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Transition metal complexes with thiosemicarbazide-based ligands: Part 59. Synthesis, structures and electrochemical properties of cobalt(III) complexes with 2-acetylpyridine S-methylisothiosemicarbazone

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ABSTRACT

The paper is concerned with the crystal structure and electrochemical characteristics of the cobalt(III) complexes with 2-acetylpyridine S-methylisothiosemicarbazone (HL), of the coordination formulas $[CoL_2]NO_3 \cdot MeOH$ (**1**), $[CoL_2]Br \cdot MeOH$ (**2**), $[CoL_2]HSO_4 \cdot MeOH$ (**3**), $[CoL_2]_2[Co^{II}(NCS)_4]$ (**4**), $[Co(HL)(L)]I_2 \cdot 2\,MeOH$ (**5**), and $[Co(HL)(L)][Co^{II}Cl_4] \cdot MeOH$ (**6**), as well as of the structure of HL. In all the complexes, Co(III) is situated in a slightly deformed octahedral environment formed by six nitrogen atoms of the two HL molecules in the meridional positions. The ligands coordinate with Co(III) in a usual way, i.e. via the pyridine, azomethine, and isothioamide nitrogen atoms, each forming two five-membered metallocycles. Electrochemical studies of the ligand and the complexes in DMF show that the electrode processes are accompanied by chemical reactions and the corresponding mechanism was proposed. The obtained complexes were also characterized by elemental analysis, conductometric measurements and UV–Vis and IR spectroscopy.

1. Introduction

Thiosemicarbazones $R^1R^2C{=}N^1{-}N^2H{-}C^3({=}S){-}N^4H_2$ and isothiosemicarbazones $R^1R^2C{=}N^1{-}N^2{=}C^3({-}SR^3){-}N^4H_2$, as well as their complexes, have been attracting attention of the researchers for a number of years, not only because of their interesting physicochemical and structural characteristics, but also because of the biological properties. In favor of this speak also several reviews of thiosemicarbazones [1], and a monograph about isothiosemicarbazones [2]. The α(N) heterocyclic thiosemicarbazones, including also 2-acetyl pyridine thiosemicarbazone, and especially their N^4-substituted derivatives, show a wide spectrum of biological activities as they can act as: antituberculous, antiviral, antifungal, antimalaric, and antitumor agents [1,3–5]. The biological significance of this class of compounds can be judged from the data that they belong to the most important inhibitors of ribonucleotide reductase. On the other hand, between the activity of this enzyme and the rate of replication of cancer cells there is a positive correlation [6,7]. The data about biological activity of S-alkylisothiosemicarbazones are rather scarce, but a recent study showed that they possess antituberculous activity [8].

A large number of complexes of 2-acetylpyridine thiosemicarbazone (HL′) and its N^4-substituted derivatives with both transition and non-transition metals have been prepared [1], of which, to our knowledge, only two cobalt complex have been structurally characterized, viz. Co(III) complexes $[CoL'_2]ClO_4 \cdot 2H_2O$ and $[CoL'_2]ClO_4 \cdot 1.5EtOH$ [9]. Considering the structural data deposited in CSD (Nos. 286570 and 286574) we claim that authors [9] have misinterpreted results of structural analysis and erroneously described the obtained compounds as cobalt(II) instead of cobalt(III) complexes.

In the majority of cases, this group of ligands coordinate in a tridentate manner through the pyridine and azomethine nitrogen atoms and sulfur atom of the thioamide group. However, there are also several examples of complexes involving S-monodentate, NS-bidentate, as well as the NNS-tetradentate coordination mode with a bridging role of the sulfur atom [6,10–15].

In contrast to this, there have been known only a limited number of transition metal complexes with 2-acetylpyridine S-methylisothiosemicarbazone (HL) [16,17], of which only three mono-ligand complexes of Cu(II) have been characterized up to now [17]. It has been found that this ligand coordinates as a neutral NNN tridentate ligand, which is in agreement with the general mode of coordination of isothiosemicarbazones, in which, instead of the sulfur atom, the isothioamide nitrogen atom is engaged in coordination [2]. With the aim of a further investigation of the

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coordination chemistry of 2-acetylpyridine S-methylisothiosemicarbazone, this work deals with the structure of HL, as well as the synthesis, structure, spectral and electrochemical characteristics of two types of bis(ligand) octahedral complexes of cobalt(III), viz. the monocationic $[CoL_2]^+$ and dicationic $[Co(HL)(L)]^{2+}$.

