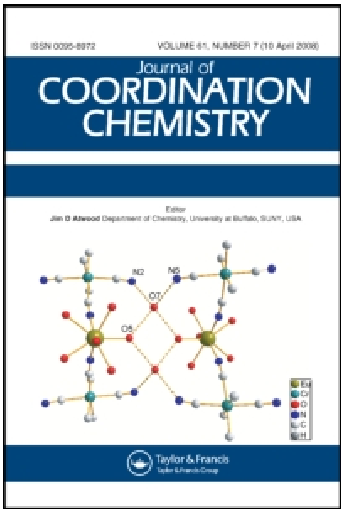

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Roman Boča[a]; Mária Hvastijová[a]; Jiří Kohout[a]
[a] Department of Inorganic Chemistry, Slovak Technical University, Bratislava, Slovakia

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A MOLECULAR ORBITAL APPROACH TO COLIGAND ISOMER FORMATION

ROMAN BOČA,* MÁRIA HVASTIJOVÁ and JIŘÍ KOHOUT

Department of Inorganic Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovakia

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Coligand isomerism is exemplified by a pair of [Cu(dmpz)$_2$(NCO)$_2$] and [Cu(dmpz.NCO)$_2$] complexes (dmpz = 3,5-dimethylpyrazole). The former isomer (**I**) contains dmpz and NCO$^-$ ligands whereas the latter (**II**) consists of 1-carbamoyl-3,5-dimethylpyrazolate anions chelated to the copper(II) central atom. This new ligand is formed by nucleophilic addition of the dmpz ligand to the cyanate group in the Cu(II) coordination sphere. The cyanate complex transforms under heating to the more stable isomer **II**. On the contrary, isomer **II** disolves in DMSO and DMF and its counterpart **I** is formed. A molecular-orbital study (quasirelativistic INDO/1 method) rationalizes this behaviour and maps the reaction path of the hydrogen transfer over the molecular skeleton.

KEYWORDS: coligand isomerism, quasirelativistic INDO calculations, copper(II), isocyanate, dimethylpyrazole

INTRODUCTION

Recently, a series of isomeric pairs which can be considered as coligand isomers have been discovered. One of them is the pair of compounds [Cu(dmpz)$_2$(NCO)$_2$] and [Cu(dmpz.NCO)$_2$], dmpz being 3,5-dimethyl-pyrazole. The former compound (I), according to the results of spectroscopic (mostly IR) data, contains two cyanate and two dmpz ligands in the complex plane. X-ray structure analysis of the latter compound (II)[1] proved suggestions based on IR data (appearance of a characteristic ν_{as}(NCO) vibration at 1694 cm^{-1}) that a new ligand, 1-carbamoyl-3,5-dimethylpyrazolate (dmpz.NCO) is chelated to copper(II) in this isomer. It was deduced that this new ligand is formed by nucleophilic addition of the dmpz ligand to the cyanate carbon within the Cu(II) coordination sphere.

The greater stability of isomer **II** relative to its precursor **I** is important; the latter transforms spontaneously to the former with heating, with $\Delta H = -8.15$ kJ mol^{-1} (maximum of the exothermic excursion, $T_{max} = 377.3$ K). Isomer **II** is soluble in certain solvents, *e.g.*, in dimethylsulfoxide (DMSO) and dimethylformamide (DMF). In these solutions the characteristic ν_{as}(NCO) vibration shows a typical value of 2221 cm^{-1} so that transformation to isomer **I** proceeds. The above solvents exhibit high donor numbers: DN(DMSO) = 29.8 and DN(DMF) = 26.6. Thus the strong axial interaction of the complex with two molecules of the solvent

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* Author for correspondence.

results in a weakening of the bonds in the square plane. Such a decrease of the chelation effect may manifest itself in the splitting of the pertinent C–N bond and thus a transformation to isomer **I** is enabled.

