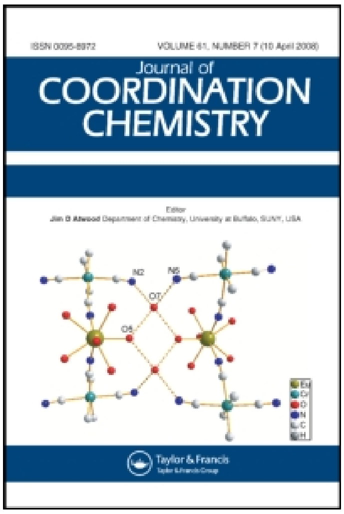

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Studies on mononuclear transition metal chelates derived from a novel (<i>E</i>,<i>E</i>)-dioxime: synthesis, characterization and biological activity

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To cite this Article Kurtoğlu, Mükerrem and Baydemır, S. Ayşe(2007) 'Studies on mononuclear transition metal chelates derived from a novel (<i>E</i>,<i>E</i>)-dioxime: synthesis, characterization and biological activity', Journal of Coordination Chemistry, 60: 6, 655 — 665

To link to this Article: DOI: 10.1080/00958970600896076

URL: http://dx.doi.org/10.1080/00958970600896076

Journal of Coordination Chemistry
Vol. 60, No. 6, 20 March 2007, 655–665

Studies on mononuclear transition metal chelates derived from a novel (*E*,*E*)-dioxime: synthesis, characterization and biological activity

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(*Received 20 November 2005; revised 18 January 2006; in final form 19 January 2006*)

A novel *vic*-dioxime ligand with a thiourea moiety, (*4E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)-methylene]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime (**4**) ($bmdH_2$) has been synthesized from *N*,*N′*-*bis*{4-[(4-bromophenylamino)methylene]phenyl}thiourea and (*E*,*E*)-dichloroglyoxime. The $bmdH_2$ ligand (**4**) forms transition metal complexes $[M(bmdH)_2]$ with a metal : ligand ratio of 1 : 2 with M = Ni(II), Co(II), and Cu(II). The mononuclear Ni(II), Co(II) and Cu(II) complexes, $[Ni(bmdH)_2]$ (**5**), $[Co(bmdH)_2]$ (**6**) and $[Cu(bmdH)_2]$ (**7**) have the metal ions coordinated through the two *N*,*N* atoms, as do most *vic*-dioximes. Elemental analyses, molar conductivity, magnetic susceptibility, IR, ^1H NMR spectra, and UV-Visible spectroscopy were used to elucidate the structures of the ligand and its complexes. Conductivity measurements have shown that the mononuclear complexes are non-electrolytes. In addition, the ligands and metal complexes were screened for antibacterial and antifungal activities by agar well diffusion techniques using DMF as solvent.

Keywords: Synthesis of *vic*-dioxime; Metal complexes; Transition metal

1. Introduction

Complexes of metal ions with macrocyclic ligands are similar to many natural systems, such as porphyrins and cobalamines. The main interest in new macrocyclic bifunctional chelating agents arise from their use in antibody labeling, cancer diagnosis, and magnetic resonance imaging as permagnetic ions [1–9].

Coordination compounds of oximes receive considerable attention due to their structural features. Since Tschugaeff introduced dimethylglyoxime as a reagent for nickel in 1905, the oximes have played an important role in coordination chemistry. A vast amount of fascinating chemistry has been accumulated affecting areas such as structural, stability and reactivity studies, biochemical modeling, analytical and organometallic chemistry, and synthesis of molecules with unusual electronic properties [10].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600896076

The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes *vic*-dioximes amphoteric ligands, which form square-planar, square-pyramidal or octahedral complexes with transition metal ions such as Ni(II), Co(II) and Cu(II) [11]. We have an ongoing effort to synthesize new *vic*-dioximes (figure 4 and 5) and investigate their reactions with various metal ions.

In previous studies we investigated the synthesis and characterization of various transition metal complexes of novel *vic*-dioximes and some mono and bidentate compounds [12–15]. In this article, we report the synthesis and characterization of a novel dioxime ligand, (*4E*,*5E*)-1,3-*bis*{4-[(4-bromophenylamino)methylene]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime, (**4**) bmdH$_2$, prepared from *anti*-dichloroglyoxime and *N*,*N'*-*bis*{4-[(4-bromophenylamino)methylene]phenyl}thiourea, and its mononuclear complexes with Ni(II), Co(II) and Cu(II).