2. Experimental

2.1. Materials and physical measurements

All chemicals for the synthesis were analytical reagent grade. Elemental analysis (C, H, N and S) of air-dried compounds was carried out by standard micro-methods in the Center for Instrumental Analyses, ICTN in Belgrade. Magnetic susceptibility measurements were conducted at room temperature on an MSB-MK1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Molar conductivity of freshly prepared 1 mM solutions were performed on a Jenway 4010 conductivity meter. IR spectra were recorded on a Nicolet Nexus 670 FTIR (Thermo Scientific) spectrophotometer, in the range of 400–4000 cm^{-1} by KBr pellet technique. Melting points were measured on a Nagema hot stage microscope Rapido. Electronic spectra of DMF solutions of the ligand and complexes were recorded on a T80+ UV–Vis Spectrometer (PG Instruments Ltd.), in the spectral range of 270–1000 nm.

2.2. Preparation of the ligand

Single crystals of 2-acetylpyridine S-methylisothiosemicarbazone were obtained according to a slightly modified procedure [16], and used without further purification. Namely, 2-acetylpyridine (3 mL), $Na_2CO_3 \cdot 10H_2O$ (3.34 g) and S-methylisothiosemicarbazide hydrogen-iodide (5 g) were added to EtOH (20 mL). The mixture was refluxed at a moderate temperature for about 3 h with constant stirring. After 48 h at room temperature, by overpouring "thick" mass with water, light-yellow single crystals were filtered off, and washed with water. Yield 3.08 g (74%). *Anal.* Calc. for $C_9H_{12}N_4S$: C, 51.90; H, 5.81; N, 26.90; S, 15.39. Found: C, 51.81; H, 5.36; N, 26.19; S, 15.04%. M.p. 86–87 °C. Conductivity [$\Lambda_M/\Omega^{-1}\,cm^2\,mol^{-1}$]: 8 in DMF. IR [$\tilde{\nu}/cm^{-1}$]: 3359 m, 3246 m, 3152 m, 3004 w, 2930 w, 1596 s, 1559 m, 1520 s, 1468 s, 1426 s, 1360 m, 1297 m, 990 m, 780 m. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 315 (4.38).

2.3. General procedure for preparation of the complexes

HL was added to the solution of cobalt(II) salt in MeOH and stirred at room temperature until clear solution was formed. After 24 h at room temperature, crystals suitable for X-ray crystallographic analysis were filtered off, washed with EtOH and dried with Et_2O.

2.3.1. Complex **1** $[CoL_2]NO_3 \cdot MeOH$

$Co(NO_3)_2 \cdot 6H_2O$ (150 mg, 0.5 mmol) in MeOH (5 mL) and HL (104 mg, 0.5 mmol) were treated by the general procedure to afford **1** as red crystals. Yield: 80 mg (28%). *Anal.* Calc. for $C_{19}H_{26}CoN_9O_4S_2$: C, 40.21; H, 4.62; N, 22.21; S, 11.30. Found: C, 40.20; H, 23.51; N, 4.22; S, 12.49%. M.p. >330 °C. Conductivity [$\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$]: 78 in DMF, 81 in MeOH. IR [$\tilde{\nu}/cm^{-1}$]: 3398 br, 3211 br, 2923 w, 1600 m, 1552 m, 1493 s, 1452 s, 1383 s, 1357 s, 1312 s, 1149 s, 979 m, 782 m, 680 w, 688 w. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 317 (4.51), 433 (4.11).

2.3.2. Complex **2** $[CoL_2]Br \cdot MeOH$

$CoBr_2$ (50 mg, 0.25 mmol) in MeOH (10 mL) and HL (104 mg, 0.5 mmol) were treated by the general procedure to afford **2** as red crystals. Yield: 50 mg (34%). *Anal.* Calc. for $C_{19}H_{26}CoN_9O_4S_2$: C, 48.52; H, 7.86; N, 17.56; S, 8.93. Found: C, 48.14; H, 8.00; N, 17.31; S, 8.88%. M.p. >330 °C. Conductivity [$\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$]: 70 in DMF, 80 in MeOH. IR [$\tilde{\nu}/cm^{-1}$]: 3348 w, 3236 br, 2978 w, 1599 s, 1551 m, 1493 s, 1448 s, 1358 s, 1315 s, 1293 s, 1165 s, 1143 s, 917 m, 778 sh. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 318 (4.45), 433 (4.11).

