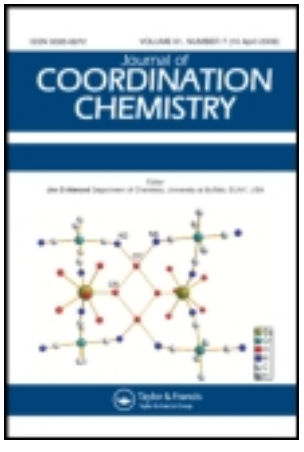

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Syntheses, solvatochromism, and antimicrobial activities of new binuclear copper(II) mixed-ligand complexes in a ternary system with β-diketones and diamine ligands

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Published online: 26 Jul 2011.

To cite this article: A.A. Abou-Hussein, Nelly H. Mahmoud & Wolfgang Linert (2011) Syntheses, solvatochromism, and antimicrobial activities of new binuclear copper(II) mixed-ligand complexes in a ternary system with β-diketones and diamine ligands, Journal of Coordination Chemistry, 64:15, 2592-2605, DOI: 10.1080/00958972.2011.602402

To link to this article: http://dx.doi.org/10.1080/00958972.2011.602402

Journal of Coordination Chemistry
Vol. 64, No. 15, 10 August 2011, 2592–2605

Syntheses, solvatochromism, and antimicrobial activities of new binuclear copper(II) mixed-ligand complexes in a ternary system with β-diketones and diamine ligands

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(*Received 23 February 2011; in final form 13 June 2011*)

Ternary complexes of binuclear copper(II) nitrate with bis(β-diketones) [β-diketones = 2-phenyl-1,3-bis-(tetraacetyl-propane), L_1, or 2-(*o*-hydroxyphenyl-1,3-bis-(tetraacetyl-propane), L_2] and diamines [diamines = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen), 2,2′-bipyidine (bipy) and 1,10-phenanthroline (phen)] have been synthesized, where NO_3^- groups are counter or coordinated anions. The structures of the complexes and their solvatochromic behavior were investigated by elemental analysis, spectroscopic, magnetic, molar conductance, and thermal analysis. Solvatochromism was observed for only three complexes where they displayed a drastic color change with increasing donor strength of the solvent. This behavior is due to the solute–solvent interaction between the chelate cation and the solvent. Spectroscopic studies of the complexes implicate tetragonal distortions in strongly polar solvents and square planar or square pyramidal geometries in the presence of weakly coordinating molecules. Biological studies of the ligands and their complexes showed a significant inhibition on the growth of selected Gram-positive bacteria and moderate effect against two kinds of Gram-negative bacteria as well as one kind of pathogenic fungi.

Keywords: Mixed-Cu(II) chelates; Ternary complexes; Solvatochromism; Antimicrobial activities

1. Introduction

Complexes of the Cu(II)-ternary system containing β-diketones with diamine ligands are of considerable interest due to their thermochromic properties [1–3]. They can be used as thermosensitive coloring materials which are chromotropic as a result of exhibiting color change when exposed to solvent or environmental pollutants [4].

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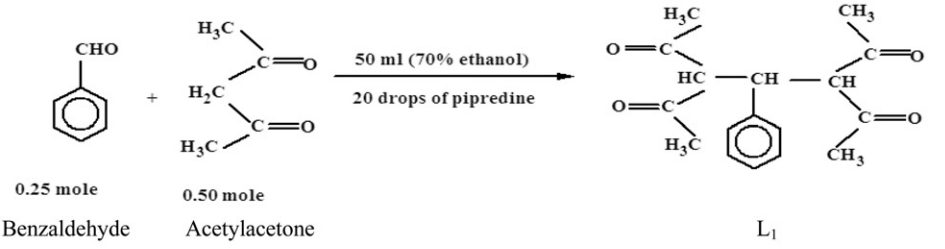
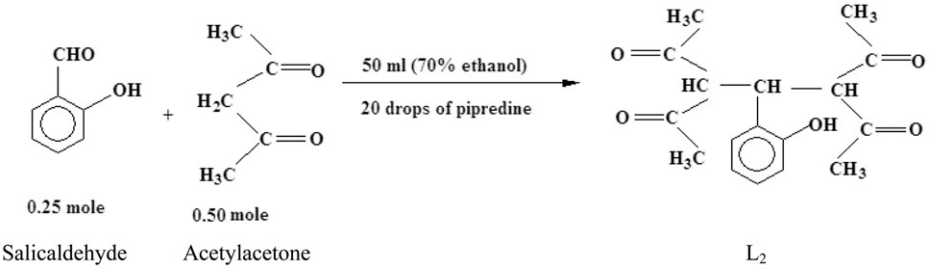
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.602402



