

New soluble coordination chain polymers of nickel(II) and copper(II) ions and their biological activity

Mükerrem Kurtoğlu* and Esin İspir

Department of Chemistry, Kahramanmaraş Sütçü İmam University, K. Maraş, 46050-9 Turkey

Nurcan Kurtoğlu

Engineering Faculty, Kahramanmaraş Sütçü İmam University, K. Maraş, 46050-9 Turkey

Sevil Toroğlu

Department of Biology, Kahramanmaraş Sütçü İmam University, K. Maraş, 46050-9 Turkey

Selahattin Serin

Department of Chemistry, Çukurova University, Adana, 01330 Turkey

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Abstract

A new tetraoxime ligand, (2E, 3E, 9E, 10E)-1, 4, 8, 11-tetraazacyclotetradecane-2, 3, 9, 10-tetrone tetraoxime has been prepared by the template condensation of 1,3-propanediamine and cyanogen-*di-N*-oxide, obtained by treating (*E, E*)-dichloroglyoxime in CH₂Cl₂ with Na₂CO₃ at –10 °C. The coordination chain polymers $\{[(pnngH_2)_2Ni]_n(5)$ and $\{[(pncgH_2)_2Cu]_n(6)\}$ of two transition metal ions, [Ni(II) and Cu(II)] with the *vic*-dioxime ligand have been prepared. The oxime ligand acts as a polydentate ligand bending through nitrogen atoms in the presence of a base, as do most of the *vic*-dioximes. In the complexes, the chloride ions coordinate to the nickel and copper ions. The structures of these novel *vic*-dioxime compounds are proposed on the basis of the elemental analyses, molar conductance data, i.r., and U.v.–visible are presented. Elemental analyses indicate a ligand metal ratio of 1:1 in the coordination polymers. Conductivity measurements have shown that mono- and polynuclear complexes are non-electrolytes. In addition, anti-microbial activities of the compounds have been investigated.

Introduction

Polymers containing metals have emerged as a new generation of material with tremendous potential in fields like superconducting materials, ultra-high strength materials, liquid crystals, catalysts, and bio-compatible polymers [1–6]. The structures of some polymer–metal ion complexes have been reported in the literature [3, 7–10]. One of the major interests in coordination chemistry is to study the interaction of a central atom with surrounding atoms, ions, or molecules. Coordination compounds containing *vic*-dioxime ligands have been known and studied since the beginning of this century.

The transition metal complexes of macrocyclic ligands have been the subject matter of great interest. In most of the synthetic routes, the template effect of the metal is significant. The numerous dioximes and their transition metal complexes have been investigated [11–15]. The exceptional stability and unique electronic properties of the complexes can be attributed to their planar structure, which is stabilised by hydrogen bonding. Oximes and their metal complexes are of cur-

rent interest for their rich physicochemical properties, reactivity patterns and potential applications in many important chemical processes in the areas of medicine [16–19], bioorganic systems [20, 21], catalysis [22], electrochemical [23] and electrooptical sensors [24, 25]. Diamines react with (*E, E*)-dichloroglyoxime or cyanogen-*di-N*-oxide to yield macrocyclic *vic*-dioximes. The (*E, E*)- and (*E, Z*)-stereoisomers of *vic*-dioximes coordinate through their *N, N* or *N, O* sites and, in a far cases, interconversion of (*E, E*)- and (*E, Z*)-complexes is possible.

The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes *vic*-glyoximes amphoteric ligands which form corrin-type square planar square-pyramidal and octahedral complexes with metal ions such as nickel(II), cobalt(II) and cobalt(III) as central atoms [13].

In our previous studies we investigated the synthesis and characterization of various transition metal complexes of novel *vic*-dioximes and some bidentate compounds [13–15, 26]. In this paper, we report the isolation and characterisation of a new tetradentate oxime ligand, (2E, 3E, 9E, 10E)-1, 4, 8, 11-tetraazacyclotetradecane-2, 3, 9, 10-tetrone tetraoxime derived from 1,3-propanediamine and cyanogen-*di-N*-oxide

* Author for correspondence.

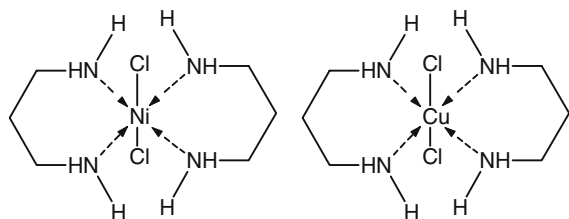


Fig. 1. Structures of octahedral Ni(II) (pnn) (1) ve Cu(II) (pnc)(2) complexes of 1,3-propanediamine.

