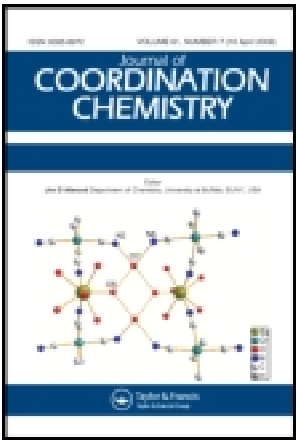

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Synthesis and characterization of a binuclear copper(II) complex $[Cu(H_2slox)]_2$ from polyfunctional disalicylaldehyde oxaloyldihydrazone and its heterobinuclear copper(II) and molybdenum(VI) complexes

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Synthesis and characterization of a binuclear copper(II) complex [Cu(H_2slox)]$_2$ from polyfunctional disalicylaldehyde oxaloyldihydrazone and its heterobinuclear copper(II) and molybdenum(VI) complexes

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The binuclear copper complex [Cu(H_2slox)]$_2$ (**1**) and heterobinuclear copper and molybdenum complexes [Cu(slox)MoO_2(A)$_2$] (slox = tetranegative disalicylaldehyde oxaloyldihydrazone) (A = H_2O (**2**), py (**3**), 2-pic (**4**), 3-pic (**5**), 4-pic (**6**)) and [Cu(slox)MoO_2(NN)] (NN = bpy (**7**) and phen (**8**)) have been synthesized from disalicylaldehyde oxaloyldihydrazone in methanol and characterized by various physico-chemical and spectroscopic techniques. The stoichiometry of the complexes has been established based on elemental analyses and thermoanalytical studies. The μ_{eff} values for the complexes rule out metal–metal interaction between the metal centers in the structural unit of the complexes. The dihydrazone has keto-enol forms; in **1**, it is a dibasic tetradentate bridging ligand in enol form and in heterobinuclear complexes as a tetrabasic hexadentate bridging ligand. Electronic spectra of the complexes show that copper(II) is square-planar in binuclear and heterobinuclear complexes; molybdenum is a distorted octahedral stereochemistry in heterobinuclear complexes. EPR spectra suggest that in all complexes, the unpaired electron is in the d_{x2-y2} orbital of copper and that the copper in heterobinuclear complexes is tetrahedrally distorted.

Keywords: Heterobinuclear complexes; Copper(II); Dioxomolybdenum(VI); Disalicylaldehyde oxaloyldihydrazone; Spectral studies

1. Introduction

Copper is essential for proper functioning of copper-dependent enzymes, including cytochrome c oxidase (energy production), superoxide dismutase (antioxidant protection), tyrosinase (pigmentation), dopamine hydroxylase (catecholamine production), lysyloxidase (collagen and elastin formation), clotting factor V (blood clotting), ceruloplasmin (antioxidant protection), iron metabolism, and copper transport [1].

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Copper occurs in the active site of particulate methane monooxygenase (pMMO) coupled sites where copper is present in di- or trinuclear assemblies. It has been proposed that the copper centers of pMMO are organized into a trinuclear catalytic or electron transfer cluster on the basis of magnetic susceptibility data. The electron paramagnetic resonance (EPR) spectra of fully oxidized enzymes obtained from three different pMMO-containing bacteria have also supported this formulation [2, 3]. However, a mononuclear active center has been supported by another interpretation of EPR spectra from similarly isolated pMMO samples. Copper occurs in nature in combination with molybdenum in the unique heterobimetallic enzyme carbon monoxide dehydrogenase (CODH) [4, 5]. This enzyme catalyzes the oxidation of CO to CO_2, thereby providing carbon and energy to the organism and maintaining sub-toxic levels of CO in the troposphere. Molybdenum ions show antagonistic function with regard to copper in humans and animals [6–9]. Molybdenum–copper complexes or tungsten–copper complexes combining polyfunctional ligands constitute an interesting system of research due to their diverse structural chemistry [10, 11] and their relevance to biological systems [12, 13]. Besides such importance of copper either alone or in combination with molybdenum in biological system, copper plays a significant role in combination with other metals such as zinc and iron in the active sites of several enzymes. Copper occurs in superoxide dismutase in combination with zinc where it catalyzes disproportionation of superoxide, produced in biological systems from action of enzymes on O_2^- to O_2 and H_2O [14]. Copper also occurs in cytochrome oxidase in combination with iron [15] where it catalyzes the oxidation of Fe^{2+} to Fe^{3+}.

