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Mononuclear copper(II) complexes of bis-triazole-based macrocyclic Schiff base hydrazones: direct synthesis, EPR studies, magnetic and thermal properties

Hamid Khanmohammadi · Malihe Erfantalab · Edward J. Reijerse

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Abstract Mononuclear copper(II) complexes of 1,2,4-triazole-based Schiff base macrocyclic hydrazones, **III** and **IV**, have been reported. The prepared amorphous complexes have been characterized by spectroscopic methods, electron spray ionization mass spectrometry, and elemental analysis data. Electrochemical studies of the complexes in DMSO show only one quasi-reversible reduction wave at $+0.43$ V ($\Delta E = 70$ mV) and $+0.42$ V ($\Delta E = 310$ mV) for **III** and **IV**, respectively, which is assigned to the Cu(II) → Cu(I) reduction process. Temperature dependence of magnetic susceptibilities of **III** and **IV** has been measured within an interval of 2–290 K. The values of χ_M at 290 K are 1.72×10^{-3} cm^3 mol^{-1} and 1.71×10^{-3} for **III** and **IV**, respectively, which increases continuously upon cooling to 2 K. EPR spectra of **III** and **IV** in frozen DMSO and DMF were also reported. The trend $g_{\parallel} > g\perp > g_e$ suggests the presence of an unpaired electron in the d_{x2-y2} orbital of the Cu(II) in both complexes. Furthermore, spectral and antimicrobial properties of the prepared complexes were also investigated.

Keywords 1,2,4-Triazole · Schiff base · Macrocyclic copper(II) complex · Magnetic properties · EPR study

Introduction

During the past decade great attention has been devoted to the construction of transition metal complexes of heterocycle-based ligands due to their interesting chemical and physical properties as well as their biological importance [1–5]. 1,2,4-Triazole-based ligands constitute a dominant class of these compounds which have attracted a great number of researchers in recent years [6, 7]. This is due to the key role played by 1,2,4-triazole group which has unique structural characteristics such as (i) bridging capability and (ii) structural flexibility [7, 8]. On the other hand, the electronic properties of 1,2,4-triazole-based ligands are also unique. The tendency of 1,2,4-triazole moiety to coordinate with metal ions is dependent on the presence of other groups, such as phenolic and azomethine groups [9–11]. Hence, the incorporation of 1,2,4-triazole unit into acyclic and/or macroacyclic Schiff bases is of considerable interest due to their capabilities to bind with various metal ions and also their possibility of generating magnetically interesting complexes [7, 12–14].

Prior to this work, other groups, most notably Alcade et al. [15] have reported the synthesis and structural characterization of several metal-free triazole-based macrocycles. Foroughifar et al. [16] and Abbas [17] have reported synthesis and spectral characterization of metal-free 1,2,4-triazole and thiadiazole-based Schiff base macrocyclic ligands via condensation reaction of various dicarbonyles with triazole and/or thiadiazole-based diamines, Fig. 1a. However, attempts to prepare the metal-free Schiff base macrocycles from 3,5-diacetyl-1,2,4-triazole were unsuccessful [18–21]. The first dinuclear metal complexes of 1,2,4-triazole-based Schiff base ligand of that dicarbonyl have been reported by Torres and co-workers [22–24], but none of them were structurally characterized to date.

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H. Khanmohammadi (✉) · M. Erfantalab
Department of Chemistry, Arak University,
Arak 38156-8-8349, Iran
e-mail: h-khanmohammadi@araku.ac.ir

E. J. Reijerse
Max Planck Institute for Chemical Energy Conversion,
Mülheim an der Ruhr, Germany

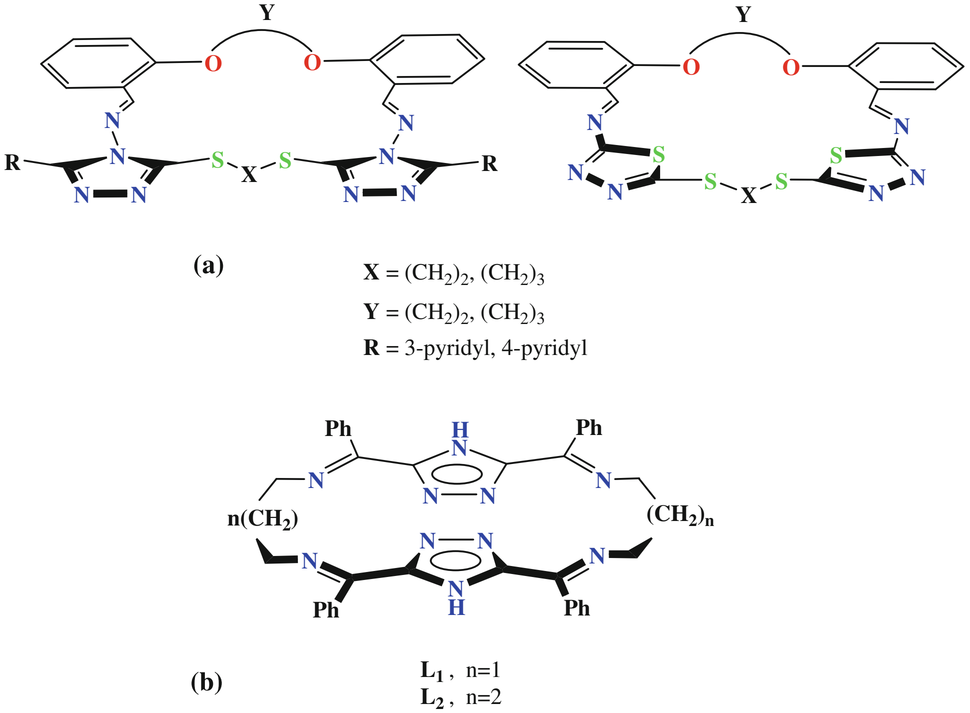

Fig. 1 Reported triazole and tiadiazole-based Schiff base macrocyclic ligands

Binuclear Pb(II) complexes of symmetric [2 + 2] 1,2,4-triazole-based Schiff base macrocycles, L_n ($n = 1,2$), Fig. 1b, were formed by cyclocondensation of 3,5-diacetyl-1,2,4-triazole with diamine components in the presence of Pb(II) ion [18]. Up to now, based on our knowledge, almost all transition metal complexes of triazole-based Schiff-base macrocyclic ligands have been prepared via transmetalation procedure and attempts to direct synthesis of mononuclear complex of 1,2,4-triazole-based Schiff-base ligands in the presence of transition metal ions were not successful [18].

