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XAFS study of metal chelates of phenylazo derivatives of Schiff bases

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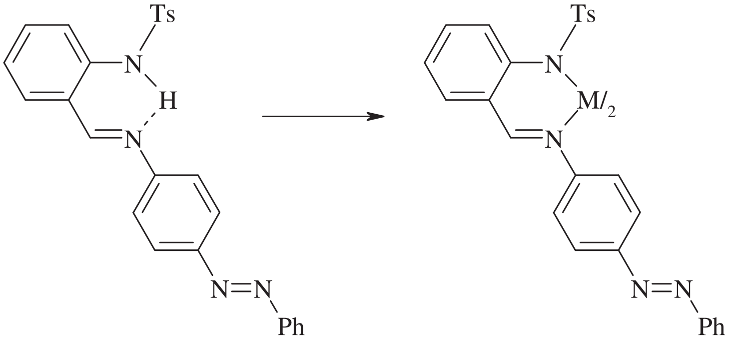
HIGHLIGHTS

- Four complexes (**3a–d**) synthesized on the base of bidentate *N,N*-ligand **2**.
- The structure of imine **2** was determined by X-ray crystallography.
- Parameters and geometry of the local donor environment for **3a–c** were established by XAFS.

GRAPHICAL ABSTRACT



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ABSTRACT

The Schiff base derived from *o*-tosylaminobenzaldehyde and *p*-aminoazobenzene and its metal chelates (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) have been synthesized and investigated (IR, ^1H NMR, XANES, EXAFS spectroscopy, X-ray diffraction, magnetic measurements). It was found that the azomethine exists in the amino-imine tautomeric form both in solutions and solid state. XAFS investigations reveal that the complexes adopt either distorted tetrahedral or octahedral (due to additional coordination of oxygen atoms of the tosylamino group) ligand environment.

1. Introduction

Schiff bases are among the most important ligands of the modern coordination chemistry [1–12] since their complex-forming activity makes them attractive for the design of novel multifunctional materials, e.g., molecular magnets [13–16], luminophores [17,18], and bioactive chelates [19,20].

Coordination compounds of Schiff bases bearing an azo group are represented by complexes of ligands containing an Ar—N=N— fragment in the aldehyde moiety, which are essentially chelates of azomethines of arylazosalicylaldehyde **1** [8,15,21,22–24].

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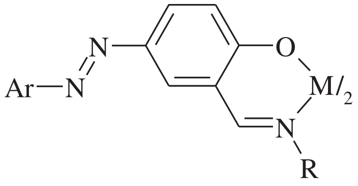
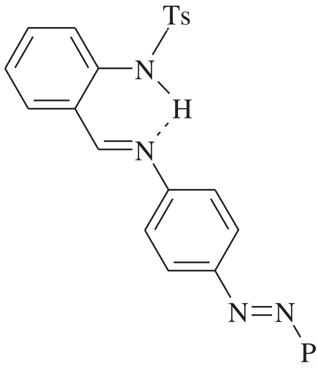
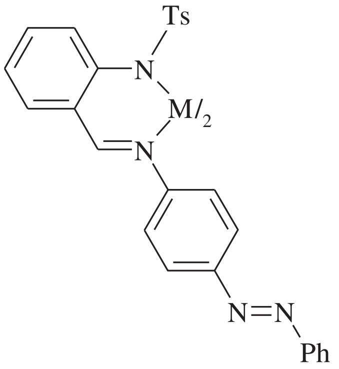


1



2: Ts = -$SO_2C_6H_4CH_3$-*p*



3: M = Co (a), Ni (b), Cu (c), Zn (d)

Metallocomplexes of azomethines containing arylazo-group in the amine moiety presented only by chelates on the base of ligands with N_2O_2 donor atoms set [25,26].

So synthesis and investigation of the same complexes with N_4 donor environment is a matter of interest.

We have synthesized and investigated Schiff base **2** with an azo group within the amine moiety and its metal complexes **3**, and have studied of influence of the character of such substituent on their structural and magnetic characteristics.

2. Experimental

2.1. Materials

All solvents, metal acetates and organic precursors were purchased from Aesar, Lancaster.

2.2. Synthesis of the azoderivative 2

A hot solution of 1.97 g (0.01 mol) of 4-aminoazobenzene in 30 ml of methanol was added to a hot solution of 2.75 g (0.01 mol) of 2-tosylaminobenzaldehyde in 20 ml of the same solvent. Resulting mixture was refluxed for 1 h. Precipitate formed after cooling to the room temperature was filterred off, washed with cool methanol, dried in air and recrystallized from the chloroform–methanol mixture (1:2). Obtained crystals were available for X-ray structural investigations. Red–orange crystals, m.p. 204–205 °C, yield 84 %. Found, %: C, 68.75; H, 4.95; N, 12.41. Calculated for $C_{26}H_{22}N_4O_2S$, %: C, 68.71; H, 4.88; N, 12.32. NMR ^{1}H ($CDCl_3$), δ (ppm): 2.36 (3H, s, CH_3), 7.11 (1H, t, C-H_{Ar}), 7.21 (1H, d, C—H_{Ar}), 7.23 (1H, d, C—H_{Ar}), 7.36–7.57 (7H, m, C—H_{Ar}), 7.70 (1H, d, C—H_{Ar}), 7.79 (1H, d, C—H_{Ar}), 7.80 (1H, d, C—H_{Ar}), 7.94 (1H, d, C—H_{Ar}), 7.96 (1H, d, C—H_{Ar}), 8.01 (1H, d, C—H_{Ar}), 8.04 (1H, d, C—H_{Ar}), 8.56 (1H, s, HC═N), 12.75 (1H, s, NH). IR spectrum, ν (cm^{-1}): 2700–3100 (br, NH), 1617 (s, C═N), 1334 (vs SO_2, as), 1152 (vs SO_2, sym).