Dihydrazones derived from condensation of acyldihydrazines, aroyldihydrazines, and pyridoyldihydrazines with o-hydroxy aromatic aldehydes and ketones are potential polyfunctional ligands with as many as eight or nine bonding sites, phenolic/naphtholic-OH, azomethine, secondary –NH, and carbonyl oxygen in duplicate and pyridoyl nitrogen in their molecular skeleton [16, 17], capable of giving mononuclear and polynuclear complexes [16, 17]. A survey of literature reveals that although work on metal complexes of monohydrazide-based ligands and their Schiff bases has been carried out in some detail [18–21], those on metal complexes of dihydrazones are quite meager [16, 17, 22–27]. It further reveals that work on heterobimetallic complexes of dihydrazones is virtually absent [26, 27]. The importance of copper either alone or in combination with other metals in biological systems and virtually no work on heterometallic complexes of dihydrazones led to this article describing the synthesis of some heterobimetallic complexes containing copper and molybdenum derived from the polyfunctional disalicylaldehyde oxaloyldihydrazone (H_4slox, figure 1).

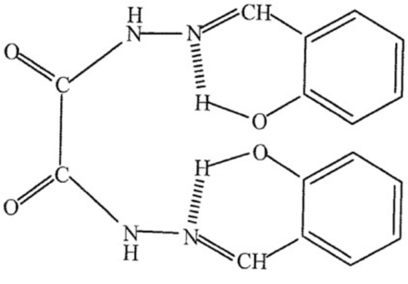


Figure 1. Disalicylaldehyde oxaloyldihydrazone (H_4slox).

Further, it describes the synthesis and characterization of a binuclear copper complex of the title ligand, which has been used as precursor for the synthesis of heterobimetallic complexes.

2. Experimental

2.1. *Materials*

The metal salts, ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$)], copper acetate monohydrate ($Cu(OAc)_2\cdot H_2O$), diethyl oxalate ($(CO_2Et)_2$), hydrazine hydrate ($N_2H_4\cdot H_2O$), and salicylaldehyde ($C_6H_4(OH)(CHO)$), were E-Merck, Qualigens, Hi-Media or equivalent grade reagents and used without purification. Acetyl acetone, pyridine, 2-picoline, 3-picoline, 4-picoline, 2,2′-bipyridine, and 1,10-phenanthroline were Lancaster or equivalent grade reagents. Bis(acetylacetonato)dioxomolybdenum(VI), $MoO_2(acac)_2$ was prepared by the literature method [28].

2.2. *Elemental analyses*

Copper and molybdenum were determined by standard literature procedures [29]. Room temperature magnetic susceptibility measurements were made on a Sherwood Magnetic Susceptibility Balance MSB-Auto. Diamagnetic corrections were applied using Pascal's constants. Electronic spectra of the complexes were recorded in DMSO at $\sim 10^{-3}\,\mathrm{mol\,L^{-1}}$ on a Perkin-Elmer Lambda-25 spectrophotometer. EPR spectra of the complexes were recorded at X-band frequency on a Varian E-112 E-Line Century Series EPR Spectrometer using TCNE ($g = 2.0027$) as an internal field marker. All conductance measurements were made at 1 KHz using a Wayne-Kerr B905 Automatic Precision Bridge. A dip-type conductivity cell having a platinized platinum electrode was used. The cell constant was determined using a standard KCl solution. Infrared spectra were recorded on a BX-III/FT-IR Perkin-Elmer Spectrophotometer from 4000 to $400\,\mathrm{cm^{-1}}$ as KBr discs.

2.3. *Preparation of the complexes*

2.3.1. Preparation of [$Cu(H_2slox)]_2$ (1). Oxaloyldihydrazine (ODH) (0.60 g, 5.08 mmol) was dissolved in H_2O (20 mL). To this solution, $Cu(OAc)_2\cdot 2H_2O$ (1.00 g, 5.01 mmol) dissolved in methanol (60 mL) was added slowly accompanied by gentle stirring and the resulting solution was stirred for 10 min. This solution was then added dropwise to 1.6 mL of salicylaldehyde in methanol (150 mL) over a period of 30 min accompanied by vigorous stirring. This precipitated a green compound which was refluxed for 15 min, then filtered, washed three times with methanol (30 mL each time) followed by ether and finally dried over anhydrous $CaCl_2$.

2.3.2. Preparation of [$Cu(slox)MoO_2(H_2O)_2$] (2). 1.00 g (1.29 mmol) of [$Cu(H_2slox)]_2$ (**1**) was suspended in methanol (60 mL) with stirring for 15–20 min to make a homogeneous suspension. To this homogeneous suspension, a solution of $MoO_2(acac)_2$ (1.00 g, 3.07 mmol) in methanol (20 mL) was added dropwise over a period of 30 min, and the mixture thus obtained was refluxed for 1 h, giving a greenish yellow compound which was isolated following the same procedure.

2.3.3. Preparation of [Cu(slox)MoO$_2$(A)$_2$] {where A = pyridine (py) (**3**), 2-picoline (2-pic) (**4**), 3-picoline (3-pic) (**5**) and 4-picoline (4-pic) (**6**)}**.** In order to prepare [Cu(slox)$MoO_2(py)_2$] (**3**), about 1.00 g (1.82 mmol) of [Cu(slox)$MoO_2(H_2O)_2$] (**2**) was suspended in methanol (50 mL) with constant stirring to make a homogeneous suspension. To this homogeneous suspension 1.44 mL of pyridine was added dropwise over a period of 30 min accompanied by constant stirring. The mixture was then subjected to reflux for 1 h when a greenish yellow compound precipitated, was suction filtered hot and washed several times with minimum quantity of hot methanol followed by ether, and finally dried over anhydrous $CaCl_2$.

