

The Synthesis and Characterization of a Novel (*E,E*)-Dioxime and Its Mono- and Polynuclear Complexes

S. Zeki Yıldız, M. Nedim Mısır, Nuray Tüfekçi and Yaşar Gök*

Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey

Yıldız, S. Z., Mısır, M. N., Tüfekçi, N. and Gök, Y., 1998. The Synthesis and Characterization of a Novel (*E,E*)-Dioxime and Its Mono- and Polynuclear Complexes. – Acta Chem. Scand. 52: 694–701. © Acta Chemica Scandinavica 1998.

A bidentate (*E,E*)-dioxime ligand, 2,3-bis(hydroxyimino)-7,16-dioxa-10,13-bis(toluene-*p*-sulfonyl)-1,4,10,13-tetrazacyclooctadecane (H_2L), has been synthesized by the addition reaction of (*E,E*)-dichloroglyoxime with 1,14-diamino-6,9-bis(toluene-*p*-sulfonyl)-3,12-dioxa-6,9-diazatetradecane. The free macrocyclic ligand is neutral and coordinates with nickel(II) and copper(II) through its hydroxyimino nitrogen donors in the equatorial position by the loss of one of the oxime protons, with the concomitant formation of two intramolecular hydrogen per oxime molecule. The series of homo- and heterotrinnuclear complexes Cu^{II}_3 or Ni^{II}_3 and $Cu^{II}Ni^{II}_2$ or $Ni^{II}Cu^{II}_2$, respectively, containing the oximate tetra-anion as a bridging ligand and 2,2'-bipyridine (L') or 1,10-phenanthroline (L'') as end-capping ligands have been synthesized by using $[Cu(HL)_2]$ or $[Ni(HL)_2]$ as the ligand for the ML^{n+} center. The macrocyclic ligand and its transition metal complexes have been characterized on the basis of 1H , ^{13}C NMR, IR, UV-VIS and MS spectroscopy and elemental analytical data.

The inorganic chemist can transform matter in order to design a novel system exhibiting desired physical or chemical properties. When dealing with magnetic properties of homo- or polynuclear systems, this necessitates many iterations of the steps of a cycle.¹ One of the most important steps of this phenomenon is the synthesis and characterization of new compounds, which one thinks will exhibit magnetic properties. For two or three decades, the inorganic chemist has been increasingly interested in polynuclear compounds. When the transition metal ions are not isolated from each another, these systems can acquire extraordinary physical properties or new physical and chemical reactivity. For this reason, the physical properties, such as magnetic behaviour, of the polynuclear complex are totally different from the sum of the magnetic properties of each transition metal center surrounded by its nearest neighbours.² Additionally, the importance of exchange coupling in multimetal proteins³ has stimulated much interest in exploring the ability of binding multi-atom ligands to mediate exchange coupling in $M(\text{bridging ligand})-M'(\text{end-cap ligands})$ systems. Both homo- and heteropolynuclear complexes provide an opportunity for experimental and theoretical studies of fundamental electronic processes such as electron exchange in biological metallic systems and their model compounds.⁴

The dependence of the magnitude of the exchange

interaction upon the nature of the bridging ligand, such as oximate or oxamidate, in a series of polynuclear complexes has been investigated extensively.⁵ One of the best strategies to design and synthesize polynuclear compounds is the use of mononuclear complexes as ligands which contain potential donor moieties for another metal ion carrying end-cap ligands.⁶ It is known that the oximate group ($=N-O-$) can function as a bridge between two transition metal ions through the imino nitrogen and the deprotonated oxygen, to afford polynuclear complexes.⁷ The best examples of these are represented by the copper(II) or nickel(II) oximate complexes. These complexes have played a relevant role in molecular magnetism because of the remarkable efficiency of the oximate bridge to transmit electronic effects between the transition metal ions. In particular, bis(oximate) copper(II) or bis(oximate)nickel(II) complexes are suitable candidates, because they can coordinate easily to another transition metal ion carrying end-cap moieties to obtain polynuclear complexes. On the other hand, the oximate bridges are able to mediate stronger magnetic interactions than other bridge groups such as oxamidate.⁸

In previous papers⁹ we described the synthesis and characterization of trinuclear copper(II) complexes bridged by substituted (*E,E*)-dioximate groups containing macrocyclic moieties and double oximate bridges in a *cis* arrangement. Here we report the synthesis and characterization of a new (*E,E*)-dioxime ligand carrying

* To whom correspondence should be addressed.