In order to try to direct synthesis of Cu(II) complexes of new 1,2,4-triazole-based Schiff base macrocycles and also to investigate the influence of the substituents on the electronic and magnetic properties of the resulting complexes, we developed direct synthesis of 1,2,4-triazole-based copper(II) complexes. Here we report the synthesis of mononuclear copper(II) complexes of bis-1,2,4-triazole-based Schiff base macrocycles, **III** and **IV**, by cyclocondensation of *N*,*N*'-ethylene-bis(3-formyl-5-methylsalicylaldimine)copper(II), **CuL**, with 1,2,4-triazole-based diamines, **I** and **II**, in MeOH, Fig. 2. The powder XRD data indicated that the prepared complexes are amorphous. The complexes were characterized by electron spray ionization mass (ESI–MS) spectrometry. Variable temperature magnetic measurements were also carried out on complexes in the temperature range 2–290 K. Furthermore, the EPR spectra of **III** and **IV** exhibited well-resolved features characteristic of mononuclear Cu(II) complexes which is also supported by the magnetic data. However, the EPR spectra of frozen-solution of **III** and **IV** also exhibited a half-field, $\Delta M_s = 2$, transition with a seven line pattern, demonstrating interaction between two copper (II) centers.

In addition, in vitro antimicrobial activities of **III** and **IV** were screened against *Escherichia coli* (*E. coli*), *Staphylococcus aureus,* and *Candida albicans* using disc diffusion method. The data showed that the antimicrobial activities of **III** and **IV** are too low, probably due to their low solubility in DMSO. Spectral property of the prepared complexes in DMSO and DMF were also evaluated.

Experimental section

General information

All chemicals and solvents were of analytical grade and purchased commercially. 4-Amino-3-(4-pyridyl)-5-mercapto-1,2,4-triazole [25], *N*,*N*'-ethylene-bis(3-formyl-5-methylsalicylaldimino)copper(II), **CuL**, [26], and bis(4-amino-1,2,4-triazolepyridylsulfanyl)ethane, **I**, [17] were prepared as described previously. ^{1}H NMR spectra were obtained with a Bruker Avance 300 MHz spectrometer. Electronic spectral measurements were carried out using a Perkin-Elmer Lambda spectrophotometer in the range 200–600 nm. Thermal analyses were performed on a Perkin-Elmer Thermogravimetric Analyzer TG/DTA 6300 instrument. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Infrared spectra were recorded as pressed KBr discs, using a

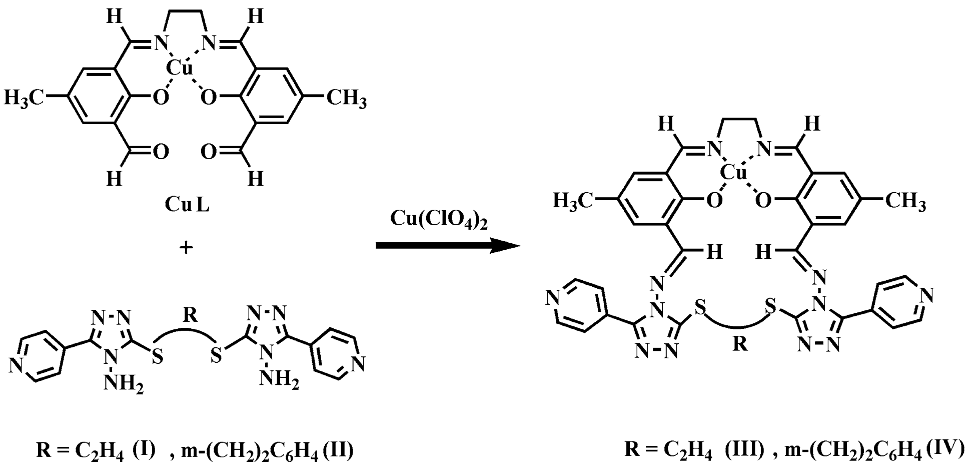

Fig. 2 Triazole-based Schiff base macrocyclic complexes

Unicam Galaxy Series FT-IR 5000 spectrophotometer (400–4,000 cm^{-1}). Electron paramagnetic resonance (EPR) was obtained from frozen solutions at 10–50 K with a Bruker ELEXSYS E500 spectrometer operating at X-band utilizing microwave frequencies around 9.5 GHz. The concentrations of copper complexes were in range of 1×10^{-4} M–2×10^{-3} M in DMSO and DMF solvents. The $g_{||}$, $g\perp$, $A_{||}$, and $A\perp$ parameters were evaluated using Easy Spin software [27, 28]. The variable temperature magnetic measurements were carried out in a superconducting quantum interference device (SQUID) magnetometer in the range 2–290 K and the data were simulated using julX [27, 28]. The positive electrospray mass spectra (ESI–MS) in DMF: Methanol (50:50) solutions were recorded on a Q-ToF Ultima, Waters apparatus. Electrochemical measurements were recorded on an Autolab 30 V potentiostat/Galvanostat of Eco Chemical Company. All readings were taken using a three-electrode potentiostatic system in DMSO with 0.1 mol cm^{-3} tetrabutylammonium perchlorate (TBAP, electrochemical grade, Acros) as supporting electrolyte. A three-electrode assembly composed of a glassy carbon working electrode, a platinum auxiliary electrode, and Ag–AgCl reference electrode was used with sample concentrations of 1×10^{-3} $molcm^{-3}$. X-ray diffraction studies were performed in a X-Pert PW 3710 powder diffractometer with Cu-K_{α} radiation (1.5406 Å) at 40 kV and 35 mA current.

Procedure for biological activity study

Newly prepared copper(II) complexes were screened for their activity against *E. coli*, *S. aureus,* and *C. albicans* strains by disc diffusion method as gram-negative, gram-positive, and fungal organisms, respectively.

The muller hinton agar and subro dextrose agar were used to culture bacterial and fungal, respectively. The culture media was poured into sterile plates and microorganisms were introduced onto the surface of agar plates individually. The blank sterile discs measuring 6.4 mm in diameter were soaked in a known concentration of the test compounds. Then the soaked discs were implanted on the surface of the plates. A blank disc was soaked in the solvent (DMSO) and implanted as negative control on each plate along with the standard drugs. The plates were incubated at 37 °C (24 h) and 27 °C (48 h) for bacterial and fungal strain, respectively.

Synthesis of bis(4-amino-1,2,4-triazolepyridylsulfanyl)-1,3-methylbenzene, **II**

1,3-Bis(bromomethyl)benzene (0.264 g, 1 mmol) was added to an alkaline (0.112 g, 2 mmol of KOH), solution of 4-amino-3-(4-pyridyl)-5-mercapto-1,2,4-triazole (0.386 g, 2 mmol) in ethanol (50 mL). The reaction mixture was stirred and heated under reflux for 1 h. The solvent was removed in vacuum and the remaining solid was collected and washed with water. Yield: 81 %, m.p. = 208–209 °C. ^{1}H NMR (d_6-DMSO, ppm): 8.72 (dd, 4H, $J = 6.00$ Hz), 7.98 (dd, 4H, $J = 6.00$ Hz), 7.56 (s, br, 1H), 7.29 (m, 3H), 6.23 (s, 4H), 4.46 (s, 4H). IR (KBr, cm^{-1}); IR (KBr, cm^{-1}); 3,340, 3,267 $\upsilon_{(NH2)}$, 1,602 $\upsilon_{(C=C)}$, 1,556 $\upsilon_{(C=C–N)}$, 1,232 $\upsilon_{(N–N)}$, 825 $\upsilon_{(NCN)}$. Anal. Calcd. for $C_{22}H_{20}N_{10}S_2$: C, 54.08; H, 4.13; N, 28.67; S, 13.13. Found: C, 54.23; H, 4.28; N, 28.34; S, 13.01.

