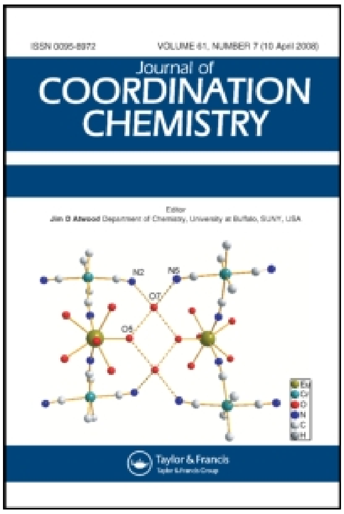

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Synthesis and characterization of a new (*E,E*)-dioxime and its mono and polynuclear complexes containing a 14-membered dithiadiaza macrocyclic moiety

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SYNTHESIS AND CHARACTERIZATION OF A NEW (*E*,*E*)-DIOXIME AND ITS MONO AND POLYNUCLEAR COMPLEXES CONTAINING A 14-MEMBERED DITHIADIAZA MACROCYCLIC MOIETY

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A novel (*E*,*E*)-dioxime,5,6:13,14-di(4′-*t*-butylbenzo)-2,3-bis(hydroxyimino)-8,11-dithia-1,4-diazacyclotetradecane (H_2L), containing a 14-membered dithiadiaza macrocyclic unit has been synthesized by the reaction of 1,2-bis(4-*t*-butyl-2-aminobenzylthio)ethane (**1**) and cyanogendi-*N*-oxide (**2**). A mononuclear nickel(II) complex (**3**) with a metal : ligand ratio of 1 : 2 was also prepared. A heterotrinuclear complex $[Cu_2Ni(HL)_2](PF_6)_2$ (**4**) was synthesized by using the mononuclear complex **3** and $[Cu(CH_3CN)_4]PF_6$. A heteropentanuclear complex $[Cu_2(UO_2)_2(phen)_2Ni(HL)_2](PF_6)_2(NO_3)_2$ (**5**) containing the oximato tetraanion as a bridging ligand and 1,10-phenanthroline as an end-capping ligand was obtained by using the heterotrinuclear ligand for the $Cu_2Ni(HL)_2^{n+}$ center. The ligand and its complexes have been characterized by ^1H and ^{13}C NMR, IR and mass spectroscopy, elemental analysis and semiempirical quantum chemical calculations.

Keywords: (*E*,*E*)-Dioxime; N_2S_2-Donor macrocycle; Heterotrinuclear complex; Heteropentanuclear complex; $[UO_2]^{2+}$; Ni(II); Cu(I)

INTRODUCTION

The chemistry of complexes containing mixed-donor macrocyclic ligands with cation complexing abilities has been explored extensively over the past 35 years [1]. A rapidly emerging area of chemical interest in recent years is the synthesis of heterobinucleating compounds and the coordination chemistry of the polynuclear complexes derived from these compounds [2]. Examples of heterobinucleating ligands that could serve as ‘‘polytopic receptor molecules’’ for the binding of metal cations include molecules containing macrocyclic functionalities appended with tetrathia [3] or dithiadiaza centers [4].

The coordination chemistry of (*E*,*E*)-dioximes has been investigated actively since the beginning of the twentieth century, and aspects such as traditional synthetic

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routes leading to *vic*-dioxime complexes and structural and analytical applications of the oxime species have been reviewed extensively [5]. The presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms means that (*E*,*E*)-dioximes are amphoteric compounds that can form corrin-type square-planar, square-pyramidal, tetrahedral or octahedral complexes with transition metal cations [6]. The high stability of the complexes prepared from (*E*,*E*)-dioxime ligands has been exploited for various purposes, such as models for some biological systems [7] and as compounds having columnar stacking thought to be the reason for their semiconducting properties [8].

The heteropolymetallic *vic*-dioxime systems are of interest to both biologists and bioinorganic chemists investigating the structure and functions of polynuclear metal centers in proteins and searching for new magnetic materials [9].

In this study, our goal was to undertake the synthesis of a new *vic*-dioxime containing a 14-membered macrocycle with multidonor groups able to bind more than one transition metal cation simultaneously.

