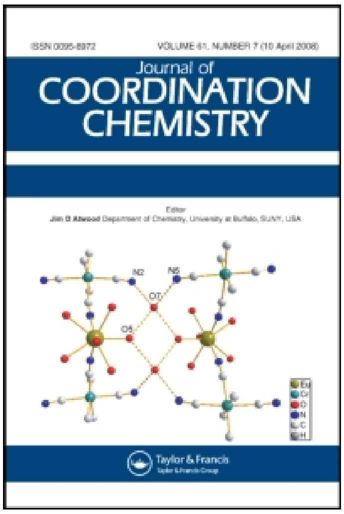

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THE SYNTHESIS AND CHARACTERIZATION OF A NOVEL (*E, E*)-DIOXIME AND ITS MONO, TRI AND PENTANUCLEAR COMPLEXES CONTAINING A NITROGEN-SULFUR MIXED 15-MEMBERED MACROCYCLIC MOIETY

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THE SYNTHESIS AND CHARACTERIZATION OF A NOVEL (*E*, *E*)-DIOXIME AND ITS MONO, TRI AND PENTANUCLEAR COMPLEXES CONTAINING A NITROGEN-SULFUR MIXED 15-MEMBERED MACROCYCLIC MOIETY

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A novel (*E*, *E*)-dioxime 5, 6:14,15-dibenzo-9,11-pyrido-2,3-*bis*(hydroxyimino)-1,4-diaza-7, 13-dithiacyclopentadecane (H_2L) has been synthesized from the reaction of cyanogendi-*N*-oxide and 2,6-*bis*(2-aminothiophenoxymethyl)pyridine (**3**), which has been prepared from 2,6-bis(chloromethyl)pyridine (**1**) and 2-amino thiophenol. The cobalt (III) complex $[Co(HL)_2L'Cl]$ of H_2L has been obtained with L' = 2,6-lutidine together with chloride as axial ligands. In addition the synthesis of a new cobalt complex containing BF_2^+ bridges is achieved with the hydrogen bridged cobalt(III) complex. Three new mono-, tri- and pentanuclear copper(II) complexes of formula $[Cu_3(HL)_2]$, $[Cu_5(HL)_2(bipy)_2]$ and $[Cu_5(HL)_2(phen)_2]$ have been synthesized. The structures of the oxime and its complexes were identified by elemental analysis, ^1H, ^{13}C NMR, IR and MS data.

Keywords: *vic*-Dioximes; heterocycles ; macrocycle; copper(II)

INTRODUCTION

Over the past three decades, numerous examples of macrocyclic ligands and their transition metal complexes have been investigated.[1] Macrocyclic ligands which incorporate heterocyclic groups within the polydentate donor set have been particularly investigated.[2] Macrocyclic ligands containing both nitrogen and sulfur donor atoms are of interest because of their potential for providing molecules capable of mimicking various aspects of macromolecular biological systems.[3] Some work has been carried out on azathia mixed donor compounds either as podand [4] or macrocyclic ligands.[5] Some of these compounds contain the group 2,6 *bis*(thiomethyl)pyridine, which is the source of the azathia coordinating moiety.[6]

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Studies on ligands containing only thiaether sulfur donor atoms have primarily been limited to reaction with transition metal cations such as Cu(II), Hg(II) and Ag(I). In the case of ligands with all amine nitrogen donors (cyclic polyamines), the strongly basic character of the nitrogens leads to extensive ligand protonation at pH values accessible to most aquometal ions.[7] As might be anticipated, the macrocyclic polyamino-polythiaether ligands (nitrogen-sulfur mixed donor) exhibit an interesting range of properties intermediate between those of macrocyclic polythiaethers and macrocyclic polyamines.