General procedure for the synthesis of copper(II) complexes, **III** and **IV**

A solution of diamine, **I** and/or **II**, (0.5 mmol) in MeOH:CH_3COOH (5:1) (5 mL) was added to a suspension of *N,N′*-ethylene-bis(3-formyl-5-methylsalicylaldimino) copper(II) (1 mmol) and copper perchlorate (1 mmol) in methanol (15 mL) at 60 °C. The mixture was heated for

Table 1 Tentative assignments of some selected IR[a] frequencies (cm^{-1}) and UV–Vis data of the prepared complexes

Compound	υ(C–O)	υ(C=N/C=C)	υ (phenol ring)	υ(ClO_4^-)	υ(Cu–N) and (Cu–O)	λ_{max} (nm) (ε ($M^{-1}cm^{-1}$)) in DMSO
III	1,309	1,637, 1,606, 1,448	1,572	–	684, 586, 509	275 (49,967), 419 (22,077), 596 (1,333)
IV	1,307	1,637, 1,602, 1,446	1,574	–	696, 584, 513	275 (69,165), 423 (30,000), 607 (1,500)

[a] KBr discs

15–17 h at same temperature. The isolated green solid was filtered and washed well with warm absolute methanol.

Complex **III**

The isolated green solid was recrystallized from DMF. IR (KBr, cm^{-1}); 1,652 (shoulder), 1,637 υ(C=N), 1,606, 1,572, 1,539, 1,448, 1,383, 1,309, 1,236, 991, 831, 705, 684, 586, 509. UV–Vis λ_{max} (nm)(ε ($M^{-1}cm^{-1}$)) in DMF: 275 (49,967), 419 (22,077), 596 (1,333). Anal. Calc. for $C_{36}H_{30}N_{12}O_2S_2Cu$. 0.5 DMF: C, 54.47; H, 4.08; N, 21.17; S, 7.76; Cu, 7.69 %. Found: C, 54.61; H, 4.43; N, 21.17; S, 7.71; Cu, 7.94 %. $g_{\|} = 2.23$, $A_{\|} = 560 \times 10^{-4}$ cm^{-1}. $\mu_{eff} = 2.00 \pm 0.05$ BM.

Complex **IV**

IR (KBr, cm^{-1}); 1,637 υ(C=N), 1,602, 1,574, 1,541, 1,446, 1,379, 1,307, 1,234, 1,091, 991, 775, 696, 623, 584, 513. UV–Vis λ_{max} (nm)(ε ($M^{-1}cm^{-1}$)) in DMSO: 275 (69,165), 423 (30,000), 607 (1,500). Anal. Calc. for $C_{42}H_{34}N_{12}O_2S_2Cu$. 0.5 CH_3OH: C, 57.84; H, 4.11; N, 19.05; S, 7.27; Cu, 7.20 %. Found: C, 57.80; H, 4.43; N, 18.62; S, 7.10; Cu, 7.14 %. $g_{\|} = 2.23$, $A_{\|} = 500 \times 10^{-4}$ cm^{-1}. $\mu_{eff} = 1.99 \pm 0.05$ BM.

Result and discussion

New macrocyclic copper(II) complexes, **III** and **IV,** have been prepared by direct synthesis. The complexes are amorphous solids, air stable, and moderately soluble in DMSO and DMF at ambient temperature. ESI(+)-MS data provided evidence for the presence of mononuclear complexes in solution.

Infrared spectra

In the absence of X-ray crystal structure data, infrared spectroscopic data were used to find relatively narrow bonding pattern of the amorphous complexes. The positions of some of the prominent bands in the IR spectra of the prepared compounds and their assignments based on extensive data available for related compounds [29, 30] are given in Table 1. The total absence of **CuL** υ(C=O) absorption band at 1,686 cm^{-1} together with the appearance of new υ(C=N) absorption band in the IR spectra of **III** and **IV** at 1,637–1,640 cm^{-1} clearly indicated that a cyclic Schiff-base had formed. The bands located at 1,541, 991, and 700 cm^{-1} in the IR spectra of **III** and **IV** can be assigned to υ(C=C) and υ($C=N_{py}$) of the in plane ring

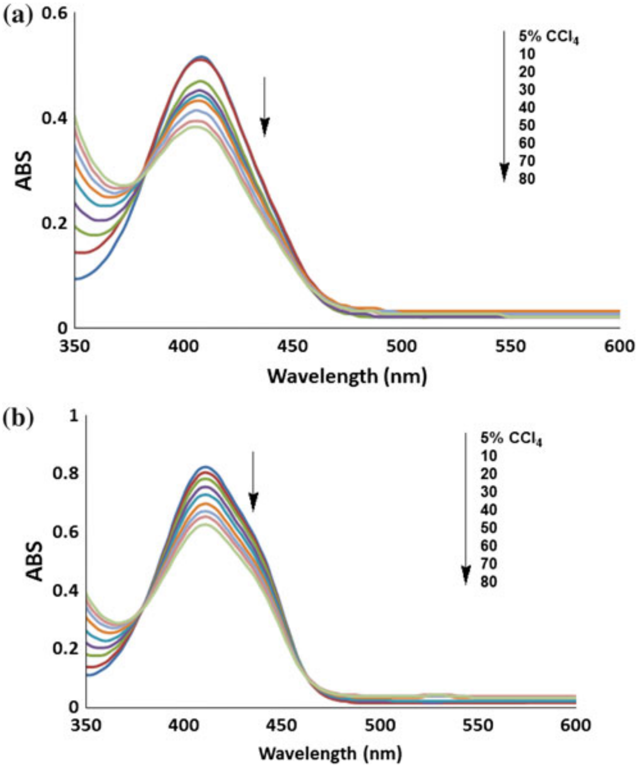

Fig. 3 The absorption spectra of (**a**) 1.0×10^{-5} M of **III** (**b**) 2.0×10^{-5} M of **IV** in mixture of DMSO: CCl_4

Table 2 Zone inhibition of the prepared compounds

Compounds	*Staphylococcus aureus* (mm)	*Escherichia coli* (mm)	*Candida albicans* (mm)
III	3	–	–
IV	4	–	–
DMSO	–	–	–
Standard drugs	Penicillin 33 mm	Gentamicin 18 mm	Nistatin 25 mm

– Indicates bacteria are resistant to the compounds. Zone of inhibition are reported in mm of diameter. Discs were inoculated with 5 mg of the compounds dissolved in DMSO deformation and out of plane ring deformation mode, respectively [29, 31]. The coordination mode of the ligands is supported by the appearance of ν(Cu–N) and ν(Cu–O) bands at 480–580 cm^{-1} [32, 33]. These bands are in accordance with data found in the literature and strongly support the hypothesis that the metal ion is coordinated through the imine nitrogen and phenolic oxygen atoms. The total absence of perchlorate bands in the IR spectra of **III** and **IV** implies that the complexes have no counter ions. The bands at 1,645 cm^{-1} and 706 cm^{-1} in the IR spectrum of **III** may be assigned to a coordinated DMF molecule [34], as was confirmed by their disappearance after drying of **III** at 150 °C over night.