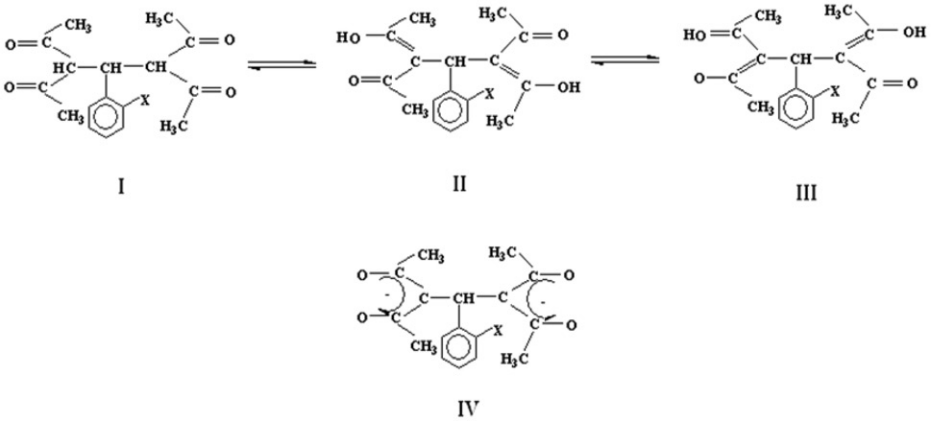
Scheme 1. Representative structures for the preparation of 2-phenyl-1,3-bis(tetraacetyl)-propane, L_1.



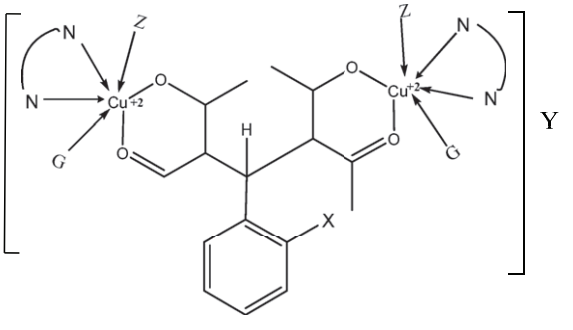
Scheme 2. Representative structures for the preparation of 2-(*o*-hydroxyphenyl)-1,3-bis-(tetraacetyl)-propane, L_2.

These complexes are also of great importance due to their solvatochromic behavior since they can be used as Lewis acid–base indicators where the color changes can be ascribed to d–d transitions with a strong Jahn–Teller effect which explains the regular changes in their electronic spectra according to the strength of interactions with the solvent molecules at the axial sites [5–12].

Herein we report the syntheses, spectral, thermal, and solvatochromic behavior of six new mixed-ligand binuclear copper(II) nitrate complexes with bis(β-diketones) [β-diketones = 2-phenyl-1,3-bis-(tetraacetyl-propane), L_1, or 2-(*o*-hydroxyphenyl-1, 3-bis-(tetraacetyl-propane), L_2] and diamines [diamines = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen), 2,2′-bipyidine (bipy) and 1,10-phenanthroline (phen)], while NO_3^- groups are counter or coordinated anions. The two ligands were prepared by the method reported in [13] (schemes 1 and 2). Scheme 3 shows that the ligands undergo tautomeric behavior. The structures of the newly synthesized mixed ligand complexes were proved by elemental analysis, spectroscopic techniques, and thermal gravimetric analysis. These copper chelates are easily soluble in various organic solvents and show color changes due to characteristic solvatochromism phenomenon. Scheme 4 is a representative structure of Cu(II) mixed-chelate complexes. Thermal decomposition and kinetics studies were carried out and the parameters (ΔH, ΔS, and ΔG) of all the thermal decomposition stages have been calculated using the Coats–Redfern equations [14] (Supplementary material). Microbial studies of the ligands and complexes on the growth of two Gram-positive bacteria strains (*Streptococcus pyogenes* and *Staphylococcus aureus*), two Gram-negative bacteria (*Pseudomonas fluorescens* and *Pseudomonas phaseolicola*), and one selected pathogenic fungi (*Aspergillus fumigates*) have been investigated to assess their biological activities.



Scheme 3. Representation of the tautomeric forms (I–III) of the β-diketones, where X = H for L_1 or X = OH for L_2. Form IV is a general structure.



Complex	N–N	X	Y	Z	G	Geometry
1	tmen	H	$2NO_3^-$	–	–	Square planar
2	bipy	H	–	$2NO_3^-$	$2H_2O$	Octahedral
3	phen	H	–	$2NO_3^-$	–	Square pyramidal
4	tmen	OH	$2NO_3^-$	–	–	Square planar
5	bipy	OH	–	$2NO_3^-$	$2H_2O$	Octahedral
6	phen	OH	–	$2NO_3^-$	$2H_2O$	Octahedral

Scheme 4. Schematic representation of the mixed-chelate Cu(II) complexes.

2. Experimental

2.1. *Materials*

Copper nitrate trihydrate $Cu(NO_3)_2{\cdot}3H_2O$, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen), bipy, phen, anhydrous sodium carbonate, benzaldehyde, salicylaldehyde,

acetylacetone, and piperidine were of analytical reagent grade and obtained from either Merck or Aldrich and used without purification. Acetonitrile, methanol, ethanol, acetone, methylene chloride, DMF, and DMSO used for spectral studies were of spectro-grade and used without purification.