an 18-membered diaxatetraaza macrocyclic moiety and its mononuclear copper(II) or nickel(II) complexes, as a double oximate bridge, to prepare homo- or heteropolynuclear complexes such as $[\text{Cu}(\text{L})_2\text{Cu}_2(\text{dipy})_2]^{2+}$, $[\text{Cu}(\text{L})_2\text{Cu}_2(\text{phen})_2]$, $[\text{Cu}(\text{L})_2\text{Ni}_2(\text{phen})_2]^{2+}$, $[\text{Ni}(\text{L})_2\text{Cu}_2(\text{phen})_2]^{2+}$, $[\text{Ni}(\text{L})_2\text{Cu}_2(\text{dipy})_2]^{2+}$, $[\text{Ni}(\text{L})_2\text{Ni}_2(\text{dipy})_2]^{2+}$ or $[\text{Ni}(\text{L})_2\text{Cu}_2(\text{phen})_2]^{2+}$.

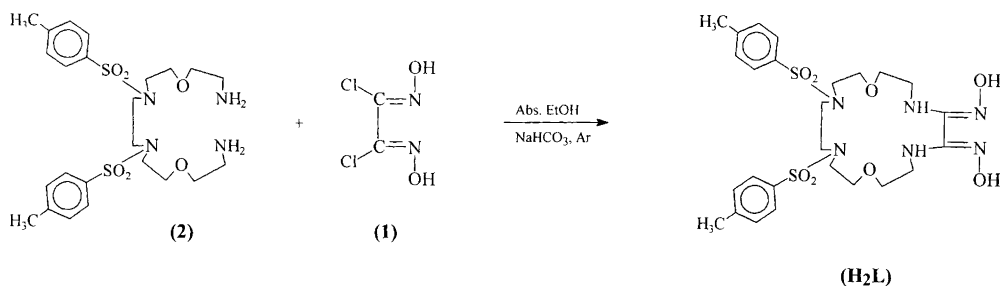
Results and discussion

2,3-Bis(hydroxyimino)-7,16-dioxa-10,13-bis(toluene-*p*-sulfonyl)-1,4,10,13-tetraazacyclotetradecane (H_2L) has been synthesized by the reaction of 1,14-diamino-6,9-bis(toluene-*p*-sulfonyl)-3,12-dioxa-6,9-dizahexadecane¹⁰ (**1**) with (*E,E*)-dichloroglyoxime¹¹ (**2**) in absolute ethanol with an excess of NaHCO_3 as a buffer to neutralize under an argon atmosphere, HCl formed during the condensation reaction (Scheme 1). The synthesis of mononuclear complexes of formula $[\text{Cu}(\text{HL})_2]$ or $[\text{Ni}(\text{HL})_2]$ was performed by the reaction between H_2L and metal salts. Then homo- or heteronuclear complexes of H_2L were obtained using mononuclear complexes of ligand and metal salts (Cu^{II} or Ni^{II}) containing end-cap ligands such as 1,10-phenanthroline or 2,2'-bipyridine. ^1H and ^{13}C NMR, IR, MS and UV-VIS spectral and elemental analysis data were combined to identify the structure of the ligand and its complexes.

Treatment of **1** with (*E,E*)-dichloroglyoxime (**2**) in the presence of an excess amount of NaHCO_3 in absolute ethanol under an inert atmosphere gave the target compound containing the 18-membered dioxatetraaza macrocyclic moiety (H_2L) in high yield (ca. 85%) by a simple work-up procedure. In the ^1H NMR spectrum of H_2L the absence of amine functional groups belonging to the precursor diamine compound (**1**) and NH groups and N-OH chemical shifts appearing at $\delta=5.49$ and 9.46 ppm indicate the occurrence of a macrocyclization reaction. On the other hand, the deuterium exchangeable properties of these protons also show the formation of the desired compound (H_2L). The single chemical shifts for the hydroxyimino protons ($=\text{N-OH}$) can be attributed to the oxime groups, which are in the (*E,E*)-structure.¹² In the proton-decoupled ^{13}C NMR spectrum of H_2L , the carbon resonance of azomethine groups is found to lower field at $\delta=143.49$ ppm, as given in the literature.¹³ This equivalent carbon resonances con-