2. Experimental

2.1. *Reagents*

p-Nitrobenzaldehyde, hydrazinemonohydrate, carbon disulphide, 10% Pd/C, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ (Merck) were used as purchased with no additional purification. *p*-Bromoaniline were purchased from Aldrich. All solvents were reagent grade and used without further purification. (*E*,*E*)-dichloroglyoxime and cyanogen-di-*N*-oxide were prepared as described previously [16–18].

2.2. *Physical measurements*

Elemental analyses (C, H, N) and proton NMR spectra were determined in the TUBİTAK Laboratories (Centre of Science and Technology Research of Turkey). IR spectra (KBr disc) were recorded in the range 4000–400 cm^{-1} on a Shimadzu 8300 FT-IR spectrometer. Electronic spectra were obtained on a Shimadzu 160A UV spectrometer. Melting points were obtained with a Electrothermal LDT 9200 Apparatus in open capillaries.

2.3. *Synthesis of* N-*(4-bromophenyl)*-N-*[(4-nitrophenyl) methylene]amine (1) (bma)*

This Schiff-base ligand was prepared by condensing (3.44 g, 0.02 mol) *p*-bromoaniline in EtOH (15 mL) with *p*-nitrobenzaldehyde (3.02 g, 0.02 mol) in 15 mL of EtOH by boiling the mixture under reflux for 4 h. The precipitated yellow compound was filtered off, recrystallized from Me_2CO/C_6H_{12} and dried in a vacuum desiccator. Yield: 4.1 g (68%). m.p.: 135–137°C. Elemental analyses for $C_{13}H_9BrN_2O_2$ (F.W. 305.12 g mol^{-1}): Calcd (%): C, 51.17; H, 2.97; N, 9.18. Found (%): C, 51.28; H, 3.09; N, 9.04.

2.4. *Synthesis of* N-*(4-aminobenzyl)*-N-*(4-bromophenyl)amine (2) (bpa)*

N-(4-Bromophenyl)-*N*-[(4-nitrophenyl)methylene]amine (4.57 g, 0.014 mol) was dissolved in EtOH (100 mL) and the solution was heated to 80°C. 1.5 g Pd/C (10%) was then added to this solution at the same temperature followed by dropwise addition of $N_2H_4 \cdot H_2O$ (2.5 mL). The mixture was then stirred and refluxed for 2 h. After cooling to room temperature, it was filtered and the light yellow solid product was extracted with $CHCl_3$. The extract was reduced under vacuum and cooled in a refrigerator at −10°C. The resulting white crystals were filtered and washed with cold *n*-hexane. Yield: 1.62 g (39%). m.p.: 230°C. Elemental analyses for $C_{13}H_{13}BrN_2$ (F.W. 277.16 g mol^{-1}): Calcd (%): C, 56.34; H, 4.73; N, 10.11. Found (%): C, 56.21; H, 4.59; N, 10.24.

2.5. *Synthesis of* N,N′-bis*{4-[(4-bromophenylamino)methyl]phenyl}thiourea (3) (bft)*

N-(4-Aminobenzyl)-*N*-(4-bromophenyl)amine (1.1 g, 0.0051 mol) was dissolved in CS_2 (1.5 mL, 0.075 mol) and EtOH–acetone mixture (3 : 1) in a 250 mL capacity flask fixed with a long refluxer. The solution was refluxed for 2 h in a water bath and yellow precipitate formed. The excess CS_2 and EtOH were removed in a rotary evaporator. The residue was washed with water and Et_2O and filtered through a Gouch filter. The light yellow product was insoluble in water but soluble in Me_2CO, DMSO and DMF. Yield: 0.66 g (56%) m.p: 236–238°C (dec.). Elemental analyses for $C_{27}H_{24}Br_2N_4S$ (F.W. 596.38 g mol^{-1}): Calcd (%): C, 54.38; H, 4.06; N, 9.39. Found (%): C, 54.27; H, 4.15; N, 9.50.