2.2. *Synthesis of 2-phenyl-1,3-bis-(tetraacetyl)-propane, L_1*

Acetylacetone (50.00 g, 0.50 mol) and benzaldehyde (26.60 g, 0.25 mol) were dissolved in 50 g of 70% ethanol. Following the addition of 20 drops of piperidine, the mixture was allowed to stand, solidifying after 1 week. The product (35.40 g) was filtered, washed with 50% ethanol, and recrystallized from benzene.

2.3. *Synthesis of 2-(o-hydroxyphenyl)-1,3-bis-(tetraacetyl)-propane, L_2*

Acetylacetone (50.00 g, 0.50 mmol) and salicylaldehyde (30.50 g, 0.25 mmol) were dissolved in 50.00 g of 70% ethanol. About 20 drops of piperidine were added and the mixture was solidified after 2 days of standing. The product (43.80 g) was filtered, washed with 50% ethanol, and recrystallized from a mixture of water and 95% ethanol.

2.4. *Syntheses of Cu(II) mixed-ligand complexes*

These complexes were prepared by adding a mixture of 5.00 mmol of β-diketone in 20 mL absolute ethanol and 10.00 mmol of anhydrous Na_2CO_3 to an ethanolic solution of 10.00 mmol of $Cu(NO_3)_2{\cdot}3H_2O$. The mixture was stirred for 30 min resulting in a green solution, which was then filtered. A solution of 10.00 mmol of diamine represented by tmen, bipy, or phen in 10.00 mL absolute ethanol was added dropwise to the filtrate under continuous stirring for an additional 30 min. Complexes were filtered off, left to stand overnight, and then recrystallized from CH_2Cl_2 where violet crystals were obtained for $[Cu_2(L_1)(tmen)_2](NO_3)_2$ (**1**) and $[Cu_2(L_2)(tmen)_2](NO_3)_2$ (**4**), bluish-violet crystals for $[Cu_2(L_1)(phen)_2(NO_3)_2]$ (**3**) and green crystals for $[Cu_2(L_1)(bipy)_2(NO_3)_2(H_2O)_2]$ (**2**), $[Cu_2(L_2)(bipy)_2(NO_3)_2(H_2O)_2]$ (**5**), and $[Cu_2(L_2)(phen)_2(NO_3)_2(H_2O)_2]$ (**6**). The following detailed preparation routes are given as examples and the other complexes were obtained similarly.

2.4.1. Synthesis of 1. A mixture of (0.72 g, 5.00 mmol) of 2-phenyl-1,3-bis-(tetraacetyl)-propane, (L_1) in 20.00 mL absolute ethanol and (1.060 g, 10.00 mmol) of anhydrous Na_2CO_3 was added to an ethanolic solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.2079 g, 10.00 mmol). The mixture was stirred for 30 min to give a green solution, which was filtered. Then a solution of (0.7546 mL, 10.00 mmol) of tmen in 10.00 mL absolute ethanol was added dropwise to the filtrate under continuous stirring for an additional 30 min. After filtration the complexes were left to stand overnight and then recrystallized from CH_2Cl_2 yielding violet crystals. The yield was 1.024 g (77.50%).

2.4.2. Synthesis of 5. A mixture of (0.76 g, 5.00 mmol) of 2-(*o*-hydroxyphenyl)-1,3-bis-(tetraacetyl)-propane (L_1) in 20.00 mL absolute ethanol and (1.060 g, 10.00 mmol) of

anhydrous Na_2CO_3 was added to an ethanolic solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.2079 g, 10.00 mmol). The mixture was stirred for 30 min resulting in a green solution, which was filtered. Then a solution of (0.99 g, 10.00 mmol) of phen in 10.00 mL absolute ethanol was added dropwise to the filtrate under continuous stirring for an additional 30 min. The solution was filtered off, left to stand overnight, and then recrystallized from CH_2Cl_2. Green crystals were formed. The yield was 0.8738 g (63.9%).

2.5. *Physical measurements*

Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer 2400 Series II Analyzer. Copper was determined by EDTA solution using muroxide as an indicator. FT-IR spectra (4000–200 cm^{-1}) of the compounds were recorded using an FT-IR (Shimadzu) spectrophotometer Model 4000. UV-VIS spectra of the compounds were obtained on a JASCO model V-550 UV-VIS spectrophotometer. Mass spectra were obtained on a Shimadzu-GC–MS–QL mass spectrometer model 1000EX using a direct inlet system. TGA curves were obtained using a NETZSCH-Gerateban Beste ll-Nr 348472c. The magnetic susceptibilities were measured using a Johnson Matthey Alfa balance. Diamagnetic corrections were calculated from Pascal's constants [15] to obtain the molar paramagnetic susceptibility. Conductance measurements were made at 25°C with a Corning conductivity meter Model NY 14831 model 441(USA).

2.6. *Biological studies*

The *in vitro* biological screening of the synthesized ligands and complexes were carried out against phytopathogenic bacteria and fungi at the Faculty of Agriculture, Department of Plant Pathology, Al-Azhar University.