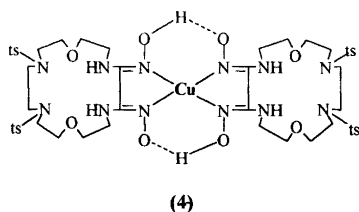
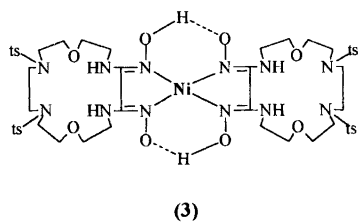
cerning oxime groups confirm the (*E,E*)-structure, which is in good agreement with literature.¹⁴ The other carbon resonances belonging to aromatic and ethylene groups are very similar to those of the precursor amine compound (**1**). The IR spectrum of H_2L was found to be consistent with the assigned structure. The broad absorptions at 3371 and 3216 cm^{-1} for H_2L are assignable to the N-H and O-H stretching vibrations, respectively. The C=N absorption of ligand is well resolved and appears as a defined, high-intensity and sharp band at ca. 1649 cm^{-1} . Distinct stretching vibrations of the azomethine groups are also assignable to a (*E,E*)-dioxime structure.¹⁵ The metal-sensitive, strong bands appearing at 1001 and 827 cm^{-1} may be attributed to N-O stretching and C=N-O^- deformation vibrations, respectively. The mass spectrum (FAB positive, matrix *m*-nitrobenzylalcohol) of H_2L , which shows a molecular ion peak at $m/z=627 [M+1]^+$, confirms the proposed structure and rules out any polymeric form.

In order to prepare nickel(II) and copper(II) complexes we have used a standard procedure¹⁶ by reaction of H_2L with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. A mixture of ligand, metal(II) chloride and an equivalent amount of KOH (0.1 M) in methanol gave the desired complexes $[\text{Ni}(\text{HL})_2]$ and $[\text{Cu}(\text{HL})_2]$ in 77.22% and 52.25% yield, respectively. These mononuclear nickel(II) and copper(II) complexes have a metal:ligand ratio of 1:2 according to the elemental analysis and mass spectral data, as is the case for most (*E,E*)-dioximes (Scheme 1).¹⁷ The fast atom bombardment mass spectra of **3** and **4** showed the expected molecular ion peaks at $m/z=1309 [M+1]^+$ and 1313 $[M+1]^+$, respectively. Both of the complexes have IR spectra very similar to those of the free ligand, except for the disappearance of the O-H stretching vibrations. Weak and low intensity bands at ca. 1725–1716 cm^{-1} indicate intramolecular O-HO bending vibrations.¹⁸ This indicates the formation of a hydrogen bond during the complexation of the ligand, since the hydrogen bond reduces the strength of the O-H bond. The occurrence of hydrogen bridges by the loss of one oxime proton per oxime molecule during the complexation of the ligand accounts for the two non-identical $=\text{N-O-}$ linkages, C=N-O-H and C=N-OH , in the complexes.¹⁹ The stretching vibrations of azomethine groups appearing at 1649 cm^{-1} in the free ligand are shifted to 1626 and 1621 cm^{-1} in the mononuclear complexes.

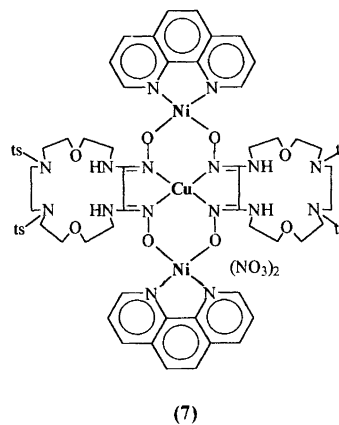
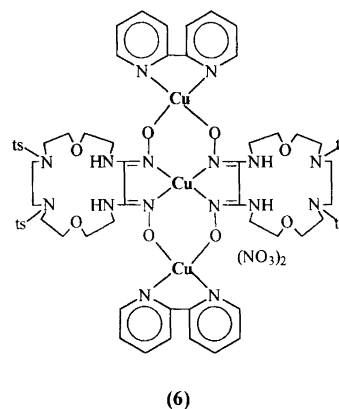
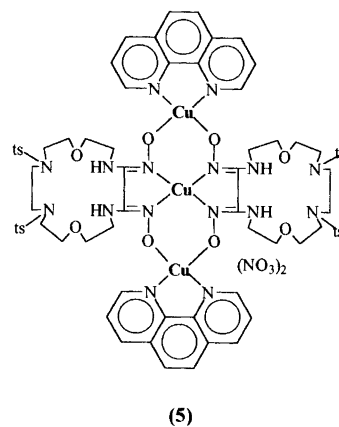


Scheme 1.

