, 2251 s *v*(N≡C). ^{1}H NMR in CD$_2$Cl$_2$, δ: 1.39 (t, 6H, Et), 2.32 (s, 9H, Me), 2.54 (s, 9H, Me), 3.25 (q, 4H, Et), 6.01 (s, 3H, CH$_{pyrazolyl}$), 7.75 (s, 1H, CH$_{pyrazolyl}$). ^{13}C{^{1}H} NMR in CD$_2$Cl$_2$, δ: 10.7 (Me), 12.7 (Et), 13.32 (Me), 46.1 (Et), 67.6 (CH), 106.6 (CH$_{pyrazolyl}$), 139.8, 150.6 (C$_{pyrazolyl}$), NCN was not detected. Λ_m = 90 Ohm^{-1} cm^{-1} mol^{-1}.

$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNC_5H_{10})][BF_4]$ (**3**). Yield 85 mg, 96%. Anal. Calcd for $C_{22}H_{32}N_8BCuF_4$: C, 47.28; H, 5.77; N, 20.05%. Found: C, 47.40; H, 5.69; N, 20.01%. HRESI$^+$-MS, *m/z*: 471.2037 ($[M]^+$, calcd 471.2035). IR spectrum in KBr, selected bands, cm^{-1}: 2209, 2242 s $\nu(N{\equiv}C)$. ^1H NMR in CD_2Cl_2 δ: 1.67 (m, 2H, C_5H_{10}), 1.74 (m, 4H, C_5H_{10}), 2.32 (s, 9H, Me), 2.54 (s, 9H, Me), 3.34 (q, 4H, C_5H_{10}), 6.01 (s, 3H, $CH_{pyrazolyl}$), 7.74 (s, 1H, CH). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 10.7 (Me), 13.3 (Me), 22.8 (C_5H_{10}), 24.7 (C_5H_{10}), 50.1 (C_5H_{10}), 67.6 (CH), 106.56 ($CH_{pyrazolyl}$), 139.8, 150.6 ($C_{pyrazolyl}$), NCN was not detected. Λ_m = 87 Ohm^{-1} cm^{-1} mol^{-1}. Crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of the reaction mixture at room temperature.

$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNC_4H_8O)][BF_4]$ (**4**). Yield 85 mg, 96%. Anal. Calcd for $C_{21}H_{30}N_8OBCuF_4$: C, 44.97; H, 5.39; N, 19.98%. Found: C, 44.79; H, 5.46; N, 19.81%. HRESI$^+$-MS, *m/z*: 473.1823 ($[M]^+$, calcd 473.1828). IR spectrum in KBr, selected bands, cm^{-1}: 2216, 2248 s $\nu(N{\equiv}C)$. ^1H NMR in $CDCl_3$, δ: 2.28 (s, 9H, Me), 2.57 (s, 9H, Me), 3.30 (q, 4H, C_4H_8O), 3.83 (q, 4H, C_4H_8O), 5.91 (s, 3H, $CH_{pyrazolyl}$), 7.82 (s, 1H, CH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, 10.9 (Me), 13.7 (Me), 48.5 (C_4H_8O), 65.6 (C_4H_8O), 67.8 (CH), 106.6 ($CH_{pyrazolyl}$), 140.4, 150.4 ($C_{pyrazolyl}$), NCN was not detected. Λ_m = 73 Ohm^{-1} cm^{-1} mol^{-1}.

$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNC_4H_8)][BF_4]$ (**5**). Yield 83 mg, 96%. Anal. Calcd for $C_{21}H_{30}N_8BCuF_4$: C, 46.29; H, 5.55; N, 20.57%. Found: C, 46.20; H, 5.72; N, 20.53%. HRESI$^+$-MS, *m/z*: 457.1876 ($[M]^+$, calcd 457.1879). IR spectrum in KBr, selected bands, cm^{-1}: 2208, 2242 s $\nu(N{\equiv}C)$. ^1H NMR in $CDCl_3$, δ: 2.02 (v, 4H, C_4H_8), 2.28 (s, 9H, Me), 2.58 (s, 9H, Me), 3.60 (q, 4H, C_4H_8), 5.91 (s, 3H, $CH_{pyrazolyl}$), 7.84 (s, 1H, CH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.9 (Me), 13.7 (Me), 25.9 (C_4H_8), 67.8 (CH), 106.6 ($CH_{pyrazolyl}$), 140.5, 150.4 ($C_{pyrazolyl}$), NCN was not detected. Λ_m = 85 Ohm^{-1} cm^{-1} mol^{-1}.