Electronic spectra of **III** and **IV**

The electronic spectra of **III** and **IV** in DMSO display three main features at 260–280, 410–430, and 590–610 nm, Table 1. The intense absorption band located at 260–280 nm can be assigned to the moderate-energy

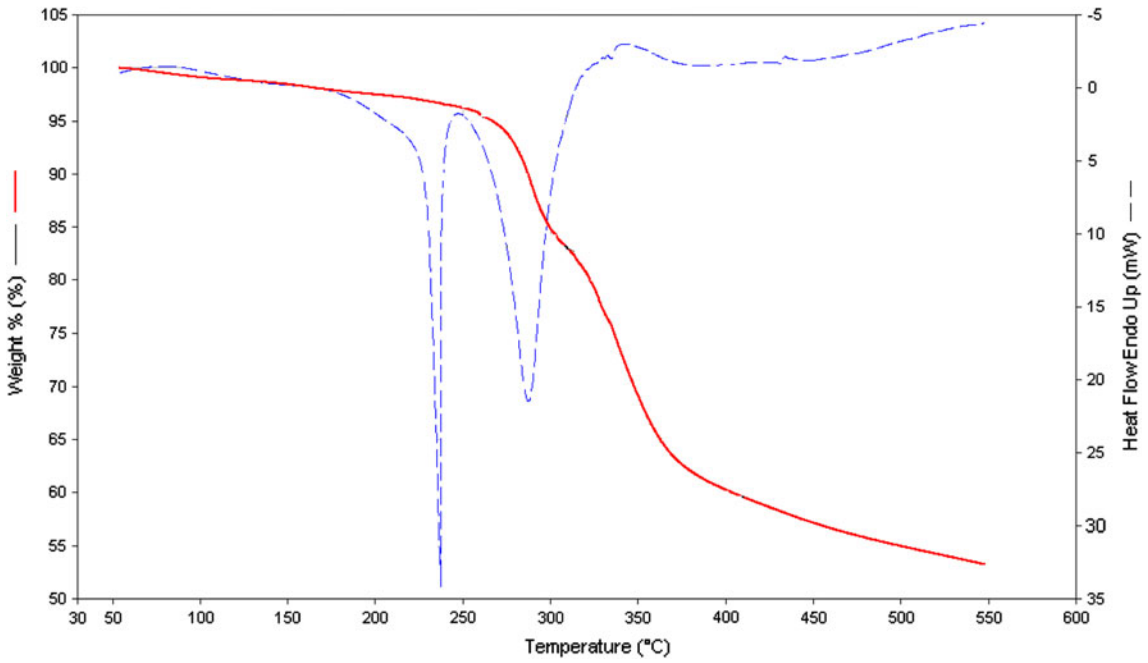

Fig. 4 TGA-DTA analyses curve of **IV** (see supplementary data)

Table 3 Thermal analyses data for **III** and **IV**

Compound, M.F. (M. Wt.)	Dissociation stages	Temperature range in TG (°C)	Weight loss, found (calculated) (%)	Decomposition assignment	Td[a] (°C)
III $C_{36}H_{30}N_{12}O_2S_2Cu.0.5DMF$ (826.93)	Stage I	50–250	4.50 (4.42)	The loss of 0.5 mol DMF	307
	Stage II	250–370	50.66 (49.90)	The loss of $C_{16}H_{12}N_9S_2$	
	Stage III	370–550	–	The loss of remaining organic parts	
IV $C_{42}H_{34}N_{12}O_2S_2Cu.0.5MeOH$ (882.50)	Stage I	50–200	2.20 (1.82)	The loss of 0.5 mol CH_3OH	287
	Stage II	200–310	13.97 (14.44)	The loss of C_3HN_4S	
	Stage III	310–390	28.89 (29.30)	The loss of $C_9H_7N_5S$	
	Stage IV	390–550	–	The loss of remaining organic parts	

[a] Decomposition temperature

($\pi \rightarrow \pi^*$) transition of the aromatic rings while the second band at 410–430 nm is due to low-energy ($\pi \rightarrow \pi^*$) transition involving the π-electrons of the azomethine groups [35]. The low-intensity band at ca. 600 nm is due to the d–d transition of Cu(II) ion.

The UV–Vis spectra of **III** and **IV** were also recorded in mixture of DMSO/CCl_4 to study the effect of a non-polar solvent on solvent–solute interactions and tautomeric equilibrium in solution, Fig. 3. Upon the addition of CCl_4, the intensity of absorption band at 410–430 nm, in pure DMSO, was decreased gradually and simultaneously the intensity of band at 260–280 was increased with isosbestic points at 386 nm and 384 nm for **III** and **IV**, respectively, indicating the establishment of equilibrium between various tautomers. The position of band was also shifted to lower wavelength during the addition of CCl_4.

Antibacterial and antifungal activities

The investigation of antibacterial screening data revealed that **III** and **IV** did not show any antibacterial activity against *E. coli*, *S. aureus,* and *C. albicans* (Table 2). The low inhibition of complexes may be due to their low solubility in DMSO.

Thermal properties

In order to obtain more insight into the structure of **III** and **IV**, thermal studies of the prepared complexes have been carried out using TGA/DTA techniques. The thermogravimetric studies have been made in the temperature range 25–550 °C under N_2 atmosphere.

The TG curve of **III** refers to three stages of mass loses within the temperature range 50–550 °C. The first stage at 50–250 °C with a mass loss of 4.50 % (calc. 4.42 %) corresponds to the loss of DMF. The second stage at 250–370 °C with a mass loss of 50.66 % (calc. 49.90 %) corresponds to the loss of $C_{16}H_{12}N_9S_2$ fragment, accompanied by an exotherm in the DTA curve, and the thermal decomposition of the complex. Another stage of decomposition at the temperature range 370–550 °C is roughly assigned to the loss of the remaining organic part of the complex (See supporting information).