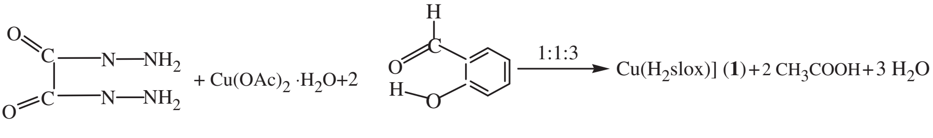
[Cu(slox)$MoO_2(A)_2$] {where A = 2-picoline (2-pic) (**4**), 3-picoline (3-pic) (**5**) and 4-picoline (4-pic) (**6**)} were also prepared by the above procedure using 1.70 mL of picolines instead of 1.44 mL of pyridine.

2.3.4. Preparation of [Cu(slox)MoO$_2$(NN)] {where NN = 2,2′-bipyridine (bpy) (**7**) and 1,10-phenanthroline (phen) (**8**)}**.** [Cu(slox)$MoO_2(H_2O)_2$] (1.00 g, 1.82 mmol) was suspended in methanol and stirred for 10–15 min. To this homogeneous suspension, a solution of bipyridine (0.8 g, 5.12 mmol) in methanol (20 mL) was added dropwise over a period of 30 min. The mixture was then refluxed for 1 h which precipitated the complex. The complex was isolated by the same procedure.

[Cu(slox)MoO_2(phen)] (**8**) was also obtained by following the above procedure using 1.02 g (5.15 mmol) of phenanthroline instead of bipyridine.

3. Results and discussion

Synthesis of pure samples of heterobimetallic complexes is a difficult task because of the possibility of scrambling to other undesired bimetallic products. The synthesis of heterobimetallic products is accessible by strategies developed by Lintvedt *et al.* [30] *via* a monometallic intermediate with polyfunctional ligands and Davies *et al.* [31] *via* transmetallation beginning with a complex of discrete molecularity as target and another metal complex as transmetallator. Accordingly, **1** is synthesized by template method by reacting oxaloyldihydrazine, $Cu(OAc)_2{\cdot}H_2O$, and salicylaldehyde in 1 : 1 : 3 molar ratio in methanol.



The heterobimetallic complex (**2**) was synthesized by reacting the binuclear complex $[Cu(H_2slox)]_2$ with $MoO_2(acac)_2$ in 1 : 2.4 molar ratio in methanol. Further, **3–6** were prepared by reacting **2** with pyridine bases in 1 : 10 molar ratio (**7** and **8** by reacting **2** with bipyridine and 1,10-phenanthroline in ~1 : 3 molar ratio in methanol). These complexes are dark green, light green, or greenish yellow, air-stable compounds, decomposing above 300°C without melting. All complexes are air stable and insoluble in water and common organic solvents such as methanol, ethanol, chloroform, carbon tetrachloride, ether, benzene, but soluble in highly coordinating solvents such as DMF and DMSO. Effort to crystallize the complexes either from a saturated solution or by diffusion into saturated solutions in DMSO and DMF in a closed system led to the precipitation of amorphous products, preventing analysis by X-ray crystallography.

3.1. *Thermal analyses*

Detailed decomposition studies [32] of the complexes were carried out from 70°C to 250°C and the vapors evolved were identified by passing through a test tube containing anhydrous copper sulfate, a test tube containing chloroform solution with a drop of 5 mol L^{-1} sodium hydroxide, a test tube containing solution of iodine and sodium hydroxide and a test tube containing cyanogen bromide solution. None of the complexes showed loss of weight from 100°C to 120°C ruling out the possibility of lattice water; **2** showed loss of weight corresponding two water molecules from 160°C to 180°C. The vapors evolved in this temperature range turned the test tube containing anhydrous copper sulfate blue, confirming water. The loss of weight at such a high temperature indicates coordinated water [32]. Complexes **3–6** showed weight loss at 220°C corresponding to pyridine, 2-picoline, 3-picoline, and 4-picoline, respectively. The vapors evolved at this temperature in **2** turned a solution of $CHCl_3$ containing a drop of 5 mol L^{-1} NaOH solution red, confirming that they originated from a pyridine base [33]. The vapors evolved in **6** at this temperature turned the cyanogen bromide solution blue on treatment with phloroglucinol solution, suggesting its origin from 4-picoline molecule [33]. The expulsion of these molecules at such a high temperature indicates that they are coordinated to the metal [32].

3.2. *Molar conductance*

Molar conductance values for the complexes in DMSO at 10^{-3} mol L^{-1} dilution are 4.9–8.9 Ω^{-1} cm^2 mol^{-1}, consistent with non-electrolytes [34].