2.6. *Synthesis of (4*E*,5*E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime (4) bmdH$_2$*

A solution of cyanogen-di-*N*-oxide prepared from (*E,E*)-dichloroglyoxime (0.33 g, 0.0021 mol) in CH_2Cl_2 (10 mL) and an aqueous solution of Na_2CO_3 (10 mL, 1 N), was added to a cold solution (−10°C) of *N,N′-bis*{4-[(4-bromophenylamino)methyl]-phenyl}thiourea (1 g, 0.0021 mol) in Me_2CO (30 mL) under nitrogen atmosphere. The reaction was continued for 10 h at −10°C and the reddish brown product formed separated by filtration, washed with CH_2Cl_2 and Et_2O, and then dried *in vacuo*. The reddish brown, bmdH$_2$ ligand is soluble in DMF, DMSO, hot EtOH, MeOH and insoluble in *n*-heptane and water. Yield: 0.51 g (45%). m.p.: 248–250°C. Λ_M (Ohm^{-1} cm^2 mol^{-1}): 10.55. Elemental analyses for $C_{29}H_{24}Br_2N_6O_2S$ (F.W. 680.41 g mol^{-1}): Calcd (%): C, 51.19; H, 3.56; N, 12.35; S, 4.71. Found (%): C, 51.32; H, 3.65; N, 12.13; S, 4.84. UV-Vis (λ_{max}, nm, DMSO): 371, 260, 235. ^{1}H NMR (ppm, d$_6$-DMSO): 11.35 (C=N–OH, 2H, s), 9.45 (N–H, t), 8.30 (Ar–H, d), 7.70, 7.60, 7.40 (Ar–H, d), 3.30 (–CH$_2$, d).

2.7. *Synthesis of* bis*[(4*E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioximato]nickel(II) (5) [Ni(bmdH)$_2$]*

A solution of $NiCl_2 \cdot 6H_2O$ (0.0167 g, 0.07 mmol) in EtOH (10 mL) was added to a solution of (*4E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime, bmdH$_2$ (0.1 g, 0.14 mmol) in EtOH (50 mL) at 60–65°C, and a change in colour from reddish yellow to brown with a decrease in pH was observed. While heating and stirring at the above mentioned temperature, an equivalent amount of ethanolic solution of NaOH (0.1 M) was added and a brown precipitate of [Ni(bmdH)$_2$] (**5**) formed. After heating the mixture for 3 h in a water-bath, the brown precipitate was filtered off, washed several times with H_2O, EtOH and Et_2O and then dried *in vacuo*. Yield: 0.052 g (50%): m.p.: 257–258°C. Λ_M ($Ohm^{-1} cm^2 mol^{-1}$): 17.75. Elemental analyses for $C_{58}H_{46}N_{12}Br_4NiO_4S_2$ (F.W. 1417.52 g mol^{-1}): Calcd (%): C, 49.14; H, 3.25; N, 11.85; S, 4.52. Found (%): C, 49.35; H, 3.36; N, 11.94; S, 4.65. UV-Vis (λ_{max}, nm, DMSO): 369, 255, 232.

2.8. *Synthesis of* bis*[(4*E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioximato]cobalt(II) (6) [Co(bmdH)$_2$]*

A solution of $CoCl_2 \cdot 6H_2O$ (0.17 g, 0.7 mmol) in 15.0 mL hot EtOH was slowly added with stirring to a solution of (*4E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime, bmdH$_2$ (0.1 g, 0.14 mmol) in 50 mL EtOH at room temperature. The pH of the mixture was about 3. NaOH solution in EtOH was added to the mixture to adjust the pH of the mixture and to complete the precipitation after the mixture had been heated on a water-bath for 5 h. Finally, the mixture was centrifuged several times with diethyl ether and EtOH and the product dried *in vacuo* to afford a brown powder. This brown coordination compound is soluble in DMF and DMSO, and insoluble in water, cold EtOH and Et_2O. Yield: 0.08 g (77%), m.p.: 253°C. Λ_M ($Ohm^{-1} cm^2 mol^{-1}$): 18.10. Elemental analyses for $C_{58}H_{46}Br_4CoN_{12}O_4S_2$ (F.W. 1417.76 g mol^{-1}): Calcd (%): C, 49.13; H, 3.24; N, 11.85; S, 4.52. Found (%): C, 48.93; H, 3.09; N, 11.67; S, 4.38. UV-Vis (λ_{max}, nm, DMSO): 399, 357, 259, 234.