Other coligand isomeric pairs have been found. They cover the combinations of the central atoms and ligands as listed in Table 1. In order to rationalize the interesting behaviour of the pseudohalide and pyrazole ligands in the metal coordination sphere of the dmpz system with copper, a molecular-orbital study of **I** and **II** has been performed.

METHOD

Calculations

For molecular orbital studies a *quasi*-relativistic INDO/1 method has been chosen.[15] The method spans a novel class of approximate, but non-empirical methods which cover the dominant relativistic effects (if relevant). The results of precise atomic Dirac-Fock calculations (orbital energies and orbital exponents) are used in the parametrization scheme of the INDO/1 method. The calculations have been performed by the program MOSEM7.[16]

As the parameteriztion scheme for transition metals needs a proper selection of the reference electron configuration, the $3d^9 4s^2 4p^0$ configuration has been chosen for the Cu atom. This is closer to the behaviour of Cu(II) complexes than the (experimental) free-atom alternative of $3d^{10} 4s^1 4p^0$.

The systems under study contain 37 atoms (105 valence orbitals) for free isomers **I** and **II** and eventually 57 atoms (149 valence orbitals) for an adduct of **II** with two DMSO molecules. An *ab initio* study of such complexity would be very costly and the most popular versions of semi-empirical methods, like MNDO, AM/1 or PM/3, suffer for lack of parameters. The choice of the QR-INDO/1 method was motivated by the fact that not only Cu(II) but also Pd(II) and Pt(II) complexes are candidates for subsequent studies and thus a partial inclusion of relativistic effects adopts a significance for them. The method is capable of reproducing at least molecular geometries. The energy differences, however, may be highly overestimated due to effects of approximations applied for interelectronic repulsions.

Table 1 Metal/ligand combinations for coligand isomer pairs.

Metal	Ligand		References
	Pseudohalide	Pyrazole derivative [a]	
Cu(II)	NCO^-	pz, mpz, dmpz, tmpz, inz, 4-NH_2-pz, 4-NO_2-pz, 4-Br-pz, 4-I-pz	1–9
Ni(II)	NCO^-	tmpz	10
Cu(II)	$N(CN)_2^-$	pz, inz, 4-Br-pz, 4-NO_2-pz	8, 9, 11, 12
Ni(II)	$N(CN)_2^-$	pz, 4-I-pz, 4-NO_2-pz	8, 9, 12
Cu(II)	$C(CN)_3^-$	pz	13
Co(II)	$NOC(CN)_2^-$	tmpz	14

[a] Abbreviations: pz = pyrazole, mpz = 3(5)-methylpyrazole, dmpz = 3,5-dimethylpyrazole, tmpz = 3,4,5-trimethylpyrazole, inz = indazole.

Data Analysis

Chemical bonds are characterized by three quantities: the bond length (on input) R_{A-B}, the calculated Wiberg (bond-strength) index W_{A-B}[17] and the bicentric (interaction) part of the total energy, E_{A-B}.[18] These parameters are generally interrelated in such a way so that with decreasing R_{A-B} the value of W_{A-B} increases and simultaneously the (negative) value of E_{A-B} decreases. An effective atomic charge, Q_A, despite its rather problematic definition, is calculated for each centre; this gives information about electron density distribution and is capable of indicating nucleophilic and/or electrophilic sites throughout the molecular skeleton. The d-orbital population, d^x, and the spin density, ρ(Cu), give further information about distribution of charge/spin density over the chromophore.

Molecular geometry

The molecular geometry of isomer **II** has been taken from X-ray data.[1] It has been slightly idealized, keeping a centre of inversion at the copper atom. As the hydrogen atom coordinates were undetermined, a limited geometry optimization has been performed for **II** in order to localize the positions of three types of the hydrogen atoms. The optimized bond lengths and bond angles are listed in Table 2. Figure 1 shows a final visualization of isomer **II**.

