

# Nucleophilic addition reaction in coordinated non-linear pseudohalides: experimental charge density analysis in *trans*-bis(cyanamidonitrato-*N*:*O*)bis-(imidazole-*N*<sup>3</sup>)copper(II) complex

Jozef Kožíšek,<sup>a\*</sup> Niels K. Hansen<sup>b</sup>  
and Hartmut Fuess<sup>c</sup>

<sup>a</sup>Department of Physical Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, <sup>b</sup>Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, CNRS-7036, Université Henri Poincaré - Nancy I, BP 239, F 54506 Vandoeuvre-lès-Nancy CEDEX, France, and <sup>c</sup>Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany

Correspondence e-mail: kozisek@cvt.stuba.sk

Received 2 October 2001  
Accepted 5 February 2002

The experimental crystal charge density of the complex [Cu(iz)<sub>2</sub>(can)<sub>2</sub>] (I) (where iz = imidazole, can = cyanamidonitrato anion), [Cu(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(CN<sub>3</sub>O<sub>2</sub>)<sub>2</sub>], crystallizing in centrosymmetric space group *P*2<sub>1</sub>/*c*, has been determined at 120.0 (2) K, using Hansen and Coppens' aspherical atom multipole model. The central Cu atom is pseudo-octahedrally coordinated by four N atoms in an equatorial plane [two from iz molecules, 1.9660 (4) Å, two from can anions, 2.0273 (5) Å] and by two O atoms (from two adjacent molecules) in axial positions [2.5566 (5) Å]. The *d*-orbital population analysis shows that the oxidation state for the copper is +2 with the *d*<sup>9</sup> configuration and that there is a hole in the *d*<sub>*x*<sup>2</sup>−*y*<sup>2</sup></sub> orbital, located in the plane of the four nitrogen-ligating atoms. Electron lone pairs of these four N atoms are pointing into these regions of depleted electron density. In accordance with the medium-length Cu—O axial bonds, the *d*<sub>*z*<sup>2</sup></sub> orbital is almost fully occupied [1.79 (3) electrons]. The non-bonding *d*<sub>*xy*</sub> orbital is fully occupied [2.05 (3) electrons]. Analysis of the atomic charges does indicate a deficit of +0.35 (4) e<sup>−</sup> on the nitrile carbon, which provides evidence of β-carbon activation for a possible nucleophilic addition reaction. This reaction has been indirectly confirmed experimentally.

## 1. Introduction

The bonding properties of transition metals in coordination compounds are of great importance for inorganic as well as bio-inorganic chemistry. In enzymes, metal centres are important for their activity. In order to understand the kinetics and thermodynamics of the reactions of biological systems, knowledge of the structure and bonding properties of the active site is essential. For this purpose it is useful to study simple model compounds for which accurate data can be obtained.

The great interest in copper(II) coordination compounds is illustrated by the large number of such crystal structures in the Cambridge Structural Database (CSD). Considerable efforts were made to understand the fundamental character of the chemical bonds. Chemical reactions in coordination compounds are studied to elucidate how small changes in molecular composition affect the distribution of bonding electrons, which modifies their physical and chemical properties.

It is generally accepted that there are two basic effects: steric and electronic. A large amount of information on

stereochemistry is available in crystallographic databases. However, the different degrees of precision and various systematic errors in the structures reported hampers comparative studies. On the other hand, studying the charge density is a more direct way of estimating the electronic properties of the compound under investigation. For this it is absolutely necessary to obtain highly accurate data, which to a large extent depends on the quality and stability of the crystal. There are not many compounds, which meet all requirements for such an experiment. From 11 902 entries for copper crystal structures (CSD, August 2000), there are only 822 entries (789 different) with a crystallographic  $R$  value less than 0.03. An optimistic estimation is that  $\sim 10\%$  of copper crystal structures are suitable candidates for charge density studies. This number could increase, if time-consuming recrystallization under different conditions is applied.

In the last few years, using CCD detectors, data collection times have been reduced to a few days. The brilliance of synchrotron radiation sources enables us to use much smaller crystals. Improved techniques for low-temperature data collection as well as more sophisticated software allows a rapid application of charge density analyses for solving chemical problems.

We are studying the bonding properties of non-linear pseudohalides such as dicyanamide, tricyanomethanide, nitrosodicyanomethanide and cyanamidonitrate in coordination compounds of 3d-transition metals,  $[M(L)_n(X)_m]$ , where  $M$  is  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{III}}$ ,  $X$  is a non-linear pseudohalide and  $L$  is a neutral ligand such as imidazole or pyrazole and their methyl derivatives. From a crystallographic point of view the non-linear pseudohalides have strictly planar arrangements of atoms with possibly more donor atoms connected by delocalized  $\pi$ -electron density. All the changes in electron density

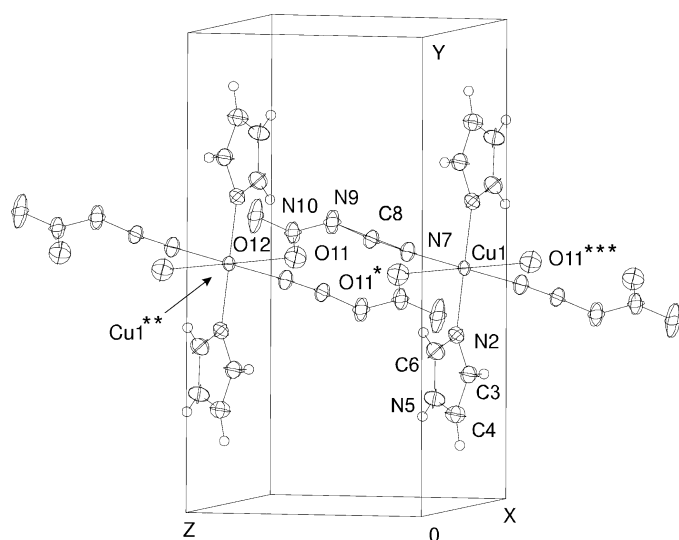
distribution on donor atoms due to coordination bonding are compensated by a delocalized system over the whole pseudohalide anion. On the other hand, the neutral ligand of the pyrazole and imidazole type represents so-called standard electronic states, which can be smoothly changed by substituents at different positions. A systematic study of these types of complexes is rather difficult because suitable single crystals can only be prepared for a small number of these compounds.