In vitro antibacterial activity studies were carried out using the standardized disc-agar diffusion method [16] to investigate the inhibitory effect of the synthesized compounds against Gram-positive bacteria, *Sta. aureus* (ATCC25923) and *Str. pyogenes* (ATCC19615), and Gram-negative bacteria, *P. fluorescens* (S 97) and *P. phaseolicola* (GSPB 2828), as well as the fungi *A. fumigatus*.

The antibiotic chloramphencol was used as standard reference for Gram-negative bacteria, cephalothin was used as standard reference for Gram-positive bacteria, and cycloheximide as antifungal standard reference [17]. An inhibition zone diameter indicates that the tested compounds are active against bacteria and fungi.

3. Results and discussion

The ternary metal complexes were prepared in the molar ratio 1 : 2 : 2 from bis-β-diketone, bidentate nitrogen bases (tmen, bipy and phen), and copper ions in absolute ethanol. The new bis-β-diketone possesses two mono basic bidentate dioxide units on both sides, so the resulting Cu(II) complexes have two positive charges balanced by nitrates.

The new Cu(II) complexes were identified by ultraviolet, infrared, electronic, mass spectra, and thermal gravimetric analysis. Solvatochromic properties were studied to

investigate the effect of ligands on the chromotropic behavior. The Cu(II) complexes exhibit square planar, square pyramidal, or octahedral geometrical arrangements. Table 1 lists the physical and analytical data of the complexes.

3.1. *Infrared spectra*

All the complexes show two weak intensity bands at 2916–2922 and 2827–2884 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of the aromatic C–H groups [18]. The broad band at 3423–3442 cm^{-1} for **2**, **5**, and **6** is assigned to ν(OH) of water, in accord with thermal studies and supported by elemental analyses [19].

One feature in the infrared spectra of the complexes is the coordination behavior of nitrate. NO_3^- is coordinated unidentate for **2**, **3**, **5**, and **6** with three non-degenerate modes of vibration for C_{2v} symmetry (ν_s, ν'_s and ν_{as}), where $\nu_s(NO_3^-)$ is 1360–1380 cm^{-1}, $\nu'_s(NO_3^-)$ 1232–1270 cm^{-1}, and $\nu_{as}(NO_3^-)$ 1018–1027 cm^{-1}. The $\nu_s(NO_3^-)$ of unidentate NO_3^- is markedly shifted to lower frequency compared to that of free nitrate (1384 cm^{-1}), providing a measure of the covalent bond strength. The frequencies of the two nitrates in **1** and **4** are at 1384 cm^{-1} [19, 20]. The molar conductivities of the complexes in DMF, shown in table 2, reveal that the measured values of **2**, **3**, **5**, and **6** are higher than expected due to uncoordinated nitrates, perhaps DMF replaced NO_3^- in the complexes, resulting in 1 : 1 or 1 : 2 electrolytes [21]. The conductivity data reveal that NO_3^- is only a counter ion for **1** and **4** (Table 2).

Infrared spectra of the β-diketones in the complexes exhibit two stretching frequencies at 1637–1697 and 1522–1582 cm^{-1}, assigned to ν_{as}(COO) and a single band at 1457–1484 cm^{-1} for ν_s(COO). Generally, the free β-diketone showed a strong broad band at 1739 cm^{-1} [22]. This shift may be due to the chelation of oxygen of the β-diketone. These observations are consistent with the presence of a new medium band at 432–519 cm^{-1} assigned to ν(Cu–O) [23]. Characteristic bands of tmen, bipy, and phen [19, 24] are shifted to lower frequencies on complexation. A new medium band at 520–591 cm^{-1} appears due to ν(Cu–N) [25].

3.2. *Electronic spectra of the complexes in various solvents*

The absorption spectra of complexes were measured in different organic solvents with different donor numbers (DNs) (table 3). The spectra of Cu(II) mixed-chelate complexes are studied in CH_2Cl_2 (Supplementary material). The spectra of the ligands show four absorptions corresponding to $^1L_a \rightarrow {}^1A_1$ and $^1L_b \rightarrow {}^1A_1$ of the aromatic ring of phen and bipy, $\pi \rightarrow \pi^*$ transition of the phenyl rings of phen and bipy and $n \rightarrow \pi^*$ from carbonyl of β-diketones. The transition at 367–479 nm is assigned to intermolecular charge transfer [26].

The green Cu(II) complexes (**1** and **4**) have a broad band at 586 and 566 nm, assigned to $^2B_{1g} \leftarrow {}^2A_{1g}$ of a square planar geometry. The band due to $^2B_{1g} \leftarrow {}^2E_g$ may be obscured by the high-intensity absorption of the ligand. The magnetic moments for **1** and **4** are 1.92 and 1.87 B.M., respectively, in accord with the previous spectral data. Electronic spectra of **2**, **5**, and **6** show one unsymmetrical band, 681, 665, and 703 nm, respectively, assigned to $^2T_{2g}(G) \leftarrow {}^2E_g$ transition in a distorted octahedral geometry. The measured value of the magnetic moments for **2**, **5**, and **6** lie in the range 1.81–178 B.M., while for **3** absorption spectra show λ_{max} at 609 nm, attributed to $^2B_1 \rightarrow {}^2E_g$,

Table 1. The physical and analytical data of Cu(II) complexes.