(Figure 2). We also describe the synthesis and spectroscopic properties of coordination polymers $\{[(pnn\text{gH}_2)_2\text{Ni}]_n$ (5) and $\{[(pnc\text{gH}_2)_2\text{Cu}]_n$ (6) of (2E, 3E, 9E, 10E)-1, 4, 8, 11-tetraazacyclotetradecane-2, 3, 9, 10-tetrone tetraoxime with Ni(II) and Cu(II) ions.

Experimental

Materials

The metal salts, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 1,3-propanediamine were obtained from Fluka. EtOH was used after distillation over CaCl_2 . All other solvents obtained commercially were used without purification. (E, E)-dichloroglyoxime and cyanogen-di-N-oxide were prepared as described previously [27].

Physical measurements

Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Marmara Research Centre. I.r. spectra were obtained using KBr discs ($4000\text{--}400\text{ cm}^{-1}$) on a Shimadzu 8300 FTIR spectrophotometer. The electronic spectra in the $200\text{--}900\text{ nm}$ range were obtained using EtOH on a Shimadzu UV-160 A spectrophotometer. Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The microorganisms tested in this study were provided from the culture collections of the Microbiology Laboratory of KSU, in Kahramanmaraş, Turkey. In the study, *Pseudomonas aeruginosa* DSM 5007, *Micrococcus luteus* LA 2971, *Enterococcus faecalis* ATCC 15753, *Listeria monocytogenes* SCOTT A, *Bacillus cereus* EU, *Bacillus*

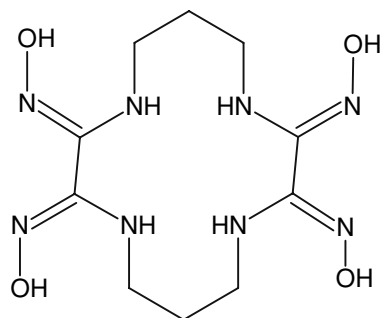


Fig. 2. Structure of (2E, 3E, 9E, 10E)-1, 4, 8, 11-tetraazacyclotetradecane-2, 3, 9, 10-tetrone tetraoxime ligand.

brevis FMC 3 bacteria, *Kluyveromyces fragilis* DC 98, *Candida albicans* CCM 314 fungi were used.

Synthesis of dichloro-bis(propanediamine)nickel(II), (pnn) (1)

A solution of 1,3-propanediamine (1.48 g, 20 mmol) in EtOH (40 cm^3) was carefully added with stirring to a solution of nickel(II)dichloride (2.37 g, 10 mmol) in EtOH (30 cm^3). The resulting mixture was allowed to stir magnetically under reflux for 2–3 h. After cooling the resulting precipitate was filtered, washed with cold EtOH and dried *in vacuo*. The light purple product is soluble in water and hot EtOH. Yield: 1.61 g (58%). m. p.: $200\text{--}202\text{ }^\circ\text{C}$ (dec.). Elemental analyses for $\text{C}_6\text{H}_{20}\text{N}_4\text{NiCl}_2$ (F. W. = 277.65 g/mol): Found = C, 25.85; H, 7.3; N, 20.3%; Calcd. = C, 25.9; H, 7.2; N, 20.2. Λ_M ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$): 16.88. U.v.-vis. (λ_{max} , nm) ($\log\epsilon$): 378 (sh) (2.3), 335(sh) (2.7), 265 (10.91).

Synthesis of dichloro-bis(propanediamine)copper(II), (pnc) (2)

1,3-Propanediamine (1.48 g, 20 mmol) dissolved in EtOH (40 cm^3) was carefully added with stirring to a solution of CuCl_2 (1.70 g, 10 mmol) in EtOH (30 cm^3). The resulting mixture was allowed to stir magnetically under reflux for 2–3 h. After cooling the resulting precipitate was filtered, washed with cold EtOH and dried *in vacuo*. The dark blue product is soluble in water and hot EtOH and insoluble common organic solvents such as acetone, DMF, and *n*-heptane. Yield: 1.44 g (51%). m. p.: $280\text{--}282\text{ }^\circ\text{C}$. Elemental analyses for $\text{C}_6\text{H}_{20}\text{N}_4\text{CuCl}_2$ (F. W. = 282.51 g/mol): Found = C, 25.35; H, 7.2; N, 19.9%; Calcd. = C, 25.5; H, 7.1; N, 19.8. Λ_M ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$): 19.64. U.v.-vis. (λ_{max} , nm) ($\log\epsilon$): 378 (sh) (2.3), 335(sh) (2.7), 265 (10.91).