2.9. *Synthesis of* bis*[(4*E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioximato]copper(II) (7) [Cu(bmdH)$_2$]*

To a stirring solution of (*4E,5E*)-1,3-*bis*{4-[(4-bromophenylamino)methyl]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime, bmdH$_2$ (**4**) (0.1 g, 0.14 mmol)) in 10 mL EtOH, a solution of (0.0119 g, 0.07 mmol) $CuCl_2 \cdot 2H_2O$ in 10.0 mL of EtOH was added dropwise at r.t. The colour of the solution turned greenish yellow. The pH of the mixture was adjusted to about 4–5 by adding NaOH. Then the mixture was heated on a water bath until the precipitation was completed. It was brought to r.t., then the product was filtered, washed with water, EtOH, and dried *in vacuo*. This dark green compound is soluble in DMF and DMSO, slightly soluble in Me_2CO and insoluble in water and *n*-hexane. Yield: 0.076 g (73%), m.p.: 268°C. Λ_M ($Ohm^{-1} cm^2 mol^{-1}$): 16.30. Elemental analyses for $C_{62}H_{58}Br_4CuN_{12}O_4S_2$ (F.W. 1422.37 g mol^{-1}): Calcd (%): C, 48.97; H, 3.23; N, 11.81; S, 4.50. Found (%): C, 49.17; H, 3.30; N, 11.96; S, 4.40. UV-Vis (λ_{max}, nm, DMSO): 484, 359, 251, 229.

2.10. *Biological studies*

In this study, a new *vic*-dioxime ligand containing thiourea and its transition metal complexes were evaluated for their *in vitro* antibacterial activity against *Klebsiella pneumoniae*, *Micrococcus luteus*, *Streptococcus faecalis*, *Enterobacter cloaca*, *Bacillus megaterium* and antifungal activity against *Candida albicans*, *Kluyveromyces marxianus* and *Rhodotorula rubra* by the agar-well diffusion method. All the bacteria mentioned above were incubated at 30 ± 0.1°C for 24 h by inoculation into Nutrient Broth (Difco), and the fungi studied were incubated in Malt Extract Broth (Difco) for 48 h. Mueller Hinton Agar (Oxoid), sterilized in a flask and cooled to 45–50°C, was distributed into sterilized Petri dishes having a diameter of 9 cm, by using pipettes in the amount of 15 cm^3 after injecting cultures of bacteria prepared as mentioned above and mold for 24 h in the amount of 0.01 $cm^3 \times 10^5$ bacteria per cm^3 and 10^3 fungi spores per cm^3 and providing the distribution of food medium in Petri dishes homogenously. By using a sterilised cork borer (11 mm diameter), wells were dug in the culture plates. Compounds dissolved in DMF were added (50 µL) to these wells. The compounds to be tested were dissolved in DMF to a final concentration of 1000 ppm. After Petri dishes so obtained were placed at 4°C for 2 h, plates inoculated with fungi were incubated at 25 ± 0.1°C for 24 h. At the end of the period, values for the diameter of the inhibition zones for the growth of various microorganisms, created in response to treatment with the compounds were measured. These studies were performed in triplicate with Gentamicin and Nystatin as standards.

3. Results and discussion

3.1. *Synthesis of compounds*

This study focuses on the preparation of a novel *vic*-dioxime ligand containing –C=S and three metal complexes. The new ligand bmdH_2 (**4**), was prepared in a four stage process as shown in figures 1–4. Ni(II), Co(II) and Cu(II) complexes of

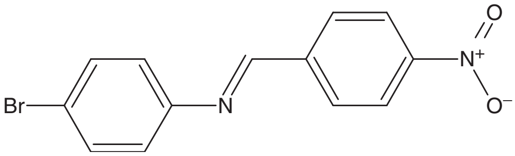

Figure 1. *N*-(4-Bromophenyl)-*N*-[(4-nitrophenyl)methylene]amine, (**1**) (bma).