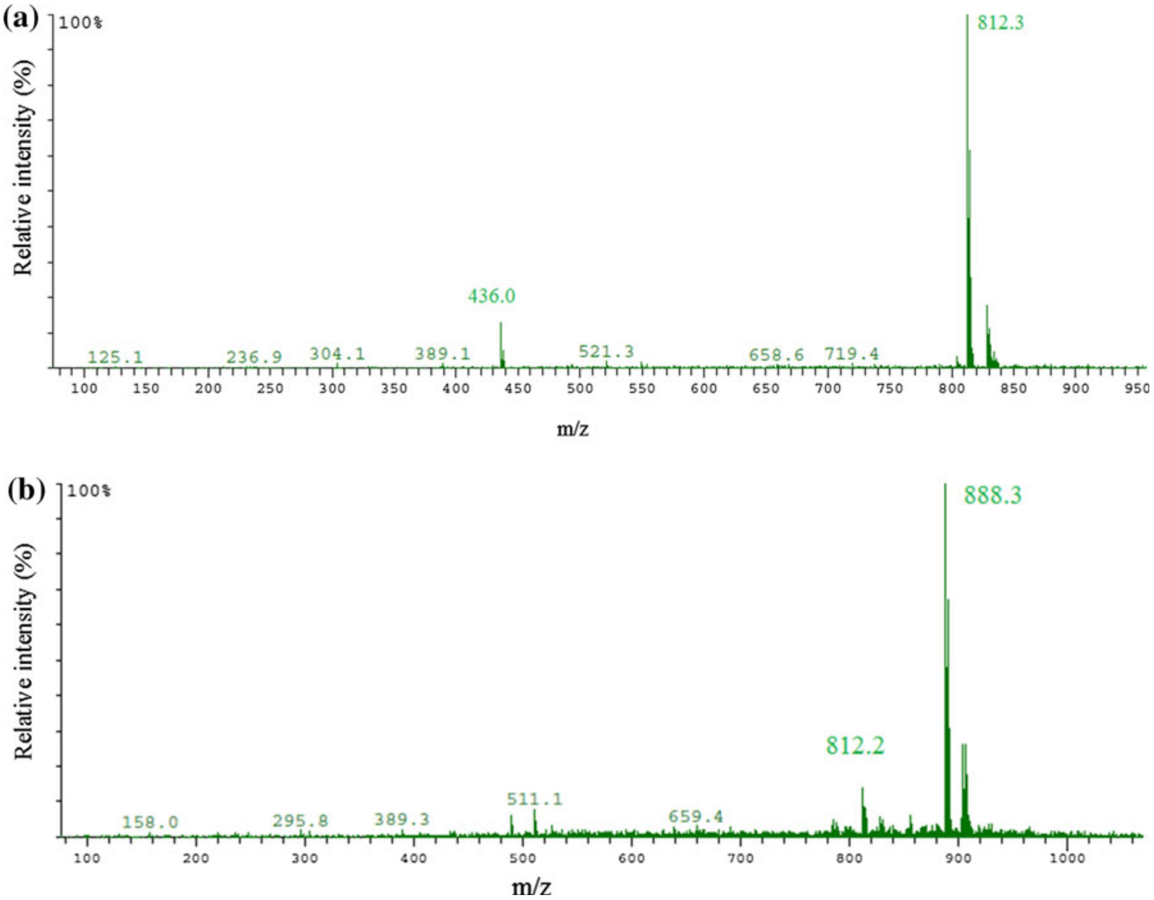

Fig. 5 Positive ion ESI mass spectra of (**a**) **III**, (**b**) **IV** in DMF: Methanol (50:50) solution

Table 4 Relevant magnetic data for the prepared copper(II) complexes, **III** and **IV**

Complexes	χ_M (cm^3 mol^{-1}), 290 K	χ_M (cm^3 mol^{-1}), 2 K	g[a]	R[a]
III	1.72×10^{-3}	0.20	2.162	1.56×10^{-5}
IV	1.71×10^{-3}	0.178	2.142	1.61×10^{-5}

[a] The best fit parameters

The TG curve of **IV**, refers to four stages of mass loses within the temperature range 50–550 °C (Fig. 4). In the first stage, methanol molecule was released 2.20 % (calc. 1.82 %). The second and third stages at temperature range of 200–310 °C and 310–390 °C indicate the loss of organic parts of complex, C_3HN_4S 13.97 % (calc. 14.44 %) and $C_9H_7N_5S$ 28.89 % (calc. 29.30 %) fragments, respectively. The fourth stage at the temperature range 390–550 °C is assigned to the loss of the remaining organic part of the complex. The comparison of $\mathbf{T_d}$ (decomposition temperature) showed that the thermal stability of the complexes increases in order **III > IV** (Table 3).

Electron spray ionization mass spectra

Electrospray ionization mass spectra, ESI–MS, were found to be fully compatible with the proposed structure of **III** and **IV**, Fig. 5. The ESI–MS of **III** and **IV** exhibit similar features and containing two types of positively charged species: m/z 812.3 (m/z 812.12 calculated for

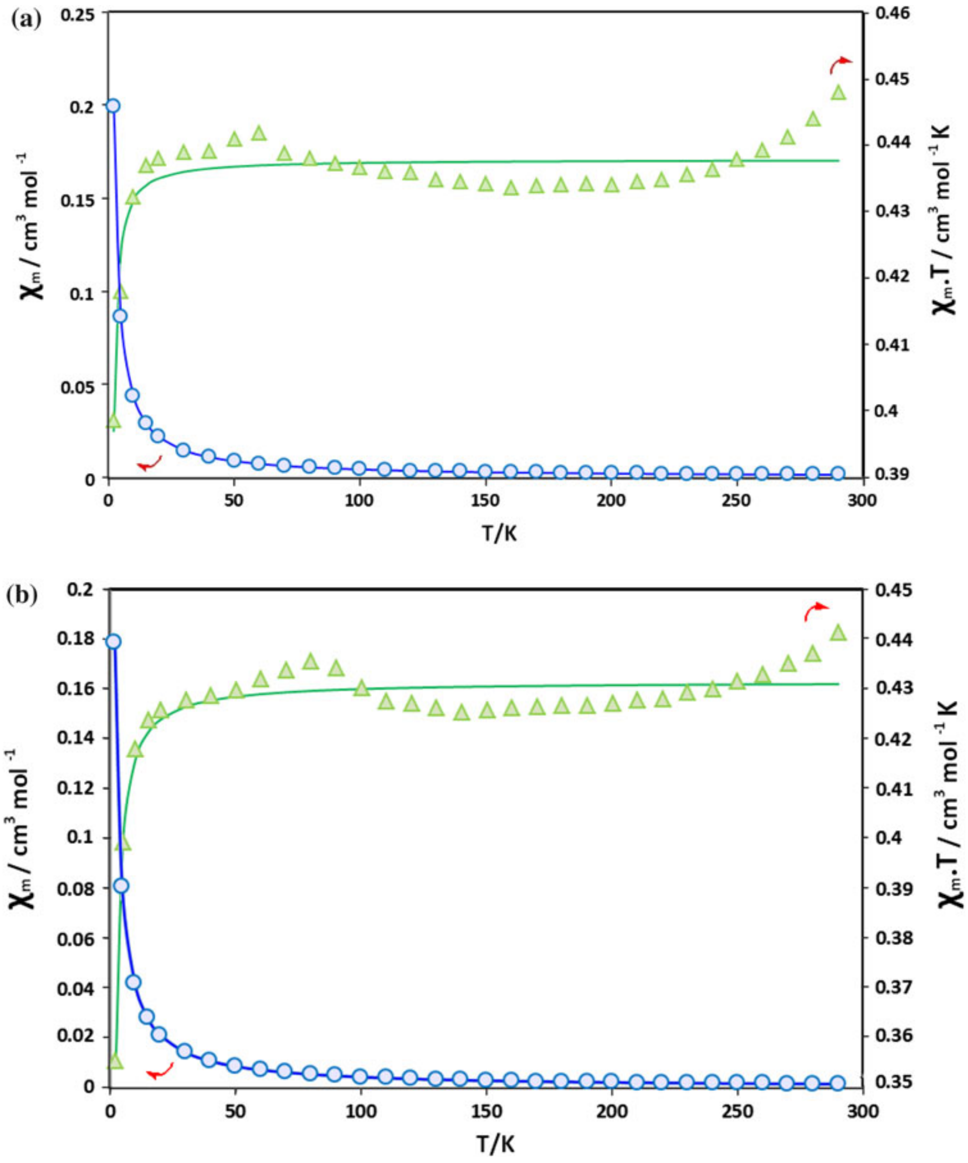

Fig. 6 Thermal evolution of the magnetic susceptibility for (**a**) **III** and (**b**) **IV**

