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Synthesis and calculated structure of a copper(II) complex with 1-(1-silatranylmethyl)pyrrole

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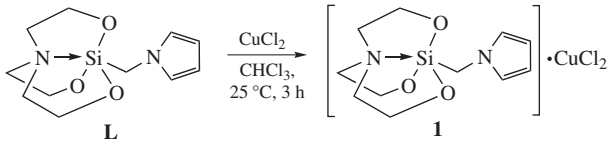
The calculated structural and electron density characteristics of a new copper(II) complex with 1-(1-silatranylmethyl)pyrrole indicate the coordination of the oxygen atom and the π-electron system of the pyrrole ring with the Cu atom.

Silatranes, hetero-tricyclic compounds with a transannular N→Si bond, have attracted attention due to their high stability, unique structure, architectural beauty and wide applications in biology, medicine and agriculture.[1] However, their complexation studies involving endo/exocyclic heteroatoms (O, N) of silatranyl and carbofunctional groups are not widespread. Recently, we reported the synthesis and molecular structure of two metal(II) complexes $[HetCH_2Si(OCH_2CH_2)_3N]\cdot MCl_2$ (Het is 3,5-dimethylpyrazolyl, M = Zn, Co).[2] The structure analysis showed that the metal atom is connected both with the pyridinic heterocycle nitrogen atom and the cage oxygen atom so that a six-membered ring is closed. Here, we report the synthesis of new copper(II) complex with 1-(1-silatranylmethyl)pyrrole **1** and a computational study of its structure.



L **1**

Scheme 1

For the synthesis of neutral complex **1**, we used a reaction of $CuCl_2$ with 1-(1-silatranylmethyl)pyrrole (**L**) (Scheme 1). The mixing of a starting copper(II) salt with the ligand in chloroform gave complex **1**, which was isolated as a black powder stable in air.† The compound is only soluble in DMSO. According to the microanalysis data, the resulting product $CuCl_2\cdot$**L** has a 1 : 1 stoichiometry.

The 1-(1-silatranylmethyl)pyrrole molecule has four potential basicity centers: three oxygen atoms of the silatranyl group and the pyrrole cycle. The basicity of the oxygen atom is higher in silatranes than such in their tetracoordinated analogues, as was proved theoretically and experimentally.[1(d)] The high electron-releasing inductive effect of the silatranyl group ($\sigma^* = -3.49$) increases the π-coordinating ability of the substituents around the Si atom.[1(a)] Quantum-chemical calculations of the energy of aromatic stabilization indicate an increase in the aromaticity of a pyrrole ring on passing from pyrrole to 1-(1-silatranylmethyl)-pyrrole.[3] The IR spectra of complex **1** in a solid state revealed the bonding of 1-(1-silatranylmethyl)pyrrole through the O atom of the silatranyl group and the π-electron system of the pyrrole ring with the Cu atom. The decrease observed in ν_{as}(C–O–Si) absorption band is due to the coordination of the Lewis acid through the O atom of the $Si(OCH_2CH_2)_3N$ group. The decrease in $\nu(C_4H_4N)$ in complex **1** denotes the π-coordination of the transition metal to the pyrrole cycle.

According to calculations,‡ complex **1** can exist as two isomers **1a** and **1b**, in which the distances from the Cu atom to one of the endocyclic O atoms of the silatranyl group and to the C atoms of the pyrrole ring are shortened.

The structures and relative energies of isomers **1a** and **1b** in a gas phase and in DMSO are given in Figure 1. Both isomers **1a** and **1b** are in equilibrium in the gas phase. The transition from the gas phase to a polar solvent in both isomers is accompanied by shortening the dative N→Si bond length and the Cu···C distance and by lengthening the Si–C bond. The Cu···O distance in isomer **1b** increases, and it substantially decreases in isomer **1a**, whereas isomer **1b** is stabilized relative to isomer **1a**.

† Copper(II) chloride dihydrate $CuCl_2\cdot 2H_2O$ was dehydrated upon heating *in vacuo* (0.002 bar, 150 °C, 2 h). Solvent was purified by a standard method. Initial compound 1-(1*H*-pyrrol-1-ylmethyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane was synthesized as described previously.[6] Melting points were determined using Micro-Hot-Stage PolyTherm A. IR spectra were recorded on a Bruker Vertex 70 instrument in a spectral range of 4000–500 cm^{-1} with the sample in the form of KBr pellet. Microelemental analysis was carried out on a Flash EA 1112 elemental analyzer and confirmed by electron-scanning X-ray microanalysis with a Hitachi TM-3000 X-ray microanalysis instrument.

*Synthesis of [$CuCl_2\cdot$**L**] [**L** = 1-(1-silatranylmethyl)pyrrole].* A solution of 1-(1-silatranylmethyl)pyrrole (430.0 mg, 1.7 mmol) in dry chloroform (10 ml) was added dropwise to $CuCl_2$ (230.0 mg, 1.7 mmol) in dry chloroform (5 ml) within 2 min at 25 °C. The reaction mixture was stirred for 3 h. The resulting black precipitate was filtered, washed with 10 ml of dry chloroform and dried *in vacuo*. Yield, 640 mg (97%). IR (ν/cm^{-1}): 1019, 1084, 1116 (C–O–Si), 1487, 1269 (C_4H_4N). Found (%): C, 33.93; H, 4.38; Cl, 18.62; Cu, 16.73; N, 7.51; Si, 6.90. Calc. for $C_{11}H_{18}Cl_2CuN_2O_3Si$ (%): C, 33.98; H, 4.67; Cl, 18.23; Cu, 16.34; N, 7.21; Si, 7.22.

