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Bis- and tris-chelates of Ni^{II}, Cu^{II}, Co^{II} and Fe^{III} bound to N,N-dialkyl/alkyl



Bis- and tris-chelates (1-5) of Ni(II), Cu(II), Fe(III) and Co(II) with two O.S donor substituted benzovlthiourea based ligands 3,3-diethyl-1-benzoylthiourea (HL¹) and 3-methyl-3-phenyl-1-benzoylthiourea (HL²) have been synthesized and structurally characterized by X-ray crystallography. The keto-thione form of the free ligands transform to the keto-thiol form during coordination through neutral O and anionic S atoms. Crystallographic characterizations with supportive spectroscopic signatures confirm the cis-conformation in *bis*-chelates and *facial* binding to the *tris*-chelates.

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enantioselective organic transformations [16-18], selective chelating extractants for precious metals [19-22] and as effective chemical corrosion inhibitors [23]. Mononuclear $M(O,S)_n$ (n = 2 or 3) type complexes are thus expected to show interesting structures, isomerism, magnetic and electrochemical properties. These O,Sdonor ligands present high inhibitory activity towards xanthine oxidase in nanomolar concentration range [24]. Photoinduced cis-trans isomerism in bis-chelates of similar O,S-donor ligands is rare and interesting [25].

In this work two O,S-donor ligands, 3,3-diethyl-1-benzoylthiourea (HL^1) and 3-methyl-3-phenyl-1-benzovlthiourea (HL^2) were synthesized and examined for the type of complexation to Co(II), Fe(III), Ni(II) and Cu(II) ions. The bis-chelates in cis-form are close to ideal square planar geometries whereas the tris-chelate in distorted octahedral environment remains in fac-form.

2. Experimental

2.1. Materials

Hydrated perchlorate salts of copper(II), nickel(II) and cobalt(II) were prepared by treating corresponding metal carbonates with 1:1 conc. HClO₄-water mixture and crystallized after concentration on water bath. The ligands HL¹ and HL² were synthesized following modified procedure [26]. The other chemicals used were obtained from the following sources: diethylamine from SRL Chem. (India), triethylamine and ferric nitrate nonahydrate from S. d. Fine-Chem Ltd., benzoyl chloride from Merck, India, potassium

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1. Introduction

Benzylisothiocyanate (PhCH₂NCS, BITC) has been shown to inhibit the cell growth and induces apoptosis in few types of human cancer cell lines through generation of reactive oxygen species (ROS) [1,2]. The related species, benzoylisothiocyanate (PhCONCS, BIT) readily reacts with hydrazone derivatives to provide 1,2,4triazoline-5-thiones [3]. Self-condensation of two benzoylisothiocvanate molecules have led to the formation of novel tridentate OCS ligand [4]. It smoothly reacts with different secondary amines to yield substituted benzoylthioureas. Complexes of iron, cobalt, nickel and copper in O and S environments are fascinating in establishing the distortions in coordinating polyhedron around the metal centers in identifying the distorted environments around these metal ions in living organisms [5]. Planar nickel(II) complexes have been shown to be excellent G-quadruplex DNA stabilizers [6]. Nickel(II) complex in N₂S₂ coordination environment has shown model behavior for nickel-containing superoxide dismutase [7]. The redox and magnetic properties of Co^{II}, Ni^{II} and Cu^{II} are dependent on the nature of the ligands having varying steric and electronic properties. The thiourea backbone is important in antithyroid drug methimazole, used to treat hyperthyroidism [8]. Moreover substituted thioureas and their metal complexes are potentially useful mainly because of their in vitro activities against common pathogens [9–14], catalysts for alcohol oxidation [15],



aryl-N'-benzoylthiourea ligands

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thiocyanate and *N*-methylaniline from Aldrich Chemical Co. Inc. All other chemicals and solvents were reagent grade materials and were used as received without further purification.

2.2. Synthesis

2.2.1. 3,3-Diethyl-1-benzoylthiourea (HL¹)

