Spectroscopic studies on isomerisation of coordinated polyfunctional dihydrazones in going from monometallic to bimetallic complexes: Zinc(II), copper(II) and dioxouranium(VI) complexes of bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone

R A Lal* & A Kumar
Department of Chemistry, Tripura University, Agartala 799004, Tripura, India
Received 10 October 1997; revised 8 April 1999

The monometallic complexes of the type [Zn₂(H₄L)₂(SO₄)₂] (1), [Zn₂(H₂L)₂(H₂O)₄] (2), K₂[Zn₂(H₂L)₂F₄] (2a), and the heterobimetallic complexes of the type [UO₂]Zn₂(L)₂(H₂O)₄ (3), K₄[UO₂]Zn₂(L)₂F₄(H₂O)₄ (3a), [Cu₂Zn₂(L)₂(H₂O)₄] (4) and K₄[Cu₂Zn₂(L)₂F₄(H₂O)₄] (4a) have been synthesized and characterized by analytical, molar conductance, and magnetic data and electronic, IR and IH NMR spectroscopic studies. Monometallic complexes have been shown to contain the coordinated dihydrazones in syn-cis-configuration while the heterobimetallic complexes contain the coordinated dihydrazone in the anti-cis-configuration.

Heterobimetallic chemistry is an area of active current research due to the importance of heterobimetallic complexes in homogeneous catalysis¹, heterogeneous catalysis² and in multimetallic enzymes³,⁴. A synthetic approach for preparing pure samples of heterobimetallic complexes involves preparing monometallic precursor complex from polynucleating ligands in which the first metal ion assembles the ligands in a manner that facilitates the incorporation of the second metal ions⁵. Bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone is a polynucleating ligand possessing amide, azomethine and phenol functions in duplicate in its molecular skeleton. A survey of literature reveals that although some isolated studies on dihydrazones-metal complexes have been carried out⁶-¹⁰, the heterobimetallic complexes derived from them have not been studied at all. The present paper reports the results of synthesis and characterization of heterobimetallic complexes of zinc(II), dioxouranium(VI), and copper(II) derived from the title ligand, bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H₄L).

Experimental

All chemicals used were of AR grade. The determination of Cu¹¹⁺, Zn¹¹⁺ and U¹¹⁺ was carried out by following the literature procedures. Microanalyses were carried out by microanalyzer Heraeus Carlo Erba 1108. Water molecules were determined by heating the samples in an oven and passing the vapours through anhydrous copper sulphate trap and estimating the weight loss. The molar conductances of the complexes at 10⁻³ M dilution in DMSO were determined using a Systronics-304 conductivity meter. The magnetic measurements were made on a Faraday balance using Hg[Co(NCS)₄] as the calibrant. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. The ¹H NMR spectra were recorded on a EM-390, 90 MHz spectrometer in DMSO-d₆ solution using TMS as an internal standard. The electronic spectra of the ligand and the complexes were recorded on a DMR-21 spectro-photometer. The EPR spectra of the compounds in powdered form at RT and LNT were recorded at X-band frequency on a Varian E-112 X/Q band spectro-meter using DPPH as an internal field marker.

Bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone was prepared by the literature method².

Preparation of complexes

[Zn₂(H₄L)₂(SO₄)₂] (1) was prepared by adding bis (2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (1.0 g, 47 mmol) in hot water-ethanol medium (50 ml, 90:10) to metal sulphate solution (2.02 g, 46.9 mmol) in water (150 ml). The reaction mixture was refluxed for 6 h. The lemon yellow product so obtained was filtered hot, washed with hot water, ethanol and finally with ether and dried in vacuo, yield 92%.

The complex (1) (1.0 g, 17 mmol) suspended in water (50 ml) and refluxed with CH₂COOK (0.84 g, 428 mmol) in water (20 ml) yielded [Zn₂(H₂L)₂(H₂O)₄] complex (2) (yield 76%). K₂[Zn₂(H₂L)₂F₄] (2a) was obtained by suspending complex (2) (1.0 g, 19.7 mmol) in ethanol (50 ml) and stirring for ½ h at 60-70°C followed by addition of KF (0.57 g, 981 mmol) dissolved in water (10 ml), yield 72%.
The complex [Zn(H2L)2(SO4)2] (1) is formed when ZnSO4·7H2O and H2L in 3:1 molar ratio are refluxed in water-ethanol medium. This complex loses SO42− when refluxed with excess CH3COOK yielding the complex [Zn2(H2L)2(H2O)6] (2). The loss of SO42− may be attributed partly to the increase in acidity of

