COMPLEXES OF METALS WITH PARAMAGNETIC 3-IMIDAZOLINE SCHIFF BASES

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Methods for the synthesis of intracomplex bischelates CuL₂, NiL₂, CoL₂, and the mixed-ligand complex NiL₂Py₂, where L is a deprotonated derivative of the stable nitroxide 4-(2'-hydroxyphenyl)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl, were developed. In the solid state, the compounds have a molecular structure. The most significant difference in the structure of ML₂ molecules lies in the values of the angle between the chelate rings (56.9° for CuL₂, 78.8° for CoL₂, and 0° for NiL₂). In complexes with paramagnetic metal ions, the intramolecular exchange interactions are ferromagnetic in character and are close in the order of magnitude (5.7 cm⁻¹ for CuL₂ and 6.8 cm⁻¹ for NiL₂Py₂) to the values for complexes with deprotonated enaminketone derivatives of 3-imidazoline. The NiL₂ molecules, having a square coordination of the central atom, are biradicals with antiferromagnetic exchange interactions between the unpaired electrons of nitroxyl groups (-3.6 cm⁻¹). The transformation of NiL₂ into NiL₂Py₂ leads to a transition of Ni(II) from the low- to high-spin state and to ferromagnetic exchange between the unpaired electrons of the paramagnetic centers.

In the course of our systematic investigations of the coordination compounds of metals with stable 3-imidazoline nitroxides [1, 2], we synthesized and studied the structure and magnetic properties of heterospin compounds based on the complexes of Cu(II), Ni(II), and Co(II) with a Schiff base 4-(2'-hydroxyphenyl)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (below HL). The paramagnetic HL attracted our attention because in ML₂ complexes the structure of the metalloccycle must be analogous to that in complexes with deprotonated enaminketone derivatives of 3-imidazoline nitroxide (ML₂), for which magnetic structure correlations are available. Comparing the properties of ML₂ and ML₂ allows us to trace the effect of the aromatic π-system in the side chain of the ligand on the intramolecular exchange parameters of the complex.

Coordination compounds with 3-imidazoline Schiff bases were not studied previously.
EXPERIMENTAL

Syntheses of the complexes

CuL2. To a solution of 0.043 g (0.21 mmole) of Cu(CH3COO)2(H2O) in 10 ml of water was added a solution of 0.1 g (0.42 mmole) of HL in 15 ml of ethanol. After the reagents were mixed, a brown precipitate immediately settled. The precipitate was filtered off and washed with water. The product (0.105 g) was dissolved in a mixture of 20 ml of methanol and 4 ml of dichloromethane. The resulting dark brown solution was stored at room temperature in a flask stoppered with cotton. Dichloromethane gradually evaporated during several days to form perfectly shaped black (or dark-green in transmitted light) crystals of the complex that were suitable for an X-ray diffraction analysis. Yield 80%. Tm = 229°C (decomp.). The compound is actually insoluble in alcohols (methanol, ethanol) even with heating, but is soluble in dichloromethane or chloroform, from which it settles on cooling as long dark-green needles. Found, %: C 58.6, H 6.2, N 10.3; calculated for CuC26H32N4O4, %: C 59.1, H 6.1, N 10.6.

NiL2. To a solution of 0.088 g (0.21 mmole) of NiBr2(CH3OH)6 in 10 ml of methanol was added in sequence a solution of 0.1 g (0.42 mmole) of HL in 15 ml of methanol and 0.12 ml of triethylamine. The resulting reaction mixture colored brown was kept at room temperature in a flask stoppered with cotton. In a day, dark-green crystals with a yellowish tint, suitable for an X-ray diffraction analysis, were filtered off and washed in a small amount of methanol. Yield 54%. Tm = 233°C (decomp.). The compound is well soluble in alcohols, benzene, chloroform, and acetone and is partially hydrolyzed by water. Found, %: C 58.8; H 6.4, N 10.3; calculated for NiC26H32N4O4, %: C 59.7, H 6.2, N 10.7.

NiL2Py2 was synthesized according to a procedure analogous to that for NiL2, except for the fact that an excess of pyridine was introduced into the starting reaction mixture. The compound crystallizes as green crystals suitable for an X-ray diffraction study. When heated in air above 120°C, the complex loses pyridine and then behaves as NiL2. Yield 75%. Found, %: C 62.9, H 6.2, N 12.3; calculated for NiC36H42N6O4, %: C 63.5, H 6.2, N 12.3.

CoL2 was synthesized according to a procedure that is completely analogous to that for NiL2, except the fact that Co(CH3COO)2(H2O)4 was used as a starting salt of the metal. CoL2 is formed as red crystals suitable for an X-ray diffraction investigation. Yield 67%, Tm = 240°C (decomp.). The compound is well soluble in alcohols, benzene, chloroform, and acetone and is partially hydrolyzed by water. Found, %: C 59.2, H 6.2, N 10.3; calculated for CoC26H32N4O4, %: C 59.7, H 6.2, N 10.7.

NiBr2(CH3OH)6. Commercial NiBr2 of pure grade contained a small amount of water; therefore, it was preliminarily calcinated on a stove at 300°C for half an hour. The substance changed color from light-yellow to brown, and its mass decreased by 4%. Then 6 g of calcinated NiBr2 was dissolved with heating in 40 ml of methanol. The resulting solution of light-yellow-green color (dark-green when cooled to room temperature) was filtered off from a small amount of the undissolved residue through a tight glass filter, and the filtrate was evaporated on a rotary evaporator until light-green crystals appeared on the walls of the flask. The compound was quickly filtered off and placed in a weighing bottle filled with argon. (The crystals of NiBr2(CH3OH)6 are stable in air for 4-5 min.). Yield 30%. Found, %: Ni 14.2, C 17.1, H 5.6; calculated for NiBr2C6H24O6, %: Ni 14.3, C 17.6, H 5.9.

Physical Measurements

The melting temperatures were determined on a "Boetius" heating table. The infrared spectra in the region of 400-4000 cm⁻¹ were recorded for KBr pellets of the samples on an ISF-66 BRUKER IR spectrometer.

Magnetic susceptibility of the polycrystalline samples of the complexes was measured by the Faraday method in the temperature range of 4.2-300 K and in magnetic fields of up to 10.9 kOe. The effective magnetic moment was calculated by the formula \( \mu_{eff} = (8\chi_M T)^{1/2} \), where \( \chi_M \) is the molar magnetic susceptibility corrected for diamagnetism.

The X-ray diffraction study was performed for CuL2, NiL2, and CoL2 single crystals. The crystal data of the complexes and some experimental details are given in Table 1. The structures were solved by direct methods using the SHELXS-86 program [3] and refined by full-matrix least-squares analysis for all nonhydrogen atoms. In the final cycle of the refinement, all hydrogen atoms were localized and then included in the refinement in an isotropic approximation. The final residuals are not higher than 4%. All calculations aimed at structure refinement were performed using the SHELXL-93 programs [4]. Tables 2, 4, and 6 list the coordinates and equivalent thermal parameters of nonhydrogen atoms; Tables 3, 5, and 7 give selected bond lengths. (The coordinates of the hydrogen atoms and the geometrical characteristics of the C-H bonds are available from the authors.)