2.3. Synthesis of the complexes 3a–d

All complexes have been obtained according to the below common method. A hot solution of 0.001 mol of the acetate of the corresponding *d*-metal in 10 ml of methanol was added to a hot solution of 0.91 g (001 mol) of azomethine **2** in 50 ml of the same solvent. The resulting mixture was refluxed for 1 h and cooled for the room temperature. Precipitates of complexes was filtered off, washed with hot methanol and dried *in vacuo*.

3a. Red-brown powder, m.p. 241–242 °C, yield 98%. Found, %: C, 64.68; H, 4.42; N, 11.58. Calculated for $C_{52}H_{42}N_8O_4S_2Co$, %: C, 64.66; H, 4.38; N, 11.60. IR spectrum, ν (cm^{-1}): 1604 (s, C═N), 1258 (vs SO_2, as), 1134 (vs SO_2, sym). μ_{eff} = 4.29 BM (294 K).

3b. Brown powder, m.p. > 250 °C, yield 88%. Found, %: C, 64.65; H, 4.40; N, 11.65. Calculated for $C_{52}H_{42}N_8O_4S_2Ni$, %: C, 64.68; H, 4.38; N, 11.60. IR spectrum, ν (cm^{-1}): 1603 (s, C═N), 1257 (vs SO_2, as), 1125 (vs SO_2, sym). μ_{eff} = 3.89 BM (294 K).

3c. Dark-brown powder, m.p. > 250 °C, yield 85%. Found, %: C, 64.42; H, 4.38; N, 11.60. Calculated for $C_{52}H_{42}N_8O_4S_2Cu$, %: C, 64.35; H, 4.36; N, 11.54. IR spectrum, ν (cm^{-1}): 1606 (s, C═N), 1261 (vs SO_2, as), 1130 (vs SO_2, sym). μ_{eff} = 1.74 BM (294 K).

3d. Orange powder, m.p. > 250 °C, yield 75%. Found, %: C, 64.34; H, 4.30; N, 11.62. Calculated for $C_{52}H_{42}N_8O_4S_2Zn$, %: C, 64.23; H, 4.35; N, 11.52. NMR ^{1}H (DMSO-d_6), δ (ppm): 2.25 (6H, s, CH_3), 6.70–7.87 (34H, m, C—H_{Ar}), 8.87 (1H, s, HC═N). IR spectrum, ν (cm^{-1}): 1607 (s, C═N), 1261 (vs SO_2, as), 1133 (vs SO_2, sym).

2.4. Physical measurements

C, H, and N analyses were performed with a Carlo Erba Instruments TCM 480 analyzer. IR spectra of powder samples and as KBr pellets were recorded using a Varian Excalibur-3100 FT-IR spectrophotometer. ^{1}H NMR spectra (in $CDCl_3$ for organic derivative and in DMSO-d_6 for complexes) were measured with a Bruker Avance-600 spectrometer (600 MHz) with the signal of residual ^{1}H in solvent as the internal standard.

2.5. X-ray diffraction

Orange-red crystals of *N*-(4-phenylazo)phenyl-(2-tosylamino)benzaldimine $C_{26}H_{22}N_4O_2S$ (**2**) are monoclinic: a = 11.7576 (12) Å, b = 11.7288(12) Å, c = 16.7054(17) Å, α = 90°, β = 100.899 (5)°, γ = 90°, V = 2262.2(4) Å^3, M = 454.54, F(000) = 952, ρ_{calcd} = 1.318 g cm^{-1}, μ = 0.175 g cm^{-1}, Z = 4, space group P 21/c, T = 120(2) K.

Experimental data for **2** were obtained with an Bruker SMART 1000 diffractometer (λ Mo Kα, graphite monochromator, $\theta/2\theta$-scanning, θ_{max} = 28°). Intensities of 874 reflections were measured.

The structure of this compound was determined by direct methods (SHELXS PLUS) [27], refined by full-matrix least-squares on F^2 in the anisotropic approximation for all non-hydrogen atoms. Hydrogens were placed in the calculated positions and refined according to the riding model with fixed Debye factors of U_H = 0.08 Å^2.

The final fitting parameters for **2** are: R_1 = 0.0593, wR_2 = 0.1311 on 874 reflections with $F_o \geqslant\_2\sigma(F_o)$, R_1 = 0.1021, wR_2 = 0.1565 on all reflections, 299 variable parameters, index range: $-15 \leqslant h$