Synthesis of pnn gH_4 (3)

To a solution of dichloro-bis(propanediamine)nickel(II), pnn (1) (2.77 g, 10 mmol) in 50 cm^3 of CH_2Cl_2 was added a solution of cyanogen-di-N-oxide which was obtained by treating a suspension of (E,E)-dichloroglyoxime (3.14 g, 20 mmol) in 50 cm^3 of CH_2Cl_2 with 1 N Na_2CO_3 at $-10\text{ }^\circ\text{C}$. The mixture was stirred at the same temperature for 6 h. The precipitate was then filtered, washed with CH_2Cl_2 and dried. The reddish brown product is soluble in water and insoluble common organic solvents such as DMF, EtOH and MeOH. Yield: 2.80 g (63%). m.p.: $245\text{--}246\text{ }^\circ\text{C}$. Elemental Analyses for $\text{C}_{10}\text{H}_{20}\text{N}_8\text{O}_4\text{NiCl}_2$ (F. W. = 445.69 g/mol): Found = C, 27.0; H, 4.6; N, 25.2%; Calcd. = C, 26.95; H, 4.5; N, 25.1. Λ_M ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$): 30.6. U.v.-vis. (λ_{max} , nm) ($\log\epsilon$): 378 (sh) (2.3), 335(sh) (2.7), 265 (10.91).

Synthesis of pncgH_4 (4)

A solution of cyanogen *di-N*-oxide, obtained by treating (*E, E*)-dichloroglyoxime (3.14 g, 20 mmol) 50 cm³ of CH₂Cl₂ with 1 N Na₂CO₃ at -10 °C to a stirred solution of dichloro-bis(propanediamine)copper(II), pnc (2) (2.82 g, 10 mmol) in 50 cm³ of CH₂Cl₂. The reaction mixture was stirred at -10 °C for 5 h, then allowed to warm to room temperature. The black solid product which precipitated was filtered, washed with cold EtOH and then with CH₂Cl₂. Recrystallization from water (50 cm³) afforded a black crystalline solid. The dark green product is soluble in water, and insoluble in DMF, EtOH and MeOH. Yield: 2.75 g (61%). m.p.: 225–226 °C (dec.). Elemental Analyses for C₁₀H₂₀N₈O₄ CuCl₂ (F. W. = 450.5 g/mol): Found = C, 26.7; H, 4.5; N, 24.95%; Calcd. = C, 26.7; H, 4.4; N, 24.9. $\Lambda_M(\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1})$: 19.20. U.v.-vis. (λ_{max} , nm) (log ϵ): 380(sh) (2.5), 330 (sh) (2.9), 270 (11.15).

Synthesis of $[(\text{pnngH}_2)_2\text{Ni}]_n$ (5)

A quantity of 2.5 mmol pnngH₄ (3) (1.10 g) was dissolved in absolute EtOH (40 cm³). Then the solution of 2.5 mmol NiCl₂·6H₂O (0.43 g) in MeOH (20 cm³) was added dropwise with stirring. The pH of the reaction mixture was ca. 3.5–4.0 and was adjusted to 5.5–6.0 by adding 1% NaOH solution. The precipitated complex was kept on a water bath at 75 °C for 2 h in order to complete the precipitation. The precipitated compound was filtered, washed with cold EtOH and dried *in vacuo* over CaCl₂. The brown product is soluble in water and insoluble in common organic solvents such as DMF, CHCl₃ and THF. Yield: 0.83 g (67%). m.p.: 234–236 °C. Elemental Analyses for C₁₀H₁₈N₈O₄ Ni₂Cl₂ (F. W. = 502.38 g/mol): Found = C, 24.3; H, 3.4; N, 22.2; Ni, 23.3%; Calcd. = C, 23.9; H, 3.6; N, 22.3; Ni, 23.4%. $\Lambda_M(\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1})$: 40.5. U.v.-vis. (λ_{max} , nm) (log ϵ): 430 (sh) (2.1), 370 (sh) (3.6), 260 (9.1).