$[C_{36}H_{30}N_{12}O_2S_2Cu + Na]^+$) and m/z 828.0 (m/z 828.10 calculated for $[C_{36}H_{30}N_{12}O_2S_2Cu + K]^+$) for **III** and also m/z 888.3 (m/z 888.16 calculated for $[C_{42}H_{34}N_{12}O_2S_2Cu + Na]^+$) and m/z 904.0 (m/z 904.13 calculated for $[C_{42}H_{34}N_{12}O_2S_2Cu + K]^+$) for **IV**. The numbers of peaks, m/z values and the relative peak heights observed for all cations are in excellent agreement with the calculated spectral patterns obtained by taking into consideration the relative abundances of the isotopes of the constituent elements.

Magnetic properties

The temperature dependence of magnetic susceptibilities of **III** and **IV** were measured in the range 2–290 K. The values of χ_M at 290 and 2 K are given in Table 4. The magnetic moment (μ_{eff}) of **III** and **IV** at 290 K is 2.00 ± 0.05 BM and 1.99 ± 0.05 BM, respectively, slightly larger than the spin-only value (1.73 BM) for one isolated Cu(II) center. This deviation may be arising from spin–orbit interaction which consistent with the common behavior of copper(II) ion with square pyramidal geometry [36–40]. The plot of χ_M vs T and also $\chi_M T$ vs T for **III** and **IV** are depicted in Fig. 6 (χ_M is the magnetic susceptibility per one copper atom). The χ_M values of **III** and **IV** increases continuously upon cooling from 1.72×10^{-3} cm^3 mol^{-1} and 1.71×10^{-3} at 290 K to 2.21×10^{-2} cm^3 mol^{-1} and 2.15×10^{-2} cm^3 mol^{-1} at 20 K, respectively. Upon further cooling, the χ_M values exponentially increase up to 0.20 cm^3 mol^{-1} and 0.178 at 2 K for **III** and **IV**, respectively, indicating the predominance of interaction between copper(II) ions through the solvent bridge.

The magnetic data were analyzed using the program julX [27]. The best-fit parameters of **III** are $g = 2.162$ and $R = 1.56 \times 10^{-5}$. R is the agreement factor defined as

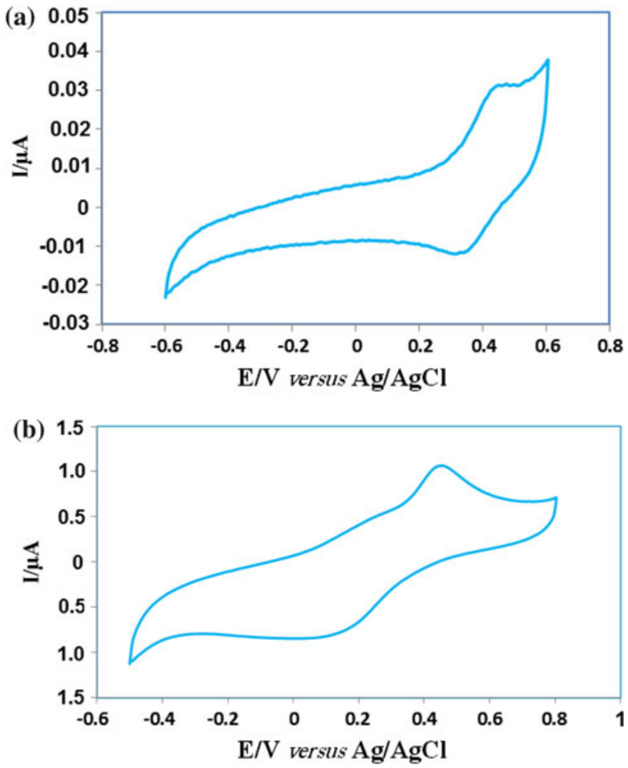

Fig. 7 Cyclic voltammgram for (**a**) **III** and (**b**) **IV** in DMSO (0.1 mol cm^{-3} TBAP, glassy carbon, Ag–AgCl, 100 mV/s)

Table 5 Voltammetric data for **III** and **IV** versus Ag/AgCl in DMSO-TBAP

Complexes	E_{pc}	$E_{1/2}$ [a]	E_{oa}	Process
III	+0.36	+0.40	+0.43	Cu^{2+}/Cu^+
IV	+0.12	+0.27	+0.42	Cu^{2+}/Cu^+

[a] $E_{1/2}$ values (vs. SEC) were taken as the average of the anodic and cathodic peaks potentials

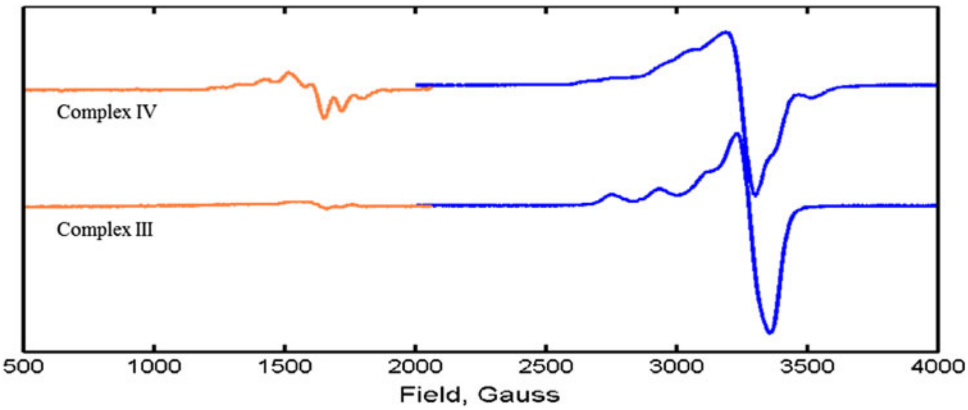

Fig. 8 The EPR spectra of **III** and **IV**

Table 6 EPR parameters of **III** and **IV** in frozen DMSO

Complexes	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$(G)
III	2.23	2.01	199
IV	2.23	2.06	175

$$\sum_i \left[(\chi_M T)_{obs} - (\chi_M T)_{calc}\right]^2 / \sum_i \left[(\chi_M T)_{obs}\right]^2$$

The best-fit parameters of **IV** are $g = 2.145$ and with $R = 1.61 \times 10^{-5}$.