The coordination chemistry of vicinal dioximes is an intensive area of study and numerous transition metal complexes of this kind of ligand have been widely investigated.[8] The high stability of these complexes prepared with (*E*, *E*)-dioximes has been applied to model compounds for vitamin B_{12}[9] or trace metal analysis.[10]

It is known that the oximate group can function as a bridge between two metal ions through the imino nitrogen and the deprotonated oxygen, to afford bi- and trinuclear complexes.[11] Typical examples are trinuclear copper(II) complexes with double oximate bridges in a *cis* arrangement (**4**) may be obtained by the use of (*E*, *E*)-glyoxime ligands. This family of complexes has played a role in studies of molecular magnetism because of the remarkable efficiency of the oximato bridge to transmit electronic effects between metal ions.[12]

We have previously reported the synthetic chemistry of MN_4 core-containing complexes, such as (*E*, *E*), (*E*, *Z*)-dioximes[13] and phthalocyanines,[14] with additional tetraaza,[15] tetrathia[16] or nitrogen-oxygen mixed donor macrocyclic substituents. Herein we report the synthesis and characterization of novel (*E*, *E*)-dioxime-containing a 15-membered N_3S_2 mixed donor macrocyclic moiety. This paper deals with the synthesis and characterization of mono-, tri- and pentanuclear copper(II) complexes of general formula $[Cu_3(HL)_2]$ or $[Cu_5(HL)_2L']$ (L' = bipy or phen).

RESULTS AND DISCUSSION

5,6:14,15-Dibenzo-9,11-pyrido-2,3-*bis*(hyroxyimino)-1,4-diaza-7,13-dithiacyclopentadecane (H_2L) was prepared of 2,6 –*bis* (2-aminothiophenoxymethyl) pyridine (**3**) which was obtained in turn by the reaction of 2-aminothiophenol (**1**) with 2,6-*bis*(chloromethyl)-pyridine (2) with cyanogendi-*N*-oxide. The latter was prepared by treating a suspension of (*E*, *E*)-dichloroglyoxime in dichloromethane with 0.5M aqueous solution of Na_2CO_3 at -15°C.[17]

The desired precursor **3** was prepared in good yield by a slight modification of the literature[3] involving the reaction of 1 equivalent of 2,6-*bis*-(chloromethyl)pyridine with 2 equivalents of 2-aminothiophenol in DMF in the presence of 2 equivalents of KOH under reflux conditions for 5 h (Scheme 1).

TABLE I 13C NMR data for 3 (ppm)

C1	137.79
C2	130.96
C3	150.47
C4	41.41
C5	136.97
C6	117.11
C7	118.33
C8	115.57
C9	122.34
C10	158.71

The EI mass spectrum of the precursor compound (**3**) exhibits a strong parent ion at *m/z* = 353, which is in accord with the formation of proposed structure. The ^{1}HNMR spectrum of a CD_3CN solution of this compound is also consistent with proposed formulation, and exhibits resonances for pyridine [$\delta = 7.44$ (t), 6.90 (d)] and phenyl rings [$\delta = 7.10$ (d), 7.02 (d), 6.71 (d), 6.61 (d)], respectively, and the singlets at $\delta = 4.72$ and 3.92 ppm indicates NH_2 and methylene chemical shifts, respectively. The proton-decoupled carbon-13 NMR spectrum of this compound (Table I) is consistent with the proposed formulation.

Infrared spectra confirm the presence of aromatic primary amine groups [ν 3444, δ 1617 cm^{-1}] and the absence of mercapto (-SH) functional groups of the starting materials. The presence of strong absorptions at 1594 cm^{-1} was strongly indicative of the presence of the 2,6-disubtituted pyridine.

The free ligand (H_2L) has been prepared by the reaction of 2,6-*bis* (2-aminothiophenoxymethyl)pyridine (3) with cyanogendi-*N*-oxide (Scheme 1). The macrocyclization reaction was carried out without metal ions and the corresponding vicinal dioxime (H_2L) in dichloromethane over *ca* 10 h at −15°C was produced by 40% yield.

