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Mixed-ligand nickel(II) and copper(II) complexes of tridentate ONS and NNS ligands derived from *S*-alkyldithiocarbazates with the saccharinate ion as a co-ligand

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ABSTRACT

New mixed-ligand complexes of the general formula, [M(L)(sac)] (M = Ni^{2+}, Cu^{2+}; L^- = anionic forms of the salicylaldehyde Schiff base of *N*-methyl-*S*-methyldithiocarbazate (Hsalsme), the salicylaldehyde 2-*N*-methyl-3-thiosemicarbazone (Hsaltsc), the methylpyruvate Schiff base of *S*-methyldithiocarbazate (Hmpsme) and the quinoline-2-methoxycarboxaldehyde Schiff base of *S*-methyldithiocarbazate (quinolsme); sac^- = the saccharinate anion) have been synthesized and characterized by IR, electronic and magnetic susceptibility measurements. Magnetic and spectroscopic data support a distorted square-planar structure for the [M(ONS/NNS)(sac)] complexes (ONS/NNS = salsme, saltsc, mpsme or quinolsme).

The structures of Hsalsme, [Cu(salsme)sac] and [Cu(quinolsme)sac] have been determined by X-ray diffraction. The complex, [Cu(salsme)sac] has a distorted square-planar structure with the Schiff base acting as a uninegatively charged ONS tridentate chelating agent coordinating the copper(II) ion via the phenolic oxygen, the azomethine nitrogen and the thione sulfur atoms, the fourth coordination position being occupied by an N-bonded saccharinate anion.

The reaction of $[Cu(sac)_4(H_2O)_2]\cdot 2H_2O$ with the 2-quinolinecarboxaldehyde Schiff base of *S*-methyldithiocarbazate (Hqsme) in boiling methanol does not lead to the formation of the expected mixed-ligand complex, [Cu(qsme)(sac)], but an unusual substitution of the hydrogen atom attached to the azomethine carbon by a methoxy group occurs with the concomitant formation of the complex [Cu(quinolsme)(sac)] of a new ligand (quinolsme = anionic form of the quinolone-2-methoxycarboxaldehyde Schiff base of *S*-methyldithiocarbazate). An X-ray crystal structure determination reveals that the Schiff base Hquinolsme is coordinated to the copper(II) ion in its deprotonated thiolate form as an NNS tridentate chelating agent and the fourth coordination position of the square-planar copper(II) centre is occupied by an N-bonded saccharinate anion.

1. Introduction

Thiosemicarbazones [1–5] and Schiff bases derived from *S*-alkyl/aryl esters of dithiocarbazic acid [6–10] have attracted considerable attention as chelating agents. These ligands possess both hard nitrogen and soft sulfur donor atoms in their backbones by virtue of which they are capable of coordinating with a wide range of metal ions, forming stable and intensely coloured metal complexes, of which some have been found to exhibit interesting physicochemical properties [11] and potentially beneficial biological activities [1,5,9,12]. Although a very large number of metal complexes of thiosemicarbazones [1–5] and dithiocarbazates [6–10] have been reported, mixed-ligand complexes containing ONS and NNS tridentate dithiocarbazates and the saccharinate ion as a co-ligand have not been studied thoroughly. Saccharine (1,2-dioxo-1,2-benzothiazol-3-one or o-sulfobenzoimide) is a well-known sugar substitute which also exhibits interesting coordination chemistry as it has three potential donor atoms, the carbonyl oxygen, the imino nitrogen and the two sulfonyl oxygen atoms. The presence of these donor atoms allows it to coordinate to transition metal ions either as a monodentate ligand, via the imino nitrogen or its carbonyl oxygen atom, or as a bidentate ligand via both donor atoms [13]. In view of the interesting coordination chemistry and potentially useful biological activities of both dithiocarbazates and the saccharinate ion and as part of our on-going work on metal complexes of ligands containing nitrogen and sulfur donor atoms, we report here the preparation and characterization of some new

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mixed-ligand nickel(II) and copper(II) complexes of the type [M(ONS/NNS)sac] (ONS/NNS = a uninegatively charged tridentate thiosemicarbazone or dithiocarbazate ligand; sac^- = the saccharinate anion), together with the X-ray crystal and molecular structures of Hsalsme, [Cu(salsme)(sac)] and [Cu(quinolsme)(sac)].

2. Experimental

2.1. Materials

All the chemicals and solvents were of analytical reagent grade and were used without any further purification. They were purchased from either Aldrich, Merck or Fluka.