The geometry of isomer **I** has been estimated as follows: no relaxation was expected for the dmpz ring and eventually a linear arrangement of the NCO group was fixed. Again a geometry optimization gave the final values of 8 or 13 bonding

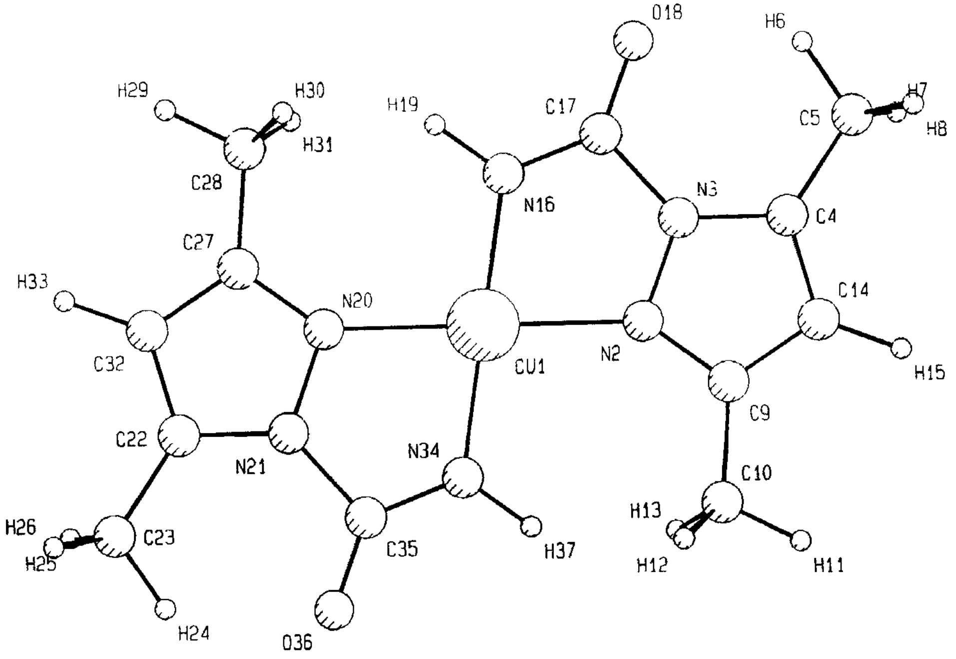


Figure 1 Molecular structure of the isomer [Cu(dmpz.NCO)$_2$], **II**.

Table 2 Structural parameters of isomers I and II.[a]

Distance/angle[b]	II	Ia	Ib	dmpz	NCO$^-$
Distances (10^{-10} m)					
Cu1-N2	[1.990]	1.936	1.890		
N2-N3	[1.363]	[1.363]	[1.363]	1.330	
N3-H19		1.0612	1.081	1.037	
N3-C17	[1.429]				
N3-C4	[1.368]	[1.368]	[1.368]	1.403	
C4-C5	[1.481]	[1.481]	[1.481]	1.468	
C5-H6	1.099	[1.099]	1.111	1.100	
N2-C9	[1.316]	[1.316]	[1.316]	1.377	
C9-C10	[1.493]	[1.493]	[1.493]	1.470	
C9-C14	[1.367]	[1.367]	[1.367]	1.437	
C14-H15	1.096	[1.096]	1.096	1.092	
Cu1-N16	[1.908]	1.945	1.955		
N16-C17	[1.306]	1.242	1.302		1.209
C17-O18	[1.218]	1.269	1.309		1.294
N16-H19	1.042				
Angles (deg)					
Cu1-N2-N3	[110.4]	110.4]	[110.4]		
N2-N3-C4	[110.2]	[110.2]	[110.2]	113.6	
N3-C4-C5	[124.0]	[124.0]	[124.0]	124.0	
C4-C5-H6	112.8	[112.8]	112.2	113.3	
N3-N2-C9	[106.2]	[106.2]	[106.2]	108.1	
N2-C9-C10	[122.0]	[122.0]	[122.0]	123.3	
N2-C9-C14	[110.3]	[110.3]	[110.3]	106.7	
C9-C14-H15	125.9	[125.9]	126.2	125.8	
N2-Cu1-N16	[81.0]	93.8	95.9		
Cu1-N16-C17	[119.8]	159.7	140.1		
N16-C17-O18	[131.6]	[180.0]	134.0		180.0
Cu1-N16-H19	118.1				
N2-N3-H19		113.4	109.5	120.2	
Total energy E_T (eV)[c]	-6624.48	-6608.44	-6613.13	-1706.73	-900.79