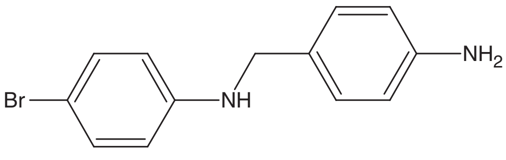

Figure 2. *N*-(4-Aminobenzyl)-*N*-(4-bromophenyl)amine, (**2**) (bpa).

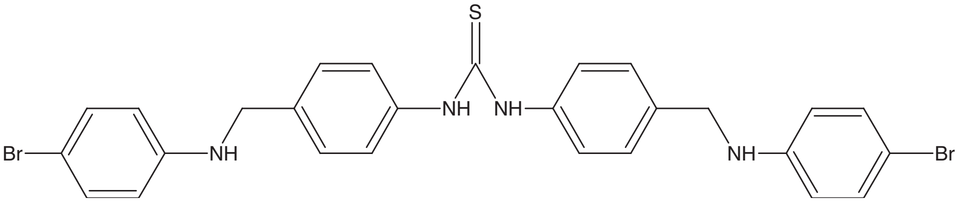

Figure 3. *N,N′-bis*{4-[(4-bromophenylamino)methyl]phenyl}thiourea, (**3**) bft.

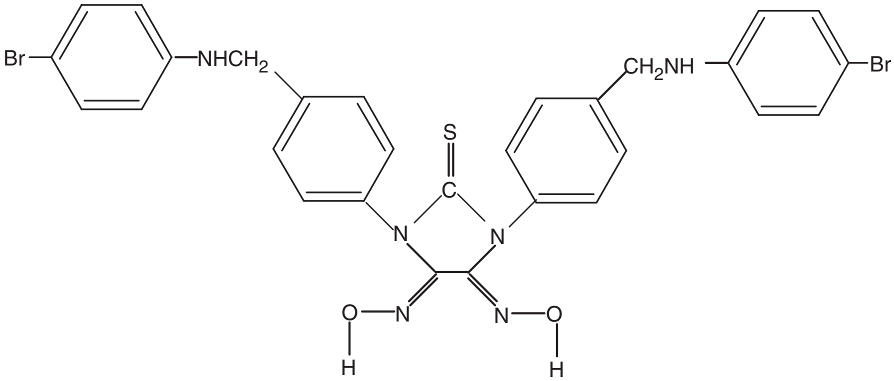

Figure 4. (*4E, 5E*)-1,3-*Bis*{4-[(4-bromophenylamino)methylene]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime, (**4**) bmdH_2.

(*4E,5E*)-1,3-*bis*{4-[(4-bromoyphenlyamino)methly]phenyl}-2-thiooxaimidazoline-4,5-dione dioxime (**4**), were synthesized.

In ethanolic solution (pH = 4–5), **4** undergoes deprotonation to form 1 : 2 mononuclear complexes with the metal ions.

$$MCl_2 \cdot xH_2O + 2bmdH_2 \longrightarrow [M(bmdH)_2] + 2HCl + xH_2O$$
$$M = Ni(II),\ Co(II)\ and\ Cu(II)$$

The level of impurity in the product was checked by thin layer chromatography (TLC). The structures of the ligand and corresponding complexes were elucidated with use of ^{1}H NMR, IR, and UV-Vis spectra, elemental analysis, magnetic susceptibility and molar conductivity. The melting points, colours and the microanalytical data of the complexes and their formulas are presented in experimental section.

3.2. *Elemental analyses*

The elemental analysis data of the compounds are given in the experimental section and are in good agreement with the theoretical calculations. The data show the complexation of 1 : 2 [M: bmdH_2] ratio [M(bmdH)$_2$], where M represents Ni(II), Cu(II) and Co(II) ions, while bmdH (**4**) represents the deprotoned oxime ligand, bmdH_2.