‡ Geometry optimization of complex **1** in a gas phase and a polar solvent (DMSO) was carried out at the UPBE0/6-311+G(d,p) level of theory. The PBE0/6-311G(d,p) method has recommended itself well for studying silatranes.[7] For the reliable description of the paramagnetic character of **1**, the 6-311G(d,p) basis set was augmented with diffusion function on heavy atoms. The calculations in DMSO were performed to study the medium effect (close to that in crystals)[1(a)] on the structure of **1**. Solvent effect was estimated with the conductor-like polarizable continuum model (C-PCM).[8] The correspondence of the calculated structures to the minima on the potential energy surface was confirmed by the positive eigenvalues of the corresponding Hessians. Relative stabilities of isomers **1a** and **1b** were estimated as a difference in their electronic energies corrected for the zero-point vibrational energies (ΔE^{ZPE}) and as a difference in their Gibbs free energies under standard conditions (ΔG^{298}). The calculations were performed with the Gaussian 09.[9] The AIMAll[10] program was employed for the AIM[4] analysis of the UPBE0/6-311+G9(d,p) electron distribution $\rho(\boldsymbol{r})$ of calculated complex **1**.

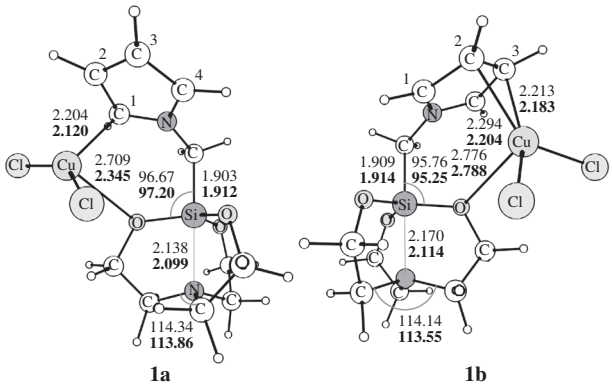


Figure 1 UPBE0/6-311+G(d,p) optimized geometry and relative energies of isomers **1a** and **1b** of the copper(II) complex with 1-(1-silatranylmethyl)-pyrrole in the gas phase and DMSO (boldfaced, C-PCM model). Bond distances are given in Å, bond angles in degree, energies in kcal mol^{-1}.

The existence of the Cu–O and Cu–C^1 bonds in isomer **1a**, and the Cu–O and Cu–C^3 bonds in isomer **1b** was confirmed by the AIM analysis of the electron density distribution $\rho(\boldsymbol{r})$.[4] The corresponding bond critical points [bcp(3,–1)] were found in the internuclear Cu···O and Cu···C^1 regions of isomer **1a** and in the Cu···O and Cu···C^3 regions of isomer **1b** (Table 1).

The Bader analysis of complex **1** indicates the formation of the Cu–C bond with only one C atom of the pyrrole ring. The values of $\rho(\boldsymbol{r}_c)$, the Laplacian $\nabla^2\rho(\boldsymbol{r}_c)$ and the electron energy density $E(\boldsymbol{r}_c)$ in the corresponding bcps suggest that the Cu···O bonds in isomers **1a** and **1b** are ionic, and the Cu–C bonds have a covalent component according to the Cremer–Kraka criterions.[5]

Thus, the analysis of the calculated structural and electron density characteristics of complex **1** demonstrates that not only the oxygen atom but also the π-electron system of the pyrrole ring in this structure are involved in the interaction with the Cu atom.

Table 1 Electron density [$\rho(\boldsymbol{r}_c)$/e Å^{-3}], the Laplacian of electron density [$\nabla^2\rho(\boldsymbol{r}_c)$/e Å^{-5}], and electron energy density [$E(\boldsymbol{r}_c)$/hartree Å^{-3}] at bond critical points bcp(3,–1) of the Cu–O and Cu–C bonds in isomers **1a** and **1b** calculated at the UPBE0/6-311+G(d,p) level of theory.[a]

Isomer	State	Cu–O			Cu–C		
		$\rho(\boldsymbol{r}_c)$	$\nabla^2\rho(\boldsymbol{r}_c)$	$E(\boldsymbol{r}_c)$	$\rho(\boldsymbol{r}_c)$	$\nabla^2\rho(\boldsymbol{r}_c)$	$E(\boldsymbol{r}_c)$
1a	Gas	0.119	1.440	–0.01	0.414	2.766	–0.12
	DMSO	0.247	3.282	–0.04	0.496	2.866	–0.16
1b	Gas	0.103	1.262	0.00	0.400	3.609	–0.10
	DMSO	0.099	1.228	0.00	0.436	4.272	–0.11

[a] 1 a.e. $\rho(\boldsymbol{r}_c)$ = 1 e/a_0^3 = 6.748 e Å^{-3}, 1 a.e. $\nabla^2\rho(\boldsymbol{r}_c)$ = 1 e/a_0^5 = 24.099 e Å^{-5}, 1 a.e. $E(\boldsymbol{r}_c)$ = 1 e^2/a_0^4 = 6.748 hartree Å^{-3}.

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