2.3.3. Complex **3** $[CoL_2]HSO_4 \cdot MeOH$

$CoSO_4 \cdot 7H_2O$ (71 mg, 0.25 mmol) in MeOH (10 mL) and HL (104 mg, 0.5 mmol) were treated by the general procedure to afford **3** as brown crystals. Yield: 180 mg (12%). *Anal.* Calc. for $C_{19}H_{26}BrCoN_8OS_2$: C, 37.87; H, 4.52; N, 18.60; S, 15.96. Found: C, 38.22; H, 4.21; N, 19.31; S, 16.82%. M.p. >330 °C. Conductivity [$\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$]: 47 in DMF, 70 in MeOH. IR [$\tilde{\nu}/cm^{-1}$]: 3440 br, 3198 br, 1599 w, 1552 w, 1493 m, 1451 m, 1359 m, 1315 m, 1147 vs, 1057 m, 916 m, 774 m. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 318 (4.43), 433 (4.11).

2.3.4. Complex **4** $[CoL_2]_2[Co^{II}(NCS)_4]$

$Co(NCS)_2$ (170 mg, 1 mmol) in MeOH (10 mL) and HL (208 mg, 1 mmol) were treated by the general procedure to afford **4** as green crystals. Yield: 300 mg. (23%). *Anal.* Calc. for $C_{42}H_{48}Co_2N_{22}S_{10}$: C, 38.82; H, 3.72; N, 23.71; S, 24.67. Found: C, 37.02; H, 3.15; N, 22.19; S, 21.91%. M.p. 295 °C. Conductivity [$\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$]: 172 in DMF, 169 in MeOH. Magnetic moment [μ/BM]: 4.65. IR [$\tilde{\nu}/cm^{-1}$]: 3442 br, 3176 br, 2107 w, 2052 s, 2067 m, 1598 m, 1534 w, 1492 s, 1447 s, 1384 s, 1360 s, 1309 s, 1169 vs, 1151 vs, 918 m, 770 m. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 318 (4.70), 433 (4.34), 584 sh (1.62), 620 (2.34).

2.3.5. Complex **5** $[Co(HL)(L)]I_2 \cdot 2MeOH$

CoI_2 (180 mg, 0.5 mmol) in MeOH (10 mL) and HL (208 mg, 1 mmol) were treated by the general procedure to afford **5** as brown crystals. Yield: 265 mg. (64%). *Anal.* Calc. for $C_{20}H_{31}CoI_2N_8O_2S_2$: C, 30.32; H, 3.94; N, 14.14; S, 8.09. Found: C, 30.14; H, 3.21; N, 14.00; S, 7.98%. M.p. >330 °C. Conductivity [$\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$]: 100 in DMF, 130 in MeOH. IR [$\tilde{\nu}/cm^{-1}$]: 3398 m, 3239 br, 2919 w, 1631 w, 1598 m, 1552 m, 1492 m, 1445 s, 1358 m, 1312 s, 1164 s, 1142 vs, 916 m, 767 m. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 317 (4.60), 432 (4.18).

2.3.6. Complex **6** $[Co(HL)(L)][Co^{II}Cl_4] \cdot MeOH$

$CoCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) in MeOH (5 mL) and HL (208 mg, 1 mmol) were treated by the general procedure to afford **6** as green crystals. Yield: 248 mg. (35%). *Anal.* Calc. for $C_{19}H_{27}Cl_4Co_2N_8O_2S_2$: C, 32.26; H, 3.94; N, 15.84; S, 9.07. Found: C, 32.56; H, 4.04; N, 16.08; S, 9.62%. M.p. 287 °C. Conductivity [$\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$]: 75 in DMF, 290 in MeOH. Magnetic moment [μ/BM]: 4.52. IR [$\tilde{\nu}/cm^{-1}$]: 3295 s, 3052 m, 2927 m, 1633 m, 1599 s, 1557 s, 1497 s, 1456 s, 1358 s, 1314 s, 1161 vs, 1151 vs, 1105 s, 1025 s, 917 m, 781 s, 685 m, 541 m. UV–Vis [λ_{max}/nm ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 318 (4.45), 433 (4.15), 596 (2.31), 606 (2.13), 628 (2.04), 677 (2.60).

2.4. X-ray crystal structure determination

Suitable single crystals of the complexes were selected and glued on glass fiber. However, HL crystals were oversized and twined, and could not be cut without severe damaging. Therefore, a large block-shaped twined crystal was glued on a fiber, and its size was reduced by dissolving in acetone until the remaining crystal gave a satisfactory diffraction image. Diffraction measurements were performed on a Gemini S diffractometer (Agilent Technologies) equipped with Sapphire CCD detector. The crystal-to-detector distance was 45 mm, and graphite monochromated Mo Kα (0.71073 Å) radiation was used. Data integration, scaling and