The fast atom bombardment (FAB positive) mass spectrum of H_2L exhibits a strong molecular ion peak at *m/z* = 438 [M+1], which is in accord with the formation of the 15-membered macrocyclic *vic*-dioxime. On the basis of the ^{1}H and ^{13}C NMR data, H_2L has an (*E*, *E*)-structure. The deuterium-exchangeable protons of the hydroxyimino groups show chemical shifts at $\delta = 12.35$ ppm as a singlet which indicates an (*E*, *E*)-structure for H_2L.[18] The NH protons in H_2L can also be identified easily, because of the disappearance of this signals ($\delta = 9.32$ ppm) by proton exchange in D_2O. In the ^{13}C NMR spectrum in DMSO-d_6, the carbohyroximamide and the CH_2 carbon resonaces are found at $\delta = 141.79$ and 42.15 ppm, respectively (Table II). It is noteworthy that the chemical shifts belonging to the phenyl and pyridine carbons are of a similar magnitude to comparable values of the precursor compound (**3**). Infrared specta of this compound confirm the presence of hydroxy

TABLE II ^{13}C NMR data for H_2L and cobalt(III) complexes (ppm)

	H_2L	$[Co(HL)_2L'Cl]$	$[Co(LBF_2)_2L'Cl]$
C1	139.16	139.31	139.43
C2	129.19	129.25	129.34
C3	152.47	152.66	152.89
C4	42.15	42.24	42.36
C5	137.90	138.08	138.19
C6	117.34	117.29	117.42
C7	119.54	119.67	119.76
C8	116.40	116.45	116.53
C9	122.13	122.18	122.24
C10	156.64	156.70	156.81
C11	141.79	142.44	142.98

(*ca* 3215 cm^{-1}) and azomethine (*ca* 1653 cm^{-1}) and the absence of aromatic primary amine functional groups of the previously prepared starting material.

To prepare the cobalt(III) complex of H_2L, a solution of the ligand and the metal salt in EtOH was heated to 60° C for at least 1 h while oxygen was bubbled through a suspension of the cobalt(II) complex in the presence of 2,6-lutidine as axial ligand. This complex has a metal:ligand ration of 1:2, and the ligand is coordinated only by the *N,N'* atoms of the vicinal dioxime. The FAB mass spectrum of the cobalt(III) complex exhibited intense peaks at m/z = 1090 and 966 corresponding to $[M+H_2O]$ and [M-L'+1]. No peak of higher mass was observed. This strongly suggests that a complex of metal:ligand ration 1:2 has been formed. It shows the characteristic features of (*E*, *E*)-dioxime, **5**. ^1H NMR specta confirm the hydrogen bridge structure with a chemical shift at lower field (δ = 16.94 ppm) for the deuterium exchangeable O—H··O protons.[19] Observation of NH shifts (δ = 9.44 ppm) also indicates the formation of desired compound. The carbon-13 NMR spectrum of the octahedral cobalt(III) complex is similar to that of the corresponding free ligand. Because of coordination to the metal ion, the ligand signals are slightly shifted. Additional signals at δ = 164.27, 137.94, 124.55 and 13.02 ppm due to the presence of the coordinated 2,6-lutidine molecule are also present. The disappearance of the N—OH bands and the shift of the C=N vibrations to lower frequency in the IR spectrum of $[Co(HL)_2L'Cl]$ can be attributed to *N,N'*-chelation.[20] In this octahedral complex, a weak deformation band assigned to the intramolecular hydrogen-bonded (O—H—O) bending vibration is observed at 1720 cm^{-1}.

Template synthesis of *bis*(dioximato)cobalt(III) complexes containing difluoroboron moieties, **6** was carried out by reaction of the cobalt(III) precursor with boron trifluoride etherate in refluxing solution. The fast atom bombardment mass spectrum of this compound does not exhibit molecular ion peak. However, the peaks at m/z = 1111 and 1071 are indicative of $[M\text{-}Co+2]^+$ and $[M\text{-}Co\text{-}2F]^+$, respectively. The ^1H NMR spectrum of the BF_2^+ -capped octahedral complex showed no peak assignable to hydrogen bridges belonging to the precursor cobalt(III) complex. Other chemical shifts (^1H and ^{13}C NMR) are similar to those of the hydrogen-bridged cobalt(III) complex. In IR spectrum a shift of the C=N stretches to higher frequency 22 cm^{-1} due to the strong electron-withdrawing influence of the difluoroboron groups was observed. The bands at 1182 and 804 cm^{-1} arise from B—O stretching vibrations and other bands near 1027 and 958 cm^{-1} have been assigned to B-F stretches of BF_2 and BF_4-groups.[21]