3.3. *Magnetic moment*

In the complexes, the magnetic moment value is close to the spin-only value of 1.73 BM, indicating that there is no appreciable spin–spin interaction between metals. According to Figgis [35], magnetic moment values less than 1.90 BM indicate square planar as well as octahedral stereochemistry and magnetic moment value greater than 1.90 BM indicate tetrahedral stereochemistry. On the basis of the magnitude of magnetic moment, the copper center in the complexes has been suggested to have square-planar stereochemistry.

3.4. *Electronic spectra*

Complex **1** and all the heterobimetallic complexes have been characterized by electronic spectroscopy, listed in table 1. All the complexes show a single broad band in the 610–670 nm region with a comparatively low molar extinction coefficient (60–100 $dm^3\,mol^{-1}\,cm^2$). Hence, this band is assigned to $^2E_g \rightarrow {}^2T_{2g}$. In octahedral and tetrahedral complexes of copper(II), the d–d transition occurs at ~800 nm and ~1200 nm, respectively. The 800 nm band in octahedral complexes is considerably blue shifted due to Jahn–Teller distortion and in extreme cases, it falls from 600 to 700 nm, reported for the square planar complexes [36]. The ligand field band in the complexes at 610–670 nm suggests that they have square-planar stereochemistry. The band at 610–670 nm suggests that it is the combination of three transitions ($^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2E_g$) [37].

3.5. *EPR spectra*

All the complexes have been characterized by EPR spectroscopy, recorded only for powder and solution samples at RT and LNT; the results are described in table 2. EPR spectra of **1**, **2**, and **8** are provided in Supplementary material as representative examples. The EPR spectra are isotropic both in the solid state and DMSO at RT. The complexes show single-line spectra in the solid state at RT but show copper hyperfine splitting in DMSO. The isotropic nature of the spectra of the complexes without any copper hyperfine splitting at RT in the solid state is due to intermolecular interaction. However, at RT in solution, since the molecules are sufficiently diluted, the complexes show hyperfine spectral features. This is due to the interaction of an unpaired electron of copper(II) with nuclear spin ($I = 3/2$) in DMSO. The isotropic EPR spectra in DMSO are due to tumbling of the molecules at room temperature. Only three signals are observable in solution. The g_{av} values for copper(II) complexes are 2.038–2.065 and 2.035–2.069 at RT in the solid state and DMSO solution, respectively. The complexes show anisotropic spectra at LNT in DMSO. Complexes **1–6** show hyperfine splitting in $g_{||}$ and $g_{\perp}$ with hyperfine splitting constants $A_{||}$ and $A_{\perp}$ at 150–180 and 40–70 G, respectively. Heterobimetallic complexes **7** and **8** show hyperfine splitting in $g_{||}$ only. Although four hyperfine lines should be observed for copper(II) complexes, in practice, only three components are observable in the $g_{||}$ region. The superhyperfine structure in $g_{\perp}$ has been observed in **1** at LNT. The superhyperfine structure shows seven lines in **1** with superhyperfine coupling constant $A_{\perp N} = 12$ G, corresponding to coupling of electron spin with the nuclear spin of two nitrogens. This indicates coordination of two nitrogens of the dihydrazone. The appearance of seven lines in the EPR spectrum shows that nitrogens bonded to the metal center are in different environments. This reveals that two nitrogens which coordinate to the metal originate from two different ligands. The DMSO solution spectrum of **1** shows a pattern typical of a weak dimer Cu···Cu interaction with an absorption corresponding to $\Delta Ms = 2$ at $g = 4.45$, although, it is not well-resolved. While the EPR spectrum is indicative of dimer structure involving weak Cu···Cu interaction, the observed magnetic moment of $\mu_B = 1.79$ BM suggests the presence of only a negligible or very weak Cu···Cu interaction. Complexes **2–8** show no such absorption at lower field ruling out a weak Cu···Cu interaction.

Table 1. Complex, color, decomposition point, analytical, molar conductance, magnetic moment, and electronic spectral data.

