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Coordination behaviour of Schiff base 2-acetyl-2-thiazoline hydrazone (ATH) towards cobalt(II), nickel(II) and copper(II)

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Abstract

The synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes of 2-acetyl-2-thiazoline hydrazone (ATH) are reported. Elemental analysis, IR spectroscopy, UV–Vis–NIR diffuse reflectance and magnetic susceptibility measurement, as well as, in the case of copper complex EPR spectroscopy, have been used to characterize the complexes. In addition, the structure of $[NiCl_2(ATH)_2]$ (**2**) and $[\{CuCl(ATH)\}_2(\mu\text{-}Cl)_2]$ (**3**) have been determined by single crystal X-ray diffraction. In all complexes, the ligand ATH bonds to the metal ion through the imine and thiazoline nitrogen atoms. X-ray data indicates that the environment around the nickel atom in **2** may be described as a distorted octahedral geometry with the metallic atom coordinated to two chlorine atoms, two thiazoline nitrogen atoms and two imino nitrogen atoms. With regard to **3**, it can be said that its structure consists of dimeric molecules in which copper ions are bridge by two chlorine ligands. The geometry about each copper ion approximates to a distorted square pyramid with each copper atom coordinated to one thiazoline nitrogen atom, one imine nitrogen atom, one terminal chlorine ligand and two bridge chlorine ligands. In compound **3**, magnetic susceptibility measurements in the temperature range 2–300 K show an intradimer antiferromagnetic interaction ($J = -7.5\ cm^{-1}$).

Keywords: Crystal structure; Cobalt complex; Nickel complex; Copper complex; Thiazoline; Hydrazone

1. Introduction

In the last few year a renewed interest in metal based therapy has been raised: in fact, on coordination, bioactive ligands might improve their bioactivity profiles, while inactive ligands may acquire pharmacological properties [1–5]. In addition, metal coordination is one of the most efficient strategies in the design of repository, slow release or long-acting drugs [6]. Furthermore, metal complexes have gained importance as enzyme inhibitors [7].

In this way, the synthesis, structural investigation and reaction of transition metal Schiff bases have received a special attention, because of their biological activities as antitumoral, antifungal and antiviral activities [8]. Thus, Schiff base hydrazones are also interesting from the point of view of pharmacology. Hydrazone derivatives are found to possess antimicrobial [9], antitubercular [10], anticonvulsant [11] and antiinflammatory [12] activities. Particularly, the antibacterial and antifungal properties of bis acyl hydrazone and their complexes with some first transition metal ions was studied and reported by Carcelli et al. [13]. In addition, complexes of salicylaldehide benzoylhydrazone was shown to be a potent inhibitor of DNA synthesis and cell growth [14]. This hydrazone also has mild bacteriostatic activity and a range of analogues has been investigated as potential oral ion chelating drugs for genetic disorders such as thalasemia [15,16].

Following all these observations and as part our program concerning the chelating behaviour of hydrazones [17,18] we report here the synthesis and the characterization by elemental analysis, IR, UV–Vis–NIR diffuse reflectance and magnetic susceptibility measurement of Co(II), Ni(II) and Cu(II) complexes with 2-acetyl-2-thiazoline

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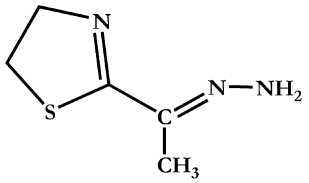
hydrazone (ATH). The Ni(II) and Cu(II) complexes have also been characterized through single crystal X-ray diffraction, as well as electronic paramagnetic resonance (EPR) of the latter.

2. Experimental

2.1. General procedures

All reagents were commercial grade materials and were used without further purification. The ligand 2-acetyl-2-thiazoline hydrazone (ATH) was synthesized according to a reported procedure [17].



ATH

Chemical analyses of carbon, hydrogen, nitrogen and sulphur were performed by means of microanalytical methods using a Perkin–Elmer 240C microanalyser. IR spectra were recorded on a Perkin–Elmer FT-IR 1720 spectrophotometer, from a KBr pellet in the 4000–370 cm^{-1} range and on a Perkin–Elmer FT-IR 1700X spectrophotometer, from a polyethylene pellet in the 500–150 cm^{-1} range. The UV–Vis–NIR reflectance spectra for complexes in the 200–1500 nm range were registered from a pellet of the sample, using a Shimadzu UV-3101 PC spectrophotometer and $BaSO_4$ as reference. Magnetic susceptibility measurements were performed on polycrystalline samples using a magnetometer with pendulum MANICS DSM8, equipped with helium continuous-flow cryostat and an electromagnetometer DRUSCH EAF 16 UE. Data were corrected for temperature-independent paramagnetism and diamagnetic contributions, which were estimated from the Pascal constants. EPR spectra were recorded at room temperature in solid state and at 77 K in methanol solution employing a BRUKER ESP-300E spectrometer using the X band of microwave.