In contrast to the cobalt(II) ion which gives only a mononuclear complex with H_2L, trinuclear complexes are obtained with copper(II). Copper(II) is coordinated to azathia donor atoms of the macrocycles while the third copper(II) ion is **7** coordinated by the *N,N'* atoms of each (*E*, *E*)-dioxime group in two ligand molecules, **7**. These complexes have a metal:ligand ratio of 3:2 as confirmed by the fast atom bombardment mass spectrum which gives a molecular ion m/z = 1058 $[M+1]^+$.

The IR spectrum of the trinuclear copper(II) complex is very similar to that of the mononuclear cobalt(III) complex except for the disappearance of the N—H stretching vibrations. A shift of the C=N stretch to lower frequencies indicates coordination through the *N*-atoms of vicinal dioxime groups. The basicity of *N* donors in this macrocycle is rather low because of their position near the oxime groups. However, the trinuclear complex has been obtained by deprotonation of the *NH* groups.[22] The planar phenyl and pyridine rings and adjacent azomethines contribute to the tendency toward planar coordination by this kind of ligand.[23] S—C vibrations of the free macrocycle appear as split bands at 701 and 590 cm^{-1}; these shift in the spectrum of the trinuclear copper(II) complex to 678 and 581 cm^{-1}, suggesting bonding of copper to sulfur atoms.[24]

In this study we have accomplished the synthesis of the pentanuclear Cu(II) complexes formulated as $[L_2Cu_5(phen)_2](NO_3)_2$ or $[L_2Cu_5(bipy)_2](NO_3)_2$ (**8**) with $Cu_3(HL)_2$ as the bridging ligand and 1,10-phenanthroline or 2,2'-bipyridine as the end-cap ligand. Elemental analyses indicate a metal:trinuclear copper(II) complex ratio of 2:1. Formation of $[L_2Cu_5(phen)_2](NO_3)_2$ or $[L_2Cu_5(bipy)_2]$ $(NO_3)_2$ is verified by the molecular ion peaks at 1720 $[M+3H_2O+1]^+$, 1485 $[M\text{-phen}]^+$ and 1618 $[M+1]^+$, 1400 $[M\text{-dipy-Cu}]^+$, respectively, by fast atom bombardment mass spectrometry. Apart from the copper(II) ions in the trinuclear copper(II) complex, the other two copper(II) ions in the pentanuclear complexes are coordinated to two nitrogen atoms of phen or bipy and two oxygen atoms of adjacent oxime groups. In the IR spectra the disappearance of O—H—O stretching vibrations at around 1705 cm^{-1} indicate the formation of the suggested compounds (**8**). The nitrate ions are not coordinated by NO vibrations around 1376–1384 cm^{-1} are typical of ionic nitrate groups.[22,25]

EXPERIMENTAL

Proton and proton-decoupled carbon-13 NMR spectra were recorded in DMSO-d_6 on a Varian XL-300 spectrometer. IR spectra were recorded on a ATIunicam FT-IR spectrophotometer calibrated with polystyrene. Fast atom bombardment (FAB positive, matrix: *m*-nitrobenzylalcohol) mass spectra were measured on a VG AutoSpec from VG Analytical. Elemental analyses and metal contents of the complexes were determined on a Hewlett-Packard 85 CHN Analyzer and on a Hitachi 180-80 atomic absorption spectrophotometer, respectively. (*E*, *E*)-Dichloroglyoxime[26] and cyanogen di-*N*-oxide[27] were prepared by reported procedures. Melting points were determined on a Electrotermal apparatus and are uncorrected. All solvents were reagent grade and used without purification.