Potassium thiocyanate (2.332 g, 24 mmol) was taken into a 250 mL round bottom flask and at about 40 mL acetone was added followed by addition of benzoyl chloride (2.8 mL, 24 mmol). The resulting mixture was gently refluxed at 50 °C for 45 min after that a dilute solution of diethylamine (2.5 mL, 24 mmol) was added to the cold reaction mixture and magnetically stirred for about 30 min followed by warming at 35 °C during next 1 h and finally the cooled mixture was stirred overnight by adding water (500 mL) and the white suspension thus formed was suction filtered and recrystallized from methanol (Scheme 1). Yield: 4.92 g, 87%. Anal. Calc., for $C_{12}H_{16}N_2OS$ (236.33 g mol⁻¹): C, 60.98; H, 6.82; N, 11.85. Found: C, 60.93; H, 6.88; N, 11.91%. Selected FT-IR bands: (KBr, cm^{-1} ; s = strong, vs = very strong, m = medium, br = broad) 3219(br), 2970(s), 1681(vs), 1532(vs), 1458(s), 1284(m), 1228(vs), 1134(m), 715(m). ¹H NMR (CDCl₃): δ = 1.28 (t, *J* = 6.0 Hz, 3H, CH₃), 1.34 (t, *J* = 6.2 Hz, 3H, CH₃), 3.59 (q, *J* = 6.0 Hz, 2H, CH₂), 4.00 (q, J = 6.2 Hz, 2H, CH₂), 7.42–7.45 (m, 3H, Ph), 7.85 (m, 2H, Ph), 8.51 (s, 1H br, NH) ppm. 13 C NMR (CDCl₃): $\delta = 11.6$ (CH₃), 13.3 (CH₃), 47.8 (CH₂), 48.0 (CH₂), 127.9, 128.9 (2C), 132.7 (C_a), 132.9(2C), 163.9 (CO), 179.5 (CS) ppm.

2.2.2. 3-Methyl-3-phenyl-1-benzoylthiourea (HL²)

HL² was synthesized following the above mentioned adapted procedure and *N*-methylaniline was used (2.6 mL, 24 mmol) in place of diethylamine (Scheme 1). The crystalline white solid was directly employed for complexation. Yield: 5.40 g, 83%. *Anal.* Calc. for C₁₅H₁₄N₂OS (270.35 g mol⁻¹): C, 66.64; H, 5.22; N, 10.36. Found: C, 66.69; H, 5.26; N, 10.32%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3196(br), 1696(vs), 1516(vs), 1437(m), 1382(s), 1262(vs), 1117(s), 1024(m), 763(m), 708(s). ¹H NMR (CDCl₃): δ = 3.75 (s, 3H, CH₃), 7.26 (t, *J*₁ = 4.0 Hz, *J*₂ = 6.8 Hz, 2H, Ph), 7.32–7.37 (m, 5H, Ph), 7.45 (s, 1H, br), 7.48 (t, *J*₁ = 6.8 Hz, *J*₂ = 14.0 Hz, 2H, Ph), 8.49 (s, 1H br, NH) ppm. ¹³C NMR (CDCl₃): δ = 45.7 (CH₃), 125.6, 127.7 (CH₂), 127.9 (CH₂), 128.8 (2C), 129.5 (2C), 132.8, 132.9, 145.2, 163.1 (CO), 180.7 (CS) ppm.

2.2.3. Cis-bis-(3,3-diethyl-1-benzoylthioureato)nickel(II), cis-NiL¹₂(**1**)

To a MeCN (20 mL) solution of HL¹ (0.47 g, 2 mmol), a methanolic solution of nickel(II) perchlorate (0.37 g, 1 mmol) was added slowly by room temperature magnetic stirring. A red solution was developed gradually upon addition of triethylamine (0.27 mL, 2 mmol) and the reaction mixture was stirred for 1 h further. The solid separated thus was filtered and the filtrate was kept for slow evaporation. On standing at room temperature it afforded deep red crystalline complex **1**. Yield: 0.430 g, 82%. *Anal.* Calc.. for C₂₄H₃₀N₄O₂S₂Ni (529.35 g mol⁻¹): C, 54.46; H, 5.71; N, 10.58. Found: C, 54.39; H, 5.74; N, 10.61%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3446(br), 1493(vs), 1412(vs), 1335(m), 1250(m), 708(s). Molar



conductance, $\Lambda_{\rm M}$: (MeCN solution at 25 °C) 6.3 S m² mol⁻¹. UV– Vis spectra [$\lambda_{\rm max}$, nm (ϵ , L mol⁻¹ cm⁻¹)]: (MeCN solution) 505 (145), 293 (13330), 265 (12903).