[a] Numbering of atoms according to Figures 1 and 2. [b] Parameters in brackets were fixed. [c] Energy of the free Cu^{2+} ion is -1303.57 eV.

coordinates, respectively, listed in Table 2 (see also Figure 2). For comparision, the geometries of the free NCO^- and dmpz ligands have been optimized separately (Table 2).

By relaxing some geometry parameters the energy profile of the expected reaction coordinate was followed as shown in Figure 3. It starts at the geometry of isomer **I**, point 1, and ends at that of isomer **II** (point 5). Intermediate situations (2 to 4) are represented by different H and NCO atoms positions.

RESULTS AND DISCUSSION

Energy Profile

First principal findings based on the calculated total molecular energy show that isomer **II** is considerably more stable than isomer **I**. Although the absolute value of the energy separation (ΔE = 11.3 eV) is evidently overestimated, the above finding

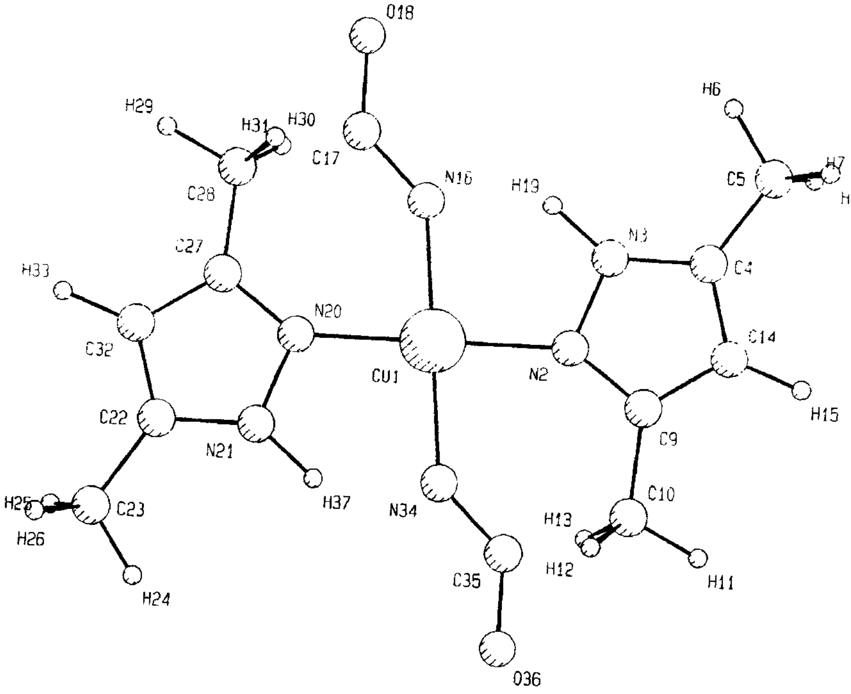


Figure 2 Expected molecular structure of the isomer [Cu(dmpz)$_2$(NCO)$_2$], **I**.