To the complex (2) (1.0 g, 19.7 mmol) suspended in ethanol (50 ml) was added UO2(OAc)2·2H2O (0.90 g, 85 mmol) in ethanol (25 ml). The reaction mixture was refluxed for 6 h. The deep brown precipitate so obtained was filtered while hot, washed with ethanol, ether and dried in vacuo to obtain complex [(UO2)Zn2(L)2(H2O)6] (3) in 74% yield. The complex [Cu2Zn2(L)2(H2O)6] (4) was also prepared by the above procedure using Cu(OAc)2·H2O instead of UO2(OAc)2·2H2O in methanol medium.

For preparing the complex K4[(UO2)Zn2(L)2F4(H2O)2] (3a), the complex (3) (1.0 g, 12.3 mmol) was suspended in ethanol (50 ml) and stirred for ½ h at 60-70°C. KF (0.72 g, 620 mmol) dissolved in the minimum amount of water (20 ml) was added to this suspension. The reaction mixture was refluxed for 6 h resulting in a dark orange solution. On concentrating the solution to 25 ml by evaporation and cooling, a light orange precipitate separated out. This was filtered, and washed with water, ethanol, ether and dried in vacuo, yield 65%. The complex K4[Cu2Zn2(L)2F4(H2O)2] (4a) was prepared by the above procedure using complex (4) as the starting material instead of the complex (3).

### Results and discussion

The complex [Zn2(H2L)2(SO4)2] (1) is formed when ZnSO4·7H2O and H2L in 3:1 molar ratio are refluxed in water-ethanol medium. This complex loses SO42− when refluxed with excess CH3COOK yielding the complex [Zn2(H2L)2(H2O)6] (2). The loss of SO42− may be attributed partly to the increase in acidity of

---

**Table 1** — Analytical, magnetic moment and electronic spectral data for the complexes

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complex, colour</th>
<th>Found (Calc.)%</th>
<th>Magnetic moment*</th>
<th>Electronic spectral bands, λmax (nm) (εmax)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn Cu/U C H N</td>
<td>μB (BM)</td>
<td>Solid state</td>
</tr>
<tr>
<td>1.</td>
<td>[Zn(H2L)2(SO4)2] Lemon yellow</td>
<td>11.34 — 48.72 3.13 9.81</td>
<td>—</td>
<td>320, 330 (13170); 330, 375 (9870); 370, 450 (6030); 445</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11.13) — (49.03) (3.07) (9.52)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>[Zn(H2L)2(H2O)2] Reddish orange</td>
<td>13.21 — 56.29 3.60 11.29</td>
<td>—</td>
<td>330, 330 (12270); 380, 390 (8750); 440, 455 (6805)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12.89) — (56.76) (3.55) (11.04)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a.</td>
<td>K4[Zn(H2L)2F4] Dark orange</td>
<td>11.28 — 53.09 2.90 10.50</td>
<td>—</td>
<td>335, 335 (14890); 375, 400 (10980); 470, 470 (7045)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11.94) — (52.61) (2.92) (10.23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>[(UO2)2Zn2(L)2(H2O)6] Orange</td>
<td>8.29 29.01 35.92 2.42 7.12</td>
<td>—</td>
<td>330, 340 (13790); 390, 410 (14750); 450, 460 (7340); 550 (535)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8.08) (29.33) (35.50) (2.47) (6.90)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a.</td>
<td>K4[(UO2)2Zn2(L)2F4(H2O)2] Light orange</td>
<td>7.31 26.25 32.75 1.87 6.02</td>
<td>—</td>
<td>345, 335 (12780); 385, 405 (14210); 460, 450 (6270); 450, 460 (7340)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(7.34) (26.70) (32.31) (1.80) (6.28)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>[Cu2Zn2(L)2(H2O)6] Dark brown</td>
<td>10.82 10.59 49.42 3.00 9.28 2.80</td>
<td>—</td>
<td>366, 340 (8790); 480, 405 (14210); 590, 485 (6270); 605 (290)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11.14) (10.83) (49.07) (3.07) (9.54) (1.98)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a.</td>
<td>K4[Cu2Zn2(L)2F4(H2O)2] Black brown</td>
<td>11.02 9.52 42.51 2.30 8.39 2.73</td>
<td>—</td>
<td>367, 340 (11209); 482, 400 (13710); 760, 490 (7330); 770 (25)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11.39) (9.28) (42.05) (2.34) (8.18) (1.93)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values in the brackets correspond to empirical formulation. λmax for monometallic copper complex, solid state: 400, 435, 475, 550; DMSO solution: 345 (9809), 360 (10120), 440 (8910), 480 (7605), 550 (170), εmax in units of dm³ mol⁻¹ cm⁻¹.
the naphtholic-OH group of coordinated H4L and partly to the buffer action of alkali metal acetate and acetic acid produced in the reaction medium which raises its pH. For the same reasons, the reactions of complex (2) with UO2(OAc)2·2H2O and Cu(OAc)2·H2O in ethanol and methanol, respectively, yielded heterobimetallic complexes [UO2(Zn2(L)2(H2O)4)3] (3) and [Cu2(Zn2(L)2(H2O)4)] (4), without requiring use of any base for the removal of secondary protons. When complexes (2) to (4) were treated with excess KF, the corresponding fluoro complexes K2[Zn2(H2L)2F2] (2a), K4[Cu2Zn2(L)2F4(H2O)2] (3a) and K4[Cu2Zn2(L)2F4(H2O)2] (4a), respectively, were obtained.

