Organometallic Chemistry

Synthesis, structures, and spectral properties of biomimetic azomethine metal chelates with chromophores CuN₂S₂, CuN₂O₂, and CuN₂Se₂. Crystal structure of bis[4-(benzyl)aldimino-3-methyl-1-phenyl-5-pyrazolothiolato]copper(II)


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Copper(II) chelates of composition CuL₂ were synthesized based on 4-aminomethylene derivatives of 5-thiopyrazoles (LH). The complexes were studied by UV, IR, ESR, and EXAFS spectroscopy, magnetocchemistry, and X-ray diffraction analysis. The coordination polyhedra in the complexes are pseudotetrahedra or octahedra of the types CuN₂S₂ or CuN₄S₂, respectively, which are distorted due to the Jahn–Teller effect. The UV and ESR spectra of copper chelates with a six-coordinate metallocycle formed by the N and S atoms of the azomethine ligand and the nitrogen atom of the quinolyl substituent (R) of the C=N–R fragment are most similar to the spectra observed for metals involved in the active centers of natural metalloenzymes ("blue" copper proteins).

Key words: azomethine, copper, pyrazolines, chelates, biomimetic models, "blue" copper proteins, X-ray diffraction analysis, UV, ESR, and EXAFS spectroscopy.

The construction of biomimetic models of "blue" copper proteins responsible for the outer-sphere electron transfer in bioinorganic systems1–9 have attracted the continuing interest over many years. The active centers in these metalloenzymes contain the chromophore CuN₂Süp, which is characterized by a "blue" band (λ = 600 nm, ε = 4000–6000), the specific ESR spectrum (Δμ < 100 · 10⁻⁴ cm⁻¹), and a rather high reduction potential of the Cu[I]/Cu[II] pair.3,4,9,10 The reasons for the fact that "blue" copper proteins exhibit the above-mentioned peculiar properties have been discussed in the literature many times.5,9 Two factors re-
Responsible for the manifestation of these properties were revealed, viz., the high degree of covalence of the Cu—S bond and the low symmetry of the coordination polyhedron. The latter factor is difficultly reproducible in the case of simple biomimetic complexes. That is the reason why only one class of compounds, which adequately reproduce the physicochemical properties of the metalloenzymes under consideration, was found among several tens of models of “blue” copper proteins. This class involves a series of copper chelates containing tris(pyrazolyl)borate ligands of type 1.\textsuperscript{11–13}

However, this complex was not considered\textsuperscript{15} as a biomimetic model of the active center of “blue” copper proteins.

In the present work, we developed and used a procedure for the directed synthesis of biomimetic models of active centers of “blue” copper proteins based on a choice of ligands of type 4 for the preparation of metal chelates with open structures 5, including metal chelates with coordinatively active substituents (R) at the N atom of the azomethine fragment.

\[ R = \text{CPh}_3, \text{Bu}, \text{C}_6\text{F}_5 \]

Adequate synthetic models of active centers of copper-containing proteins with the N,S-ligand environment are limited in number due to oxidation of the thiolate group of the ligand by Cu\textsuperscript{2+} ions.\textsuperscript{2,9} The synthesis of stable metal chelates with the CuNS chromophore were primarily based on the use of rigid macrocyclic ligands and tetridentate Schiff’s bases containing a bridging fragment (for example, complex 2).\textsuperscript{2,9,14}

The tetrahedral distortion of the chelate unit of the complexes was achieved by either lengthening the bridges or introducing bulky substituents located in close proximity to the metal center. Up to now, complex 3 in which the dihedral angle between the NCuS planes of two different coordination units is 57° was the only example of an open structure containing the CuNS\textsubscript{2} coordination unit, which was characterized by X-ray diffraction analysis.\textsuperscript{15}

\[ \text{Me} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{Cu/2} \quad \text{Pr'} \] 3

Results and Discussion

Compounds of type 4 (LH), like other analogous complexes,\textsuperscript{16–20} have aminomethylene structure 4 with a strong NH...X hydrogen bond, which is confirmed by the fact that the \textsuperscript{1}H NMR spectra of systems 4a–m have doublet signals for the protons of the NH groups (at δ 13–15) with \( J_{\text{NH-CH}} = 12 \text{ Hz} \).

Metal chelates 5 of composition ML\textsubscript{2} were synthesized according to known procedures\textsuperscript{14,22,23} (Table 1). The IR spectra of these compounds have absorption bands of stretching vibrations of the coordinated pyrazoloazomethine fragment (at \(-1630 \text{ cm}^{-1} (X = O)\) and 1590 cm\textsuperscript{-1} (X = S)). In the studies of the magnetic properties of the metal chelates performed at \(-20 \text{ °C}\) and at the temperature of liquid nitrogen, magnetic moments typical of the mononuclear Cu\textsuperscript{II} complexes were obtained (1.76–2.0 \( \mu \text{B}\); see Table 2).

These data provide evidence in favor of formula 5, which we assigned to the chelates under consideration. Actually, X-ray diffraction study demonstrated that complex 5a in the crystal occupies a special crystallographic position on a twofold axes (C\textsubscript{2}) passing through the Cu atom (Fig. 1). The geometry of the bidentate ligand is