No.	Complex (color)	d.p. (°C)	Elemental analyses: Found (Calcd) (%) Cu	Mo	C	H	N	Molar conductivity, Λ_M (Ω^{-1} cm^2 mol^{-1})	Magnetic moment, μ_{eff} (BM)	Electronic spectral band, λ_{max}(nm) (ε_{max}) (dm^3 mol^{-1} cm^{-1})
1	$[Cu(H_2slox)]_2$	> 300	16.83	–	49.78	3.09	14.90	1.8	1.79	293(8554), 303(8518), 339(8743),
	(Dark green)		(16.40)		(49.59)	(3.12)	(14.46)			423(1276), 618(65)
2	$[Cu(slox)MoO_2(H_2O)_2]$	> 300	11.24	17.63	35.12	2.60	10.45	6.6	1.79	292(12,442), 302(12,550),
	(Greenish yellow)		(11.56)	(17.46)	(34.97)	(2.57)	(10.20)			337(12,371), 420(3064), 666(59)
3	$[Cu(slox)MoO_2(py)_2]$	> 300	9.75	14.01	46.61	3.03	12.67	4.9	1.74	292(12,140), 302(12,270),
	(Greenish yellow)		(9.46)	(14.28)	(46.49)	(3.00)	(12.51)			337(11,950), 423(3340), 608(97)
4	$[Cu(slox)MoO_2(2\text{-pic})_2]$	> 300	8.83	13.99	48.32	3.49	12.29	7.1	1.75	291(12,211), 303(12,310),
	(Greenish yellow)		(9.08)	(13.71)	(48.06)	(3.46)	(12.01)			338(12,000), 424(3128), 612(82)
5	$[Cu(slox)MoO_2(3\text{-pic})_2]$	> 300	8.96	13.46	48.17	3.42	11.88	5.4	1.76	292(12,321), 303(12,432),
	(Greenish yellow)		(9.08)	(13.71)	(48.06)	(3.46)	(12.01)			338(11,900), 423(3024), 614(88)
6	$[Cu(slox)MoO_2(4\text{-pic})_2]$	> 300	9.49	13.63	48.40	3.44	12.34	6.5	1.78	292(12,911), 304(12,951),
	(Greenish yellow)		(9.08)	(13.71)	(48.06)	(3.46)	(12.01)			340(12,040), 416(2424), 625(76)
7	$[Cu(slox)MoO_2(bpy)]$	> 300	9.72	14.02	46.35	2.74	12.76	8.0	1.82	302(12,738), 338(12,694),
	(Light green)		(9.49)	(14.33)	(46.63)	(2.71)	(12.55)			414(2189), 619(87)
8	$[Cu(slox)MoO_2(phen)]$	> 300	8.95	14.17	48.50	2.58	12.41	8.9	1.76	293(12,560), 304(12,442),
	(Light green)		(9.16)	(13.83)	(48.48)	(2.62)	(12.11)			340(11,600), 418(2331), 622(78)

Table 2. EPR spectral data for bimetallic complexes at LNT in DMSO.

Complex	$g_{\|\|}$	$g_{\perp}$	g_{av}	$A_{\|\|}$ (G)	$A_{\perp}$ (G)	A_{av}	G	$g_{\|\|}/A_{\|\|}$	α^2
1	2.289	2.091	2.157	180	70	106.7	70 3.18	136.4	0.82
2	2.298	2.118	2.178	50 160	50	86.7	– 2.53	154.0	0.80
3	2.254	2.097	2.149	150	40	80.0	– 2.62	161.2	0.72
4	2.424	2.095	2.153	160	45	83.3	2.82	152.0	0.76
5	2.268	2.081	2.145	165	50	88.3	50 3.37	147.8	0.77
6	2.292	2.085	2.154	160	45	83.3	45 3.43	153.7	0.78
7	2.278	2.071	2.140	170	–	–	3.92	143.7	0.79
8	2.280	2.082	2.153	160	–	–	3.41	152.9	0.76

The frozen solution spectra of heterobimetallic complexes show hyperfine lines at LNT and no features characteristic of a homobimetallic copper(II) complex. This is also supported by the magnetic moments of 1.74–1.82 BM which confirms the presence of only one copper per ligand in **2–8**.

The spin Hamiltonian parameters, calculated for the copper(II)–molybdenum(VI) heterobimetallic complexes are characteristic of dilute copper(II) systems. The $g_{||}$ and $g_{\perp}$ values fall in the ranges 2.254–2.298 and 2.071–2.118, respectively. The shifting of g from 2.0023 in a transition metal complex is due to mixing *via* spin–orbit coupling of the metal orbitals involved in molecular orbitals containing unpaired electron(s), with the empty or filled ligand orbitals. When the mixing is with empty ligand orbitals, the result is negative g shift, whereas the mixing with the filled ligand orbitals leads to a positive g shift. The positive shift of g-values in the present complexes suggests that metal orbitals are mixed with filled ligand orbitals. The shift depends on the amount of the unpaired electron density at the donor sites of the ligands, i.e., on the degree of covalency of the complex. The g tensor values of the complexes can be used to derive the ground state. In square-planar complexes, the unpaired electron lying in the $d_{x^2-y^2}$ orbital gives $g_{||} > g_{|} > 2.0023$, while the unpaired electron lying in the d_{z^2} orbital gives $g_{|} > g_{||} > 2.0023$. In the present complexes, the observed g-values fall in the order $g_{||} > g_{|} > 2.0023$, suggesting that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital. The in-plane σ covalency parameter, α^2_{Cu}, was calculated for the copper(II) complexes using the following equation [38]; values obtained are listed in table 2.

$$\alpha^2_{\mathrm{Cu}} = -(A_{||}/0.036) + (g_{||} - 2.0023) + 3/7(g_{|} - 2.0023) + 0.04.$$

The α^2_{Cu} values for the complexes are 0.72–0.82 < 1, indicating that these complexes have some covalent character. The nature of the ligand forming the complex is evaluated from G-values obtained using the following equation:

$$G = (g_{||} - 2)/(g_{|} - 2).$$

If $G < 4.0$, the ligand forming the complex is regarded as strong field. For square planar complexes, G is usually in the range [39] 2.03–2.45. G-values for the present complexes are 2.53–3.92, suggesting that the dihydrazone has intermediate field strength in the complexes. Further, if $G > 4.0$, the local tetragonal axes are aligned parallel or only slightly misaligned. If $G < 4.0$, significant exchange coupling is present and the misalignment is appreciable. The observed G-values for the exchange interaction parameter for the complexes ($G = 2.53$–3.92) suggest that the local tetragonal axes are misaligned, and the unpaired electron is in the $d_{x^2-y^2}$ orbital.

