Complexes of nickel(II) and copper(II) chlorides with a nitroxide radical derivative of 4-tetrazolyl-3-imidazoline-3-oxide

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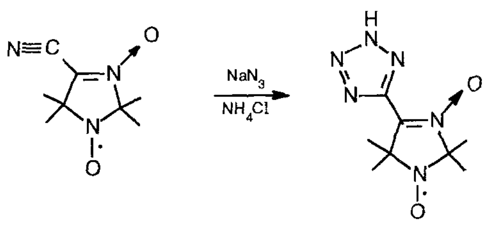
$NiCl_2$ and $CuCl_2$ complexes with a new stable nitroxyl radical, 2,2,5,5-tetramethyl-4-(tetrazol-5-yl)-3-imidazoline-3-oxide-1-oxyl (L), $NiLCl_2 \cdot H_2O$ and $CuLCl_2$, have been synthesized. The μ_{eff} values attest to a weak exchange interaction between the paramagnetic centers in the temperature interval of 78—300 K.

Key words: nitroxyl radical, complexes; exchange interaction; IR spectroscopy.

Earlier we synthesized and investigated complexes of paramagnetic transition-metal ions with various diamagnetic tetrazol derivatives that exhibit unusual magnetic properties. In particular, exchange interactions between unpaired electrons of metal ions in a $NiCl_2$ complex with 1,5-diaminotetrazole and a $CuCl_2$ complex with 1-vinyltetrazole are ferromagnetic in character.[1,2] It was of interest to synthesize Ni^{II} and Cu^{II} chloride complexes with paramagnetic tetrazole derivatives and to explore their magnetic properties. The key characteristic of this type of compound is that not only the central atoms, but also the ligands have unpaired electrons. In the present work a new nitroxyl radical, 2,2,5,5-tetramethyl-4-(tetrazol-5-yl)-3-imidazoline-3-oxide-1-oxyl (L), was used as a paramagnetic tetrazole derivative. It was prepared according to the following scheme:



L

In complexes of transition metals, the unpaired electron of the nitroxyl group of the stable free radicals derived from imidazoline can participate in exchange interactions, which results in the low temperature conversion into the ferromagnetic state.[3,4]

Results and Discussion

$NiLCl_2 \cdot H_2O$ (**1**) and $CuLCl_2$ (**2**) complexes were prepared by the reaction of equimolar amounts of the metal salts with radical L. X-ray analysis shows that the compounds obtained are crystalline.

The IR spectrum of the free ligand L exhibits absorption bands in the high-frequency area at 3200 and 3000—2900 cm^{-1} (for ν(NH) and ν(CH) of the tetrazol ring, respectively). The absorption bands at 1000—1100, 1250, and 1535 cm^{-1} may be also due to vibrations of the tetrazole ring.[5] Assignment of the absorption band for the $\nu(\mathrm{N}\dot{-}\mathrm{O})$ valent vibrations in the IR spectrum is complicated by their low intensity and the fact that they overlap with $\delta(CH_3)$ bands. However, the nitroxyl group vibration can be unequivocally identified in the Raman spectra, where $\nu(\mathrm{N}\dot{-}\mathrm{O})$ manifests itself as an intense band at 1438 cm^{-1}. The absorption band at 1300 cm^{-1} (in the IR spectrum of L) may be assigned to the vibration of the N→O fragment.[6]

The IR spectra of complexes **1** and **2** exhibit ν(NH) and ν(CH) absorption bands in the high-frequency area. The position of the ν(OH) band in the spectrum of complex **1** (3400 cm^{-1}) suggests that the water in this complex is either coordinated with the metal, or bound with the anion by strong hydrogen bonds, and the latter seems to be more probable. In the spectra of both complexes, the high-frequency band of the tetrazole cycle vibration is shifted downfield by 35 cm^{-1} relative to that in the spectra of L, which points to the coordination of L with the metal through the N atom of the tetrazole cycle. It should be noted that the formation of Ni^{II} and Cu^{II} complexes with other tetrazole deriva-