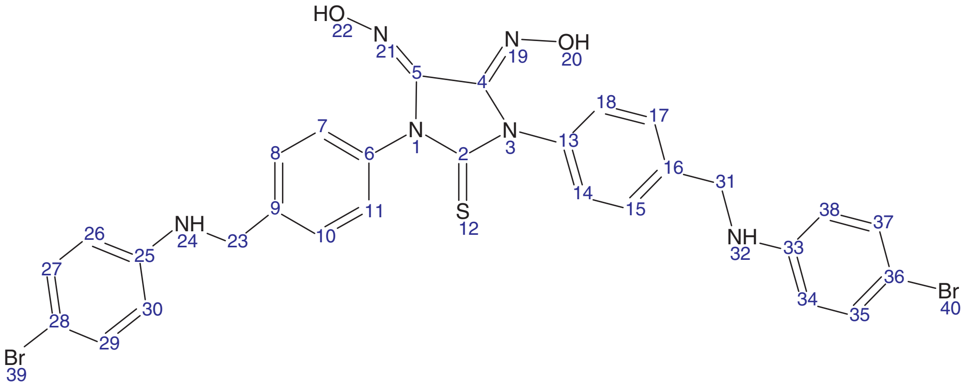

Figure 5. The suggested structure of **4**.

3.3. *Solubility and molar conductance*

All the complexes are sparingly soluble in EtOH but are soluble in DMSO and DMF to give stable solutions at room temperature. The molar conductances of the complexes are given in the experimental section. Conductivity values for **5**, **6** and **7** in DMF are in the range of 10–19 ($Ohm^{-2}\,cm^{2}\,mol^{-1}$) indicating that they are non-electrolytes.

3.4. *Magnetic susceptibility*

Magnetic susceptibility measurements revealed that **5** is diamagnetic as expected for Ni(II) and that **6** and **7** complexes are paramagnetic [19]. Magnetic susceptibility measurements were determined at 295 K on a Gouy balance. Experimental magnetic susceptibilities were corrected for diamagnetism. The magnetic susceptibility values of the complexes were calculated by the spin formula. The μ_{eff} values of the dioxime complexes are 1.90 and 2.07 BM, respectively.

3.5. *^{1}H NMR spectrum of the ligand*

In the ^{1}H NMR spectrum of **4** in DMSO a peak corresponding to –C=N–OH characteristic of oximes appears as a singlet at 11.35 ppm [11]. The peak occurs as a singlet due to protons present in hydroximino group in (*E*,*E*)-dioximes. In *amphi*-dioximes, there appear singlets in two different regions due to the protons in this group. The reason for this is one of the oxime protons that forms an intramolecular H-bond. In *anti*-dioximes the singlet disappears with addition of D_2O. Therefore *anti* and *amphi* forms of dioximes can easily be distinguished with the use of ^{1}H NMR. The triplet at 9.45 ppm was attributed to –N–H protons in the structure. Aromatic protons were observed as doublets in 8.30–7.40 ppm. The doublet observed at 3.30 ppm was attributed to –CH_2– [20].

Table 1. Infrared data for the *vic*-dioxime ligand and its complexes, bma (**1**), bpa (**2**), bft (**3**), bmdH$_2$ (**4**), [Ni(bmdH)$_2$] (**5**), [Co(bmdH)$_2$] (**6**) and [Cu(bmdH)$_2$] (**7**) (KBr, cm^{-1}).

Compound	υ(NH$_2$)	υ(OH)	υ(ArC–H)	υ(R–C–H)	υ(C=N)	υ(C=S)	υ(N–O)
bma (**1**)	–	–	3041 m	–	1627 m	–	935 m
bpa (**2**)	3377 m	–	3043 m	2930 s	–		–
bft (**3**)	–	–	3040 m	2928 s	–	1300 m	–
bmdH$_2$ (**4**)	–	3217 vs	3045 m	2923 s	1598 m	1299 m	968 m
[Ni(bmdH)$_2$] (**5**)	–	–	3029 m	2924 s	1596 w	1301 m	972 m
[Co(bmdH)$_2$] (**6**)	–	–	3033 m	2930 s	1587 w	1344 m	972 m
[Cu(bmdH)$_2$] (**7**)	–	–	3043 m	2928 s	1599 w	1307 m	974 m

vs: very strong, s: strong, m: medium, w: weak.

3.6. *IR spectra*

The characteristic IR bands of the metal complexes are given in table 1. Generally, oximes are characterized by three IR absorptions at 3300–3150 cm^{-1} (O–H str.), 1690–1620 cm^{-1} (C=N str.), and 950 cm^{-1} (N–O str.) [21].