Synthesis of $[(\text{pncgH}_2)_2\text{Cu}]_n$ (6)

A solution of CuCl₂·2H₂O (0.59 g, 2.5 mmol) in MeOH (20 cm³) was added to a solution of the ligand pncgH₄ (4) (1.10 g, 2.5 mmol) in absolute EtOH (40 cm³). The mixture was refluxed for 2–4 h at 80 °C. The precipitated compound was filtered, washed with cold EtOH and dried *in vacuo* over P₄O₁₀. The dark green product is soluble in water and insoluble in common organic solvents such as DMF, CHCl₃ and THF. Yield: 0.81 g (65%). m. p.: 250–252 °C (dec.). Elemental Analyses for C₁₀H₁₈N₈O₄Cu₂Cl₂ (F. W. = 512 g/mol): Found = C, 23.6; H, 3.4; N, 21.95; Cu, 24.9%; Calcd. = C, 23.45; H, 3.5; N, 21.9; Cu, 24.8. $\Lambda_M(\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1})$: 27.50. U.v.-vis. (λ_{max} , nm) (log ϵ): 390 (sh), (2.15), 345(sh) (2.5), 335 (sh) (2.7), 255 (12.50).

Biological studies

The ligands and their complexes have been tested for *in vitro* growth inhibitory activity against the bacteria *Pseudomonas aeruginosa*, *Micrococcus luteus*, *Enterococcus faecalis*, *Listeria monocytogenes*, *Bacillus cereus*, *Bacillus brevis* and the fungi *Kluyveromyces fragilis*, *Candida albicans*. All the bacteria mentioned above were incubated at 30 ± 0.1 °C for 24 h by inoculation of 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 in sterilized Petri dishes having a 9 cm, diameter by using pipettes in the amount of 15 cm³ after injecting cultures of bacteria prepared as mentioned above and mold for 24 h in the amount of 0.01 cm³ 10⁵ bacteria per cm³ and 10³ fungi spores per cm³, and providing the distribution of food medium in Petri dishes homogeneously.

All the compounds thus obtained and the standard antibiotics were injected into empty sterilized antibiotic discs having a diameter of 6 mm (Schleicher & Shüll No: 2668, Germany) in the amount of 50 μL . The compounds to be tested were dissolved in H₂O to a final concentration of 1000 ppm and 2000 ppm and soaked in filter paper. Discs injected with complexes were located on the solid agar medium by pressing slightly. 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, inhibition zones formed on the food medium were evaluated in millimeters. These studies works were performed in triplicate. Gentamicin (Bioanalyse), Nystatin (Oxoid) were used as standards.

Results and discussion

Synthesis and solubility of coordination compounds

The tetraoxime ligand, (2E, 3E, 9E, 10E)-1, 4, 8, 11-tetraazacyclotetradecane-2, 3, 9, 10-tetrone tetraoxime was prepared by reacting 1,3-propanediamine with cyanogen-*di-N*-oxide obtained by treating a suspension of (*E, E*)-dichloroglyoxime in dichloromethane media with a 0.1 N aqueous solution of Na₂CO₃ at -10 °C (Figure 2). The structures of the *vic*-dioxime compounds were demonstrated by a combination of analytical and spectroscopic methods. The level of impurity in the product was checked by t.l.c. In the complexes, the chloride ions were found to be coordinated to the metal ions as confirmed by magnetic moments and conductivity measurements. All of the metal complexes, [pnn] (1), [pnc] (2), [pnngH₄] (3), [pncgH₄] (4), [(pnngH₂)₂Ni]_n (5), [(pncgH₂)₂Cu]_n (6), are stable in air and soluble in water, slightly DMSO and insoluble in common organic solvents.

Single crystals of the compounds could not be isolated from any organic solution, thus no definite structures can be described. However, the analytical, spectroscopic and magnetic data enables us to predict possible structures as shown in Figures 1, 2 and 3.

Experimental results of the elemental analyses of the compounds are in agreement with theoretical expectations. The elemental analyses of the complexes indicate that the metal-ligand ratios are 1:1 in the polymeric metal complexes, $[(\text{pnngH}_2)_2\text{Ni}]_n$ (5) and $[(\text{pncgH}_2)_2\text{Cu}]_n$ (6).

Conductivity measurements

The molar conductance values of complexes measured in H_2O at the concentration 10^{-3} M are in the range

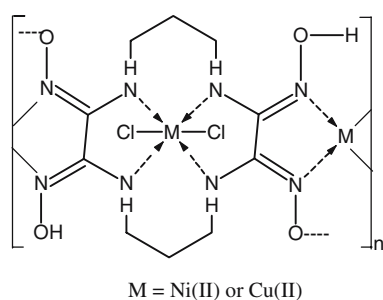


Fig. 3. The proposed general structure of polymeric metal complexes.