The ratio $g_{||}/A_{||}$ is used to find the distortion in the structure of coordination complexes. The ratio obtained for **1** is 136.4 cm while for **2**–**8** is 143.7–161.2 cm. The $g_{||}/A_{||}$ value for **1** is 90–140 cm for the square planar copper(II) complexes [40]. The value of 136.4 cm for **1** suggests that in this complex copper has square planar stereochemistry. On the other hand, for **2**–**8**, the $g_{||}/A_{||}$ is 143.7–161.2 cm^{-1}, beyond the range suggested for square-planar complexes. This indicates that in these complexes, the geometry around copper center is considerably distorted from square planar toward tetrahedral.

3.6. *Infrared spectra*

Some structurally significant IR bands for uncoordinated dihydrazone and complexes are in table 3. The free oxaloyldihydrazide shows relatively strong bands at 3292, 1651, and 1588 cm^{-1}. The band at 3292 cm^{-1} is characteristic of υNH while the bands at 1651 and 1588 cm^{-1} are characteristic of >C=O and bending of NH_2. The essential features of these bands suggest that >C=O and $-NH_2$ of dihydrazide are involved in strong intramolecular H-bonding. Complex **1** shows IR spectral features entirely different from that of ODH yet similar to that of uncoordinated dihydrazone. Complex **1** has bands at 3278 and 3204 cm^{-1} which bears similarity with the preformed dihydrazone bands, showing the presence of phenolic –OH and secondary –NH, respectively. Another strong band at 1679 cm^{-1} is similar to the band at 1651 cm^{-1} in ODH and at 1667 cm^{-1} in the dihydrazone H_4slox. Hence, this band is assigned to stretching vibration of >C=O. The position of this band is higher than ν(C=O) in ODH and dihydrazone. This rules out the possibility of coordination of >C=O group to the

Table 3. Infrared spectral data for the heterobimetallic complexes.

Ligand/ complex	ν(OH) + ν(NH)	ν(C=O)	ν(C=N)	Amide II + ν(C–O) (phenolic)	ν(NCO)	ν(C–O)	ν(N–N)	$\nu(\mathrm{MoO}_2^{2+})$	ν(M–O) (phenolic)	ν(M–O) (enolic)
H_4slox	3278(s) 3204(s)	1667(s)	1627(s) 1603(s)	1534(s)	–	1262(s)	1035(w) 1054(m)	–	–	–
1	3278(m) 3204(m)	1679(s)	1613(s)	1527(s)	–	1276(s)	1043(w)	–	598(m)	482(w)
2	3429(s)	–	1603(s)	–	1533(s)	1309(s) 1270(s)	1032(w)	942(s) 914(s)	572(w)	543(w)
3	3438(s)	–	1605(s)	–	1534(s)	1310(s) 1274(s)	1034(w)	947(s) 913(s)	573(w)	531(w)
4	3431(s)	–	1605(s)	–	1533(s)	1309(s) 1274(s)	1035(w)	948(s) 912(s)	574(w)	527(w)
5	3436(s)	–	1606(s)	–	1532(s)	1308(s) 1270(s)	1030(w)	946(s) 913(s)	574(w)	540(w)
6	3439(s)	–	1604(s)	–	1531(s)	1310(s) 1272(s)	1035(w)	944(s) 912(s)	572(w)	529(w)
7	3421(s)	–	1608(s)	–	1533(s)	1311(s)	1022(w)	914(s) 884(s)	–	532(w)
8	3410(s)	–	1608(s)	–	1531(s)	1306(s)	1035(w)	910(s) 891(s)	–	531(w)