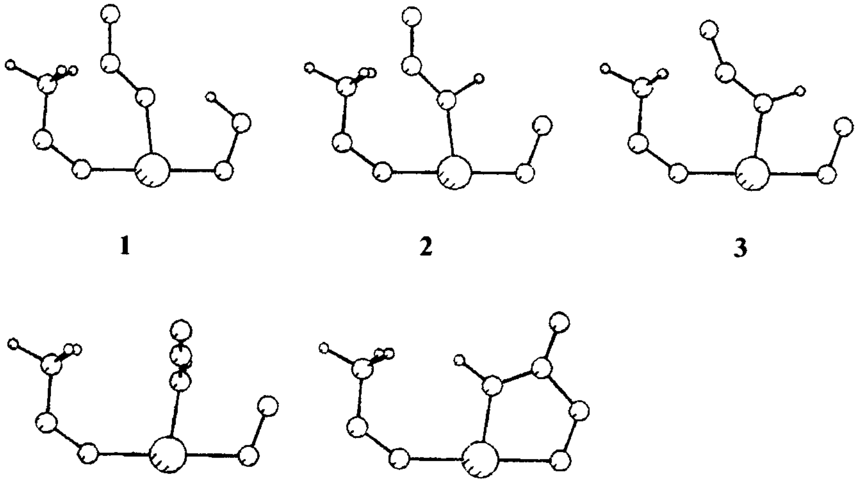
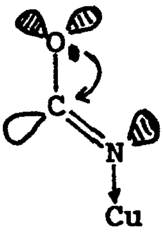


Figure 3 Structural changes along the reaction coordinate under study. Only relevant atoms are shown.

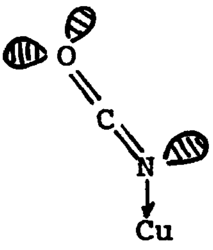
fits the experimental data: isomer **I** can spontaneously be transformed to isomer **II**, *e.g.*, under heating. The above value, however, is not comparable with the experimentally determined ΔH value since the latter accounts for the rearrangement of the crystal lattice. It should be noted that no additional axial interactions have been evidenced[1] in isomer **II** unlike in **I** where two models of pentacoordination have been proposed.[4]

Starting isomer I

The optimized geometry **Ib** differs from that of **Ia** mainly in the feature (Table 2) that the NCO unit was allowed to deviate from the expected linearity. Inspection of Figure 2 shows that a bending of ν(NCO) = 134° is stabilized by additional interactions of atoms C17... H30, H31 with contacts at 1.47Å. The final situation around the C17 atom corresponds rather to sp^2 hybridization (a) unlike the linear NCO unit with sp hybridization (b).



(a)



(b)

It is expected that any lengthening of C17... H30, H31 contacts will cause a linearization of the NCO group. The calculated stabilization energy is $\Delta E(I) = 2E(dmpz) + E(NCO^-) + E(Cu^{2+}) - E(I) = 94.5$ eV.

Charge distributions in isomer **I** indicate that the nitrogen atom of the coordinated NCO group bears a large negative charge ($O_{N16} = -0.56$ e). Simultaneously, the hydrogen atom of the pyrazole ring is rather acidic ($Q_{H19} = +0.22$ e) and thus its migration is supported. The carbon atom of the NCO group is strongly electrophile ($Q_{C17} = +0.57$ e).

Wiberg indices indicate a $Cu{-}N{=}C{=}O$ character of bonding: $W_{Cu1-N16} = 0.87$ (0.81), $W_{N16-C17} = 1.75$ (2.07) and $W_{C17-O18} = 1.52$ (1.71); values in parentheses are for the linear NCO unit, as seen in Table 3.

Intermediate Complexes

The hydrogen atom (H19) migration from the pyrazolate site to the NCO group, *i.e.*, N16... H19-N3 → N16-H19... N3 transfer, is accompanied not only by an energy increase (ΔE = 2.2 eV) but also by significant changes in charge distribution. The N3 site in 2 bears a charge of Q(N3) = − 0.25 e and therefore is capable of nucleophilic attack at the highly positive (electrophilic) centre C17 with

Table 3 Calculated bonding and atomic characteristics.[a]