16–41 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, for all the complexes. The low values of the molar conductance measured in H_2O solution of the complexes indicate the non-electrolytic nature of the complexes. Thus, the complexes may be formulated as $[\text{M}(\text{L})_2\text{X}_2]_n$ where L = ligands and X = Cl^- .

Magnetic moments

The magnetic moments of the $[\text{pnn}]$ (1) and $[\text{pnngH}_4]$ (3) are 3.03 and 3.15 B.M, respectively. In the homopolynuclear oxime complex, $[(\text{pnngH}_2)_2\text{Ni}]_n$, the nickel(II) ion has the same values per metal. These can be attributed to the octahedral geometry around the nickel(II) ion in the macrocyclic moiety. The nickel(II) ion coordinated to the oxime groups has diamagnetic character and square-planar geometry. When the

oxime nickel(II) complexes was synthesized, the result obtained from magnetic susceptibility measurements show that the geometry of the nickel(II) ion coordinated is not changed. The magnetic moments of the $[\text{pnc}]$ (2) and $[\text{pncgH}_4]$ (4), complexes are 1.82 and 1.85 B.M, respectively. These values offer the possibility of an octahedral geometry.

I. r. spectra

The i. r. spectra of the complexes have been studied to characterize their structures. The characteristic i.r. bands of the metal complexes are given in Table 1. Generally, oximes are characterized by three i.r. absorption bands at $3300\text{--}3150 \text{cm}^{-1}$ (O–H str.), $1690\text{--}1620 \text{cm}^{-1}$ (C=N str.), and 950cm^{-1} (N–O str.) [28].

In the i. r. spectrum of $[\text{pnn}]$ (1) and $[\text{pnc}]$ (2) compounds, $-\text{NH}_2$ stretching bands are observed at 3360 and 3365cm^{-1} . Aliphatic $-\text{C}-\text{H}$ band in these two octahedral metal complexes are observed in 2975 and 2976cm^{-1} , respectively. The N–H vibration bands of (3) $[\text{pnngH}_4]$, (4) $[\text{pncgH}_4]$, (5) $[(\text{pnngH}_2)_2\text{Ni}]_n$ and (6) $[(\text{pncgH}_2)_2\text{Cu}]_n$ were observed at 3246 , 3255 , 3243 and 3240cm^{-1} , respectively. The stretching vibration for $-\text{NH}_2$ disappears after the condensation of $[\text{pnn}]$ (1) and $[\text{pnc}]$ (2) compounds with (E,E)-dichloroglyoxime [29]. These results indicate that the formation of vic-dioxime compounds were completed. In the IR spectrum of $[\text{pnngH}_4]$ (3) and $[\text{pncgH}_4]$ (4) ligands containing metal ions, the $-\text{N}-\text{OH}$ stretching absorption band were observed at 3245 and 3240cm^{-1} as a broad absorption band, respectively [30]. The missing of $-\text{N}-\text{OH}$ stretching band at ca. 3200cm^{-1} in the i. r. spectrum of $[(\text{pnngH}_2)_2\text{Ni}]_n$ (5) and $[(\text{pncgH}_2)_2\text{Cu}]_n$ (6) together with the existence of a H-bridge (O–H...O) at near $1700\text{--}1720 \text{cm}^{-1}$ and the shifting of $-\text{C}=\text{N}-$ and $-\text{N}-\text{O}$ stretches in the IR spectra of the complexes $[(\text{pnngH}_2)_2\text{Ni}]_n$ (5) and $[(\text{pncgH}_2)_2\text{Cu}]_n$ (6) provide support for MN_4 -type coordination in the coordination chain polymers. These values are also in harmony with the previously reported diaminoglyoxime derivatives.

The polymeric chain metal complexes of Ni(II) and Cu(II) ions with the ligands $\{[(\text{pnngH}_2)_2\text{Ni}]_n$ (5) and $[(\text{pncgH}_2)_2\text{Cu}]_n$ (6)\} are suggested to be square-planar with a metal-ligand ratio of 1:2. It is known that Ni(II)