In some cases the redistribution of valence electrons due to coordination is changed to such an extent that the chemical properties of coordinated and non-coordinated ligands differ significantly. Such coordinated ligands are activated and may undergo nucleophilic addition reactions with small molecules like methanol, ethanol or water (Hvastijová, Kožíšek, Kohout & Jäger, 1995).

The first evidence of this type of reaction was found for dicyanamide in the crystal structure of the bis(dimethylimidodicarboimidate)copper(II) complex,  $[\text{Cu}(\text{mici})_2]$  (Kožíšek *et al.*, 1990; Boča *et al.*, 1996) (II) ( $\text{mici}^-$ : dimethylimidodicarboimidate anion). This reaction of dicyanamide is specific for the  $\text{Cu}^{\text{II}}$  cation and the methanol molecule. In the case of nitrosodicyanomethanide the reaction has not only been observed for copper(II),  $[\text{Cu}(\text{bipy})(\text{mcoe})(\text{N}(\text{CN})_2)]$  [Dunaj-Jurčo *et al.*, 1996; bipy: bipyridine,  $\text{mcoe}^-$ : methyl-2-cyano-2(hydroximino)ethaneimidate anion], but was first observed for nickel(II),  $[\text{Ni}(\text{mcoe})_2(\text{pz})_2]$  (Hvastijová, Kožíšek, Kohout & Díaz, 1995; pz: pyrazole) and cobalt(III) cations,  $[\text{Co}(\text{mcoe})_2(\text{en})_2]$  (Kožíšek, Díaz, Dvorský, *et al.*, 1997; en: ethylenediamine). In the case of  $\text{Cu}^{\text{II}}$  the added molecules were methanol (Dunaj-Jurčo *et al.*, 1996), ethanol (Tretner, 1999) and water (Hvastijová *et al.*, 1999). These new metalocyclic ligands were found in the *trans* (Hvastijová, Kožíšek, Kohout & Díaz, 1995), as well as the *cis* position (Hvastijová, Kožíšek, Kohout & Jäger, 1995). Something approximating an 'intermediate' during the nucleophilic addition reaction – the compound with one former ligand [cyanamidonitrate anion,  $\text{ONC}(\text{CN})_2$ ] and one new ligand modified by nucleophilic addition reaction ( $\text{mcoe}^-$  anion) – was prepared in the case of the compound  $[\text{Cu}(\text{bipy})(\text{mcoe})(\text{ONC}(\text{CN})_2)]$  (Dunaj-Jurčo *et al.*, 1998).

For cyanamidonitrate the appearance of nucleophilic addition reactions has not been observed until now. Thus, in order to examine the distribution of electron density in coordinated cyanamidonitrate the crystal of *trans*-bis(cyanamidonitrato- $N:O$ )bis(imidazole- $N^3$ )copper(II) complex,  $[\text{Cu}(\text{iz})_2(\text{can})_2]$  (I), has been studied by charge density analysis. The central  $\text{Cu}^{\text{II}}$  atom in this complex is pseudooctahedrally coordinated by four donor N atoms from two molecules of imidazole and two anionic ligands in the *trans* positions. The axial positions are completed by two O atoms from adjacent cyanamidonitrate ligands (Fig. 1).

The crucial problem for charge density studies is to obtain accurate values of structure factor amplitudes. One of the most severe problems is an adequate absorption correction. As the measurement of crystal faces on the diffractometer is not precise enough, the optimization of crystal shape and faces using the *X-SHAPE* software (Stoe & Cie, 1997) in the case of



**Figure 1**

The crystal structure of the title compound with 90% probability thermal displacement ellipsoids (one-dimensional chains in the  $z$  direction; Brandenburg, 1998). Symmetry codes: \*  $1 - x, 1 - y, 1 - z$ ; \*\*  $x, y, 1 + z$ ; \*\*\*  $x, y, -1 + z$ .

**Table 1**  
Experimental details.

$a$ (Å)	7.1248 (7)
$b$ (Å)	13.5995 (25)
$c$ (Å)	6.7973 (9)
$\beta$ (°)	97.821 (11)
Space group	$P2_1/c$ (No. 14)
Wavelength (Å)	0.71069
Temperature (K)	120.0 (2)
$\mu$ (mm <sup>-1</sup> )	1.638
Crystal size (mm)	0.23 × 0.40 × 0.41
Scan type	$2\theta/\omega$
Maximum $\sin \theta/\lambda$ (Å <sup>-1</sup> )	0.986
Range of indices	
$h$	−14/14
$k$	−26/24
$l$	−9/13
Number of measured reflections	14 953

a large linear absorption coefficient (which is mostly the case of coordination compounds) is highly recommended.