metal center and suggests the absence of intramolecular hydrogen bonding involving $>$C=O as in free ODH molecule. In addition, **1** shows a new band at 1613 cm^{-1}, which is similar to the band at 1627 and 1603 cm^{-1} in the free ligand and falls in the region of coordinated $>$C=N in hydrazone metal complexes. Hence, this band is assigned to ν(C=N) [41]. All these pieces of evidence suggest that NH_2 of dihydrazide and $>$C=O of salicylaldehyde condense generating the dihydrazone metal complex. In **1**, νOH, νNH, and ν(C=O) are decreased in intensity while ν(C=N) increases in intensity compared to the corresponding band in the free dihydrazone. Another important feature of the IR spectrum of **1** is that it shows a new band at 1527 cm^{-1} which masks the preformed ligand band at 1534 cm^{-1} due to amide II + ν(C–O) (phenol). This band is assigned to stretching of the newly created NCO^- produced as a result of enolization of the ligand [27]. Such a feature associated with the IR spectrum of **1** suggests that half of the dihydrazone has undergone enolization. The intensity of ν(C=N) increases due to newly created $>$C=N–N=C$<$. The strong band at 1276 cm^{-1} is assigned to ν(C–O)(phenol) in **1** as against the band at 1262 cm^{-1} in free dihydrazone. This indicates bonding of phenolate oxygen to metal. Complex **1** shows bands at 598 and 482 cm^{-1}, which are assigned to ν(M–O)(phenolate) and ν(M–O) (enolate), respectively. The bands at 3278 and 3204 cm^{-1} in the IR spectrum of $[Cu(H_2slox)]_2$ disappear in IR spectra of the heterobimetallic complexes. This suggests involvement of –OH in bonding, collapse of amide structure of the ligand, and its presence in enol form in the heterobimetallic complexes. A strong broad band at 3386–3438 cm^{-1} might be due to ν(–OH) of either lattice or coordinated water or due to ν(–OH) of moisture absorbed by KBr during pellet preparation. In order to decide whether bands in this region arise due to water or due to moisture absorbed by KBr pellets, the compounds were subjected to thermal analysis. The thermo-analytical data suggest the presence of water in the coordination sphere of **2**. Hence, it can be said that the strong broad band at 3386–3438 cm^{-1} arises due to the presence of coordinated water in **2**, whereas in the rest of the complexes the bands in this region arise due to moisture absorbed by KBr during pellet preparation.

The ν($>$C=O) at 1679 cm^{-1} in binuclear $[Cu(H_2slox)]_2$ is also absent in IR spectra of the heterobimetallic complexes confirming the pure enol form of the dihydrazone in these complexes. Two very strong bands centred at 1627 and 1603 cm^{-1} due to stretch of azomethine ($>$C=N–) in uncoordinated dihydrazone and at 1613 cm^{-1} in **1** shift to lower frequency by 5–11 cm^{-1} in all the heterobimetallic complexes. The shift of ν($>$C=N–) to lower frequency by 5–11 cm^{-1} indicates bonding between azomethine nitrogen and the metal [37]. A negative shift of 5–9 cm^{-1} in ν(C=N) in the complexes suggests that the metal–nitrogen bonds are stronger in heterobimetallic complexes as compared to those in **1**.

IR spectra of the ligand show a strong band at 1534 cm^{-1} and that of the precursor complex at 1527 cm^{-1} with composite character due to contributions of the amide II and ν(C–O) (phenol) bands. In all the complexes, a very strong band appears at 1512–1534 cm^{-1}. The position of this band is consistent with bonding through phenolate oxygen; the intensity of the band is considerably increased as compared to that of the free ligand as well as the precursor complex, suggesting that this band has contribution from the stretch of the newly created NCO. The strong intensity band due to ν(C–O) (phenol) at 1262 cm^{-1} in free dihydrazone and at 1276 cm^{-1} in **1** splits into two components in the heterobimetallic complexes at 1306–1311 and 1270–1274 cm^{-1}. The average position of these bands is shifted to higher frequency by about 23–49 and

13–35 cm^{-1}, respectively, compared to the uncoordinated dihydrazone and **1**. This shows that the phenolate oxygen is bonded to the metal [42]. The splitting of this band into two components is from formation of the heterobimetallic complex. Complexes **2–8** show a couple of bands from 884 to 948 cm^{-1}, characteristic of cis $-$ MoO_2^{2+} in the complexes. These bands arise from the symmetric and asymmetric stretches of cis $-$ MoO_2^{2+}. Complexes **3–6** show a very weak band at 1000–1070 cm^{-1}, assigned to ring stretching mode of pyridine and substituted pyridines. Complexes **7** and **8** show two strong bands at 725–727 and 841–849 cm^{-1}, assigned to out-of-plane motion of hydrogens on the heterocyclic rings and on the central ring, respectively. In **7**, only one strong band is observed at 756–758 cm^{-1} due to out-of-plane motion of hydrogens as expected for two identical groups of four hydrogens each. Apart from these bands, **7** and **8** also show very strong bands at 632, 634, 631, and 632 cm^{-1}, assigned to in-plane ring deformation of phenanthroline and bipyridine, indicating their coordination to the metal [43, 44]. The ν(M–O) (phenol) may be expected at higher frequency than ν(M–O) (enolized carbonyl) for difference in bond order. Spectra of the ligand, **1** and heterobimetallic complexes below 600 cm^{-1}, new bands at 572–574 and 483–541 cm^{-1} are, tentatively, assigned to ν(M–O) (phenol) [45] and ν(M–O) (enolate) [46], respectively. In **7** and **8**, this band appears merged with the in-plane ring deformation of bipyridine and phenanthroline, respectively.