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tives[1,2] is accompanied by a 10—30 cm^{-1} upfield shift of the vibration bands of tetrazole. Apparently, the presence of a substituent with such a complex structure as 3-imidazoline3-oxide-1-oxyl in the side chain of tetrazole, results in the essential redistribution of electron density in the ring. The formation of complexes **1** and **2** results in a slight upfield shift of the ν(C=N) band of the imidazol cycle of L (1603 cm^{-1} in the IR spectrum and 1605 cm^{-1} in the Raman spectrum). The ν(N→O) band in the IR spectra of these complexes (1300 cm^{-1}) is shifted downfield by 20 cm^{-1} relative to the spectrum of L; in addition, in the spectrum of complex **2** this band is split. These changes in the positions of the ν(C=N) and ν(N→O) bands suggest the participation of the N→O group in the coordination with the metal.

The experimentally found value of μ_{eff} for complex **1** (3.53 μ_B) also attests that the paramagnetic susceptibility of L contributes to this value. The value μ_{eff} is only somewhat higher than the spin value 3.32 μ_B calculated for the case of a weak exchange interation between the Ni^{II} and L unpaired electrons according to the equation: $\mu = 2\,[S_{Ni^{II}}(S_{Ni^{II}}+1) + S_L(S_L+1)]^{1/2}$. The difference may be explained by the fact that the orbital contribution for Ni^{II} was not taken into account. The value of μ_{eff} for Ni^{II} calculated from the equation $\mu^2_{eff\ (exp)} = \mu^2_{eff}\ (Ni^{II}) + 3$ is 3.08 μ_B, which is in accord with a high-spin state of the d^8 configuration.

The spectrum of diffuse reflection (SDR) of complex **1** contains three nonsplit bands (390, 560, and 1100 nm). The value of μ_{eff}, as well as the number and position of bands for d—d-transitions in SDR, attest most probably to a distorted octahedral configuration of Ni^{II} ($^3A_{2g} \rightarrow {}^3T_{2g} \rightarrow {}^3T_{1g} \rightarrow {}^3T_{1g}(P)$ transitions).[7] In the case of an octahedral configuration, the value of the splitting parameter by the ligand field (Δ) is equal to 9.1 kK (a relatively weak field), which indicates that not only N atoms, but also O and Cl atoms are present in the coordination center. The obtained data allow one to conclude that in the equatorial plane of compound **1** ligand L is coordinated with the Ni atom by the N(1) atom of the tetrazole ring and by the O atom of the N→O group to form a six-membered metallocycle (coordination is complemented by two Cl atoms). Since complex **1** is believed to have a distorted octahedral structure of the coordination polyhedron according to the SDR and magnetochemistry data, it is possible to conclude that the N atoms of the other tetrazole cycles are additionally coordinated with Ni^{II} (NiN_3OCl_2 center).

The experimental value of μ_{eff} for compound **2** (2.57 μ_B) is close to the value 2.45 μ_B calculated for weak exchange interactions between the Cu^{II} and L unpaired electrons. This value is virtually independent of temperature within the interval 78—300 K, which indicates the absence of any notable exchange interaction between the paramagnetic centers in the investigated temperature interval ($|J| \ll kT$). On the other hand, the ESR spectrum of compound **2** exhibits weak exchange interaction, as follows from the reduced g-factors: $g_{\parallel} = 2.16$, $g_{\perp} = 2.046$.

The SDR of complex **2** shows one broad band at 780 nm. The absence of bands in the 900—1200 nm range of the SDR of complex **2** attests that tetrahedral coordination of the central atom[8] is no possible. Apparently, ligand L is coordinated with Cu^{II} in the equatorial plane analogously to its coordination in complex **1** resulting in the formation of a square unit $CuNOCl_2$, which is complemented by the N atoms of the neighboring molecules to form the distorted octahedral coordination (4+2).