These results suggest that the ligand is coordinated to the metal ion through the nitrogen donors, as expected for *N,N*-chelated (*E,E*)-dioxime complexes. The copper(II) or nickel(II) ions probably retain the original planar configuration with four nitrogen donor atoms each in **3** and **4**. In the proton NMR spectrum of $[\text{Ni}(\text{HL})_2]$, the disappearance of the =N–OH resonance, appearance of a free ligand and the presence of a new resonance at lower field at $\delta = 17.15$ ppm can be assigned by the formation of a hydrogen bridge which can easily be identified by deuterium exchange.²⁰ The other chemical shifts of the nickel(II) complex are similar to those of the corresponding free ligand.



The nitrate salts of the trinuclear complexes were synthesized either by the reaction of monomeric $[\text{Cu}(\text{HL})_2]$ complex in THF or by the reaction of copper(II) nitrate trihydrate and an end-cap ligand (dpy or phen) in THF. Success in synthesising these complexes seems to depend upon the choice of the 'end-cap' ligands. The desired complexes can be obtained in tolerable yields (30–35%) by the use of dpy or phen as the end-cap ligand. A close investigation of the mass spectra of trinuclear copper(II) complexes **5** and **6** confirmed the proposed structure. In the case of **5**, in addition to $[M + 2.5\text{H}_2\text{O} + 1]^+$, fragment ions corresponding to loss of 2(phen) ($[M - 360]^+$) were easily identified. The spectrum of **6** was also obtained by the FAB technique using a *m*-nitrobenzyl alcohol matrix; the region of the molecular ion occurs at $m/z = 1882$, corresponding to $[M + 0.5\text{H}_2\text{O}]^+$. The compound $[\text{Cu}(\text{HL})_2]$ shows two IR absorptions near 1716 and 834 cm^{-1} which may be assigned to the $\nu(\text{O}-\text{H})$ stretching and $\gamma(\text{O}-\text{H})$ out-of-plane deformation modes of the hydrogen-bonded O–HO group, respectively.²¹ The lack of these vibrations in the IR spectra of trinuclear complexes has been attributed to the breakdown of the hydrogen bridge present in precursor copper complex by its full deprotonation to provide the $[\text{Cu}(\text{L})_2]^{2-}$ anion, as observed in **5** and **6**. The copper(II) ions in the trinuclear copper(II) complexes need to be tetracoordinated with two nitrogen atoms of a Lewis base and two oxygens of an oximate

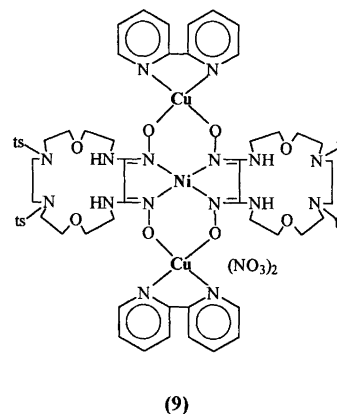
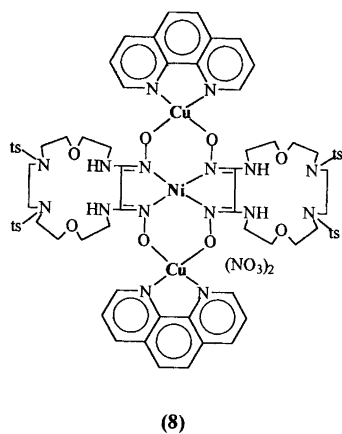


unit. The nitrate ions are out of the coordination sphere, as observed by the $\nu(\text{N}-\text{O})$ vibration at around 1370–1382 cm^{-1} , which is a typical value for an uncoordinated nitrate groups.²² On the other hand, it is noteworthy that the stretching vibration of the C=N group is shifted towards higher frequency when $[\text{Cu}(\text{HL})_2]$ coordinates to metal ions to yield trinuclear complexes.²¹

A promising way to synthesize a heterotrinuclear complex is to use a mononuclear metal complex which contains potential donor groups such as $[\text{Cu}(\text{L})_2]^{2-}$ for other metal ions.²³ $[\text{Cu}(\text{HL})_2]$ was chosen with this aim, because it can coordinate to nickel(II) or copper(II)

ions through the deprotonated oximate oxygens to afford a heterotrinnuclear complex doubly bridged by an oximate unit.²⁴ The precursor copper(II) complex shows an IR band at 1716 cm^{-1} which may be assigned to the bending vibrations of the hydrogen-bond $\delta =\text{N}-\text{O}-\text{HO}-\text{N}=\text{O}$ groups.²⁵ Evidence which indicates the formation of the trinnuclear complex is that it shows no band at vibrations belonging to the hydrogen bridge. Additional structural information comes from the observation of the stretching vibrations of C=N and N-O, which are shifted towards different frequency regions due to the formation of the trinnuclear complex $[\text{Cu}(\text{L})_2\text{Ni}_2(\text{phen})_2](\text{NO}_3)_2$. Formation of this trinnuclear complex is verified by the $[M+1]^+$ peak at $m/z=1912$, which has been measured by fast atom bombardment mass spectrometry. The other ions observed at $m/z=1733$ and 1669 , corresponding to the loss of two phenanthroline or two phenanthroline groups together with a nitrate group, also indicate the formation of the desired complex.