## 2. Experimental

### 2.1. Sample preparation

Single crystals of  $[\text{Cu}(\text{iz})_2(\text{can})_2]$  for X-ray diffraction measurements were synthesized at the Department of Inorganic Chemistry of Slovak University of Technology by Professor Mária Hvastijová (Kožíšek, Díaz, Hvastijová & Jäger, 1997). The crystal chosen ( $0.232 \times 0.401 \times 0.411 \text{ mm}^3$ ) was fixed on a glass fibre using UHU-SOFORTFEST glue and a special low-temperature goniometer head. The interior of the diffractometer box was dried by evaporation of liquid nitrogen in a 5 l Dewar container, as well as by molecular sieves.

To identify one of the products of a nucleophilic addition reaction, (III), the melting points and IR spectra for  $[\text{Cu}(\text{mici})_2]$  (II) and for (III) were measured. Melting point for (II) and (III): 520 K; IR spectrum (KBr, 4000–300 cm<sup>-1</sup>) for (II) and (III) is practically identical:  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{N})$ : 1609 v.s., 1377 v.s.  $\nu(\text{N}-\text{H})$ : 3360 m.s., 3343 m.s.,  $\delta(\text{N}-\text{H})$ : 1563 v.s.,  $\delta_{\text{as}}(\text{CH}_3)$ : 1470 v.s., 1445 m.s., 1404 s., and  $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$ : 1206 s., 1196 s.

### 2.2. Data collection

An Oxford Cryosystems low-temperature attachment providing a cold nitrogen gas stream kept the sample at 120.0 (2) K during the measurements. The X-ray diffraction intensities using the  $K\alpha$  radiation of a Mo anticathode ( $\lambda = 0.71069 \text{ Å}$ ) were recorded with a Stoe STADI4 diffractometer. The orientation matrix and unit-cell parameters were determined from setting angles of 56 reflections with  $\theta$  between 25.20 and 28.15°. Four symmetrically independent sets of low-angle reflections (8168;  $0 < \theta < 30^\circ$ ) and two independent sets of high-angle reflections (6785;  $30 < \theta < 45^\circ$ ) were measured. Three reference reflections (130), (223) and (301) were measured every 2 h in order to check the stability of the experimental conditions. A very slight decrease of the reference intensity was observed and the observed intensities were

corrected for this effect. A total of 14 953 reflections were measured. Experimental details are summarized in Table 1.

### 2.3. Data reduction

The data reduction was performed using the Stoe software (Stoe & Cie, 1991). For the absorption correction the program Stoe *X-SHAPE* (Stoe & Cie, 1997) was used. The faces of the crystal were measured and subsequently optimized. Internal  $R$  factors before and after optimization were  $R_{\text{int}} = 0.0300$ ,  $R_{\sigma(I)} = 0.0170$  and  $R_{\text{int}} = 0.0281$ ,  $R_{\sigma(I)} = 0.0170$ , respectively. The measured crystal was formed by the faces shown in the supplementary data (Table S9).<sup>1</sup> The measured distances are those from a certain point in the crystal to the face in the position *face to microscope* for the form  $\{hkl\}$ . The optimized distances are those for which the best fit for calculated and microscopically observed lengths of all edges of the crystal was obtained. Internal consistency of the data after removing outliers (*SORTAV*; Blessing, 1997) was good,  $R_{\text{int}} = 0.016$  and  $R(\sigma) = 0.020$  (*SHELX97*; Sheldrick, 1997). For the multipole refinement and all charge density calculations the *XD* (Koritsanszky *et al.*, 1997) software was used. For the electrostatic potential calculation the program *ELECTROS99* (Ghermani & Bouhmeida, 1999) was used and for the analysis of the topology the program *NEWPROP* (Souhassou, 1999).

### 2.4. Refinements

Starting parameters were taken from a previous paper (Kožíšek, Díaz, Hvastijová & Jäger, 1997) and all refinements were carried out on  $F^2$  using the *XD* (Koritsanszky *et al.*, 1997) suite of programs. Four different refinements were carried out using statistical weights throughout and the results are summarized in Table 2. Refinement I is a traditional independent atom refinement. Refinement II is a 'quasi' high-angle refinement ( $0.7 \leq \sin \theta/\lambda \leq 1.0 \text{ Å}^{-1}$ ) with the H atoms fixed at the typical distances obtained from the neutron diffraction experiments (Allen *et al.*, 1992) and isotropic thermal parameters fixed at the values obtained in refinement (I). Refinement (III) is a kappa refinement with the aim of assigning atomic charges (Coppens *et al.*, 1979). The hydrogen positional and thermal parameters were fixed as in refinement (II). A complete atom-centred multipole refinement was carried out in (IV), where the nonspherical atomic electron density (Coppens, 1997) is given by

$$\rho_{\text{at}}(r) = P_c \rho_{\text{core}}(r) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=1}^{l_{\text{max}}} \kappa^3 R_l(\kappa' r) \sum_{m=0}^l P_{lm\pm} d_{lm\pm}(\theta, \varphi).$$

The H atoms were treated with one bond-directed dipole ( $l = 1$ ); other atoms were refined up to octupoles; for the Cu atom the hexadecapoles level ( $l_{\text{max}} = 4$ ) was used. The local coordinate systems used to define multipoles are shown in Fig. 2. Isotropic extinction was accounted for in all four refine-

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0592). Services for accessing these data are described at the back of the journal.

**Table 2**

Summary of least-squares refinements.