$[Cu\{HC(3,5\text{-}Me_2pz)_3\}(NCNC_3H_6C_6H_4)][BF_4]$ (**6**). Yield 90 mg, 93%. Anal. Calcd for $C_{26}H_{32}N_8BCuF_4$: C, 51.45; H, 5.31; N, 18.46%. Found: C, 51.51; H, 5.38; N, 18.29%. HRESI$^+$-MS, *m/z*: 519.2034 ($[M]^+$, calcd 519.2035). IR spectrum in KBr, selected bands, cm^{-1}: 2214, 2248 s *ν*(N≡C). ^{1}H NMR in CDCl$_3$, δ: 2.28 (s, 9H, Me), 2.58 (s, 9H, Me), 3.06 (m, 2H, CH$_2$), 3.67 (m, 2H, CH$_2$), 4.59 (m, 2H, CH$_2$), 5.92 (s ,3H, CH$_{pyrazolyl}$), 7.13–7.35 (m, 4H, C$_6$H$_4$), 7.84 (s, 1H, CH$_{pyrazolyl}$). ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 10.9 (Me), 13.7 (Me), 27.7 (CH$_2$), 67.8 (CH), 106.6 (CH$_{pyrazolyl}$), 126.0, 127.0, 127.6, 129.3, 132.4 (C$_6$H$_4$), 140.5, 150.4 (C$_{pyrazolyl}$), NCN was not detected. Λ_m = 80 Ohm^{-1} cm^{-1} mol^{-1}.

[Cu{HC(3,5-Me$_2$pz)$_3${NCN(CH$_2$Ph)$_2$}][BF$_4$] (**7**). Yield 101 mg, 95%. Anal. Calcd for C$_{31}$H$_{36}$N$_8$BCuF$_4$: C, 55.49; H, 5.41; N, 16.70%. Found: C, 55.47; H, 5.35; N, 16.61%. HRESI$^+$-MS, *m/z*: 583.2347 ([M]$^+$, calcd 583.2348). IR spectrum in KBr, selected bands, cm^{-1}: 2210, 2239 s *ν*(N≡C). ^{1}H NMR in CDCl$_3$ δ: 2.14 (s, 9H, Me), 2.57 (s, 9H, Me), 4.36 (m, 4H, CH$_2$), 5.89 (s, 3H, CH$_{pyrazolyl}$), 7.29–7.41 (m, 10H, Ph), 7.81 (s, 1H, CH$_{pyrazolyl}$). ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 10.9 (Me), 13.6 (Me), 67.8 (CH), 106.5 (CH$_{pyrazolyl}$), 128.8, 129.1, 133.6 (C$_6$H$_4$), 140.5, 150.3 (C$_{pyrazolyl}$), CH$_2$ and NCN were not detected. Λ_m = 86 Ohm^{-1} cm^{-1} mol^{-1}.

[Cu{HC(3,5-Me$_2$pz)$_3$}(NCNMePh)][BF$_4$] (**8**). Yield 74 mg, 94%. Anal. Calcd for C$_{24}$H$_{30}$N$_8$BCuF$_4$: C, 49.62; H, 5.21; N, 19.29%. Found: C, 49.55 ; H, 5.31; N, 19.18 %. HRESI$^+$-MS, *m/z*: 493.1899 ([M]$^+$, calcd 493.1879). IR spectrum in KBr, selected bands, cm^{-1}: 2214, 2251 s *ν*(N≡C). ^{1}H NMR in CDCl$_3$, δ: 2.32 (s, 9H, Me), 2.60 (s, 9H, Me), 3.52 (3H, NMe), 5.95 (s, 3H, CH$_{pyrazolyl}$), 7.16 (m, 3H, Ph), 7.45 (m, 2H, Ph), 7.86 (s, 1H, CH$_{pyrazolyl}$). ^{13}C{^{1}H} NMR in CDCl$_3$, 10.9 (Me), 13.8 (Me), 47.6 (MeN), 67.8 (CH), 106.6 (CH$_{pyrazolyl}$), 115.3, 124.3, 129.9, (Ph), 140.6, 150.5 (C$_{pyrazolyl}$), NCN was not detected. Λ_m = 79 Ohm^{-1} cm^{-1} mol^{-1}.

The thermogravimetry/differential thermal analysis data for **1**–**8** (**Figures S42**–**S49**) demonstrate that mass loss starts in the interval ca. 130–150 °C; differential thermal analysis curves exhibit first endothermic peak in the region 165–245 °C due to the loss of NCNR$_2$. Complex **6** displays several differential thermal analysis peaks at the 130–310 °C interval from NCNR$_2$ loss accompanied with decomposition of the complex. Complexes **1**–**5** and **7**–**8** undergo further decomposition in the range 220–610 °C with one endothermic peak at 320–330 °C (**1**–**5**, and **8**) or several peaks at 360–380 °C (**7**). The mass of final product corresponds to CuF_2 (**2**–**5**) or Cu (**1**), or does not correspond to any stoichiometry of the proposed final products (**6**–**8**).

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