	Ligands and complex	Empirical formula (M.wt)	Wt. (g) Yield %	Color m.p. (°C)	Elemental analysis Found (Calcd) (%) C	H	N	Cu
I	2-Phenyl-1,3-bis-(tetraacetyl)-propane (L_1)	$C_{17}H_{20}O_4$ 288	35.4 49.0	Yellowish-white 198	71.35 (70.81)	7.11 (6.99)	–	–
II	2-(*o*-Hydroxyphenyl)-1,3-bis-(tetraacetyl)-propane (L_2)	$C_{17}H_{20}O_5$ 304	26.2 32.1	Pale yellow 176	67.54 (67.11)	6.41 (6.58)	–	–
1	$L_1 + tmen + Cu(NO_3)_2{\cdot}3H_2O \rightarrow [Cu_2(L_1)(tmen)_2](NO_3)_2$	$Cu_2C_{29}H_{50}N_6O_{10}$ 769	1.024 77.5	Violet 173	45.19 (45.25)	6.41 (6.50)	10.90 (10.92)	16.43 (16.52)
2	$L_1 + bipy + Cu(NO_3)_2{\cdot}3H_2O \rightarrow [Cu_2(L_1)(bipy)_2(NO_3)_2(H_2O)_2]$	$Cu_2C_{37}H_{38}N_6O_{12}$ 885	0.798 56.1	Green 185	50.16 (50.17)	4.34 (4.29)	9.27 (9.49)	14.28 (14.35)
3	$L_1 + phen + Cu(NO_3)_2{\cdot}3H_2O \rightarrow [Cu_2(L_1)(phen)_2(NO_3)_2]$	$Cu_2C_{41}H_{34}N_6O_{10}$ 897	1.065 37.4	Bluish-violet 234	54.73 (54.85)	3.74 (3.79)	9.52 (9.36)	14.29 (14.16)
4	$L_2 + tmen + Cu(NO_3)_2{\cdot}3H_2O \rightarrow [Cu_2(L_2)(tmen)_2](NO_3)_2$	$Cu_2C_{29}H_{50}N_6O_{11}$ 785	1.752 73.2	Violet 286	44.21 (44.33)	6.42 (6.37)	10.63 (10.70)	16.22 (16.18)
5	$L_2 + bipy + Cu(NO_3)_2{\cdot}3H_2O \rightarrow [Cu_2(L_2)(bipy)_2(NO_3)_2(H_2O)_2]$	$Cu_2C_{37}H_{38}N_6O_{13}$ 901	3.181 67.1	Green 319	49.90 (49.28)	4.55 (4.22)	9.06 (9.32)	14.23 (14.09)
6	$L_2 + phen + Cu(NO_3)_2{\cdot}3H_2O \rightarrow [Cu_2(L_2)(phen)_2(NO_3)_2(H_2O)_2]$	$Cu_2C_{41}H_{38}N_6O_{13}$ 949	1.172 45.0	Green 370	51.98 (51.85)	4.13 (4.00)	8.75 (8.85)	13.19 (13.38)

Table 2. The molecular ions of the complexes, infrared frequencies of the characteristic bands of Cu(II) complexes and molar conductance measurements.

	Complexes	Molecular ion peak m/z (intensity%)	$\nu(CH_3)$ and $\nu(CH)_{aromatic}$	$\nu(CO^-)$	$\nu(NO_3)$	ν(Cu–N)	ν(Cu–O)	Molar conductance, Ω DMF
1	$[Cu_2(L_1)(tmen)_2](NO_3)_2$	775 (14.3)	2903–2993	1693 1582 1452	1384 856	520	459	137
2	$[Cu_2(L_1)(bipy)_2(NO_3)_2(H_2O)_2]$	887 (12.1)	2928–3074	1697 1574 1439	1369 1232 1023	536	462	97
3	$[Cu_2(L_1)(phen)_2(NO_3)_2]$	899 (1.7)	2916–3057	1679 1579 1437	1375 1253 1027	545	460	125
4	$[Cu_2(L_2)(tmen)_2](NO_3)_2$	788 (0.9)	2929–2988	1665 1550 1487	1384 856	591	519	104
5	$[Cu_2(L_2)(bipy)_2(NO_3)_2(H_2O)_2]$	902 (9.1)	2870–2987	1637 1522 1465	1360 1268 1018	521	432	135
6	$[Cu_2(L_2)(phen)_2(NO_3)_2(H_2O)_2]$	953 (19.6)	2918–3051	1646 1553 1460	1380 1270 1025	582	471	121

Table 3. Electronic absorption bands λ_{max} (nm) for the Cu(II) complexes in various organic solvents.