Refinement	I	II	III	IV
$2\theta$ ( $^\circ$ )	0–90.0	60–90.0	0–90.0	0–90.0
$N_{\text{obs}}$	10 694	5572	10 694	10 694
$N_v$	111	116	25	247
$R(F)$	0.0348	0.0250	0.0232	0.0156
$R(F)^\dagger$	0.0542	0.0555	0.0425	0.0350
$wR(F)^\dagger$	0.0547	0.0307	0.0275	0.0166
$R(F^2)$	0.0568	0.0415	0.0350	0.0222
$R(F^2)^\dagger$	0.0589	0.0757	0.0371	0.0242
$wR(F^2)^\dagger$	0.1045	0.0602	0.0545	0.0325
$S$	4.63	1.33	2.32	1.42

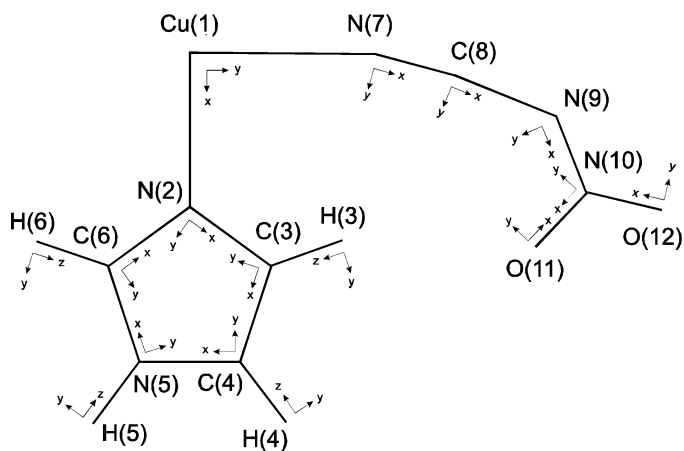
 $^\dagger$  All reflections.

ments. Symmetry constraints implied from a mirror plane were used, but their releasing did not change the results significantly. The H atoms H3, H4 and H6 were constrained to have identical multipole expansions.

### 3. Results and discussion

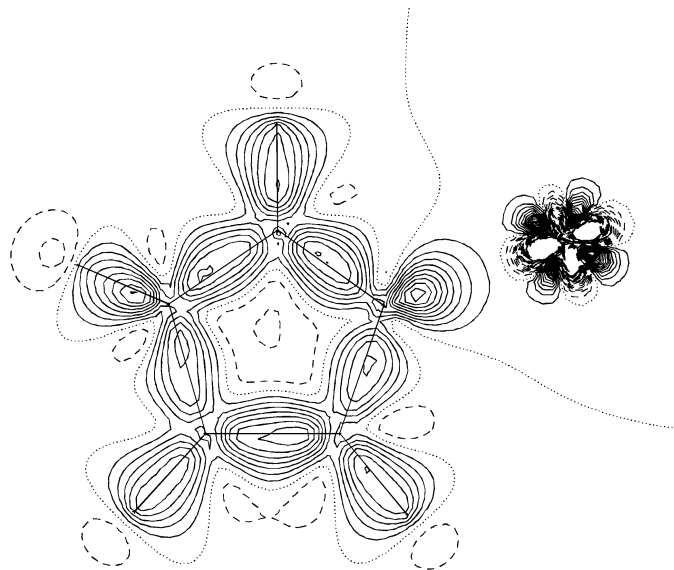
As may be seen from Table 2, the multipole refinement achieved a significant improvement of the agreement between the experimental and calculated structure factors. Residual density maps are calculated by a Fourier synthesis where the coefficients are differences between the observed and calculated structure factors corresponding to the converged multipole model. The maximum and minimum of the residual density are  $+0.16 \text{ e } \text{\AA}^{-3}$  at a distance of  $0.98 \text{ \AA}$  from the Cu1 atom and  $-0.18 \text{ e } \text{\AA}^{-3}$   $1.85 \text{ \AA}$  from the N7 atom and  $2.14 \text{ \AA}$  from the atom N2, respectively; the root-mean-square residual density is  $0.05 \text{ e } \text{\AA}^{-3}$ .

One advantage of a multipole over an independent atom refinement is the more precise values for interatomic distances. The distance for Cu–N(iz) was found to be  $1.9660(4) \text{ \AA}$ , Cu–N(can)  $2.0273(5)$  and Cu–O  $2.5566(5) \text{ \AA}$ . The interatomic distance of the N $\equiv$ C–N triple bond is  $1.136(10) \text{ \AA}$  (Allen *et al.*, 1992). More quantities related to  $\beta$ -

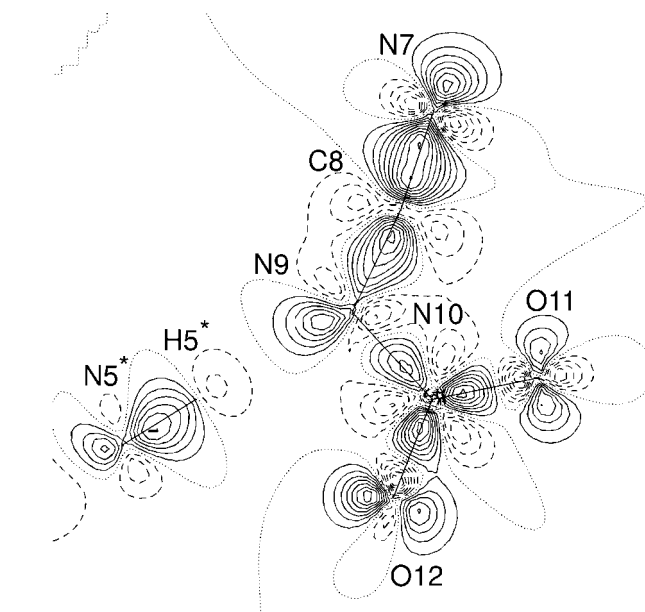
**Figure 2**

Local coordinate systems used for defining the multipole density functions.