Electrochemical analysis

Electrochemical investigation of **III** and **IV** were carried out in DMSO at a concentration of 1 mmolL^{-1}, Fig. 7 and Table 5. Only one quasi-reversible reduction wave at +0.43 V ($\Delta E = 70$ mV) and +0.42 V ($\Delta E = 310$ mV) was observed for **III** and **IV,** respectively, assigned to the Cu(II) → Cu(I) processes [41, 42]. The values are somewhat higher than those of square planer Salen-type copper(II) complexes, CuN_2O_2, indicating that the chelating ligands tend to destabilize copper(II) by π-delocalization of electron density from metal center [43]. Furthermore, Patterson and Holm [43] have shown that the redox properties of the copper(II) are influenced by coordination number, stereochemistry, and the hard/soft character of the ligand donor atoms. Therefore, the higher positive values of Cu^{2+}/Cu^{1+} redox potentials of **III** and **IV** may be due to the versatile coordination behavior of the present 1,2,4-triazole-based macrocyclic Schiff base ligands.

Electron paramagnetic resonance

The X-band EPR studies were performed in frozen DMSO solution of **III** and **IV** at 6–50 K. The EPR spectrum of **III** is characterized by a well-resolved mononuclear Cu(II) complex signal, Fig. 8. The observed $g_{||}$, $g_{\perp}$, and $A_{||}$ values are 2.23, 2.01, and 199 G, respectively, Table 6. The EPR parameters of are consistent with the assumption that (i) the copper ion located in an axial symmetry environment and (ii) the ground state orbital is d_{x2-y2} ($2.00 \approx g_{\perp} < g_{||}$) [42, 44–47]. Besides allowed transitions, $\Delta M_s = \pm 1$, around 160 mT weak signals (so called half-field) was observed corresponding to the $\Delta M_s = \pm 2$ forbidden transition, which indicates a magnetic coupling between the two Cu(II) ions [42], Fig. 9.

The EPR spectrum of **IV** is containing a much broader signal including a $g < 2$ contribution as well as a half-field signal, indicative of dimer formation and/or aggregation of the complex. To monitor the aggregation behavior, the EPR spectrum was recorded on freshly prepared and 1-week-old solutions of 1×10^{-4} M and 1×10^{-3}M of **IV** in DMSO, Fig. 10 (see also supporting information). Judging from the intensity of the $g < 2$ contribution in EPR spectra, the level of aggregation in **IV** seems to increase over time. To verify the effect of the solvent, the EPR spectrum of 1×10^{-3} M freshly prepared solution of **IV** in the strongly coordinable solvent, DMF, was recorded.

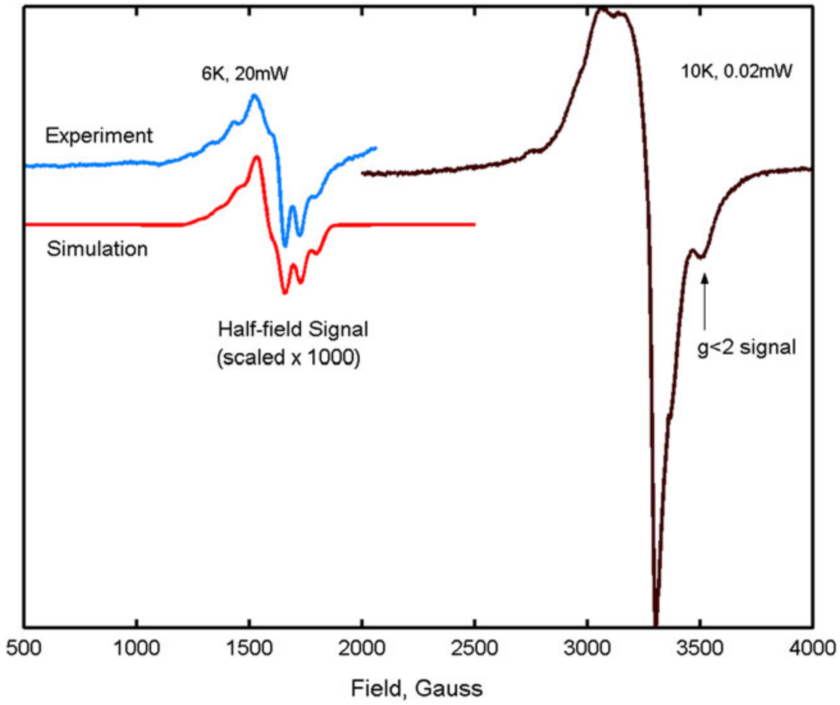

Fig. 9 The EPR and half-field spectra of s compound **IV** and their simulation diagrams

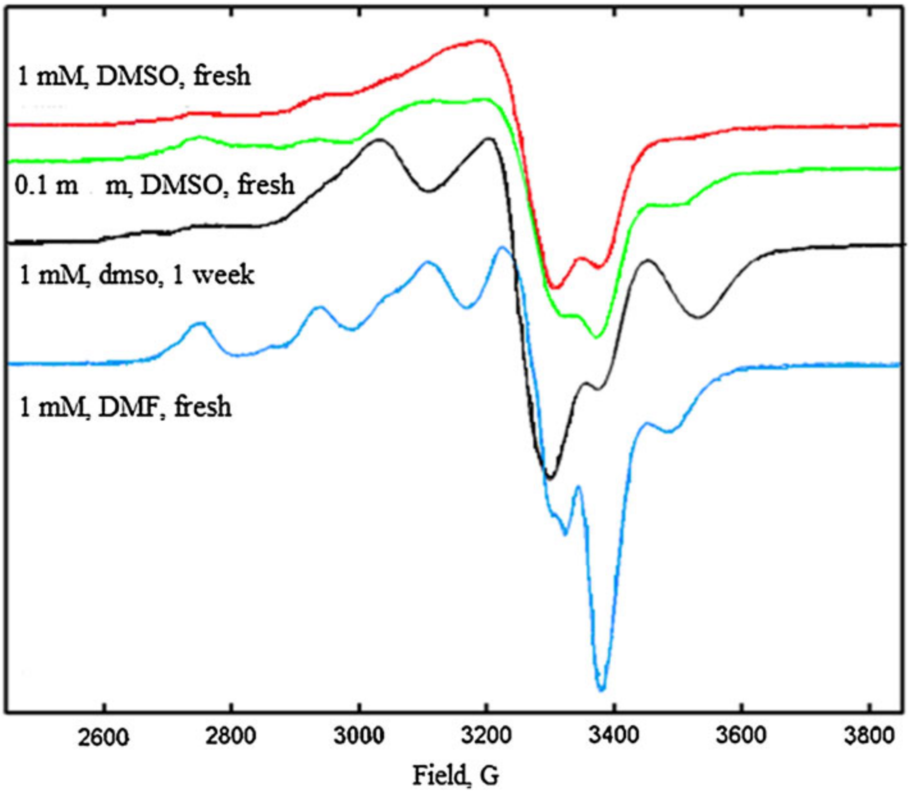

Fig. 10 The time-dependent EPR spectra of **IV** copper complex in DMSO and DMF solvents

Clearly, aggregation of **IV** is significantly diminished due to saturation of coordination sphere of metal center with DMF. In fact, the EPR spectrum of **IV** in DMF is quite similar to that of **III** in same solvent, Figs. 8 and 10.

