**Copper(II) and Nickel(II) Alkylxanthate Complexes**

**(R = C₂H₅, i-C₃H₇, i-C₄H₉, s-C₄H₉, and C₅H₁₁): EPR and Solid-State ¹³C CP/MAS NMR Studies**

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**Abstract**—Alkylxanthate complexes of the general formula [M(S(SCOR))]₂ (M = Ni, Cu; R = C₂H₅, i-C₃H₇, i-C₄H₉, s-C₄H₉, and C₅H₁₁) were synthesized and studied by EPR and high-resolution solid-state ¹³C CP/MAS NMR. In the copper(II) complexes stabilized in the matrix of nickel(II) compounds, square planar nickel(II) complexes (Cu : Ni = 1 : 1000). Such a technique allows one to stabilize [CuS₄] and the corresponding dixanthogens: [CuS₄]²⁻ + 2ROC(S)S⁻ = 2[Cu(S₂COR)₂]

EXPERIMENTAL

Ni(II) complexes of the formula [NiS(SCOR)]₂ (R = C₂H₅ (I), i-C₃H₇ (II), i-C₄H₉ (III), s-C₄H₉ (IV), and C₅H₁₁ (V)) were synthesized by reactions of Ni²⁺ with the corresponding alkylxanthate ions in aqueous solutions. Voluminous greenish yellow precipitates were washed by decantation, filtered off, and dried in air. Individual copper(II) alkylxanthate complexes cannot be isolated because they are immediately involved in the intermolecular redox reaction yielding copper(I) compounds and the corresponding dixanthogen:

2Cu²⁺ + 4ROC(S)S⁻ = 2[Cu(S₂COR)₂] + ROC(S)S⁻ + S(SCR).

Copper(II) complexes of the formula [CuS(SCOR)]₂ (R = C₂H₅ (VI), i-C₃H₇ (VII), i-C₄H₉ (VIII), and C₅H₁₁ (IX)) were synthesized in a state magnetically diluted with the corresponding Ni(II) compounds (Cu : Ni = 1 : 1000). Such a technique allows one to stabilize [CuS(SCOR)]₂ molecules in the matrix of nickel(II) complexes (except for plastic [NiS(SCOR)]₂) and study their structures and spectroscopic properties. Copper(II) complexes were obtained as isotope-substituted compounds from isotope-enriched copper salts containing ⁶⁵Cu (99.3(1) at. %) and ⁶⁴Cu (99.2(1) at. %).

Sodium and potassium alkylxanthates (Cheminova Agro A/S and Hoechst) were additionally characterized by ¹³C MAS NMR data:

Na[S₁₂CO₈C₂H₅] (δ, ppm): 231.1, 230.0, 229.5 (–S₂CO–), 73.4, 72.6 (–OCH₂–), 15.9, 14.5, 14.1 (–CH₃).

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Na\{S\_2CO\_i-C\_H\_2\} (δ, ppm): 231.8 (–S\_2CO–), 79.2 (–OCH=), 23.5, 20.6 (1 : 1, –CH₃).
Na\{S\_2CO\_s-C\_H\_3\} (δ, ppm): 231.9 (–S\_CO–), 84.0, 83.7 (–OCH=), 30.0, 29.2 (–CH=), 19.4, 17.2 (1 : 1, –CH₃), 12.0 (–CH₃).
K\{S\_2CO\_s-C\_H\_3\} (δ, ppm): 234.0, 233.5 (–S\_CO–), 80.9, 75.5 (1 : 3, –OCH=), 35.0, 28.5, 27.5, 23.2, 20.8, 17.9 (–CH=), 17.0, 14.5, 12.5 (–CH₃).

EPR spectra were recorded on a 70-02 XD/1 radio spectrometer (–9.5 GHz, MP SZ, Minsk) at ~295 K. The working frequency was measured with a CH₂-46 microwave frequency meter. g Factors were calculated with reference to DPPH. The errors in g value and HFS constant (Oe) determination were ±0.002 and ±2%, respectively. The EPR parameters were refined by simulating the experimental spectra within the second order of perturbation theory with the use of the WIN-EPR SimFonia program (Bruker Co. software, version 1.2).

The simulation was performed in two steps. First, theoretical EPR spectra were simulated for first derivatives and finally approximated for second and third derivatives characterized by substantially narrower resonance signals. In the approximation, g values, HFS constants, resonance line widths, and contributions (in percent) from the Lorentz and Gauss components to the line shape were varied.

Room-temperature ¹³C NMR spectra were recorded on a CMX-360 pulse spectrometer (90.52 MHz; Chemagnetics Infinity Co., USA) with a superconducting magnet (B₀ = 8.46 T) and a Fourier transform. The ¹³C–¹³C cross polarization technique was used. The ¹³C–¹H dipolar couplings were suppressed via proton decoupling in a magnetic field with the corresponding proton resonance frequency [3]. Samples (~350 mg) of the complexes were placed in a zirconium dioxide rotor 7.5 mm in diameter. The spinning rates in ¹³C MAS NMR experiments were 2700 to 5500 Hz; the number of scans was 256 to 2820; the duration of proton π/2 pulses was 4.5 µs; the ¹H–¹³C contact time was 2.0 to 5.0 ms; excitation pulses were spaced at 2.0 s.

Isotropic ¹³C chemical shifts δ (ppm) are referenced to a line of crystalline adamantane used as the external standard (δ 38.56 ppm relative to tetramethylsilane [4]). The width of a reference line for crystalline adamantane (2.1 Hz) was used to check the homogeneity of the magnetic field. The isotropic chemical shifts were corrected for drift of the magnetic field strength during the NMR experiments (its frequency equivalent for ¹³C nuclei was 0.051 Hz/h). Chemical shifts and integrated intensity ratios for overlapping signals in the ¹³C NMR spectra were additionally refined by fragment-by-fragment simulation considering line positions and widths and contributions from the Lorentz and Gauss components to the line shapes.

**RESULTS AND DISCUSSION**

Experimental EPR spectra of magnetically diluted copper(II) alkylxanthate complexes (Figs. 1, 2) are nearly axially symmetric, which suggests the square planar structure of chromophores [CuS₄] with predominant localization of the unpaired electron at the Cu 3dₓ²₋ᵧ² AO. Therefore, the complexes obtained contain the sp²d-hybridized copper atom (s: + pₓ + pᵧ + dₓ²₋ᵧ² AO) and, since the ⁴d AO is involved, can be classified as outer-orbital ones (in contrast to the corresponding inner-orbital nickel(II) compounds).