carbon activation are presented in Table 3. First, there is the strongest coordination bond in the *equatorial* position for the can ligand compared with all known crystal structures. Secondly, the delocalization of the  $\pi$ -electron density, which results in elongation of the N $\equiv$ C bond lengths and shortens the N–C bond. It is evident that axially bonded can in [Cu(1-meiz) $_4$ (can) $_2$ ] and [Cu(5-meiz) $_4$ (can) $_2$ ] does not follow this dependence. The decrease of the N $\equiv$ C–N angle from the value of  $180.0^\circ$  seems to indicate a small change in hybrid-

**Figure 3**

Static electron deformation densities in the plane defined by the atoms N2, C3 and C6. Positive, negative and zero contours are represented by solid, dashed and dotted curves. Contour spacing  $0.1 \text{ e } \text{\AA}^{-3}$ .

**Figure 4**

Static electron deformation densities in the plane defined by the atoms H5, N10 and O11. Contours as in Fig. 3. Symmetry code: \*  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

**Table 3**

Interatomic distances (Å) and angles (°) in coordinated cyanamidonitrate complexes.

Compound	M—N	N≡C	C—N	M—N≡C	N≡C—N	N—N	<i>R</i> ( <i>F</i> <sup>2</sup> )	Reference
[Cu(iz) <sub>2</sub> (can) <sub>2</sub> ]	2.0273 (5)	1.1607 (6)	1.3210 (6)	164.8 (1)	173.2 (1)	1.3589 (6)	0.0222	This work
[Cu(1-meiz) <sub>4</sub> (can) <sub>2</sub> ]	2.600 (3)	1.133 (4)	1.311 (4)	146.8 (3)	172.6 (3)	1.311 (4)	0.0357	Kohout <i>et al.</i> (1999)
[Cu(5-meiz) <sub>4</sub> (can) <sub>2</sub> ]	2.683 (3)	1.148 (4)	1.346 (4)	118.9 (2)	173.3 (3)	1.326 (4)	0.0401	Kohout <i>et al.</i> (1999)
[Ni(pz) <sub>4</sub> (can) <sub>2</sub> ] <sup>†</sup>	2.076 (3)	1.134 (3)	1.331 (4)	174.2 (3)	171.8 (4)	1.329 (3)	0.0337	Hvastijová <i>et al.</i> (2001)
	2.096 (3)	1.121 (3)	1.317 (4)	175.2 (3)	172.9 (4)	1.334 (3)		
[Ni(1-meiz) <sub>4</sub> (can) <sub>2</sub> ]	2.100 (3)	1.107 (4)	1.377 (5)	171.1 (3)	168.3 (4)	1.286 (5)	0.0494	Hvastijová <i>et al.</i> (2000)
[Co(iz) <sub>4</sub> (can) <sub>2</sub> ] <sup>†</sup>	2.167 (2)	1.144 (3)	1.329 (3)	174.9 (2)	172.6 (3)	1.338 (3)	0.0334	Hvastijová <i>et al.</i> (2000)
	2.164 (2)	1.140 (3)	1.335 (3)	166.1 (2)	171.4 (3)	1.332 (3)		
[Co(pz) <sub>4</sub> (can) <sub>2</sub> ] <sup>†</sup>	2.146 (1)	1.154 (2)	1.325 (2)	164.5 (1)	173.6 (1)	1.372 (2)	0.0273	Hvastijová <i>et al.</i> (2002)
	2.136 (1)	1.154 (2)	1.325 (2)	164.7 (1)	173.4 (1)	1.360 (2)		
[Ag(can)]	2.165 (4)	1.143 (6)	1.322 (5)	173.7 (4)	172.7 (4)	1.369 (5)	0.0288	Jäger <i>et al.</i> (1998)
[K(can)]	‡	1.150 (2)	1.330 (2)	—	173.8 (1)	1.337 (2)	0.0233	Jäger <i>et al.</i> (1998)

<sup>†</sup> Two independent molecules in the unit cell. <sup>‡</sup> Nine K—N/O bonds in the range 2.872 (1)–3.105 (1) Å; 1-meiz = 1-methylimidazole; 5-meiz = 5-methylimidazole; pz = pyrazole.

**Table 4**

Properties of the bond critical points.

*d*<sub>1</sub> and *d*<sub>2</sub>: distances of the critical point from the first and second, respectively, of the bonded atoms.