Experimental

The metal content in the complexes was determined by trilonometry after decomposition of samples in a mixture of concentrated $HClO_4$ and H_2SO_4. The magnetic susceptibility of polycrystalline samples was measured by the Faraday method. The effective magnetic moments were calculated with the formula $\mu_{eff} = (8\chi T)^{1/2}$, where χ is the molar susceptibility (taking into account diamagnetism). The value of μ_{eff} for $CuLCl_2$ was determined in the temperature interval 78—300 K. Diffuse reflection spectra were obtained on a Unicam-700 A spectrophotometer. IR spectra were recorded on a Specord-75 IR spectrometer in the 400—3800 cm^{-1} interval, Raman spectra were obtained on a Triplemate, Spex spectrometer, and UV spectra were registered on a Specord UV-VIS instrument. The ESR spectrum of a powder of complex **2** was recorded on a RE-1306 spectrometer. X-ray diffraction patterns of the powders of the complexes were obtained on a DRON-3M X-ray diffractometer (Cu-Kα-radiation, Ni filter).

Analytically pure hydrates of Ni^{II} and Cu^{II} chlorides were used.

2,2,5,5-Tetramethyl-4-(tetrazol-5-yl)-3-imidazoline-3-oxide-1-oxyl (L). A solution of 3.64 g (0.02 mol) of 2,2,5,5-tetramethyl-4-cyano-3-imidazoline-3-oxide-1-oxyl, 1.42 g (0.022 mol) of NaN_3, and 1.18 g (0.022 mol) of NH_4Cl in 50 mL of 50 % ethanol was refluxed for 1 h. The solvent was removed under a vacuum, the solid residue was dissolved in 50 mL of water, and the solution was washed with chloroform (3 x 20 mL). The aqueous solution was acidified to pH ~2 with 10 % HCl and extracted with chloroform (3 × 20 mL). The extract was dried with $MgSO_4$, and the solvent was removed to give a residue of 2.74 g (61 %) of compound L. After recrystallization from EtOH, the yield of radical L was 40—45 %, m.p. 184—185 °C. Found (%): C, 2.7; H, 5.8; N, 37.3 $C_8H_{13}N_6O_2$. Calculated (%): C, 43.0; H, 6.0; N, 36.6. UV (EtOH), λ_{max}/nm (log ε): 280 (3.82).

Synthesis of $NiLCl_2 \cdot H_2O$ complex (1). A solution of 0.24 g (0.001 mol) of $NiCl_2 \cdot H_2O$ in a minimal volume of EtOH and a solution of 0.23 g (0.001 mol) of radical L in EtOH were mixed with heating. Most of the solvent was removed, and ether was added to the solution. After cooling the solution to 0 °C, complex **1** was formed as a green precipitate. It was filtered off, washed with a cold ethanol—ether mixture (1 : 3), and dried in a dessicator over anhydrone. The yield of **1** was 35 %. Found (%): C, 26.3; H, 4.6; N, 22.6; Ni, 16.4. $C_8H_{15}Cl_2N_6O_3Ni$. Calculated (%): C, 25.8; H, 4.1; N, 22.5; Ni, 15.7.

Synthesis of $CuLCl_2$ complex (2). Warm concentrated solutions of $CuCl_2 \cdot 2H_2O$ (0.17 g, 0.001 mol) and radical L (0.23 g, 0.001 mol) in ethanol were mixed. After cooling, complex **2** as a dark green precipitate was filtered off, recrystallized from EtOH, and dried as in the case of complex **1**. The yield of compound **2** was 55 %. Found (%): C, 28.3; H, 4.0; N, 24.0; Cu, 17.6. $C_8H_{13}Cl_2N_6O_2Cu$. Calculated (%): C, 26.7; H, 3.7; N, 23.4; Cu, 17.7.

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