The IR spectrum of **4** as a KBr pellet revealed a broad band at 3217 cm^{-1} corresponding to vibration of O–H groups. A medium intensity band which occurred at 3149 cm^{-1} was attributed to the N–H stretching. The band observed at 3045 cm^{-1} is due to the presence of aromatic C–H in the structure and the band at 2923 cm^{-1}, points to the presence of aliphatic C–H. The band observed at 1598 cm^{-1} indicates the azomethine (–C=N–) groups, which were not present in the starting material but form in the resulting product as a result of oximation. The bands at 1299 and 968 cm^{-1} indicate (C=S) and (N–O) groups [22]. The peak at 3217 cm^{-1} in the spectrum of **4** corresponding to OH disappeared in the IR spectrum of **5**. A weak band at 1710 cm^{-1} in the spectrum of the Ni(II) complex, not present in the spectrum of the ligand, was attributed to the O–H$\cdots$O hydrogen band formed in the complex. The peaks at 3150 and 3029 cm^{-1} are due to N–H and aromatic C–H groups in the complex. The aliphatic C–H vibration is at 2924 cm^{-1}, the peak at 1596 cm^{-1} is C=N and the peaks at 1301 and 972 cm^{-1} were attributed to C=S and N–O. These values are in accord with values cited in the literature [22]. The peak at 3217 cm^{-1} in the IR spectrum of *vic*-dioxime corresponding to the OH group also disappeared in the IR spectrum of **6**. The aliphatic and aromatic C–H groups were observed at 2930 and 3033 cm^{-1}, respectively, the peak at 3152 cm^{-1} is from the N–H group, the peak at 1587 cm^{-1} corresponds to C=N and the peaks at 1344 and 972 cm^{-1} are due to C=S and N–O groups in **6**. The OH absorption also disappeared in the IR spectrum of **7**. Two bands at 3188 and 3043 cm^{-1} correspond to N–H and aromatic C–H, weak bands at ca 1700 cm^{-1} indicate O–H$\cdots$O bridges, while C=N vibrations are at lower wavenumbers, as expected for *N*,*N*-chelated *vic*-dioxime complex [23, 24]. The imine peak appeared at 1599 cm^{-1}, peaks at 1307 and 974 cm^{-1} were attributed to C=S and N–O groups for **7**.

3.7. *UV-Vis spectra*

The electronic spectra of the free *vic*-dioxime ligand, bmdH$_2$ (**4**) and its metal complexes with Ni(II), Co(II) and Cu(II) were recorded in 10^{-3} M DMSO at room temperature

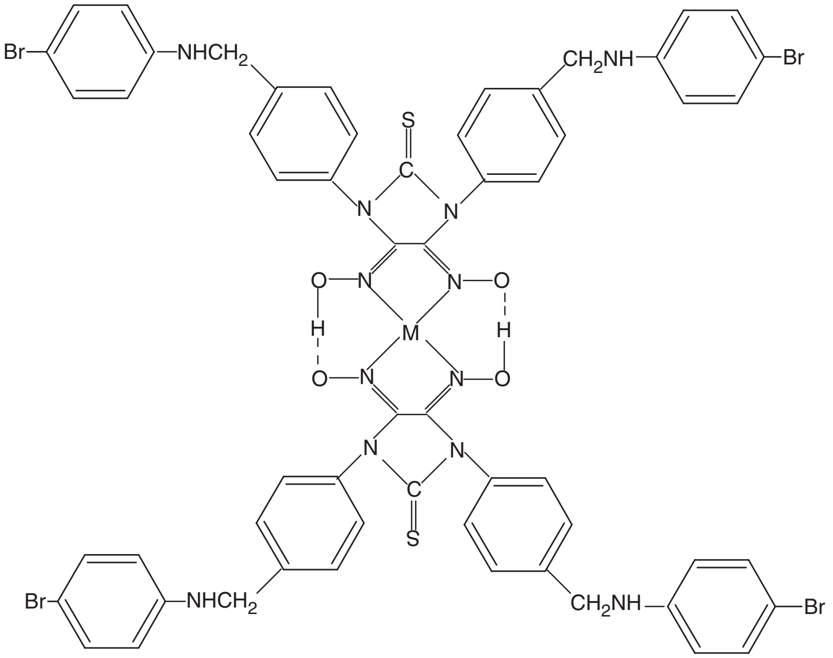

Figure 6. The proposed structure of the metal complexes.