Table 1. Some selected i.r. bands of (1) $[\text{pnn}]$, (2) $[\text{pnc}]$, (3) $[\text{pnngH}_4]$, (4) $[\text{pncgH}_4]$, (5) $[(\text{pnngH}_2)_2\text{Ni}]_n$ and (6) $[(\text{pncgH}_2)_2\text{Cu}]_n$ complexes (cm^{-1} , KBr)

| Compound | $\nu(\text{NH}_2)$ | $\nu(\text{N}-\text{H})$ | $\nu(\text{OH})$ | $\nu(\text{C}-\text{H})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{N}-\text{O})$ |
|---------------------------------------|--------------------|--------------------------|------------------|--------------------------|--------------------------|--------------------------|
| (1) $[\text{pnn}]$ | 3360 s | – | – | 2975 s | – | – |
| (2) $[\text{pnc}]$ | 3370 s | – | – | 2976 s | – | – |
| (3) $[\text{pnngH}_4]$ | – | 3246 m | 3245 m | 2975 s | 1640 w | 975 s |
| (4) $[\text{pncgH}_4]$ | – | 3255 m | 3240 m | 2973 s | 1643 w | 960 s |
| (5) $[(\text{pnngH}_2)_2\text{Ni}]_n$ | – | 3243 m | – | 2974 s | 1630 w | 967 s |
| (6) $[(\text{pncgH}_2)_2\text{Cu}]_n$ | – | 3240 m | – | 2971 s | 1635 w | 969 s |

s = strong, m = medium, w = weak.

Table 2. Antibacterial and Antimicrobial Activity Studies [Diameter of inhibition zone(mm) (Concentration:1000–2000 ppm)(50 μ l/disc)]

| Compound | Bacteria | Fungi |
|---|---|--|
| | <i>Pseudomonas Aeruginosa</i> , <i>Micrococcus Luteus</i> , <i>Enterococcus Faecalis</i> , <i>Listeria Monocytogenes</i> , <i>Bacillus Cereus</i> , <i>Bacillus Brevis</i> | <i>Kluyveromyces Fragilis</i> <i>Candida Albicans</i> |
| (1) [pnn] | – | –/10 |
| (2) [pnc] | – | –/27 |
| (3) [pnngH ₄] | – | –/8 |
| (4) [pncgH ₄] | – | –/11 |
| (5)[(pnngH ₂) ₂ Ni] _n | – | –/18 |
| (6)[(pnncH ₂) ₂ Cu] _n | – | –/8 |

and Cu(II) metal complexes of dimethylglyoxime are 5-membred chelate structures and the metal ion coordinates to the nitrogen atoms of the dioxime groups. A hydrogen atom separates each of the two oxime groups and as a result -hydrogen bridge is established. The hydrogen bridge {O–H···O} bonds of the [(pnngH₂)₂Ni]_n (5) and [(pncgH₂)₂Cu]_n (6)} complexes appear at 2320–2200 cm⁻¹, respectively. Deformation bonds of the hydrogen bonds are observation at 1700 cm⁻¹. These values are in good agreement with those reported in the literature for square-planar complexes of Ni(II) and Cu(II) ions. Furthermore, the observance of C=N bonds of the ligands at 1640 and 1643 cm⁻¹ and these of the complexes at lower field indicates that the nitrogen atoms of the C=N groups participate in the complex formation.

U.v.–visible spectra

The U.v.–vis. spectra of the complexes, (1) [pnn], (2) [pnc], (3) [pnngH₄], (4) [pncgH₄], (5) [(pnngH₂)₂Ni]_n and [(pncgH₂)₂Cu]_n, (6) in H₂O showed two or three absorption bands between 260 and 550 nm. These bands are assigned to both a charge transfer transition from the metal to anti-bonding orbital of the ligand and a spin-allowed transition of the ligand. The general character of these spectra are very similar to that of the corresponding complexes of symmetrically disubstituted dioximate ligands [31]. This is probably due to the fact that metal to ligand charge transfer and ligand to metal charge transfer transitions have similar energy differences. The d⁸ metal ion, Ni^{II} exhibits a preference for square planar geometry with dioxime complexes. The decrease in the intensities of transitions indicates the coordination to the nitrogen atoms. The metal contents of the polynuclear complexes were determined quantitatively by atomic absorption spectrophotometry.

Biological activity

The antibacterial activity of the complexes was tested by using the disc diffusion method [32]. The results

(Table 2) showed that all of the complexes exhibit moderate activity against all species of fungi, except *C. albicans* and no activity against all species of bacteria. Among the complexes tested, the complexes pnc and [(pnngH₂)Ni]_n compounds showed higher activity than the other complexes. The inhibition activity of the complexes increases with increase in the concentration of the test solution containing the new complexes, except all tested species of bacteria. The variation in the activity of different complexes against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes in microbial cells [33].

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