Conclusion

In the present study direct synthesis of new mononuclear Cu(II) complexes of 1,2,4-triazole-based macrocyclic Schiff base hydrazones have been reported. The powder XRD studies in various temperatures showed that the prepared complexes, **III** and **IV**, are amorphous. Electron spray ionization mass spectra of **III** and **IV** are in agreement with the presence of mononuclear complex in DMF/MeOH solution. The magnetic moment of **III** and **IV** at 290 K is slightly larger than the spin-only value for one isolated Cu(II) center which may be arising from weak spin–orbit interaction in square pyramidal structures. The interaction between the copper(II) ions is clearly recognizable in the EPR spectra of complexes in frozen DMSO. It seems probable that the interaction between two copper(II) ions is derived from the cooperative exchange through the coordinated bridging solvents.

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References

1. K. Tenza, M.J. Hanton, A.M.Z. Slawin, Organometallics **28**, 4852 (2009)
2. U. Beckmann, S. Brooker, Coord Chem Rev **254**, 17 (2003)
3. T. Rüther, M.C. Done, K.J. Cavell, E.J. Peacock, B.W. Skelton, A.H. White, Organometallics **20**, 5522 (2001)
4. D.W.J. Kwong, O.Y. Chan, R.N.S. Wong, S.M. Musser, L. Vaca, S.I. Chan, Inorg Chem **36**, 1276 (1997)
5. P.M. Guha, H. Phan, J.S. Kinyon, W.S. Brotherton, K. Sreenath, J.T. Simmons, Z. Wang, R.J. Clark, N.S. Dalal, M. Shatruk, L. Zhu, Inorg Chem **51**, 3465 (2012)
6. J.A. Kitchen, S. Brooker, Coord Chem Rev **252**, 2072 (2008)
7. J. Olguín, S. Brooker, Coord Chem Rev **255**, 203 (2011)
8. M.H. Klingele, S. Brooker, Coord Chem Rev **241**, 119 (2003)
9. H. Liu, J. Tian, Y. Kou, J. Zhang, L. Feng, D. Li, W. Gu, X. Liu, D. Liao, P. Cheng, J. Ribas, S. Yan, J Chem Soc, Dalton Trans **48**, 10511–10517 (2009)
10. P.A. Vigato, S. Tamburini, L. Bertolo, Coord Chem Rev **251**, 1311 (2007)
11. J.G. Haasnoot, Coord Chem Rev **200–202**, 131 (2000)
12. A. Noble, J. OlguÍn, R. Clérac, S. Brooker, Inorg Chem **49**, 4560 (2010)
13. B. Shivarama Holla, B. Veerendra, M.K. Shivananda, B. Poojary, Eur J Med Chem **38**, 759 (2003)
14. H. Khanmohammadi, M. Erfantalab, Spectrochim. Acta (A) **86**, 39 (2012)

15. E. Alcalde, M. Gisbert, C. Alvarez-Rtia, S. Garcia-Granda, Tetrahedron **52**, 15189 (1996)
16. N. Foroughifar, A. Mobinikhaledi, S. Ebrahimi, H. Moghanian, M.A. Bodaghi Fard, M. Kalhor, Tetrahedron Lett **50**, 836 (2009)
17. A.A. Abbas, Tetrahedron **60**, 1541 (2004)
18. C.D. Brandt, J.A. Kitchen, U. Beckmann, N.G. White, G.B. Jameson, S. Brooker, Supramol Chem **19**, 17 (2007)
19. U. Beckmann, J.D. Ewing, S. Brooker, Chem Commun **15**, 1690 (2003)
20. C.V. Depree, U. Beckmann, K. Heslop, S. Brooker, J Chem Soc, Dalton Trans **7**, 3071 (2003)
21. U. Beckamann, S. Brooker, C.V. Depree, J.D. Ewing, B. Moubaraki, K.S. Murray, J. Chem. Soc. Dalton Trans. **7**, 1308 (2003)
22. J.M. Alonso, M.R. Martin, J. de Mendoza, T. Torres, Heterocycles **26**, 989 (1987)
23. J.A. Duro, J.M. Ontoria, A. Sastre, W. Schafer, T. Torres, J Chem Soc, Dalton Trans **94**, 2595 (1993)
24. B. Cabezo′n, A. Sastre, T. Torres, W. Schafer, J.J. Borras-Almenar, E. Coronado, J Chem Soc, Dalton Trans **35**, 2305 (1995)
25. J.R. Reid, N.D. Heindel, J Heterocycl Chem **13**, 925 (1976)
26. H. Ōkawa, S. Kida, Bull Chem Soc Jpn **45**, 1759 (1972)
27. S. Stoll, A. Schweiger, J Magn Reson **178**, 42 (2006)
28. E. Bill. Available online at: www.cec.mpg.de
29. F. Bentiss, M. Lagrene'e, J.P. Wignacourt, E.M. Holt, Polyhedron **21**, 403 (2002)
30. K.J. Schenk, S. Meghdadi, M. Amirnasr, M.H. Habibi, Polyhedron **26**, 5448 (2007)
31. J. Madejová, L. Jankovič, M. Pentrák, P. Komadel, Vib Spectrosc **57**, 8 (2011)
32. G.A. Van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Polyhedron **26**, 2728 (2007)
33. B.T. Op‘t Holt, M.A. Vance, L.M. Mirica, D.E. Heppner, T.D.P. Stack, E.I. Solomon, J Am Chem Soc **131**, 6421 (2009)
34. Y.J. Kim, C.R. Park, Inorg Chem **41**, 6211 (2002)
35. J. Lisowski, P. Starynowicz, Inorg Chem **38**, 1351 (1999)
36. N.R.S. Kumar, M. Nethiji, K.C. Patil, Polyhedron **10**, 365 (1991)
37. V. Katović, L.T. Taylor, D.H. Busch, Inorg Chem **10**, 458 (1971)
38. G.G. Mohamed, C.M. Sharaby, Spetrochim. Acta (A) **66**, 949 (2007)
39. E.N. Baker, D. Hall, T.N. Waters, J. Chem. Soc. (A) **92**, 406 (1970)
40. R.C. Elder, M.C. Hill, Inorg Chem **18**, 729 (1979)
41. C.C. Chou, C.C. Su, H.L. Tsai, K.H. Lii, Inorg Chem **44**, 628 (2005)
42. G.E. Gurr, Acta Crystallogr B **24**, 1511 (1968)
43. G.S. Patterson, R.H. Holm, Bioinorg. Chem. **4**, 257 (1975)
44. A.W. Addison, H.M.J. Hendriks, J. Reedijk, L.K. Thompson, Inorg Chem **20**, 103 (1981)
45. M. Ciampolini, N. Nardi, Inorg Chem **5**, 41 (1966)
46. G. Albertin, E. Bordignon, A.A. Orio, Inorg Chem **14**, 1411 (1975)
47. M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Briant, K. Plein, J Chem Soc, Dalton Trans **20**, 1342 (1980)