2.2.4. Cis-bis-(3,3-diethyl-1-benzoylthioureato)copper(II), cis-CuL¹₂ (**2**)

This was synthesized as green solid following the same protocol as mentioned for complex **1**. Here nickel(II) perchlorate was replaced by copper(II) perchlorate (0.38 g, 1 mmol) and recrystallization was made from the saturated mixture of 1:1 (v/v) MeOH– MeCN. Yield: 0.390 g, 74%. *Anal.* Calc. for C₂₄H₃₀N₄O₂S₂Cu (534.21 g mol⁻¹): C, 53.96; H, 5.66; N, 10.49. Found: C, 53.89; H, 5.69; N, 10.53%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3446(br), 1491(s), 1417(vs), 1354(s), 1087(m), 715(m). Molar conductance, $\Lambda_{\rm M}$: (MeCN solution at 25 °C) 4.7 S m² mol⁻¹. UV–Vis spectra [$\lambda_{\rm max}$, nm (ε , L mol⁻¹ cm⁻¹)]: (MeCN solution) 571 (149), 283 (10600), 251 (9906).

2.2.5. Fac-tris-(3,3-diethyl-1-benzoylthioureato)iron(III), fac-FeL¹₃ (**3**·H₂O). Method A

HL¹ (0.71 g, 3 mmol) was initially dissolved separately in MeCN (15 mL) and it was drop wise added to the methanolic solution (15 mL) of iron(III) nitrate (0.4 g, 1 mmol) under stirring condition. At this stage, triethylamine (0.42 mL, 3 mmol) was introduced into the reaction vessel and immediately color changes to deep brown. The mother liquor was filtered after additional 2 h stirring. Upon air dry it gave microcrystalline sticky mass. Immediately it was dissolved in THF and kept for crystallization. After about 6 days, it produced diffraction quality brown rod-shaped single crystals. One of them was mounted for X-ray structure analysis. Yield: 0.530 g, 68%. Anal. Calc. for C₃₆H₄₇N₆O₄S₃Fe (779.84 g mol⁻¹): C, 55.45; H, 6.07; N, 10.78. Found: C, 55.43; H, 6.11; N, 10.82%. Selected FT-IR bands: (KBr, cm^{-1} ; s = strong, vs = very strong, m = medium, br = broad) 3447(br), 2975(m), 1490(s), 1419(vs), 1353(s), 1243(m), 1137(m), 825(m), 715(s). Molar conductance, $\Lambda_{\rm M}$: (MeCN solution at 25 °C) 8.4 S m² mol⁻¹. UV–Vis spectra [$\lambda_{\rm max}$, nm (ε , L mol⁻¹ cm⁻¹)]; (MeCN solution) 505 (241), 290 (10766), 267 (10352).

2.2.6. One pot synthesis of $3 H_2O$. Method B

Compound 3 was also synthesized in excellent yield using a multi-components solvent-based synthetic procedure in a single pot under stirring condition. To a 100 mL round bottom flask, solid potassium thiocyanate (0.583 g, 6 mmol) was taken with MeCN (20 mL) followed by carefully addition of benzoyl chloride (0.7 mL, 6 mmol). It was heated to reflux for about 1.5 h at 70 °C. At this stage white solid of potassium chloride formed. Under cold condition, slight excess diethylamine (1.2 mL, 12 mmol) was added and again it was refluxed for another 1 h. The *in situ* generated HL¹ was reacted with methanolic solution of iron(III) nitrate (0.8 g, 2 mmol) and stirred in air for further 2 h. The resulting brown solution on standing at room temperature for 5 days resulted in needle like brown crystals suitable for X-ray diffraction analysis. Yield: 0.550 g, 71%. Anal. Calc. for $C_{36}H_{47}N_6O_4S_3Fe$ (779.84 g mol⁻¹): C, 55.45; H, 6.07; N, 10.78. Found: C, 55.41; H, 6.12; N, 10.86%. Selected FT-IR bands: (KBr, cm^{-1} ; s = strong, vs = very strong, m = medium, br = broad) 3447(br), 2975(m), 1490(s), 1419(vs),1353(s), 1243(m), 1137(m), 825(m), 715(s).

2.2.7. Cis-bis-(3-methyl-3-phenyl-1-benzoylthioureato)cobalt(II), cis-CoL²₂ ($\mathbf{4}$ ·CH₃CN)

To a solution of ligand HL^2 (0.54 g, 2 mmol) in MeOH (15 mL), cobalt(II) perchlorate (0.366 g, 1 mmol) was added under stirring which afforded pale green solution. On addition of methanolic solution of triethylamine (0.27 mL, 2 mmol), the green product

precipitated out. After stirring at room temperature for further 45 min, it was filtered, washed with methanol and finally dried under vacuum over P_4O_{10} . A saturated solution in MeCN gave deep green single crystals suitable for X-ray analysis. Yield: 0.490 g, 78%. *Anal.* Calc. for $C_{32}H_{29}N_5O_2S_2Co$ (638.67 g mol⁻¹): C, 60.18; H, 4.58; N, 9.23. Found: C, 60.13; H, 4.60; N, 9.25%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3447(br), 3052(m), 2926(m), 1508(m), 1490(m), 1420(vs), 1374(vs), 1274(s), 1103(m), 904(s), 718(s), 696(m), 550(m). Molar conductance, Λ_M : (MeCN solution at 25 °C) 5.6 S m² mol⁻¹. UV–Vis spectra [λ_{max} , nm (ε , L mol⁻¹ cm⁻¹)]: (MeCN solution) 579 (36.6), 278 (9128), 209 (9225).