2,6-Bis(2-aminothiophenoxymethyl)pyridine, 3

A solution of 2-aminithiophenol (2.5 g, 20 mmol) in ethanol (2.5 cm^3) was added to a stirring solution of 2,6-*bis*(chloromethyl)pyridine (**1**) (1.76 g, 10 mmol in 25 cm^3 DMF) and KOH (1.12 g, 20 mmol) at room temperature under nitrogen. The solution was refluxed for 5h, cooled to room temperature, and poured onto crashed ice (200 g). After standing a few minutes, the supernatant was decanted from the gummy product. The latter was taken up in 100 cm^3 of chloroform, washed twice with H_2O, dried over anhydrous $CaCl_2$ and then the solvent was removed *in vacuo*. The oily product was purified by column chromatography [silica gel (70–230): ethyl acetate-petroleum ether (30:70)] to yield 2.76 g (78.0%) of white crystals, m.p. 62–64° C. ^{1}H NMR (CD_3CN, relative to Me_4Si): δ 7.44 (t, 1H, py), 7.10 (d, 2H, Ar—H), 7.02 (d, 2H, Ar—H), 6.90 (d, 2H, py), 6.71 (d, 2H, Ar—H), 6.61 (d, 2H, Ar—H), 4.72 (s, 4H, NH_2), 3.92 (s, 4H, CH_2). ^{13}C NMR (CD_3CN): δ 158.71, 150.47, 137.79, 136.97, 130.96, 122.34, 118.33, 117.11, 115.57, 41.41. IR (KBr pellet, cm^{-1}): 3444, 3342 (N—H), 3021 (Ar—H), 2934 (C—H), 1617 (NH_2), 1594 (C=N), 728 (C—S). Anal.: calcd. for $C_{19}H_{19}N_3S_2$ (%): C, 64.58; H, 5.38; N, 11.90. Found: C, 64.41; H, 5.23; N,11.72. Electron impact (EI) mass spectrum: $m/z = 353$

5,6:14,15-Dibenzo-9,11-pyrido-2,3-bis(hydroxyimino)-1,4-diaza-7,13 dithiacyclopentadecane, H_2L

A solution of cyanogen di-*N*-oxide in dichloromethane (50 cm^3), which was prepared from (*E*, *E*)-dichloroglyoxime (1.57 g, 10 mmol) and an aqueous solution of Na_2CO_3 (50 cm^3, 0.5 M), was added to a cold solution (–15°C) 2,6-*bis*(2-aminothiophenoxymethyl)pyridine (3.53 g, 10 mmol) in dichloromethane (600 cm^3)

The reaction was continued for 10 h at the above temperature and the yellow product formed separated by filtration, washed with cold dichloromethane and diethylether, and dried *in vacuo*. The crude product was recrystallized from ethanol. Pale yellow crystals were collected and dried *in vacuo* to yield 3.50 g (40.0%) of the macrocyclic dioxime (H_2L), m.p. 239° C (dec.). ^1H NMR (DMSO-d_6): δ 12.35 (s, 2H, OH), 9.32 (s, 2H, NH), 7.38 (t, 1H, py), 7.15 (d, 2H, Ar—H), 7.05 (m, 4H, Ar—H, py), 6.78 (d, 2H, Ar—H), 6.67 (d, 2H, Ar—H), 3.65 (s, 4H, CH_2). ^{13}C NMR (DMSO-d_6): δ 156.64, 152.47, 141.79, 139.16, 137.90, 129.19, 122.13, 119.54, 117.34, 116.40, 42.15. IR (KBr pellet, cm^{-1}): 3436 (N—H), 3215 (O—H), 3028 (Ar—H), 2912 (C—H), 1653 (C═N), 1590 $(C{=}N)_{py}$, 945 (N—O), 701 (C—S). Anal.: calcd. for $C_{21}H_{19}N_5O_2S_2$ (%): C, 57.67; H, 4.35; N, 16.02: Found: C, 57.48; H, 4.23; N, 15.89. Fast atom bombardment (FAB positive) mass spectrum: *m*/*z* = 438 $[M+1]^+$.