Structure	1 = **Ib**		2		5 = **II**		**III**[b]	
Bond A-B	$W_{A\text{-}B}$	$E_{A\text{-}B}$	$W_{A\text{-}B}$	$E_{A\text{-}B}$	$W_{A\text{-}B}$	$E_{A\text{-}B}$	$W_{A\text{-}B}$	$E_{A\text{-}B}$
Cu1-N2	0.62	-22.0	0.74	-24.5	0.63	-22.0	0.52	-19.5
N2-N3	1.15	-46.6	1.20	-47.5	1.10	-45.5	1.11	-45.8
N3-H19	0.83	-26.1						
N3-C17					0.93	-40.8	0.93	-40.8
N3-C4	1.31	-50.7	1.40	-52.6	1.26	-49.0	1.26	-49.1
Cu1-N16	0.87	-26.5	0.68	-22.9	0.84	-25.5	0.62	-21.4
N16-C17	1.75	-67.4	1.48	-59.5	1.29	-54.6	1.35	-57.5
N16-H19			0.84	-26.8	0.91	-28.3	0.91	-28.6
C17-O18	1.52	-59.4	1.61	-60.9	1.62	-61.0	1.52	-60.8
Atom A	Q_A		Q_A		Q_A		Q_A	
Cu1	-0.39		-0.33		-0.33		-0.32	
N2	0.04		0.06		-0.03		-0.05	
N3	0.06		-0.25		0.09		0.09	
C4	0.17		0.16		0.19		0.21	
N16	-0.56		-0.32		-0.35		-0.49	
C17	0.57		0.63		0.57		0.68	
O18	-0.61		-0.54		-0.52		-0.67	
H19	0.22		0.24		0.17		0.19	
d^{x}(Cu)	9.20		9.21		9.18		9.15	
ρ(Cu)	0.76		0.75		0.78		0.81	
Orbital energies /eV								
$^{\varepsilon}$LUMO	7.06		6.72		5.77		7.69	
$^{\varepsilon}$HOMO	-4.81		-5.41		-6.42		-4.90	

[a] Numbering of atoms according to Figures 1 and 2. [b] Solvent effect included through ε_r.

Q(C17) = 0.63 e. The true reaction coordinate when several atoms move is difficult to follow exactly; thus the expected pathway (Figure 3) is only an estimate based on modelling of minimum energy requirements. After some relaxation and rotation of the Cu-NH(CO) group the final geometry is reached.

Final isomer II

As the new ligand (dmpz.NCO) is formed the bonding situation relaxed to single bond C17-N3 formation with W(C17-N3) = 0.93. The new single bond N3-C17 formed as a result of nucleophilic attack is rather strong; it is stronger than the Cu-N2 and Cu-N16 bonds and only slightly weaker than the N2-N3 bond within the pyrazole ring (see data in Table 3).

Solvent Effects

Geometry optimization for the free DMSO molecule gave the following bonding coordinates at a total energy of $E_T = -1216.04$ eV: R(S-O) = 1.677, R(S–C) = 1.739, R(C–H) = 1.098 Å; ϑ(OSC) = 120.0 and ϑ(SCH) = 112°. In order to mimic the DMSO solution of isomer **II**, two molecules of DMSO were coordinated in the axial positions of **IIa**. A stepwise variation of the Cu-O distance gave optimum separation at 2.10 Å with a total energy of $E_T = -9068.41$ eV. This $[Cu(NCO.dmpz)_2(DMSO)_2]$ complex, **III**, has been recalculated by including the solvation effect. A modified Germer model[19] of the continuous class has been applied for this purpose. A value of the relative permittivity ε_r(DMSO) = 46.7 has been used in this model. According to Table 3 the Cu-N2 and Cu-N16 bonds are considerably weakened as two DMSO molecules coordinate. Such a relaxation will decrease the chelation effect and consequently the system is capable of the back transformation to isomer **I**. Our explanation is that equatorial-axial interactions in the studied systems operate.[20] Strong chelation in **II** makes the equatorial plane of the complex electronically saturated and no axial interactions apply. On the contrary, when strong donors (like DMSO and DMF) are situated on the axial ordinate, the Cu-N bonds in the equatorial plane are weakened to reflect a decrease of the chelation effect. Alternatively, electronic non-saturation in the equatorial plane of isomer **I** allows some axial interactions as evidenced in the solid state.