4. Conclusion

A binuclear copper(II) complex $[Cu(H_2slox)]_2$ has been synthesized by template method from the reaction of oxaloyldihydrazine, $Cu(OAc)_2{\cdot}2H_2O$, and salicylaldehyde in 1 : 3 molar ratio in methanol. H_4slox is present in keto-enol form in $[Cu(H_2slox)]_2$. Further, using $[Cu(H_2slox)]_2$ as a precursor, seven heterobimetallic Cu(II)-Mo(VI) complexes have been synthesized. The band due to $\nu(>C{=}O)$ is absent in IR spectra of the heterobimetallic complexes as compared to that in the precursor complex. This indicates that the ligand is transformed purely in enol form as a consequence of formation of heterobimetallic complexes compared to its keto-enol form in the precursor complex. In the binuclear precursor complex, the dihydrazone coordinates to copper as a dibasic tetradentate bridging ligand while in the heterobimetallic complexes, it coordinates to the metal centers as a tetrabasic hexadentate bridging ligand. The electronic spectral data with magnetic moment data indicate that copper(II) has a square-planar stereochemistry in the binuclear precursor and heterobimetallic complexes. The EPR spectral parameters suggest that in all complexes, the unpaired electron is in the $d_{x^2-y^2}$ orbital and that Cu in heterobimetallic complexes is tetrahedrally distorted. MoO_2^{2+} is a hard acid while Cu(II) is a relatively soft acid. Hence, given an opportunity to bind polyfunctional dihydrazone ligand, MoO_2^{2+} would prefer to bind hard carbonyl oxygen while Cu(II) would prefer to bind relatively soft phenolate oxygen and azomethine nitrogen in the heterobimetallic complexes. Assuming that copper(II) has square-planar stereochemistry and binds phenolate oxygens and azomethine nitrogens, having N_2O_2 coordination, that two monodentate donors are present in **2–6** and one bidentate molecule in **7** and **8**, and that MoO_2^{2+} is bonded to enolate oxygen in **2–8**, we suggest that the monodentate and bidentate molecules are bonded to molybdenum center. Thus, we suggest that the molybdenum

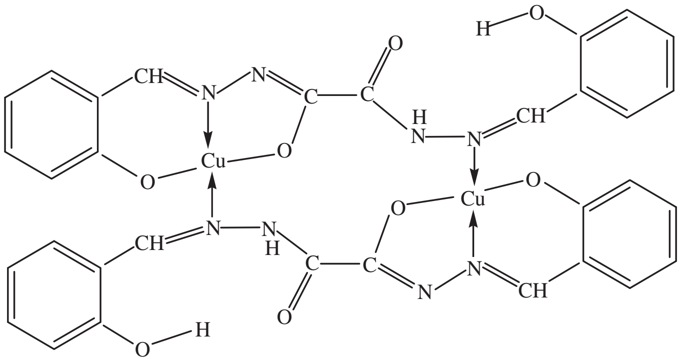


Figure 2. Suggested structure of [Cu(H_2slox)]$_2$ (**1**).

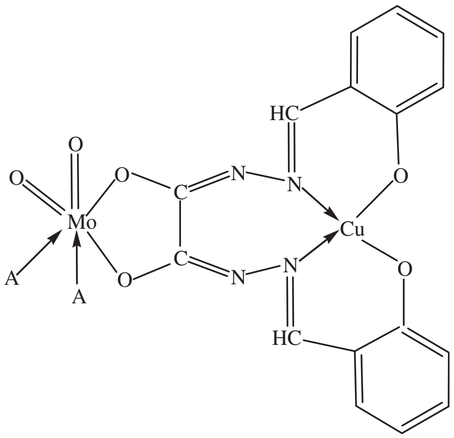


Figure 3. Suggested structures of [Cu(slox)MoO$_2$(A)$_2$] (where A = H_2O (**2**), pyridine (**3**), 2-picoline (**4**), 3-picoline (**5**) and 4-picoline (**6**)).

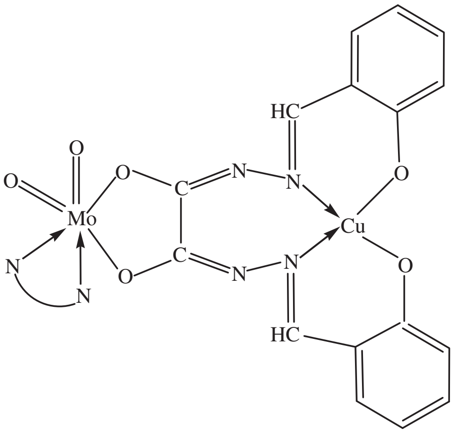


Figure 4. Suggested structures of [Cu(slox)MoO$_2$(NN)] (where A = bipyridine (**7**) and phenanthroline (**8**)).

has a distorted octahedral stereochemistry in heterobimetallic complexes **2–8**. The tentative structures for the complexes are shown in figures 2–4.

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