The complexes are lemon yellow to orange to dark orange in colour and are air-stable, decomposing above 300°C. They are soluble in highly coordinating solvents like DMF and DMSO. The complexes (2), (3a) and (4a) showed weight loss corresponding to two water molecules while the complexes (3) and (4) showed weight loss corresponding to six and four water molecules, respectively, at 180°C indicating that water molecules are coordinated to the metal centres. Molar conductance values in DMSO for complexes (2), (3) and (4) lies in the range 2.9-1.9 ohm⁻¹ cm² mol⁻¹ suggesting them to be non-electrolyte. Molar conductance values for the complex (1) (21.5 ohm⁻¹ cm² mol⁻¹) and for the complexes (2a) (3a) and (4a) lying in the range 70.5-53.7 ohm⁻¹ cm² mol⁻¹ are inconsistent with the 2:1 and 4:1 electrolytic nature, respectively, of the complexes. The molar conductance values lower than those required for 2:1 and 4:1 electrolytes may be attributed to low low ionic mobility of the anionic coordination sphere due to its large size.

The complexes (1) to (2a) showed an ¹H NMR signal in the region δ 12.78-12.65 ppm as against a signal at δ 12.72 ppm in the uncoordinated H4L assigned to δOH+δNH protons. The δ–CH=N– signal at δ 9.75 ppm in free H4L shifts downfield appearing in the region δ 9.90-9.85 ppm indicating coordination of >C=N– group. The appearance of 3δOH+3δNH or δNH and δ–CH=N– signals as a singlet in the complexes (1) and (2a) in combination with their dimeric nature as confirmed by the molecular weight measurement of the complex (2) (exptl.: 1250±50; theore.: 1014.76) indicates syn-cis-configuration of dihydrazone.

The δNH signal at δ 12.70 ppm in the precursor complex (2) disappears in the heterobimetallic complexes (3) and (3a) indicating the enol form of dihydrazone. The signal corresponding to azomethine proton splits into doublet of doublet [δ 10.10, 10.25, 10.55, 10.73 ppm in complex (3) and δ 9.70, 10.10, 10.30, 10.75 ppm in complex (3a)] and shows a downfield shift of 0.54 and 0.34 ppm indicating coordination of >C=N– group.

The δ–CH=N– signal appears as a doublet of doublet [complex (3) and (3a)] as against a singlet in the free dihydrazone. This splitting of δ–CH=N– signal may be rationalized by proposing a chair conformation, which results from isomerisation of dihydrazone from syn-cis-configuration in monometallic complexes to anti-cis-configuration in these complexes.

The IR spectral evidences confirm the inferences drawn from ¹H NMR spectroscopy. The vC=O band appears at 1655 cm⁻¹ in free dihydrazone and shifts to higher frequency in the region 1675-1670 cm⁻¹ in the monometallic complexes (1) to (2a) dismissing the possibility of coordination of >C=O group. The new bands observed in the region 575-551 cm⁻¹ are assigned to v(M–O) (naphtholic). The v(C=N) band shifts to lower frequency and appears in the region 1608-1597 cm⁻¹. The v3(S–O) band appearing at ca. 1100 cm⁻¹ for uncoordinated SO4²⁻ group is split into two strong bands at 1139 and 1101 cm⁻¹ in the complex (1) indicating its monodentate nature.