		<i>d</i> <sub>1</sub> (Å)	<i>d</i> <sub>2</sub> (Å)	Laplacian (e Å <sup>−5</sup> )	Density (e Å <sup>−3</sup> )	Ellipticity	Hessian eigenvalues (e Å <sup>−5</sup> )		
Cu	N2	0.945	1.021	10.24	0.62	0.08	−3.34	−3.10	16.68
Cu	N7	0.987	1.041	8.45	0.49	0.10	−2.42	−2.20	13.08
Cu	O11	1.270	1.287	1.94	0.11	0.01	−0.40	−0.40	2.74
C3	N2	0.589	0.793	−15.32	2.06	0.13	−16.68	−14.71	16.06
C4	C3	0.667	0.700	−18.86	2.14	0.27	−17.17	−13.53	11.84
C6	N5	0.567	0.777	−18.88	2.26	0.15	−19.16	−16.62	16.89
C6	N2	0.561	0.767	−22.13	2.41	0.15	−20.71	−18.02	16.60
C4	N5	0.586	0.788	−13.96	2.08	0.10	−16.32	−14.83	17.19
H3	C3	0.380	0.700	−19.50	1.84	0.12	−18.03	−16.12	14.64
H6	C6	0.370	0.710	−20.43	1.89	0.09	−18.49	−16.98	15.04
H4	C4	0.382	0.698	−18.30	1.81	0.06	−17.00	−16.03	14.74
H5	N5	0.225	0.785	−36.27	2.06	0.03	−29.83	−28.90	22.47
C8	N9	0.591	0.731	−16.67	2.34	0.20	−20.41	−17.07	20.81
C8	N7	0.458	0.702	−18.73	3.17	0.01	−25.58	−25.41	32.26
N9	N10	0.653	0.706	−7.17	2.31	0.23	−20.87	−16.99	30.69
O11	N10	0.619	0.623	−4.68	3.11	0.14	−29.51	−25.93	50.75
O12	N10	0.614	0.615	−7.97	3.22	0.09	−30.83	−28.19	51.05

zation state from *sp* towards *sp*<sup>2</sup>, but this is probably not so important {the angle N7≡C8—N9 of 173.2 (1)°, similar to the value of 173.8 (1)° for the ionic form in [K(can)]}. However, the real crystal structure is a compromise between the position of  $\sigma$  and  $\pi$  bonds, electron lone pairs, as well as hydrogen bonds and interatomic contacts. It is difficult to reconstruct the bonding properties of the ligands by simply analysing the correlation between angles and bond distances. The situation is somewhat more complicated than might be inferred from simple geometrical analysis.

Qualitatively, a higher level of information might be obtained from charge density studies. In Figs. 3–5 we present the multipole model static deformation density maps. The plane of the imidazole (Fig. 3) is defined by the atoms N2, C3 and C6. We can see the bonding electron density in the aromatic system, as well as the signature of the lone-pair electrons on the N atom. The difference between the acidic hydrogen H5 and the other H atoms is apparent: the electron density is shifted towards N5.

In the plane of cyanamidonitrate (Fig. 4) the maximum electron density is observed in the C≡N triple bond. Lone-pair electron lobes on both O atoms are also well resolved. The lone pair of electrons on N9 is pointing towards the regions of low electron density in the vicinity of H5 – this is evidence of a hydrogen bond (for more details see Table S4 of the supplementary data). There is not a very pronounced excess of electron density between N9 and N10; this could indicate the possibility of cleavage of this bond by thermal activation. This fact is in concordance with the weak N—N bond [1.3589 (6) Å], which is one of the weakest bonds in Table 3.

In the equatorial plane of the copper coordination polyhedron (Fig. 5) we see clearly the lone-pair electrons from the donor N atoms pointing towards the depleted  $d_{x^2-y^2}$  orbital. The non-bonding orbital  $d_{xy}$  is fully populated.

The reason for such a high quality of diffraction data might be in the fact that in the crystal structure there are many strong interactions. The imidazole rings are aligned parallel to

the distance of 3.40 Å (3.354 Å in graphite) and their orientation with regard to the equatorial plane arises as a compromise between seven strong hydrogen bonds.

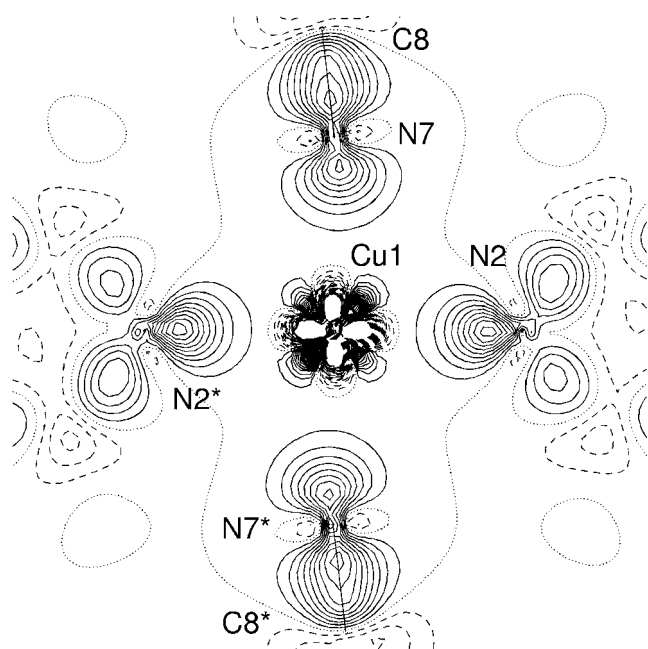
In order to obtain a more quantitative description of the bonding and atomic properties, we have carried out a topological analysis of the total static electron density following Bader (1990) and using the computer program *NEWPROP* (Souhassou, 1999).

In Table 4 we give the characteristics of the bond critical points: a bond critical point is on the gradient path connecting two adjacent atomic nuclei; it has the gradient of the electron density equal to zero and the Hessian matrix has two negative and one positive eigenvalues. Bader (1990) also introduced the notion of atomic basins; the integral of the electron density within a basin gives the number of electrons which may be associated with the atom in question and thus leads to a definition of atomic charge. In Table 5 we compile these charges for the atoms.