	Complex	CH_2Cl_2	MeCN	Me_2CO	EtOH	DMF	DMSO
1	$[Cu_2(L_1)(tmen)_2](NO_3)_2$	586	592	626	637	664	684
2	$[Cu_2(L_1)(bipy)_2(NO_3)_2(H_2O)_2]$	681	682	686	684	689	704
3	$[Cu_2(L_1)(phen)_2(NO_3)_2]$	609	619	629	645	660	681
4	$[Cu_2(L_2)(tmen)_2](NO_3)_2$	566	578	589	604	647	669
5	$[Cu_2(L_2)(bipy)_2(NO_3)_2(H_2O)_2]$	665	696	698	696	700	699
6	$[Cu(L_2)(phen)_2(NO_3)_2(H_2O)_2]$	703	704	710	708	705	709

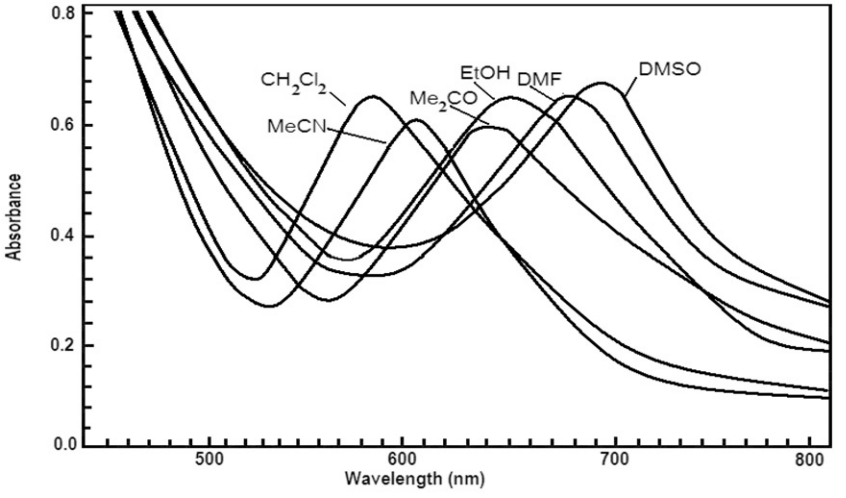


Figure 1. Electronic absorption spectra of **1** in different solvents.

corresponding to square-pyramidal structure. The values of the magnetic moment (1.63 B.M.) confirm the result [27].

The donor number proposed by Gutmann expresses a measure of coordinating ability of solvent to metal ion [28]. The spectra of the complexes show only one broad band, shifted to lower wavelength as the donor number of solvent increases [29]. This shift depends on the diamine ligands which affect the magnitude of in-plane ligand field strength, the strength of the axial bonds between copper(II) ion and solvent, and finally the counter ion to neutralize the charge of the Cu(II) mixed chelate complexes.

Thus, while a solvent of lower donor number (basicity) has less effect in the band maxima, others induce a larger red shift. The positions of the d–d absorption bands of the complexes were 566–710 nm. Solvatochromism appeared in **1**, **3**, and **4** with a color change from violet or bluish-violet through blue to green according to the DN of the solvent (figure 1). Negative solvatochromism was observed for **2**, **5**, and **6**, suggesting that short-range interactions between the dipole moment of the solute and the solvent can induce structural changes in accord with alignment of the transition moment for ground and excited states of a certain transition [30].

The solvatochromic behavior of **1**, **3**, and **4** are studied by applying the linear solvation free energy relationship $\nu_{max}/10^3 = \nu^\circ + a$ (DN), where ν_{max} is the measured d–d absorption frequency, ν° is the extrapolated frequency and a is the slope,

representing the sensitivity of the complex toward the solvent (table 4). Linearity of ν_{max} *versus* DN confirms the solvatochromic behavior of **1**, **3**, and **4**. The slope values (*a*) are in the order ($[Cu_2(L_1)(phen)_2(NO_3)_2] < [Cu_2(L_1)(tmen)_2](NO_3)_2 < [Cu_2(L_2)(tmen)_2](NO_3)_2$) (figure 2) [12, 28].

3.3. *Mass spectra*

The mass spectra of **3** and **5** show molecular ion peaks (table 2) coinciding with the formula weight of the complexes (Supplementary material).

3.4. *Thermal gravimetric analysis*

TGA–DrTGA curves of **2** and **4** were chosen as examples (Supplementary material). The stages of decomposition, temperature ranges as well as the found and calculated weight loss percentages are given in table 4.

Table 4. Relation between the absorption spectra of the Cu(II) complexes **1**, **3**, and **4** and the donor number of the solvent.