[Co(HL)$_2$L'Cl], 5

A solution of $CoCl_2.6H_2O$ (0.237 g, 1 mmol) in ethanol (15 cm^3) was added to a solution of H_2L (0.874 g, 2 mmol) in ethanol (100 cm^3) with stirring at 60° C. A distinct change in colour and a decrease in the pH of the solution (pH = 2.62) was observed. While heating, a solution of 2,6-lutidine (0.214 g, 2 mmol) in ethanol (4 cm^3) was added. The solution was allowed to cool to room temperature, and a stream of air was bubbled through it for 6 h. The reaction mixture was evaporated to 15 cm^3 and then cooled in a refrigerator overnight. Eventually the product crystallized from solution. The pale brown product was filtered off, washed with diethylether and then dried *in vacuo* to yield 0.84 g (78.4%) of the cobalt(III) complex, m. p. 350°C (dec.). ^1H NMR (DMSO-d_6): δ 16.94 (s, 2H, O—H—O), 9.44 (s, 4H, NH), 7.47-7.11 (m, 17H, Ar—H, py—H), 7.02-6.71 (m, 8H, Ar—H), 3.72 (s, 8H, CH_2), 2.70 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): δ 156.70, 152.66, 142.44, 139.31, 138.07, 129.25, 122.18, 119.67, 117.29, 116.45, 42.24. IR(KBr pellet cm^{-1}): 3429 (N—H), 3025 (Ar—H), 2842 (C—H), 1720 (O—H—O), 1625 (C═N), 1595 (C═N)py, 962 (N—O), 705 (C—S). Anal: calcd. for $C_{49}H_{45}N_{11}O_4S_4CoCl$ (%): C 54.77; H, 4.19; N, 14.34; Co, 5.48. Found: C, 54.55; H, 4.05; N, 14.20; Co, 5.27. Fast atom bombardment (FAB positive) mass spectrum: *m*/*z* = 1090 $[M+H_2O]^+$, 966 $[M\text{-}L'+1]^+$.

[Co(LBF$_2$)$_2$L'Cl], 6

A suspension of the cobalt(III) complex (0.536 g, 0.50 mmol) in 40 cm^3 of freshly distilled acetonitrile was brought to reflux in an oxygen-free nitrogen atmosphere. To this suspension, 0.25 cm^3 (2 mmol) of borontrifluoride etherate was slowly added with stirring. The resulting reaction mixture turned red immediately. Reaction was continued for 15 minutes at the above temperature and the solvent then removed under reduced pressure. The residue was dissolved in 10 cm^3 of acetonitrile and evaporated to dryness again. The crude product was crystallized from acetonitrile/diethylether, collected by filtration, washed with diethylether and dried *in vacuo* to yield 0.425 g (72.7%) of the BF_2 bridged cobalt(III) complex, m.p. 288°C. ^1H NMR ($CDCl_3$): δ 9.40 (s, 4H, NH), 7.38-7.05 (m, 17H, Ar—H, py—H), 6.92 - 6.69 (m, 8H, Ar—H), 3.65 (s, 8H, CH_2), 2.75 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 156.81, 152.89, 142.98, 139.43, 138.19, 129.34, 122.24, 119.76, 117.42, 116.53, 42.36. IR (KBr pellet, cm^{-1}): 3464 (N—H), 3016 (Ar—H), 2827 (C—H), 1647 (C=N), 1600 (C=N)py, 980 (N—O), 708 (C—S).Anal.: calcd. for $C_{49}H_{43}N_{11}O_4S_4B_2F_4CoCl$ (%): C, 50.29; H, 3.67; N, 13.17; Co, 5.03. Found: C, 50.09; H, 3.51; N, 12.96; Co, 4.88. Fast atom bombardment (FAB positive) mass spectrum: m/z = 1110 $[M\text{-}Co+1]^+$.