The vC=O band observed at 1675 cm⁻¹ in the precursor complex (2) disappears in the heterobimetallic complexes (3), (3a), (4) and (4a). These complexes show a new band in the region 1540-1537 cm⁻¹ characteristic of stretching vibrations of NCO⁻ due to enol form of dihydrazone. A new band in the complexes (3), (4) and (4a) {masked by v3(UO2²⁺) in complex (3a)} appearing in the 860-840 cm⁻¹ region indicates the presence of tetraatomic species M O M characteristic of oxo-bridging.

The complexes (3) and (3a) show another new band at 901 (s) and 862 (s) cm⁻¹ assigned to v3(UO2²⁺) stretching vibration. The v(C=N) band splits into two components separated by 16-21 cm⁻¹ as against a single band in the precursor complex (2). The splitting of v(C=N) band in all of these complexes may be attributed to isomerisation of dihydrazone to anti-cis-configuration as compared to syn-cis-configuration in
monometallic complexes as deduced from $^1$H NMR spectroscopic studies also$^{10}$. In addition to ligand bands, the monometallic complexes (1) to (2a) showed a new band in the region 470-435 nm with their molar extinction coefficient in the 7045-6030 dm$^3$ mol$^{-1}$ cm$^{-1}$ indicating that its origin lies in the charge-transfer transition from naphtholate oxygen atom to the metal centre$^{19}$. The heterobimetallic complex (3) shows a new band at 560 nm characteristic of uranyl ion in DMSO solution. In the complex (3a), this band splits into two weak bands at 550 and 570 nm indicating that uranyl ion is present in the excited state. The heterobimetallic complex (4) shows a shoulder at 590 nm to the charge-transfer band which can be attributed to $d \rightarrow d$ transition. In DMSO solution, this band shifts to longer wavelength to 605 nm ($g_e$ 2.90 dm$^3$ mol$^{-1}$ cm$^{-1}$). The corresponding band in monometallic copper complex$^{20}$ appears at 550 nm (solid) and 580 nm (DMSO), respectively. In view of very high extinction coefficient of this band, a square pyramidal geometry is suggested for copper centre$^{21}$. The complex (4a) shows a weak broad band centered at 760 nm consistent with distorted octahedral stereochemistry of copper centre in it.

The complexes (4) and (4a) have $\mu_{\text{eff}}$ value 1.98 and 1.93 B.M., respectively, per empirical formulation. This indicates no appreciable interaction, either intramolecular or intermolecular, occurs in the complexes (Table 1).

The EPR signals for the complex (4) at RT and LNT are strong, suggesting that it has five coordinated structure. Analysis of the anisotropic spectra according to Kempt's method$^{22}$ gave three $g$-values as $g_z=2.319$, $g_x=2.218$, and $g_y=2.140$ at RT ($g_z=2.319$, $g_x=2.149$ and $g_y=2.100$ at LNT). For systems with $g_y > g_x > g_z$, the ratio of $g_y - g_z$ (called R-parameter) less than one ($R=0.473$) indicates that $d_{x^2-y^2}$ is the ground state supporting the square pyramidal geometry of the complex (4).

The EPR spectra of the heterobimetallic complex (4) have essentially similar features as that of the monometallic complex$^{20,21}$ except that the $g$-values are different ($g_z=2.318$, $g_x=2.160$, $g_y=2.080$ at RT and $g_z=2.367$, $g_x=2.193$, $g_y=2.123$ at LNT for monometallic complex).

On the other hand, the complex (4a) shows axial spectra at RT as well as at LNT. The parallel $^6$Cu features are resolved due to copper hyperfine interaction showing weak four lines. The $A_z$ value for the complex is 210 G. The parameters indicate that $g_z g_x > g_y$ free spin (2.346-2.124-2.0023) which show that the unpaired electron is in the $d_{x^2-y^2}$ orbital of Cu(II). The complexes (4) and (4a) also show a well-resolved pattern with $g=4.5$ typical of dimer similar to the monometallic complex$^{20}$ with weak Cu---Cu interaction.

**Acknowledgement**

The authors are thankful to University Grants Commission, New Delhi for financial assistance through grant No. F.12-19/94 (SR-I), August 18, 1994. Further, they would like to thank the Head, RSIC, NEHU, Shillong; Head, RSIC, CDRI, Lucknow and Head, RSIC, IIT, Madras for IR and $^1$H NMR spectral studies, C, H, N analyses and EPR spectral studies.

**References**