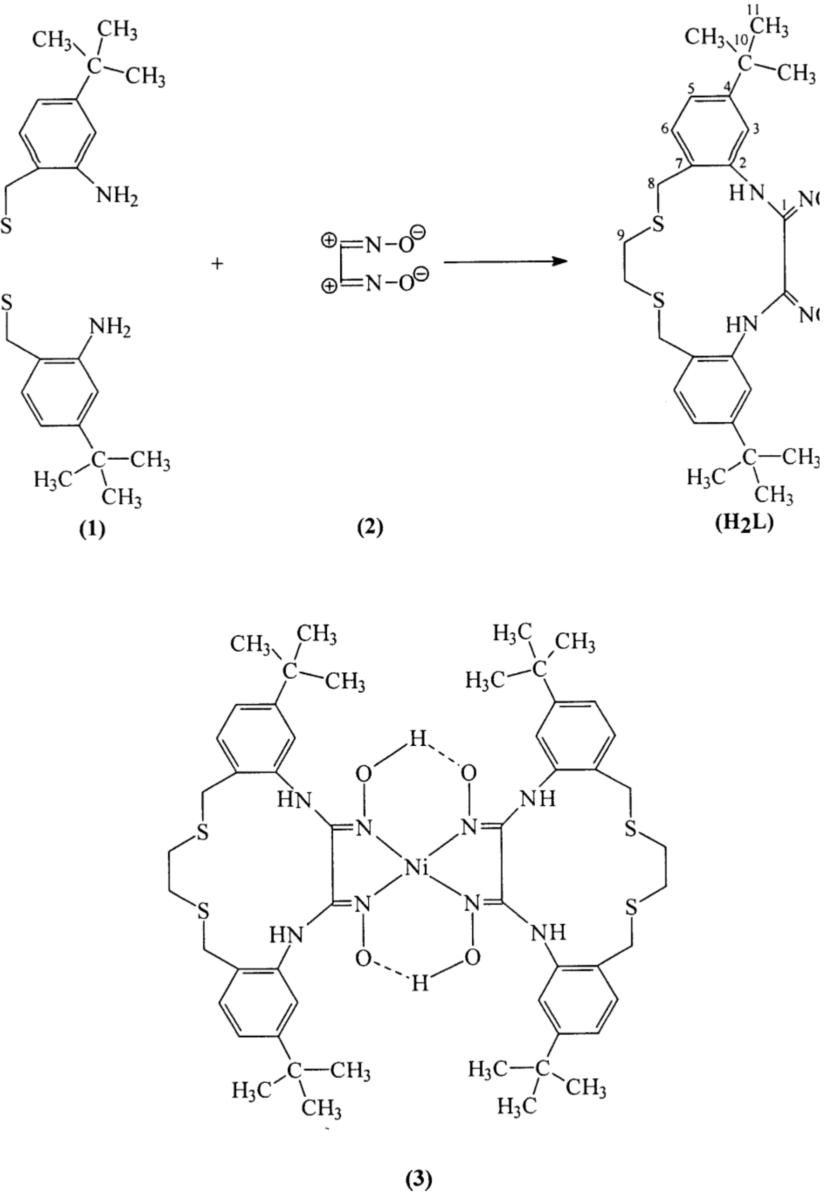
RESULTS AND DISCUSSION

1,2-Bis(4-*t*-butyl-2-aminobenzylthio)ethane (**1**) was prepared by reaction of 4-*t*-butyl-2-nitrobenzyl chloride and 1,2-ethanedithiol, which was obtained from a multistep reaction sequence according to standard procedures [10–13]. 5,6:13,14-Di(4′-*t*-butylbenzo)-2,3-bis(hydroxyimino)-8,11-dithia-1,4-diazacyclotetradecane (H_2L) was synthesized in moderate yield (60%) by condensation of **1** with cyanogendi-*N*-oxide (**2**), which was prepared by the reaction of (*E*,*E*)-dichloroglyoxime [14] and aqueous sodium carbonate (0.5 M) in dichloromethane at −10°C (Scheme 1) [15].