2.2.8. Cis-bis-(3-methyl-3-phenyl-1-benzoylthioureato)nickel(II), cis-NiL $_2^2$ (5)

Complex **5** was synthesized following same reaction protocol as mentioned for the synthesis of complex **1**. Here HL² was used instead of HL¹. The block shaped deep brown single crystals formed from the reaction mixture after 5 days. One of them was used for structure determination using X-ray diffractometer. Yield: 0.495 g, 83%. *Anal.* Calc. for C₃₀H₂₆N₄O₂S₂Ni (597.38 g mol⁻¹): C, 60.32; H, 4.39; N, 9.38. Found: C, 60.29; H, 4.36; N, 9.37%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3447(br), 3059(m), 2928(m), 1511(m), 1491(m), 1419(vs), 1378(vs), 1272(s), 1107(m), 906(s), 719(s), 692(vs), 556(s). Molar conductance, Λ_{M} : (MeCN solution at 25 °C) 6.2 S m² - mol⁻¹. UV–Vis spectra [λ_{max} , nm (ε , L mol⁻¹ cm⁻¹)]: (MeCN solution) 504 (152), 291 (13410), 264 (12927).

2.3. Physical measurements

The elemental analysis (C, H, N) were performed with a Perkin-Elmer model 240 C elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer RX1 spectrometer. Solution electrical conductivity measurements and electronic spectra were carried out using a Unitech type U131C digital

Table 1

Crystallographic	data of	complex 2	, 3 ⋅H ₂ O,	$4 \cdot CH_3CN$	and 5
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conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu 1601 UV–Vis–NIR spectrophotometer using 1 cm quartz cell pairs. In each measurement, background was subtracted using reference solvent to one of the cuvettes.

2.4. Crystal data collection and refinement for 2, 3 H₂O, 4 CH₃CN and 5

The diffraction data of the complexes 2, 3·H₂O, 4·CH₃CN and 5 were collected on a Bruker APEX-II CCD X-ray diffractometer using single crystals that uses graphite-monochromated Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$ by ω -scan method at 293 K. Information concerning X-ray data collection and structure refinement of the compounds are summarized in Table 1. For complex 2, a total of 5988 reflections were recorded with Miller indices $h_{\min} = -13$, $h_{\text{max}} = 13$, $k_{\text{min}} = -24$, $k_{\text{max}} = 24$, $l_{\text{min}} = -13$, $l_{\text{max}} = 17$. For complex 3·H₂O, a total of 4013 reflections were recorded with Miller indices $h_{\min} = -23$, $h_{\max} = 23$, $k_{\min} = -23$, $k_{\max} = 19$, $l_{\min} = -12$, $l_{\max} = 12$. For complex 4-CH₃CN, a total of 5041 reflections were recorded with Miller indices $h_{\min} = -12$, $h_{\max} = 13$, $k_{\min} = -16$, $k_{\max} = 16$, l_{min} = -22, l_{max} = 22 whereas for complex **5**, a total of 6815 reflections were recorded with Miller indices $h_{\min} = -13$, $h_{\max} = 13$, $k_{\min} = -17$, $k_{\max} = 17$, $l_{\min} = -28$, $l_{\max} = 28$. In the final cycles of full-matrix least squares on F^2 , all non-hydrogen atoms were assigned anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The structures were solved using the SHELX-97 program system [27] and were drawn using DIAMOND v. 2.1e programs [28].