2.2. Physical methods

The melting points of the compounds were determined by a Melting Point apparatus SMP1 Stuart Scientific. The electronic spectra were recorded both in the solid state (Nujol mull) and in solution with a Shimadzu UV-3100 spectrophotometer. The IR spectra were recorded with either a Perkin-Elmer 1600 FT IR spectrometer or a Perkin-Elmer 2000 spectrometer. Conductance measurements were made by means of a CMD 400 conductivity meter. All other physical method measurements were performed as described previously [6].

2.3. Synthesis of the compounds

2.3.1. Preparation of the ligands

2.3.1.1. Preparation of Hsalsme. This compound was prepared by following the published procedure [14].

2.3.1.2. Preparation of Hsaltsc·H_2O. Salicylaldehyde (2.31 g; 0.019 mol) dissolved in warm abs. ethanol (15 mL) was added to a solution of 2-methyl-3-thiosemicarbazide in a 3:1:1 mixture of dichloromethane, abs. ethanol and acetonitrile (50 mL) to yield a colourless solution. A few drops of glacial acetic acid were added and the mixture was heated on a water bath for 30 min, whereupon it was left to stand overnight with the formation of a yellow microcrystalline product. The product was filtered, washed several times with cold ethanol and dried in a desiccator over anhydrous silica gel. Yield: 2.8 g (71%); m.p.: 159–160 °C. The crude product was recrystallized from a chloroform–methanol mixture (9:1). *Anal.* Calc. for Hsaltsc·H_2O ($C_9H_{13}N_3O_2S$): C, 47.56; H, 5.76; N, 18.49. Found: C, 47.60; H, 5.70; N, 18.52%. IR (KBr, cm^{-1}): ν(NH) 3429s,sh, 3322m, ν(CN) 1584s, ν(NN) 1156s, ν(CS) 883m; UV–Vis [λ_{max} (Nujol): 336, 302sh; λ_{max} (DMSO, nm) ($\log\varepsilon$ in parenthesis): *ca.* 350sh, 338(2.46) 310(4.24), *ca.* 297sh. NMR [$CDCl_3$] (ppm) δ_H: 10.10(s, 1H, OH), 8.31 and 8.20(s, 2H, $-NH_2$), 8.06(s, 1H, N=CH), 7.25(m, 1H, Ar–H), 6.92–6.80(m, 2H, Ar–H), 3.61, (CH_3). δ_C: 182.28(CS), 157.48(CH=N), 138.07(C–O), 132.06, 127.74, 121.34, 120.24, 116.98(Ar–C), 33.48 (NCH_3).

2.3.1.3. Preparation of Hmpsme and Hqsme. These ligands were prepared following the same procedures as described previously [15,16].

2.3.2. Preparation of [$M(sac)_2(H_2O)_4$]·$2H_2O$ (M = Cu^{2+}, Ni^{2+})

These complexes were prepared according to the literature method [17].

2.3.3. General method of preparation of the [Cu(ONS/NNS)(sac))] complexes

To a solution of the copper(II)–saccharinate complex [$Cu(sac)_2(H_2O)_4$·$2H_2O$] (1.3 mmol) in boiling methanol (200 mL) was added a hot solution of the ligand (1.3 mmol) in the same solvent (30 mL). The mixture was then refluxed for 1 h, after which time it was left to stand to cool to room temperature, and the product that had formed was filtered off, washed with ethanol and dried in a desiccator over anhydrous silica gel.

[Cu(salsme)sac]: Dark-green crystals. *Anal.* Calc. for $C_{17}H_{15}N_3O_4S_3Cu$: C, 42.10; H, 3.53; N, 8.66. Found: C, 41.62; H, 2.98; N, 9.17%. μ_{eff}: 1.91 μ_B. Λ_M (10^{-3} M, DMSO, Ω^{-1} cm^2 mol^{-1}): 22.1. IR (KBr, cm^{-1}): ν(CN) 1574m, ν(NN) 1119ms, ν(CS) 871m; $\nu(SO_2)$ 1168s, $\nu(SO_2)$ 1295vs, ν(CO) 1660vs. UV–Vis spectrum λ_{max} (in Nujol, nm): 615sh, 390sh, 342,298; λ_{max} (saturated solution in DMSO, nm): 657, 427, 320sh, 300, 257, 209.