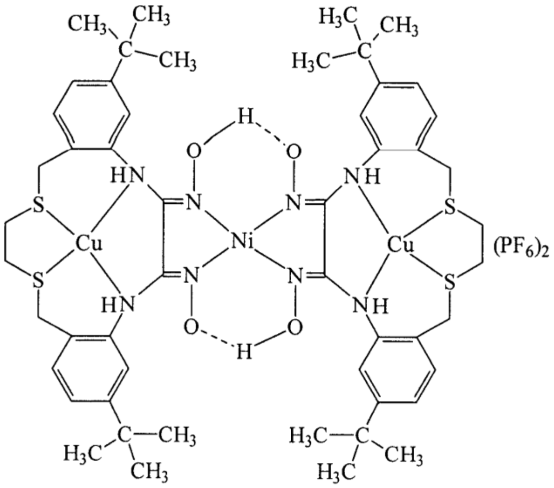
The new *vic*-dioxime was characterized by elemental analysis, ^1H, ^{13}C NMR, IR and mass spectral data. The ^1H NMR spectrum of H_2L, the disappearance of the aromatic primary amine functional groups that belong to the starting compound **1** and the N–OH and NH signals appearing at 12.07 and 10.70 ppm, respectively, which disappear upon deuterium exchange, indicate the formation of a dioxime. The single chemical shifts for N–OH protons indicate that the oxime groups are in the (*E*,*E*)-structure [16]. The carbon resonance of the azomethine groups in the proton-decoupled ^{13}C NMR spectrum of H_2L is found to be at lower fields, $\delta = 145.72$ ppm, as given in the literature [17]. The equivalent carbon signal of the oxime groups also confirms the (*E*,*E*) form of *vic*-dioxime. The IR spectrum of this compound suggested that it was the same structure, and the presence of the sharp absorptions at 3218 and 1613 cm^{-1} was strongly indicative of the presence of the hydroxyimino and azomethine groups, respectively. The fast atom bombardment (FAB) mass spectrum of H_2L exhibited an intense peak at $m/z = 501$ $[M+1]^+$, which is in accord with the expected formulation.

The reaction of H_2L with nickel(II) chloride hexahydrate gave the 1 : 2 metal : ligand ratio of the mononuclear $[Ni(HL)_2]$ (**3**) complex in 80% yield, and its composition was defined by elemental analysis and spectroscopic techniques. In the ^1H NMR spectrum of **3**, slight differences between those of H_2L and its nickel(II) complex were observed. The presence of intramolecular hydrogen bonding in this square-planar complex at around 16.82 ppm identifies the complexation product. The weak bending vibrations at 1700 cm^{-1} assigned to the O–H···O bending vibrations in the IR spectrum also indicate the same formation. As a distinct decrease in the pH of the solution was observed during complexation, deprotonation of the ligand with subsequent *N*,*N*′-chelation with the *vic*-dioxime group occurs. The FAB mass spectrum of **3** showed the expected molecular ion peak at $m/z = 1057.3$ $[M+1]^+$.

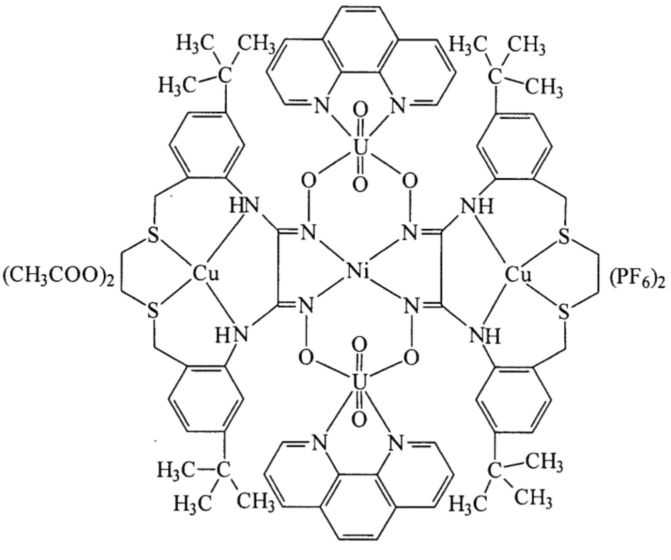
The heterotrinuclear Complex **4** was prepared in 75% yield by the reaction of the mononuclear Ni(II) Complex **3** with $[Cu(CH_3CN)_4]PF_6$ in a refluxing ethanol–dimethylformamide mixture. In this product, nickel(II) is still coordinated to the dioxime groups, and the two copper(I) ions are coordinated to two 14-membered dithiadiaza hetero atoms of the macrocycles. The planar nature of the phenyl rings and the adjacent azomethine groups contribute to the tendency toward planar coordination



SCHEME 1.