2.2. Synthesis of $[CoCl_2(ATH)_2]$ (1)

This complex was isolated from an ethanol solution (3 mL) of $CoCl_2 \cdot 6H_2O$ (166 mg, 0.7 mmol) that was added to an ethanol solution (25 mL) of ATH (200 mg, 1.4 mmol). After an hour, pink crystalline solid was isolated from the solution at room temperature (104 mg, 36%). Solid was filtered and washed with cold ether and air-dried. *Anal.* Calc. for $C_{10}H_{18}Cl_2CoN_6S_2$: C, 28.85; H, 4.35; N, 20.18; S, 15.40. Found: C, 29.23; H, 3.98; N, 20.45; S, 15.15%. IR(KBr): ν(NH_2) 3367, 3247, 3167; δ(NH_2) 1616; (ring vibration) 1603; ν(C=N) 1546; (ring vibrations) 1000, 950, 734, 682; 653, 602, 564, 448 cm^{-1}.

Table 1
Crystal data, data collection and refinement details for **2** and **3**

	2	**3**
Crystal shape	plate	prism
Colour	green	green
Size (mm)	0.62 × 0.26 × 0.10	0.48 × 0.40 × 0.20
Chemical formula	$C_{10}H_{18}Cl_2N_6NiS_2$	$C_{10}H_{18}Cl_4N_6Cu_2S_2$
Formula weight	416.0	555.3
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	16.730(1)	8.645(2)
b (Å)	9.142(1)	12.468(3)
c (Å)	12.053(1)	8.941(2)
β (°)	107.566(1)	93.333(4)
Cell volume (Å^3)	1757.4(2)	962.2(4)
Z	4	2
D_{calc} (g cm^{-3})	1.572	1.917
μ (mm^{-1})	1.646	2.989
$F(000)$	856	556
θ Range	2.6–28.3	2.8–27.5
Index ranges	$-21 \leqslant h \leqslant 21$, $-7 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$	$-11 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 11$
Independent reflections	2013	2201
Observed reflections $[F > 4.0\sigma(F)]$	1811	1703
Data completeness	0.921	0.996
Max/min transmission	0.853/0.428	0.542/0.255
Number of refined parameters	97	110
R $[F > 4.0\sigma(F)]$[a]	0.034	0.028
wR $[F > 4.0\sigma(F)]$[b]	0.085	0.067
GOF[c]	1.062	0.974
ρ_{max}, ρ_{min} (e Å^{-3})	0.465, −0.247	0.377, −0.321

[a] $R = \sum \| F_o \| - \| F_c \| / \sum | F_o |$.
[b] $R = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.
[c] The Goodness-of-fit (GOF) equals $\{\sum[w(F_o^2 - F_c^2)^2]/(N_{rf\,ln\,s} - N_{params})\}^{1/2}$.

2.3. Synthesis of $[NiCl_2(ATH)_2]$ (2)

This complex was isolated from an ethanol solution (2 mL) of $NiCl_2 \cdot 6H_2O$ (83 mg, 0.35 mmol) that was added to an ethanol solution (15 mL) of ATH (100 mg, 0.7 mmol). After several hours, 103 mg (71% yield) of a green solid was recovered filtering. This solid was recrystallized from a ethanol/acetonitrile (1:1 v/v) solution, yielding plate dark green crystals, of considerable size, suitable for X-ray diffraction. Anal. Calc. for $C_{10}H_{18}Cl_2NiN_6S_2$: C, 29.01; H, 4.38; N, 20.30; S, 15.49. Found: C, 28.99; H, 4.45; N, 20.35; S, 15.21%. IR(KBr): ν(NH_2) 3335, 3245, 3142; δ(NH_2) 1619; (ring vibration) 1601; ν(C=N) 1546; (ring vibrations) 1001, 954, 741, 683, 642, 602, 562, 435 cm^{-1}.

2.4. Synthesis of $[\{CuCl(ATH)\}_2(\mu\text{-}Cl)_2]$ (3)

This complex was isolated from a methanol solution (2 mL) of $CuCl_2 \cdot 2H_2O$ (119 mg, 0.7 mmol) that was