3. Results and discussion

The ligands 3,3-diethyl-1-benzoylthiourea (HL^1) and 3-methyl-3-phenyl-1-benzoylthiourea (HL^2) have been synthesized quantitatively following modified literature procedure (Scheme 1). The powered ligands thus obtained were next employed for complexation reaction with perchlorate salts of Ni(II), Cu(II) and

Complex	2	3 ·H ₂ 0	4-CH ₃ CN	5
Formula	$C_{24}H_{30}N_4O_2S_2Cu$	$C_{36}H_{47}N_6O_4S_3Fe$	$C_{32}H_{29}N_5O_2S_2Co$	C30H26N4O2S2Ni
M g mol ⁻¹	534.21	779.839	638.65	597.38
Space group	$P2_1/n$	РЗ	$P2_1/c$	$P2_1/c$
Crystal system	monoclinic	hexagonal	monoclinic	monoclinic
a (Å)	10.620(4)	16.6660(10)	11.3573(4)	9.8051(11)
b (Å)	18.319(7)	16.6660(10)	14.6264(6)	13.2791(15)
<i>c</i> (Å)	13.464(5)	8.5087(5)	19.4019(8)	21.669(2)
α (°)	90.00	90.00	90.00	90.00
β(°)	102.946(12)	90.00	104.3970(10)	91.597(4)
γ (°)	90.00	120.00	90.00	90.00
$V(Å^3)$	2552.7(18)	2046.7(2)	3121.8(2)	2820.3(5)
T (K)	293	293	293	293
Ζ	4	2	4	4
D _{calc} (g cm ⁻³)	1.390	1.262	1.359	1.407
F(000)	1116	818	1324	1240
μ (Mo K α) (cm ⁻¹)	10.47	5.64	7.21	8.71
Measured reflections	33744	29989	34026	37838
Unique reflections	5988	4013	5041	6815
R _{int}	0.0386	0.0284	0.0525	0.1138
Observed reflections $[I \ge 2\sigma(I)]$	4057	2967	3457	3471
$\theta_{\min} - \theta_{\max} / ^{\circ}$	1.91-27.96	1.41-30.63	1.76-24.27	1.80-28.26
Index ranges	$-13\leqslant h\leqslant 13$,	$-23\leqslant h\leqslant 23$,	$-12\leqslant h\leqslant 13$,	$-13\leqslant h\leqslant 13$,
	$-24\leqslant k\leqslant 24$,	$-23\leqslant k\leqslant 19$,	$-16\leqslant k\leqslant 16$,	$-17\leqslant k\leqslant 17$,
	$-13 \leqslant l \leqslant 17$	$-12 \leqslant l \leqslant 12$	$-22 \leqslant l \leqslant 22$	$-28\leqslant l\leqslant 28$
$R(F^2)$ (observed reflections)	0.0562	0.0617	0.0440	0.0607
$wR(F^2)$ (all refins)	0.2541	0.2112	0.1300	0.2480
No. of variables	298	151	379	352
Goodness-of-fit (GOF) on F^2	0.978	1.033	1.063	0.652
$\Delta ho_{ m max}$; $\Delta ho_{ m min}$ (e Å $^{-3}$)	1.273; -0.614	1.217; -0.413	0.393; -0.372	0.539; -0.327



Co(II) in 2:1 M ratios in MeOH–MeCN mixture in presence of triethylamine for the synthesis of **1**, **2**, **4**·CH₃CN and **5**.

For the synthesis of complex $3 \cdot H_2O$, two separate methods were followed in 3:1 M ratios of ligand and metal salts. The preliminary X-ray data analysis from unit cell determination, FT-IR spectrum and elemental analysis confirmed the formation of isostructural compounds in both the methods. In method A, triethylamine was used to deprotonate the ligand HL¹. The *in situ* generated ligand HL¹ was used in method B where excess diethylamine acts as base to abstract the proton. All these complexes were obtained as microcrystalline solid except complex **3**·H₂O in moderate to high vield (\sim 68–87%). The single crystals for **3**·H₂O were grown from the saturated solution of THF from method A whereas the same chemical structure was obtained following method B from the saturated solution of 1:1 (v/v) MeOH-MeCN mixture. The single crystals suitable for X-ray diffraction of complex **5** were grown both from MeOH and DMF separately whereas the complex 2 and 4 CH₃₋ CN were generated from MeOH-MeCN mixtures. The methoxido or hydroxido bridged dinuclear complexes were not obtained under varying alkaline conditions (complex 3, Scheme 2) [29,30].

Microanalysis and solution conductivity measurements confirmed the chemical formula and non-electrolytic nature of the synthesized complexes. All of these complexes were characterized by a combined spectroscopic technique both in solid and solution phases and four of them were structurally determined from Xray crystallography. The FTIR spectra of both the ligands and their corresponding metal complexes confirmed that the keto-thione forms are stable in the free ligands and but during complexation, tautomerized keto-thiol forms stabilized and coordinated to the metal centers.