Pyrazolate Coligand Isomers

In order to generalize the above considerations another coligand isomer pair has been chosen: $[Cu(pz)_2(NCO)_2]$, abbreviated as **IV**, and $[Cu(pz.NCO)_2]$, hereafter **V**. Results of a geometry optimization performed over nine internal coordinates for both isomers is visualized in Figure 4. The optimized parameters (distances in Å, angles in deg) are: $R(Cu\text{-}N_{pz})$ = 1.967 (2.007), R(Cu-N) = 1.957 (1.958), $\vartheta(N_{pz}\text{-}Cu\text{-}N)$ = 82.7 (86.0), R(C–N) = 1.249 (1.374), ϑ(Cu-N-C) = 106.4 (110.2), R(C-O) = 1.261 (1.305), ϑ(N–C–O) = 166.5 (126.7), R(N-H) = 1.105 (1.031) and ϑ(Cu-N-H) = 109.6 (128.8) for **IV** and **V** (in parentheses). Isomer **V** is 19.1 eV more stable than its precursor **IV**. These results match well with those presented above for the dimethylpyrazolate analogues.

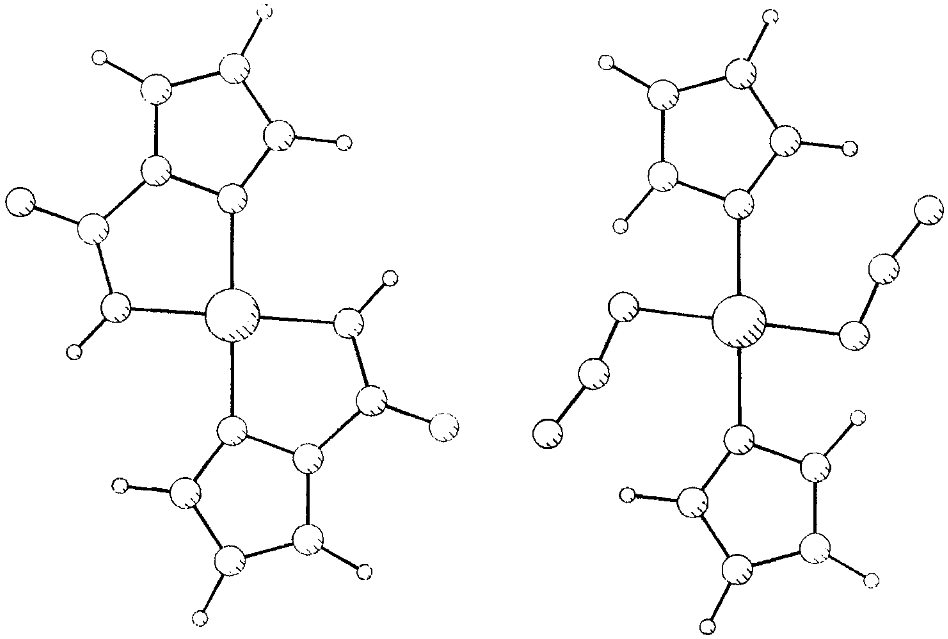


Figure 4 The optimized geometry of $[Cu(pz)_2(NCO)_2]$ and $[Cu(pz{\cdot}NCO)_2]$ coligand isomer pairs.

Note added in proof

We succeeded in *ab initio* molecular orbital calculations of $[Cu \cdot (NCO]_2(pz)_2]$ and $[Cu(NCO \cdot pz)_2]$ isomer pair using a double-zeta basis set and assuming C_{2h} symmetry: for the geometries pre-optimized by the quasi-relativistic CNDO/1 method the latter isomer being more stable by 3.31 eV at the SCF level.

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