$[Cu_3(HL)_2]$, 7

H_2L (0.874 g, 2 mmol) was dissolved in methanol (60 cm^3) with heating and stirring. A solution of $CuCl_2.2H_2O$ (0.511 g, 3 mmol) in methanol (20 cm^3) was added to the above dioxime solution with heating and stirring at 50° C. The reaction mixture was refluxed for 30 mins and 0.1 M KOH in ethanol added to adjust the pH to about 4.5 when precipitation of the complex started. After heating for another hour, the precipitated complex was filtered off, washed with hot and cold ethanol, then diethylether, and dried *in vacuo* to yield 0.85 g (85.0%) of the trinuclear copper(II) comlex, m.p. 313–315°C (dec.). IR (KBr pellet, cm^{-1}): 3035 (Ar—H), 2840 (C—H), 1705 (O—H··O), 1645 (C=N), 1592 (C=N)py, 937 (N—O), 678 (C—S). Anal.: calcd for $C_{42}H_{32}N_{10}O_4S_4Cu_3$ (%): C, 47.63; H, 3.02; N, 13.28; Cu, 18.00. Found: C, 47.41; H, 2.84; N, 13.12; Cu, 17.81. Fast atom bombardment (FAB positive) mass spectrum: m/z = 1058 $[M+1]^+$, 932 $[M\text{-}2Cu\text{-}1]^+$.

$[Cu_5(L)_2(phen\ or\ bipy)_2](NO_3)_2$, 8

The trinuclear complex of H_2L (0.264 g, 0.25 mmol) was suspansed in tetrahydrofuran (30 cm^3) with stirring. A solution of end-cap ligand (0.5 mmol, 0.09 g of phen or 0.078 g of bipy) in THF (10 cm^3) and a solution of $Cu(NO_3)_2.3H_2O$ (0.121 g, 0.5 mmol) in the same solvent (10 cm^3) was added to the mixture at reflux. Reflux was maintained for 5 h after which the precipitate which had formed was filtered off, washed with water, methanol and diethylether, and then dried *in vacuo*.

$[Cu_5(L)_2(phen)_2](NO_3)_2$

IR (KBr pellet, cm^{-1}): 3028 (Ar—H), 2852 (C—H), 1640 (C=N), 1585 (C=N)py, 1376 (NO), 930 (N—O), 682 (C—S). Anal.: calcd. for $C_{66}H_{46}N_{16}O_7S_4Cu_5$ (%): C, 47.51; H, 2.76; N, 13.44; Cu, 19.05. Found: C, 47.33; H, 2.60; N, 13.29; Cu, 18.87. Fast atom bombardment (FAB positive) mass spetrum: m/z = 1720 $[M+3H_2 O-2]^+$, 1484 $[M\text{-phen}]^+$.

$[Cu_5(L)_2(bipy)_2](NO_3)_2$

IR (KBr pellet, cm^{-1}): 3032 (Ar—H), 2845 (C—H), 1643 (C=N), 1595 $(C=N)_{py}$, 1384 (N—O), 921 (N—O), 688 (C—S). Anal.: calcd. for $C_{62}H_{46}N_{16}O_4S_4Cu_5$ (%): C, 45.95; H, 2.84; N, 13.83; Cu, 19.61. Found: C, 45.77; H, 2.69; N, 13.65; Cu, 19.48. Fast atom bombardment (FAB positive) mass spectrum: m/z = 1618 $[M+1]^+$, 1400 $[M\text{-dipy-Cu}]^+$, 1059 $[M\text{-2bipy-2Cu-2NO}_3]^+$.

References

[1] G.A. Melson, (ed.), *Coordination Chemistry of Macrocyclic Compounds*, (Plenum, New York, 1979); R.M. Izatt and J.J. Christensen, (eds.), *Synthesis of Macrocycles*, Vol. **1–3** (Wiley-Interscience, New York, 1987).

[2] E.C. Constable, J. Lewis, V.E. Marquez and P.R. Rathby, *J. Chem. Soc., Dalton Trans.*, 1747 (1986); G.R. Newkome, J.D. Sauer, J.M. Roper and D.C. Hager, *Chem. Rev.*, **77**, 513 (1977).

[3] E.C. Constable, C. Sacht, G. Palo, D.A. Tocher and M.R. Truter, *J. Chem. Soc., Dalton. Trans.*, 1307 (1993).

[4] E. Domes and P.S. Bryan, *J. Coord. Chem.*, **6**, 97 (1976); F. Teixidor, J. Casabo, M. Sanz, L.I. Escriche, E. Molins, C. Miravitlies and J. Rius, *J. Chem. Soc., Dalton Trans.*, 1739 (1989).