[Ni(salsme)sac]: Brown solid. *Anal.* Calc. for $C_{17}H_{15}N_3S_3O_4Ni$: C, 42.52; H, 3.57; N, 8.75. Found: C, 42.35; H, 3.01; N, 9.41%. μ_{eff}: 0.57 μ_B. Λ_M (10^{-3} M, DMSO, Ω^{-1} cm^2 mol^{-1}): 6.4. IR (KBr, cm^{-1}): ν(CN) 1574m, ν(NN) 1124m, ν(CS) 799s, $\nu(SO_2)$ 1295vs, $\nu(SO_2)$ 1162vs, ν(CO) 1671vs. λ_{max} (in Nujol, nm): 465, 390, *ca.* 370sh, 307; (DMSO, nm; $\log\varepsilon$ in parentheses): *ca.* 794sh, *ca.* 608sh, 430, 355(4.47), 319(4.22), *ca.* 310sh, 257(4.36).

[Cu(saltsc)(sac)].3H_2O: Apple green solid. *Anal.* Calc. for $C_{16}H_{16}N_4O_7S_2Cu$: C, 37.83; H, 3.93; N, 11.02. Found: C, 37.40; H, 3.97; N, 11.04%. μ_{eff}: 2.00 μ_B. Λ_M (10^{-3} M, DMSO, Ω^{-1} cm^2 mol^{-1}): 11.1. IR (KBr, cm^{-1}): ν(CN) 1602s, ν(NN) 1054s, ν(CSS) 918s, $\nu(SO_2)$ 1275sh, $\nu(SO_2)$ 1154m, ν(CO) 1680s, ν(OH)(H_2O) 3351br. λ_{max} (in Nujol, nm): 465, 390, *ca.* 370sh, 307; (DMSO, nm; $\log\varepsilon$ in parentheses): *ca.* 794sh, *ca.* 608sh, 430, 355(4.47), 319(4.22), *ca.* 310sh, 257(4.36).

[Cu(quinolsme)(sac)]: Dark green solid. *Anal.* Calc. for $C_{20}H_{18}CuN_4O_5S_3$: C, 43.37; H, 3.45; N, 10.6. Found: C, 43.88; H, 3.04; N, 10.78%. μ_{eff}: 1.96 B.M.; Λ_M (10^{-3} M, DMSO, Ω^{-1} cm^2 mol^{-1}): 16.4. IR (KBr, cm^{-1}): ν(CN) 1592m, ν(NN) 1128w, ν(CS) 884ms, $\nu(SO_2)$ 1296vs, $\nu(SO_2)$ 1150s, ν(CO) 1676vs, ν(OH)(MeOH) 3462br. λ_{max} (in Nujol, nm): 636, 394sh, 301; (DMSO, nm; $\log\varepsilon$ in parentheses): 580(2.41), *ca.* 415sh, 409, 350(4.67), *ca.* 339sh, *ca.* 311sh, 257(4.74).

[Cu(mpsme)(sac)]·CH_3OH: Dark-green solid. *Anal.* Calc. for $C_{13}H_{13}N_3CuO_5S_3$: C, 34.79; H, 3.54; N, 8.69. Found: C, 34.62; H, 3.21; N, 8.83%. μ_{eff}: 2.22 μ_B. Λ_M (saturated solution in DMSO, Ω^{-1} cm^2 mol^{-1}): 3.48. IR (KBr, cm^{-1}): ν(CN) 1552w, ν(NN) 1099s, ν(CS) 869s, $\nu(SO_2)$1275sh, $\nu(SO_2)$1134m, ν(CO)1680sh, ν(OH) (MeOH)3462br. λ_{max} (in Nujol): 642, 426, *ca.* 280sh; (DMSO, nm; $\log\varepsilon$ in parentheses): 669(2.14), *ca.* 320sh, 294(4.23), 257(4.70).

2.3.4. Crystal structure determination and structure refinement

A crystal of the appropriate compound was glued to the end of a thin glass fibre and transferred to a Siemens P4/S or an Enraf Nonius CAD4 diffractometer, and the structure was determined using Mo Kα radiation and a graphite monochromator. Cell dimensions and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of at least 25 accurately centred reflections. These are listed with other relevant data in Table 1. The structures were solved by direct methods using SHELXS86 [18]. Neutral atom scattering factors were used [19] with corrections for real and imaginary anomalous dispersion [20]. The structure was refined by the full-matrix least-squares method based on F^2 using SHELXL [21].

3. Results and discussion

3.1. Synthesis and characterization of the complexes

The salicylaldehyde Schiff base of both *N*-methyl-*S*-methyldithiocarbazate (Fig. 1; R = SCH_3; Hsalsme) and 2-methyl-3-thiosemicarbazone (Fig. 1, R = NH_2; Hsaltsc) can exhibit conformational isomerism due to restricted rotations about the