(4)

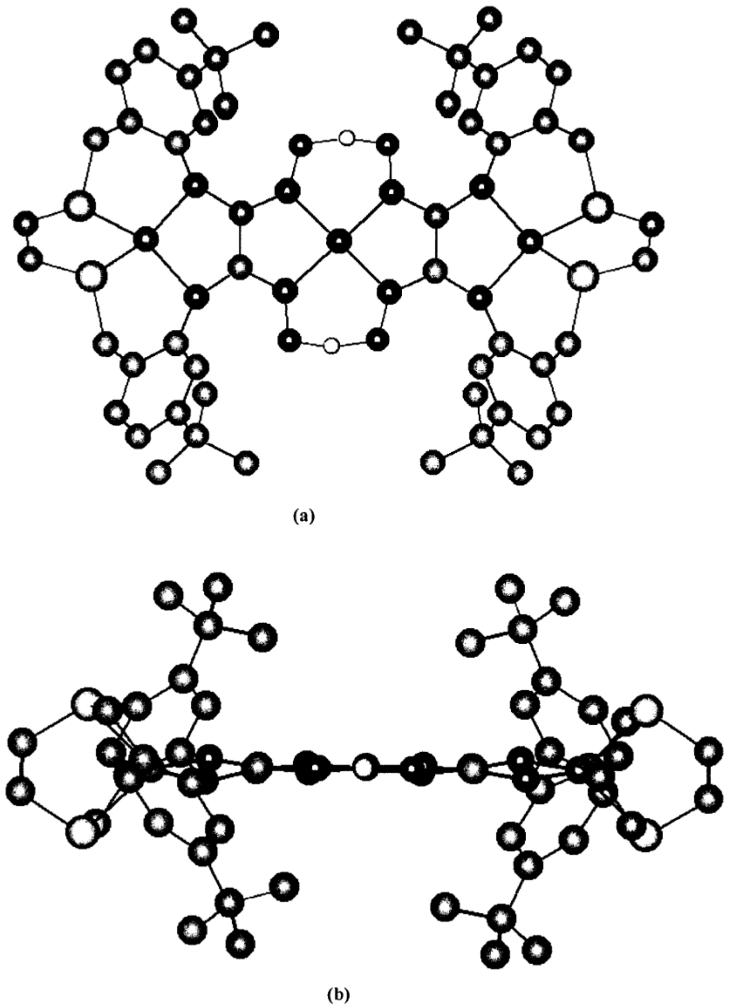


(5)

SCHEME 1 Continued.

by this kind of compound [17]. The heterotrinuclear complex has a metal : ligand ratio of 3 : 2 according to its elemental analysis. This complexation is also confirmed by the mass spectral data. The FAB mass spectrum shows a peak for $[Cu_2Ni(HL)_2](PF_6)_2$ at $m/z = 1473.4$ due to the $[M]^+$ ion. The ^1H NMR spectrum of **4** is similar to that of the precursor complex **3**, but the expected shifts due to complexation with copper(I) ions belonging to N_2S_2-macrocyclic moieties such as CH_2–N and CH_2–S are significant. The PF_6^- ion is a convenient "noncomplexing" agent that has even less coordinating ability than other anions such as ClO_4^- or BF_4^- [18]. The molar conductance value of this complex measured in DMF at room temperature is in the region of 159 $\mathrm{ohm}^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$ as expected for a 1 : 2 electrolyte for the PF_6^- complex [19]. In the IR spectrum of **4**, the vibrations at 851 and 556 cm^{-1}, assigned to $[PF_6]^-$, support a structure in which the PF_6^- ions are not coordinated to the Cu(I) ions [20].