[5] D Parker, J.M. Lehn and J. Rimmer, *J. Chem. Soc., Dalton Trans.*, 1517 (1985); F. Vögtle and E. Weber, *Chem. Ber.*, **109**, 1803 (1976); D. Parker, G. Ferguson and K. Matthes, *J. Chem. Soc., Chem. Commun.*, 1350 (1987).

[6] F. Teixidor, G. SancheCastello, N. Lucena, L. Escriche, R. Kivekös, M. Sundberg and J. Casabo, *Inorg. Chem.*, **30**, 4931 (1991).

[7] B.C. Westerby, K.L. Juntunen, G.H. Leggett, V.B. Pett, M.J. Koenigbauer, M.D. Purgett, M.J. Taschner, L.A. Ochrymowycz and D.B. Rorabacher, *Inorg. Chem.*, **30**, 2109 (1991).

[8] R.C. Mehrotra, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard and J.A. McCleverty, (Eds.), (Pergamon Press, New York, 1988), Vol. **2;** A Chakravorty, *Coord Chem. Rev.*, **13**, 12 (1974).

[9] G.N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).

[10] S. Kuse, S. Motomizu and K. Toei, *Anal. Chim. Acta*, **70**, 65 (1974).

[11] W.E. Hatfield, *Inorg. Chem.*, **11** 216 (1972); J.A. Bertrand, J.H. Smith and P.G. Eller, *Inorg. Chem.*, **13**, 1649 (1974); H. Okawa, M. Koikawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 469 (1990).

[12] R. Ruiz, J. Sanz, B. Cervera, F. Liaret, M. Julve, C. Bois, J. Faus and M.C. Munoz, *J. Chem. Soc., Dalton Trans.*, 1623 (1993).

[13] Y. Gok and H. Kantekin, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 1085 (1990).
[14] Y. Gok and S.Z. Yildiz, *J. Coord. Chem.*, **36**, 175 (1995); Y. Gok, *Z. Anorg. Allg. Chem.*, **621**, 1243 (1995).
[15] Y. Gok, H. Kantekin, H. Alp and M. Ozdemir, *ibid.*, **621**, 1237 (1995).
[16] Y. Gok, S.Z. Yildiz and M. Tüfekci, *J. Coord. Chem.*, **28**, 237 (1993).
[17] C. Grundmann, V. Mini, J.M. Dean and H.D. Frommeld, *Liebibs. Ann. Chem.*, **687**, 191 (1965).
[18] A. Gul, A.I. Okur, A. Cihan, N. Tan and O. Bekaroglu, *J. Chem. Res., (S)*, 90 (1986); Y. Gok and H. Kantekin, *Chem. Ber.*, **123**, 1479 (1990).
[19] Y. Gok, H. Ertepmar and S.Z. Yildiz, *Spect. Lett*, **23**, 713 (1990).
[20] V. Alexander, *Inorg. Chim. Acta*, **156**, 125 (1989); V. Alexander, *ibid.*, **204**, 109 (1993); Y. Gok, S. Karabocek and H. Kantekin, *Trans. Met. Chem.*, **20**, 234 (1995).
[21] B. Sahoo, N.C. Patra, A.K. Rout and B. Sahoo, *Indian J. Chem.*, **27A**, 680 (1988); B. Sahoo, A.K. Rout, N.C. Patra and B. Sahoo, *ibid*, **28A**, 400 (1989).
[22] E. Hamuryudan and O. Bekaroglu, *Chem. Ber.*, **127** 2483 (1994).
[23] M.C. Rakowski, M. Rycheck and D.H. Busch, *Inorg. Chem.*, **14**, 1194 (1975); L.F. Lindoy and D.H. Busch, *Inorg. Chem.*, **19**, 2494 (1974).
[24] Y. Gok and H. Kantekin, *New J. Chem.*, **19**, 461 (1995).
[25] K. Nakamoto, *Infrared and Raman Spectra od Inorganic and Coordination Compounds*, 3rd Edn. p.244 (Wiley, New York, 1988).