The copper ion carries, according to the multipole model and the  $\kappa$  refinement (Table 5),  $\sim 9.1$  3*d* electrons. By integration of the multipole model density over the atomic basin we find 27.1 *e* (we may interpret this as being due to 18 inner shell and 9.1 valence electrons) in perfect agreement with a formal ionic charge of +2 (Table 6). For the copper ion, the basin has the same volume as a sphere with radius 1.34 Å (the closest nucleus-to-surface distance is 0.95 Å) and within this radius we find  $\sim 97\%$  of the electrons of the 3*d* atomic orbitals.

The occupancies of the *d* orbitals calculated from multipole population parameters are given in Table 7. These values depend sensitively on a reliable absorption correction. The maximum values should not exceed 2 electrons per orbital;

this is a good check of the absorption correction. The *d*-orbital populations in Table 7 are in good agreement with the features observed in Fig. 5: The non-bonding orbital  $d_{xy}$  is fully



**Table 5**Population of the monopoles from  $\kappa$  refinement and corresponding net charges.

	Population	Charge	Kappa
Cu	9.18 (3)	+1.82 (3)	1.028 (3)
O11	6.24 (2)	−0.24 (2)	0.983 (2)
O12	6.27 (2)	−0.27 (2)	= $\kappa$ (O11)
N2	5.41 (2)	−0.41 (2)	0.977 (2)
N5	5.15 (3)	−0.15 (3)	1.011 (3)
N7	5.57 (2)	−0.57 (2)	0.977 (2)
N9	5.37 (3)	−0.37 (3)	0.987 (3)
N10	4.25 (3)	+0.75 (3)	1.048 (4)
C3	3.84 (2)	+0.16 (2)	1.048 (3)
C4	4.07 (2)	−0.07 (2)	= $\kappa$ (C3)
C6	3.84 (2)	+0.16 (2)	= $\kappa$ (C3)
C8	3.46 (3)	+0.54 (3)	1.088 (6)
H3	0.91 (2)	+0.09 (2)	1.26 (2)
H5	0.70 (2)	+0.30 (2)	= $\kappa$ (H3)

populated. The electron configuration of Cu is  $d^9$ ; the missing electron in the 3d shell has been taken to ~60% from the  $d_{x^2-y^2}$  orbital, to 20% from the  $d_{z^2}$  orbital and to ~10% from the  $d_{xz}$  and  $d_{yz}$  orbitals.

The bond critical points between the copper ion and the nitrogen ligands are close to halfway between the atoms showing a curvature of the density parallel to the bond about as strong as for a covalent bond, but with much slower variation of the density perpendicular to the bond, the result being a positive Laplacian. These findings are in good agreement with a study of  $\text{MnCu(Pba)(H}_2\text{O)}_3 \cdot 2\text{H}_2\text{O}$  (Pba = propylene-bis-amato) by Pillet (2001).

For the longer Cu—O contact a bond critical point is found, but all descriptors have much smaller values, implying rather weak bonding. It is to be expected that in such cases the results of the topological analysis will depend sensitively on the radial density functions chosen for the multipole modelling and we refrain from drawing any detailed conclusion for this interaction.

Considering the charges of the atoms on the ligands, the Bader partitioning gives (as observed in all other studies) more extreme values (Table 6) than those obtained using the  $\kappa$ -refined populations (Table 5). Nevertheless, the sign of the charges always agrees, with the exception that the C4 atom belonging to the imidazole group is close to neutral according to the  $\kappa$  refinement. The C8 atom is of special interest; the charge on this atom is strongly positive, in agreement with being strongly electrophilic.

We may compare the topological features with what was observed in the analyses by Souhassou & Blessing (1999) of *N*-acetyl-L-tryptophan-*N*-methylamide (*Actr*). For an aromatic C—C bond the ellipticity  $\varepsilon \simeq 0.20$  and for a C=C bond  $\varepsilon \simeq 0.23$ .

The ellipticities  $\varepsilon$  of the bonds correlate clearly with their nature; for the ideally cylindrically symmetric cyanide triple bond,  $\varepsilon$  is close to zero. The pronounced ellipticities of all the other bonds in the cyanoamidonitrato ligand are indicative of a strong  $\pi$ -conjugation in the chain  $\text{N}\equiv\text{C}-\text{N}-\text{N}$ .

For the bonds in the imidazole ligand, the bond C3—C4 has the highest ellipticity (0.27) and the bond distance (1.37 Å)

**Table 6**

Net electron count and charges in the atomic basins.

	Integral	Charge
Cu	27.1	+1.9
O11	8.29	−0.29
O12	8.31	−0.31
N2	7.89	−0.89
N5	8.03	−1.03
N7	7.99	−0.99
N9	7.45	−0.45
N10	6.35	+0.65 (3)
C3	5.63	+0.37
C4	5.68	+0.32
C6	5.26	+0.74
C8	4.81	+1.19
H3	0.95	+0.05
H5	0.42	+0.58
H4	0.94	+0.06
H6	0.94	+0.06

**Table 7**Population of the  $d$  orbitals.

Orbital	$d_{x^2-y^2}$	$d_{z^2}$	$d_{yz}$	$d_{xz}$	$d_{xy}$
Number of electrons	1.43 (3)	1.79 (3)	1.88 (3)	1.89 (3)	2.05 (3)

corresponds closely to a double bond. In *Actr* a similar double bond has  $\varepsilon = 0.23$ . The two adjacent C—N bonds have lower ellipticities: for C3—N2  $\varepsilon = 0.13$  and C4—N5  $\varepsilon = 0.10$  than the other two C—N bonds having  $\varepsilon$  close to 0.15.

Since we are interested in the properties of the cyanamidonitrato ligand when coordinating a copper ion, we have calculated the electrostatic potential of a cluster composed of copper with its six ligands from the multipole model charge density, including the nuclear contribution using the computer program *ELECTROS99* (Ghermani & Bouhmeida, 1999). The results for two different sections are shown in Figs. 6 and 7.