In this study, the complete geometry optimization of various configurations of the heterotrinuclear complex $[Cu_2Ni(HL)_2](PF_6)_2$ was performed using the ZINDO/1 method. Its stability was evaluated, its geometric parameters were calculated, and its electronic structures were examined in detail (Fig. 1, Table I). The calculated total energy, heat of formation and bond lengths between the metal atoms and ligating heteroatoms show that the *pseudo*-tetrahedral configuration around the outer Cu(I) macrocycle ions is more stable than the square-planar structure, while the central metal ion, [Ni(II)], is square planar. Binding distances for Cu–N and Cu–S in the macrocyclic cavity range between 1.902 and 2.338 Å, according to the quantum chemical calculations, $r_{\mathrm{Ni-Cu}}$ in **4** is 5.049 Å. However, the equatorial Ni–N distances


(a)

(b)

FIGURE 1 Top (a) and side views (b) of the trinuclear complex **4**.

TABLE I The calculated total energy, heat of formation, bond lengths and bond angles for the stable configuration of the heterotrinuclear complex $[Cu_2Ni(HL)_2](PF_6)_2$

E_{tot} (kcal mol^{-1})	−457 146.191
ΔH_f (kcal mol^{-1})	−27 316.221
Bond lengths (Å)	
Ni–N	1.902
Cu–N	1.987
Cu–S	2.338
Bond angles (°)	
N1–Ni–N2	91.813
N2–Ni–N3	88.357
S–Cu–S	97.127
S–Cu–S	93.604
N–Cu–N	97.475

(1.902 Å) in the square-planar part of the heterotrinuclear complex are in agreement with the X-ray data for Ni–N bonding distance (1.87–1.90 Å) for known vicinal dioxime complexes [21].

The pentanuclear complex **5** has been synthesized in 40% yield by the reaction of $UO_2(CH_3OO)_2 \cdot 2H_2O$ with heterotrinuclear complex **4** as the bridging ligand and 1,10-phenanthroline as an end-cap ligand at 2 : 1 : 2 ratio in tetrahydrofuran. In this complex, while Ni(II) and Cu(I) cations are still coordinated to the precursor heterotrinuclear complex **4**, $[UO_2]^{2+}$ cations are coordinated to oxygens of the oximates and two nitrogens of 1,10-phenanthroline. This complex consists of a dinuclear cation $\{[Cu_2Ni(L)_2(UO_2)_2(phen)_2](PF_6)_2\}^{2+}$ and uncoordinated acetate anions. Formation of this heteropentanuclear complex **5** is verified by elemental analysis data. The presence or absence of certain characteristic bands in the complicated IR spectrum has been used to establish the nature of the complex. The resonances concerning hydrogen bridges are missing in the spectrum of **5**, indicating that the enolic hydrogen atoms are lost upon chelation. The C=N stretching vibration in this complex observed at 1629 cm^{-1} is situated at a frequency significantly higher than that of the free ligand. This is in accord with the concept that, on pentanuclear complex formation, the positively charged $\{[Cu_2Ni(L)_2(UO_2)_2(phen)_2](PF_6)_2\}^{2+}$ unit stabilizes the negative charge on oxygen of the oximate function and thus increases the double-bond character of azomethine [22]. On the other hand, the two bands observed at 1584 and 1421 cm^{-1} concerning asymmetric and symmetric stretching vibrations [23], respectively, which belong to the uncoordinated acetate anions, also supported the formation of a heteropentanuclear complex. The former band is stronger and more characteristic [24]. The band observed at 902 cm^{-1} arises from the uranyl group and is very significant [25]. The vibrations at 838 cm^{-1} can be attributed to uncoordinated PF_6^- ions [20]. The characteristic feature of the ^{1}H NMR spectrum of the diamagnetic complex **5** is the disappearance of the intramolecular hydrogen bonding protons (O–H···O) after heteropentanuclear complex formation. Protons of the acetate anions are observed at 2.11 ppm as a singlet and other characteristic signals concerning *tert*-butyl and aliphatic groups appear at 1.31, 3.80 and 2.47 ppm as expected. Based on the molar conductance values measured in DMF at room temperature (287 ohm^{-1} cm^2 mol^{-1}), it was not possible to determine how electrolytic this complex was, as it is difficult to determine the contributions of PF_6^- and CH_3COO^- anions to the total conductivity.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Varian-Mercury 200 spectrometer. Routine IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer calibrated with polystyrene, with the samples in KBr pellets. FAB mass spectra of the compounds were measured on a Varian MAT 711 spectrometer (*m*-nitrobenzyl alcohol as matrix). Elemental analysis and metal contents of the compounds were determined with a Hewlett-Packard 185 CHN analyzer and Unicam 929 AA spectrophotometers, respectively. Melting points were measured on an electrothermal apparatus. All quantum chemical calculations were carried out using the HYPERCHEM 6 software on an HP Pentium-III 866 computer. Molar conductivities of 10^{-3} M solutions of the complexes were determined by using a Model 31 conductivity meter (Yellow Spring Instrument Co. Inc.). 1,2-Bis(4-*t*-butyl-2-aminobenzylthio)-ethane was prepared by a reported procedure [13].