		(λ_{max}, nm)[b], ($\nu_{max}/10^3$, cm^{-1})[c]		
Solvent	DN[a]	$[Cu_2(L_1)(tmen)_2](NO_3)_2$ (**1**)	$[Cu_2(L_1)(phen)_2(NO_3)_2]$ (**3**)	$[Cu_2(L_2)(tmen)_2](NO_3)_2$ (**4**)
CH_2Cl_2	00.00	586(17.06)	609(16.42)	566(17.66)
MeCN	14.10	592(16.89)	619(16.15)	578(17.30)
Me_2CO	17.00	626(15.97)	629(15.89)	589(16.97)
EtOH	19.10	637(15.69)	645(15.50)	604(16.55)
DMF	26.60	664(15.06)	660(15.15)	647(15.45)
DMSO	29.80	684(14.61)	681(14.68)	669(14.94)

[a]Donor number of the solvent.
[b]Maximum absorption in nm.
[c]Referring to the wavenumber of the d–d transition bands of the complexes.

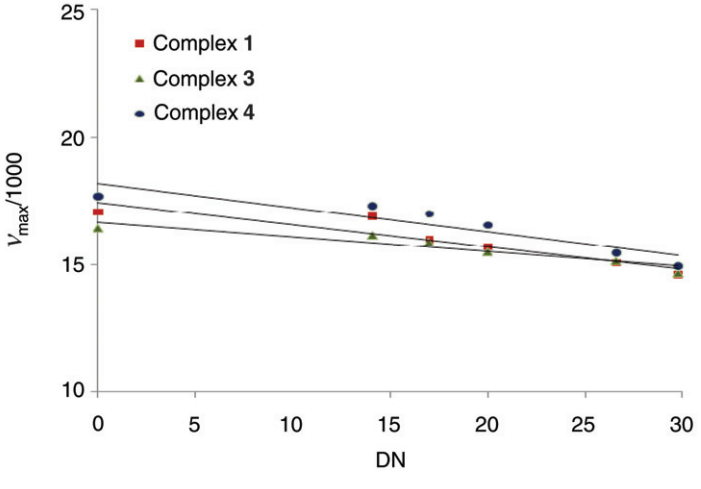


Figure 2. Solvation free energy relationship between the DN of the solvent and the maximum absorption $\nu_{max}/1000$.

Thermal decomposition of **2** involves three steps, starting at 105°C and finishing at 670°C. The first decomposition involves the removal of two H_2O at 105–170°C, accompanied by a weight loss of 4.502%. The second stage occurs at 170–422°C, corresponding to the loss of nitrate of NO_2 and (L_2), accompanied by the weight loss of 43%. The third stage involves the removal of two bipy's from 424°C to 670°C, accompanied by 35% weight loss.

Thermal decomposition of **4** also involves three steps. The first involves loss of uncoordinated nitrate as two molecules of NO_2 at 127–250°C, accompanied by a weight loss of 21%. The second stage of decomposition occurs from 252 to 410°C, corresponding to the loss of two tmen molecules (30%). The third stage involves the removal of L_2 at 415–570°C, accompanied by a weight loss of 39%.

4. Biological activities

The results of biological studies of the ligands and complexes are shown in figure 3, compared with standard antibiotics, chloramphencol for Gram-negative, and cephalothin for Gram-positive bacteria. Cycloheximide was used as standard antifungal reference. The complexes show higher antimicrobial activity than the ligands in all the tested strains (table 5), where it showed no inhibitory activity against Gram-negative strains. Coordination reduces the polarity of the metal [31, 32].

The *in vitro* antibacterial and antifungal activities (table 6) demonstrate that complexes with L_2 have higher antimicrobial activity than L_1 and its complexes; L_1 showed moderate biological activity while L_2 has no inhibitory effect against the tested strains. Complexes **5** and **6** displayed significant inhibition against the growth

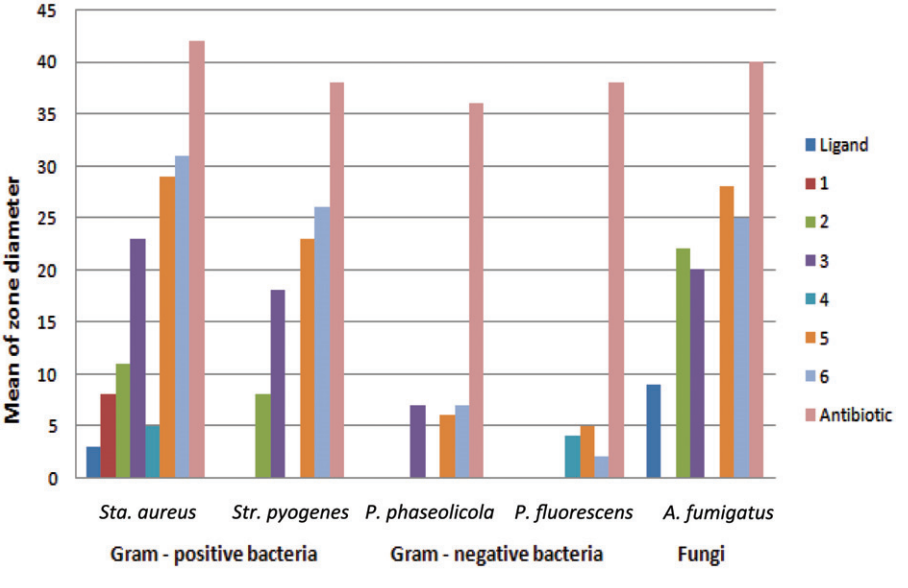


Figure 3. Biological screening data of the ligands and Cu(II) complexes against Gram-positive bacteria, Gram-negative bacteria, and fungi.