3.1. FTIR spectra

The FT-IR spectra (Figs. S1 and S2 in the Supporting information) of the free ligands and their metal complexes clearly indicate the spectral patterns of the free and metal-bound states of the ligands. The backbone N–H stretching vibrations in the region of 3190–3220 cm⁻¹ present in the free ligands disappear in the spectra of corresponding metal complexes which are in good agreement with the presence of deprotonated ligands in the respective complexes. The C=O stretching vibration in the region of 1681–1697 cm⁻¹ and C=S band within 1228–1262 cm⁻¹ of the free ligands are shifted to the lower wave-number by *ca*. 112–190 cm⁻¹ and 93–134 cm⁻¹ respectively upon complexation, confirming the lowering of C=O and C=S bond orders during coordination [vide supra]. The FTIR data clearly indicate the coordination of the ligands through C=O and C-S⁻ groups providing oxygen and sulfur donor atoms. Each ligand underwent coordination driven thiolization and deprotonation, responsible for the generation of neutral *bis*- and *tris*-chelates depending upon the coordination environments. All the above changes in the stretching vibrations support the coordination of thiol forms of the ligands as opposed to the thione forms.

3.2. Structural descriptions

The crystallographic refinement data for complexes **2**, **3**·H₂O, **4**·CH₃CN and **5** are given in the experimental section (Table 1) and the selected bond angles and bond lengths are collected in Table 2.

Complex **2** crystallizes in monoclinic $P2_1/n$ space group is shown in Fig. 1. Here Cu(II) center is surrounded by two sulfur and two oxygen atoms of two deprotonated HL¹ ligands in an approximately square planar arrangement where both oxygen and sulfur atoms are located in *cis*-conformation. The six-membered chelate rings (NC₂OS-Cu) so formed are twisted about the central N-atoms in order to attain suitable O...S bite distances in the 3.018-3.048 Å range. The amount of distortion from the ideal square planar geometry around Cu(II) ion is reflected from deviation of the cis and trans angles of 86.3-93.8° and 173.0-179.7° from ideal range of 90° and 180°, respectively. The closeness of the C-N bonds residing on the oxygen and sulfur sides indicate the facile delocalization of the single negative charge between these two donor atoms but the significantly longer C-S bond lengths (1.740-1.742 Å) compare to C-O distances (1.261–1.265 Å) is a clear indication that the negative charge is mostly on sulfur atom. Within the square-planar arrangement the Cu-O bond distances (1.92-1.93 Å) are significantly shorter than Cu–S distances (2.22–2.23 Å) as expected [31]. The six-membered chelate rings deviate from the planarity as indicated from the O-C-N-C and C-N-C-S torsion angles of 6.07-9.93° and 5.59-16.98° respectively. The dihedral angle between two O-Cu–S planes is 6.97° for a slight D_{2d} distortion from the ideal square-planar geometry.

Molecular structure of $3 \cdot H_2O$ with atom numbering scheme shown in Fig. 2 crystallizes in a hexagonal $P\bar{3}$ space group. The lattice water molecules occupy the void space between monomeric units. Three ligands around Fe^{III} ion yielded a distorted octahedral O_3S_3 environment with a stereochemical preference for a *facial* geometry [29,30]. Six-membered O,S chelate rings (NC₂OS–Fe) provide a distorted octahedral geometry with an average O...S bite distance of 3.01 Å in the complex. The substantial distortion from ideal coordination geometry is seen for the *cis* and *trans* angles at 85.5–88.1° and 169.7 from 90° and 180° respectively. The Fe–O