5,6:13,14-Di(4′-*t*-butylbenzo)-2,3-bis(hydroxyimino)-8,11-dithia-1, 4-diazacyclotetradecane (H_2L)

A cold solution (−10°C) of cyanogendi-*N*-oxide (**2**) in dichloromethane (25 cm^3), which was prepared from (E,E)-dichloroglyoxime (0.785 g, 5 mmol) and aqueous solution (−10°C) of Na_2CO_3 (25 cm^3, 0.5 M), was added to a cold solution of 1,2-bis(4-*t*-butyl-2-aminobenzylthio)ethane (**1**) (2.08 g, 5 mmol) in dichloromethane (50 cm^3). The reaction was continued for 10 h at the same temperature and then evaporated to dryness under reduced pressure. The crude product was crystallized from a benzene : hexane mixture (1 : 3) to yield pale orange crystals. Yield: 1.5 g (60%), m.p. 191°C (dec.). ^{1}H NMR (DMSO-d_6): δ (ppm) 12.07 (s, 2H, OH), 10.70 (s, 2H, NH), 7.20–6.68 (m, 6H, ArH), 3.60 (s, 4H, $ArCH_2S$), 2.50 (t, 4H, SCH_2CH_2S), 1.22 (s, 18H, $(CH_3)_3C$). ^{13}C NMR (DMSO-d_6): δ (ppm) 150.17 (C_2), 148.11 (C_4), 145.72 (C_1), 128.34 (C_6), 124.95 (C_7), 119.17 (C_5), 117.50 (C_3), 31.35 (C_8), 34.02 (C_9), 31.01 (C_{10}), 30.84 (C_{11}). IR (KBr pellets, cm^{-1}): 3330 (N–H), 3216 (O–H), 3049 (Ar–H), 2959 (C–H), 1613 (C=N), 1603 (N–H), 946 (N–O). Anal. Calcd. for $C_{26}H_{36}N_4O_2S_2$(%): C, 62.40; H, 7.20; N, 11.20. Found: C, 62.17; H, 7.41; N, 10.98. FAB positive mass spectrum: $m/z = 501$ $[M+1]^+$.

$[Ni(HL)_2]$ (3)

A solution of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) in ethanol (20 cm^3) was added to a solution of H_2L (1.0 g, 2 mmol) in ethanol (75 cm^3) at 60°C. A distinct change in color and a decrease in the pH of the solution (pH = 2.45) was observed. While heating and stirring at the same temperature, an equivalent of ethanolic triethylamine (0.1 M) was added to pH 5.0, and an orange precipitate of **3** formed. After heating the reaction mixture for 2 h in a water-bath, the precipitate was filtered off, washed several times with water, ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.84 g (80%), m.p. > 300°C. ^{1}H NMR (DMSO-d_6): δ (ppm) 16.88 (s, 2H, O–H O), 10.85 (s, 4H, NH), 7.33–6.75 (m, 12H, ArH), 3.74 (s, 8H, $ArCH_2S$), 2.65 (m, 8H, SCH_2CH_2S), 1.29 (s, 36H, $(CH_3)_3C$). IR (KBr pellets, cm^{-1}): 3368 (N–H), 3042 (Ar–H), 2961 (C–H), 1701 (O–H O), 1605 (C=N), 1600 (N–H), 957 (N–O). Anal. Calcd. for $C_{52}H_{70}N_8O_4S_4Ni$(%): C, 59.05; H, 6.62; N, 10.59; Ni, 5.55. Found: C, 58.81; H, 6.60; N, 10.75; Ni, 5.81. FAB positive mass spectrum: $m/z = 1057.3$ $[M+1]^+$.