Table 5. Thermal decomposition stages of Cu(II) complexes.

	Complexes	DrTGA peak (°C)	Temperature range (°C)	Decomposition product lost (Formula wt.)	Wt. (%) Found (Calcd)
1	$[Cu_2(L_1)(tmen)_2](NO_3)_2$	256.26	75.00–310.12	2(tmen) + $2NO_2$ (324)	42.023 (42.115)
		350.17	315.00–490.00	(L_1) (288)	37.461 (37.354)
2	$[Cu_2(L_1)(bipy)_2(NO_3)_2(H_2O)_2]$	142.00	115.00–169.84	$2H_2O$ (36)	4.502 (4.068)
		372.37	170.22–422.74	NO_2 + (L_1) (380)	43.124 (42.712)
		526.35	424.04–670.12	2(2,2′-bipyridine) (312)	35.293 (35.254)
3	$[Cu_2(L_1)(phen)_2(NO_3)_2]$	252.09	140.00–277.17	$2NO_2$ (92)	10.371 (10.256)
		411.89	280.00–550.24	2(1,10-phenanthroline) + (L_1) (648)	72.901 (72.241)
4	$[Cu_2(L_2)(tmen)_2](NO_3)_2$	248.00	127.12–250.00	$2NO_2$ (92)	11.788 (11.719)
		385.00	252.00–410.00	2(tmen) (232)	30.012 (29.554)
		557.00	415–570.20	(L_2) (304)	38.799 (38.726)
5	$[Cu_2(L_2)(bipy)_2(NO_3)_2(H_2O)_2]$	130.11	87.00–147.48	$2H_2O$ (36)	4.305 (3.996)
		255.08	150.00–296.77	$2NO_2$ (92)	10.609 (10.211)
		398.97	300.14–580.89	2(2,2′-bipyridine) + (L_2) (616)	68.564 (68.369)
6	$[Cu_2(L_2)(phen)_2(NO_3)_2(H_2O)_2]$	129.78	402.78	$2H_2O$ (36)	3.998 (3.794)
		264.00	537.00	$2NO_2$ (92)	10.025 (9.695)
		371.16	644.16	(L_2) (304)	32.488 (32.033)
		473.08	746.08	2(1,10-phenanthroline) (360)	38.024 (37.935)

Table 6. Antimicrobial activity of L_1, L_2 and their Cu(II) complexes.

	Mean of zone diameter[a], mm (mg mL^{-1})				
	Gram-positive bacteria[b]		Gram-negative bacteria[b]		Fungi[b]
Complexes	*Sta. aureus*	*Str. pyogenes*	*P. phaseolicola*	*P. fluorescens*	*A. fumigatus*
L_1	3 ± 0.4	–[(c)]	–	–	9±0.1
L_2	–	–	–	–	–
1	8 ± 0.1	–	–	–	–
2	11 ± 0.2	8 ± 0.1	–	–	22 ± 0.3
3	23 ± 0.1	18 ± 0.4	7 ± 0.3	–	20 ± 0.4
4	5 ± 0.2	–	–	4 ± 0.3	–
5	29 ± 0.2	23 ± 0.3	6 ± 0.1	5 ± 0.2	28 ± 0.8
6	31 ± 0.2	26 ± 0.5	7 ± 0.3	2 ± 0.2	25 ± 0.2
Antibiotic[d]	42	38	36	38	40

– represents no inhibitory effect.
[(a)] Calculated from three average values.
[(b)] Chloramphencol in the case of Gram-positive bacteria, cephalothin in the case of Gram-negative bacteria and cycloheximide in the case of fungi.
[(d)] Control.

of Gram-positive, Gram-negative, and fungi. In contrast, **1** and **4** did not show inhibition activity on the growth of *Str. pyogenes*, *P. phaseolicola*, and *A. funigatus*. Complexes **2** and **3** showed antimicrobial activity towards Gram-positive bacteria superior to that of the Gram-negative bacteria [33, 34].

5. Conclusions

Binuclear copper(II) bis(β-diketone) complexes derived from L_1 and L_2 have been characterized by different spectroscopic techniques as well as thermal studies. Solvatochromism is observed in **1**, **3**, and **4**, where the d–d absorptions in weak donor solvents suggest square-planar or distorted square pyramidal geometries, confirming the possibility of using these complexes as Lewis acid–base color indicators. An octahedral structure is identified for **2**, **5**, and **6**, where the electronic transition occurred in strong donor solvents. Ligands and their complexes exhibit antimicrobial activity compared with standard antibiotics.

Acknowledgments

Authors thanks the "Austrian Science Foundation" (Project 19335-N17) for financial support.

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