and data presented in the Experimental section. The dioxime ligand is characterized mainly by two or three absorption bands. The $n \rightarrow \pi^*$ transitions associated with azomethine of oximes are found in the range 380–385 nm. Other absorption bands at 260 and 235 nm, are attributed to aromatic B and K bands, respectively. In the spectra of the metal complexes, the $\pi \rightarrow \pi^*$ transitions are shifted to higher energy. These results indicate that the nitrogen atoms of the oxime groups are coordinated to the metal ion [25–29]. In the complexes, lower energy transitions can also be observed in the 399–484 nm range corresponding to d → d transitions. Formation of these complexes is verified by the spectroscopic and elemental analysis results. These complexes are stable at atmospheric pressure. The values of analytical, spectral data are in agreement with those previously reported, particularly those of substituted dioximes [21, 22–25]. Based on the above results, the structure of the coordination compounds under investigation can be formulated as figure 6.

3.8. *Biological activity*

Antifungal and antibacterial activities of the ligands, **1**, **2**, **3**, **4** and the transition metal complexes of **4**, **5**, **6** and **7** have been screened against five different bacteria and three different fungi by the agar-well diffusion method [30, 31]. The same concentration of the ligands and the metal complexes in DMF solution were used for the studies. Antifungal and antibacterial studies were done on *K. pneumoniae*, *M. luteus*, *S. faecalis*, *E. cloaca*, *B. megaterium* bacteria, *C. albicans*, *K. marxianus* and *R. rubra* fungi. The results of antibacterial and antifungal activities of the prepared ligands and the metal

Table 2. Antimicrobial effects of the synthesised compounds, **1**, **2**, **3**, **4**, **5**, **6** and **7** (Concentration: 1000 ppm; 50 µL well^{-1}).

	Diameter of inhibition zone (mm)							
Compound	*K. pneumoniae*	*M. luteus*	*S. faecalis*	*E. cloaca*	*B. megaterium*	*C. albicans*	*K. marxianus*	*R. rubra*
bma (**1**)	12	11	10	13	15	13	8	11
bpa (**2**)	16	18	14	13	17	16	8	16
bft (**3**)	11	13	12	12	14	14	15	13
bmdH$_2$ (**4**)	13	12	13	12	13	12	14	13
[Ni(bmdH)$_2$] (**5**)	16	17	14	16	19	20	19	24
[Co(bmdH)$_2$] (**6**)	14	14	13	16	19	23	22	20
[Cu(bmdH)$_2$] (**7**)	15	16	17	12	16	20	17	16

complexes are presented in table 2. All compounds tested showed antibacterial and antifungal activity. From table 2 it is clear that the zone of inhibition is much larger for metal complexes than **4**. The increased activity of the metal chelates can be explained on the basis of chelation theory; chelation tends to make ligands more powerful and potent bactericidal agents. In the complex the positive charge of the metal is partially shared with the donor atoms present in the ligands and there may be π-electron delocalization over the whole chelate ring. Other factors which also increase the activity are solubility, conductivity and bond length between the metal and ligand [32, 33].

Among the complexes tested, **6** shows the lowest activity against *K. pneumoniae*, *M. luteus* and *S. faecalis* bacteria. On the other hand this complex has high activity against *E. cloaca*, *B. megaterium bacteria*, *C. albicans*, *K. marxianus* and *R. rubra fungi*. The complexes [Ni(bmdH)$_2$] (**5**) and [Co(bmdH)$_2$] (**6**) show the same activity against *B. megaterium*. Complex **7** has high activity against *M. luteus* and *S. faecalis* bacteria and low activity against *E. cloaca* bacteria. Complex **6** showed higher antifungal activity than the other coordination compounds. The variation in the activity of different complexes against different microorganisms depends either on the impermeability of the cells of the microbes or differences in ribosomes in microbial cells [30, 34, 35].

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