Since the total charge of this fragment is positive, the potential is overall positive and dominated by the strongly charged copper ion. A nucleophilic substrate would be expected to approach this 'molecule' in regions where the potential is the most strongly positive. The most likely approach in these planes is arrowed in Figs. 6 and 7.

We have not observed any products of a nucleophilic addition reaction at room temperature, but the above results indicate that this type of reaction of the title compound in methanol should take place at a higher temperature. In fact, after 48 h at 335 K a mixture of products was obtained. One of the products from the methanol solution precipitated as violet crystals. The IR spectra proved that it was the bis(dimethyl-imidodicarboimidate)copper(II) complex,  $(\text{C}_8\text{H}_{16}\text{CuN}_6\text{O}_4)$  (III), a compound which we have already synthesized from dicyanamide (Kožíšek *et al.*, 1990). As cyanamidonitrato is stable in hot methanol, these results show that the decomposition of the complex  $[\text{Cu}(\text{iz})_2(\text{can})_2]$  and/or the nucleophilic addition reaction takes place under these conditions.

The financial support of the Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR) (Project No. SLA-005-97) and

University Henri Poincaré for an invited professorship for JK is acknowledged. We especially thank Dr N. Ghermani for helping with the electrostatic potential calculations and Dr M. Souhassou for many fruitful discussions about the topological characterization of the electron density.

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for Crystallography*, edited by A. J. C. Wilson, Vol. C, pp. 685–706. Dordrecht: Kluwer Academic Publishers.
- Bader, R. F. W. (1990). *Atoms in Molecules: A Quantum Theory, The International Series of Monographs of Chemistry*, edited by J. Halpen & M. L. H. Green. Oxford: Clarendon Press.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Brandenburg, K. (1998). *Diamond*. Bonn, Germany.
- Boča, R., Hvastijová, M., Kožíšek, J. & Valko, M. (1996). *Inorg. Chem.* **35**, 4794.
- Coppens, P. (1997). *X-ray Charge Densities and Chemical Bonding*. Oxford University Press.
- Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- Dunaj-Jurčo, M., Mikloš, D. & Potočňák, I. (1998). *Acta Cryst.* **C54**, 1763–1765.
- Dunaj-Jurčo, M., Mikloš, D., Potočňák, I. & Jäger, L. (1996). *Acta Cryst.* **C52**, 2409–2412.
- Ghermani, N. & Bouhmeida, N. (1999). *ELECTROS99*. LCM3B, Université Henri-Poincaré - Nancy I, France.
- Hvastijová, M., Bocá, R., Kohout, J., Jäger, L., Císařová, I. & Kožíšek, J. (2002). Submitted for publication.
- Hvastijová, M., Kohout, J., Díaz, J. G., Kožíšek, J. & Buchler, J. W. (2001). *Transit. Metal Chem.* **26**, 430–434.
- Hvastijová, M., Kohout, J., Kožíšek, J., Jäger, L. & Díaz, J. G. (2000). *Polyhedron*, **19**, 1021–1027.
- Hvastijová, M., Kohout, J., Kožíšek, J. & Svoboda, I. (1999). *J. Coord. Chem.* **47**, 573–579.
- Hvastijová, M., Kožíšek, J., Kohout, J. & Díaz, J. G. (1995). *Inorg. Chim. Acta*, **236**, 163–165.
- Hvastijová, M., Kožíšek, J., Kohout, J. & Jäger, L. (1995). *J. Coord. Chem.* **36**, 195–205.
- Jäger, L., Tretner, C., Hartung, H., Biedermann, M. & Wagner, C. (1998). *Z. Anorg. Allg. Chem.* **624**, 1558–1562.
- Kohout, J., Hvastijová, M., Kožíšek, J., Díaz, J. G., Valko, M., Jäger, L. & Svoboda, I. (1999). *Inorg. Chim. Acta*, **287**, 186–192.
- Koritsanzsky, T., Howard, S. T., Su, Z., Mallinson, P. R., Richter, T. & Hansen, N. K. (1997). *XD*. Free University of Berlin, Germany.
- Kožíšek, J., Díaz, J. G., Dvorský, A., Hvastijová, M. & Svoboda, I. (1997). *Progress in Coordination Chemistry*, 16<sup>th</sup> CCC, edited by G. Ondrejovič & A. Sirota, p. 123. Bratislava: STU Press.
- Kožíšek, J., Díaz, J. G., Hvastijová, M. & Jäger, L. (1997). *Acta Cryst.* **C53**, 703–705.
- Kožíšek, J., Hvastijová, M. & Kohout, J. (1990). *Inorg. Chim. Acta*, **168**, 157–158.
- Pillet, S. (2001). PhD thesis. Université Henri Poincaré – Nancy I, France.
- Sheldrick, G. M. (1997). *SHELX97*. University of Göttingen, Germany.
- Souhassou, M. (1999). *NEWPROP*. LCM3B, Université Henri-Poincaré – Nancy I, France.
- Souhassou, M. & Blessing, R. H. (1999). *J. Appl. Cryst.* **32**, 210–217.
- Stoe & Cie (1991). *REDU4*, Version 7.08. Stoe and Cie, Darmstadt, Germany.
- Stoe & Cie (1997). *X-SHAPE*, Version 1.02. Stoe and Cie GmbH, Darmstadt, Germany.
- Tretner, C. (1999). Dissertation. Universität Halle–Wittenberg, Germany.