Selected bond lengths	(Å) and bond ang	gles (°) of complex 2 , 3	3 ⋅H ₂ O, 4 ⋅CH ₃ CN and 5 .
Bond lengths (Å) Complex 2			
Cu1-01	1.918(4)	S2-C20	1.742(4)
Cu1-02	1.929(4)	S1-C8	1.740(5)
Cu1-S1	2.221(2)	01-C7	1.265(6)
Cu1-S2	2,233(2)	N1-C8	1 338(6)
02-019	1.263(2)	N1-C7	1 324(6)
N3-C20	1.339(6)	N3-C19	1.318(6)
Complex 3-H ₂ O			
Fe-O1	1.986(2)	N1-C8	1.353(3)
Fe-S1	2.4221(8)	C7-N1	1.319(3)
S1-C8	1.726(3)	C7-01	1.247(3)
Complex 4 ·CH ₃ CN			
Co1-O2	1.926(3)	C7-N1	1.320(4)
Co1-O1	1.920(3)	S2-C23	1.718(4)
Co1-S2	2.225(11)	02-C22	1.273(4)
Co1-S1	2.217(11)	C22-N3	1.321(4)
C7-01	1.270(4)	N3-C23	1.334(5)
N1-C8	1.336(5)	S1-C8	1.719(4)
Complex 5			
Ni1-01	1.865(4)	S1-C8	1.724(6)
Ni1-02	1.858(4)	01-C7	1.263(7)
Ni1-S2	2.135(17)	O2-C22	1.257(7)
Ni1-S1	2.142(17)	N3-C22	1.322(8)
S2-C23	1.728(6)	N1-C7	1.322(7)
N3-C23	1.335(7)	N1-C8	1.344(7)
Rond angles (°)			
Complex 2			
01_01_02	86 40(16)	02-Cu1-S1	170 71(13)
01-Cu1-02	03 32(12)	02-Cu1-51 01-Cu1-52	173.04(15)
01-Cu1-31 02-Cu1-52	93.32(12) 93.87(11)	C8_N1_C7	175.04(15) 125.4(4)
S1-Cu1-S2	86.39(6)	C19-N3-C20	125.8(4)
Complex 3.H-O			
01-Fe-01#	87 52(9)	01-Fe-\$1#	169 70(7)
01#-Fe-S1	85 55(6)	S1_Fe_S1*	88 13(3)
01_Fe_\$1*	99.77(7)	C7_N1_C8	125 2(2)
Symmetry code: *	=(1-y, x-y, -1)	(1 + z) and $# = (1 - x + z)$	y, 1 - x, -1 + z)
Complex 4 CH ₂ CN		, , , , , , , , , , , , , , , , , , ,	/
01-Co1-02	84.92(11)	01-Co1-S2	176.33(9)
02-Co1-S2	93.57(8)	02-Co1-S1	177.54(9)
01-Co1-S1	93.11(8)	C8-N1-C7	124.9(3)
S1-Co1-S2	88.48(4)	C22-N3-C23	125.4(3)
Complex 5	• •		. •
01-Ni1-02	84.08(18)	01-Ni1-S2	179.08(15)
S2-Ni1-S1	85.39(6)	02-Ni1-S1	177.94(18)
02-Ni1-S2	95.24(14)	C7-N1-C8	123.8(5)
01-Ni1-S1	95.27(14)	C22-N3-C23	124.3(5)
	55.2. (1.1)	322 1.5 625	12 113(3)

Table 2

separation (1.98 Å) is significantly shorter than Fe–S distance (2.42 Å). Thus the M–O and M–S distances in octahedral geometry are longer in trivalent state than the same in square-planar geometry in +2 state as observed in case of **2** [32]. In *facial* geometry the iron(III) ion is sandwiched by a slightly bigger S₃ face (average S…S distance 3.37 Å) and smaller O₃ face (average O…O distance 2.75 Å). The phenyl rings of the benzoyl ends of the ligands remain coplanar with the OCNCS–Fe chelate ring.

The perspective view of compound **4**·CH₃CN is shown in Fig. 3. The single crystal of the compound obtained from a saturated solution in MeOH-MeCN (1:1 v/v) crystallizes in monoclinic *Cc* space group. The Co(II) center is enclosed by two sulfur and two oxygen donor atoms of two deprotonated $\{L^2\}^-$ ligands in an approximately *cis*-square-planar arrangement. In *cis* orientation the Co–O separations (1.91–1.92 Å) are also shorter than and Co–S separations (2.21–2.22 Å) [32]. The dihedral angle between the two O–Co–S chelate planes is 3.55°. The inter-planar angle between the phenyl rings from C–O and C–S sides is 87.88°.

The molecular view of compound **5** displayed in Fig. 4 is in monoclinic $P2_1/c$ space group.



Fig. 1. The molecular structure of complex **2** with atom numbering scheme. Color code: Cu, brown; N, blue; O, red; S, yellow; C, grey; H, teal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Molecular structure of **3**·H₂O with partial atom numbering scheme. Solvent water molecule is removed for clarity. Symmetry code: * = (1 - y, x - y, -1 + z) and # = (1 - x + y, 1 - x, -1 + z). Color code: Fe, steel; N, blue; O, red; S, yellow; C, grey; H, teal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Like Cu(II) and Co(II) complexes, two sulfur and two oxygen atoms of two monoanionic HL² ligands bind Ni(II) ion in square planar *cis*-conformation. The six-membered (OCNCS-Ni) chelate