$[Cu_2Ni(HL)_2](PF_6]_2$ (4)

A solution of $[Cu(CH_3CN)_4]PF_6$ (0.34 g, 1.36 mmol) in dry acetonitrile (50 cm^3) was added to a solution of mononuclear nickel(II) complex (0.72 g, 0.68 mmol) in a mixture of ethanol : DMF (40 cm^3, 3 : 1) under a nitrogen atmosphere at 60°C. Then the reaction was refluxed and stirred under a nitrogen atmosphere for 27 h. The end of the reaction was determined by TLC (*n*-butanol : acetic acid : water 4 : 1 : 5). After cooling to room temperature the reaction mixture was evaporated to dryness under reduced pressure. Dry ethanol (15 cm^3) was added to the residue and the mixture allowed to stand at −18°C overnight whereupon the product separated from the solution. The dark brown product was collected by filtration, washed with cold ethanol and diethyl ether, and then dried *in vacuo*. Yield: 0.75 g (75%), m.p. > 300°C. ^1H NMR (DMSO-d_6): δ (ppm) 16.93 (s, 2H, O–H···O), 10.98 (s, 4H, NH), 7.46–6.91 (m, 12H, ArH), 3.84 (m, 8H, $ArCH_2S$), 2.81 (m, 8H, SCH_2CH_2S), 1.35 (s, 36H, $(CH_3)_3C$). IR (KBr pellets, cm^{-1}): 3298 (N–H), 3041 (ArH), 2955 (C–H), 1694 (O–H···O), 1609 (C=N), 1598 (N–H), 941 (N–O), 849 $(PF_6)^-$. Anal. Calcd. for $C_{52}H_{70}N_8O_4S_4NiCu_2P_2F_{12}$(%): C, 42.34; H, 4.74; N, 7.59; Ni, 3.98; Cu, 8.61. Found: C, 42.60; H, 4.61; N, 7.87; Ni, 3.80, Cu, 8.37. FAB positive mass spectrum: $m/z = 1473.4$ $[M]^+$.

$\{[Cu_2Ni(L)(UO_2)_2(phen)_2](PF_6)_2\}(CH_3COO)_2$ (5)

The heterotrinuclear complex (0.41 g, 0.28 mmol) was dissolved in dry tetrahydrofuran (80 cm^3) with heating and stirring at 60°C. A solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.24 g, 0.46 mmol) in dry tetrahydrofuran (30 cm^3) and a solution of 1,10-phenanthroline (0.11 g, 0.56 mmol) in the same solvent (10 cm^3) was added to the hot solution. The reaction mixture was refluxed and stirred on a water-bath for 3 h, when precipitation of the heteropentanuclear complex stopped. After cooling to room temperature, the reddish brown complex was filtered off, washed with water then with hot tetrahydrofuran and cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.25 g (40%), m.p. > 300°C. ^1H NMR (DMSO-d_6): δ (ppm) 10.90 (s, 4H, NH), 8.98 (s, 4H, ArH_{phen}), 8.55 (d, 4H, ArH_{phen}), 7.94–7.81 (m, 8H, ArH_{phen}), 7.41–6.84 (m, 12H, ArH), 3.80 (m, 8H, $ArCH_2S$), 2.77 (m, 8H, SCH_2CH_2S), 2.12 (s, 6H, CH_3COO), 1.31 (s, 36H, $(CH_3)_3C$). IR (KBr pellets, cm^{-1}): 3315 (N–H), 3049 (Ar–H), 2951 (C–H), 1629 (C=N), 1602 (N–H), 1584 $(CO)_{asym}$, 1421 $(CO)_{sym}$, 963 (N–O), 905 (U=O=U), 838 $(PF_6)^-$. Anal. Calcd. for $C_{84}H_{92}N_{12}O_{12}S_4NiCu_2P_2F_{12}U_2$(%): C, 39.68; H, 3.62; N, 6.61; Ni, 2.31; Cu, 5.00; U, 18.74. Found: C, 39.53; H, 3.49; N, 6.77; Ni, 2.55; Cu, 4.80; U, 18.99.

Acknowledgments

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