Fig. 3. The molecular structure of complex **4**·CH₃CN with atom numbering scheme. Solvent acetonitrile molecule is removed for clarity. Color code: Co, pink; N, blue; O, red; S, yellow; C, grey; H, teal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. The molecular structure of complex **5** with atom numbering scheme. Color code: Ni, green; N, blue; O, red; S, yellow; C, grey; H, teal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

rings so formed showed twisting about the central N-atoms in order to maintain suitable O···S bite distances of 2.956–2.966 Å. The Ni–O (1.858–1.865 Å) and Ni–S (2.135–2.142 Å) bond lengths are considerably shorter than the corresponding values for Cu(II) and Co(II) complexes. The dihedral angle between the two O–Ni–S planes is smallest (2.12°) for a close ideal square-planar arrangement compared to cobalt(II) and copper(II) complexes. Around the NiO₂S₂ coordination environment, the inter-planar angle between the phenyl rings of the benzoyl moieties and the phenyl rings of the N-methylaniline parts is 87.48°.

3.3. Electronic absorption spectra

The electronic absorption spectra (Figs. S3–S5 in the Supporting information) measured for all the five complexes using 10^{-3} M solute concentration in MeCN showed strong absorption bands from charge transfer transitions in near UV range. In case of nickel(II) complexes of 1 and 5, the spin forbidden d-d transitions observed at 505 nm (ε = 145 L mol⁻¹ cm⁻¹) and 504 nm (ε = 152 L mol⁻¹ cm⁻¹) can be assigned to $A_{1g} \rightarrow B_{1g}$ transition [33]. In UV region the bands at 293 nm ($\varepsilon = 13,330 \text{ Lmol}^{-1} \text{ cm}^{-1}$) and 265 nm ($\varepsilon = 12,903 \text{ Lmol}^{-1} \text{ cm}^{-1}$) for complex **1** and 291 nm $(\varepsilon = 13,410 \text{ Lmol}^{-1} \text{ cm}^{-1})$ and 264 nm $(\varepsilon = 12,927 \text{ Lmol}^{-1} \text{ cm}^{-1})$ for complex **5** were observed for nickel(II)-bound intraligand n- π^* and π - π^* charge transfer transitions overlapping with alternative MLCT transitions. For complex 2 the observed band positions for electronic transitions were 571 nm (ε = 159 L mol⁻¹ cm⁻¹), 283 nm $(\varepsilon = 10600 \text{ Lmol}^{-1} \text{ cm}^{-1})$ and 251 nm $(\varepsilon = 9906 \text{ Lmol}^{-1} \text{ cm}^{-1})$ respectively. The low energy transition may be assigned to d-d transition band centered on chelated copper(II). The two other high energy transitions were observed for copper(II)-bound intraligand n- π^* and π - π^* charge transfer transitions. In case of octahedral iron(III) complex **3**·H₂O, one of the ligand field transition appears at 505 nm (ε = 241 L mol⁻¹ cm⁻¹). Here high energy transitions were observed at 290 nm (10766 L mol⁻¹ cm⁻¹) and 267 nm $(11156 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1})$ for iron(III)-bound intraligand n- π^* and π - π^* charge transfer transitions. For square planar cobalt(II) complex **4**·CH₃CN, the ligand field transitions appear at 579 nm (ε = 36.6 L mol⁻¹ cm⁻¹) whereas the intraligand $n-\pi^*$ and $\pi-\pi^*$ charge transfer transitions appear at 278 nm (ε = 9128 L mol⁻¹ cm⁻¹) and 209 nm (ε = 9225 L mol⁻¹ cm⁻¹) respectively.

4. Concluding remarks

Two benzoylthiourea based ligands have been examined for their coordination potential to Fe^{III} , Co^{II} , Ni^{II} and Cu^{II} . The unsymmetrical O,S donor anionic ligands show systematic preferences for *facial* and *cis* isomers in mononuclear octahedral and squareplanar geometries around these metal ions. The spectroscopic signatures both in solution and solid states and X-ray crystallography confirm keto-thiol tautomerization during metal binding as well as delocalization of negative charge over the six membered chelate rings. The unique properties of square-planar 3d metal complexes reported in this paper can be successfully used to probe the duplex DNA and G-quadruplex DNA structure in live cells to elucidate the role of planar structures with perpendicular *N*-phenyl pendent ends. The *N*,*N*-diethyl ends of complex **2** make it almost planar molecule for good stacking and intercalation.

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Appendix A. Supplementary material

CCDC 922997, 922998, 922999 and 923000 contain the supplementary crystallographic data for **2**, **3**·H₂O, **4**·CH₃CN and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.ica.2014.01.044.

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