In order to gain further evidence for heteropolynuclear complexes **8** and **9** in such a *cis*-dioximate bridging system, we have synthesized trinnuclear $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$ complexes **8** and **9** by the use of $[\text{Ni}(\text{HL})_2]$.²⁶ These complexes consist of a trinnuclear cation and nitrate ions. The $\text{Ni}(\text{HL})_2$ molecule coordinates the two copper(II) ions through the deprotonated oximate oxygens to afford a trinnuclear skeleton doubly bridged by an oximate group in the *cis* arrangement. The nickel(II) ion is surrounded in the same plane by four nitrogen atoms of $\text{Ni}(\text{L})_2^{2-}$. A noticeable feature of the trinnuclear cation is that the whole cation is not coplanar, and is bent at the bridging oximate oxygens so that it assumes a butterfly shape.²⁴ The disappearance of the bridging hydrogen belong to the precursor nickel(II) compound can be assigned to the formation of the desired trinnuclear compounds. It is known that planar $[\text{M}(\text{dpy})_2]^{2+}$ and $[\text{M}(\text{phen})_2]^{2+}$ complexes are distorted from a rigid square-planar configuration because of interligand bonding within each molecule.²⁷ In the case of copper(II), this usually results in five-coordinate or distorted six-coordinate species. In this study, no ligand coordinated with copper ions except end-cap ligands was observed. The mass spectra (FAB)



of the complexes support the structure of the proposed formula; however, the peaks at $m/z=1733$ for **8** and 1557 for **9** do not confirm the presence of a Lewis base (phen or dipy). The stretching vibrations of C=N groups of the oxime for the trinnuclear complexes containing divalent metal ions are situated at a frequency significantly higher than that for the complex containing nickel(II) ions. This is accord with the concept that on trinnuclear complex formation the positively charged ML^{2+} units stabilize the negative charge on the oxygen of the oximate function, and thus increase the double-bond character of the C=N bond.⁴ All of the nitrate salts show stretching vibrations at around $1380\text{--}1374\text{ cm}^{-1}$, indicating uncoordinated nitrate anions.²²

The monomeric $[\text{Ni}(\text{HL})_2]$ dissolves in hot THF in the presence of a mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and end-cap ligands (phen or dipy) with concomitant formation of an anionic species $[\text{Ni}(\text{L})_2]^{2-}$, as is evident from the formation of the trinnuclear complexes containing a nickel-oximate unit. The anionic species produced in this way can now function as a ligand for the coordinatively unsaturated ML^{2+} moieties. In the presence of a counterion, nitrates are assembled in this manner in acceptable yields (46–38%). The presence or absence of significant vibrations in the generally complicated IR spectra has been utilized to establish the nature of the trinnuclear complexes. The monomeric $[\text{Ni}(\text{HL})_2]$ has appreciable IR absorption at around 1725 cm^{-1} due to the O-HO bending vibrations of the hydrogen bond. These absorptions are missing in the spectra of trinnuclear complexes **10** and **11**, indicating that the enolic hydrogen atoms are lost on complexation. The medium-strong bands appearing at $991\text{--}998\text{ cm}^{-1}$ are assignable to the stretching vibrations of N-O, which are shifted towards lower frequency according to the mononuclear species. The stretching vibrations of C=N groups of these complexes observed at around $1642\text{--}1645\text{ cm}^{-1}$ appear at a significantly higher frequency than that for the mononuclear complex due to formation of positively charged ML^{2+} , which stabilizes the negative charge on the oxygen of the oximate function, thus increasing the double-bond character of the C=N groups. The FAB mass spectra of these

complexes (**10** and **11**) show the expected molecular peaks at $m/z=1942$, 1876 and 1664, 1422. The latter peaks indicate the loss of $M\text{-phen-NO}_3^-$ from complexes.

The electronic spectra of the ligand and its complexes were determined in THF solutions, except for mononuclear complexes in the range 800–200 nm. All the spectra obey Beer's law in the concentration range $(1\text{--}4) \times 10^{-4}$ mol dm $^{-3}$. Significant energetic and distributional changes in the π -electron cloud of the C=N groups are observed on complex formation by the ligand, as is evidenced from IR spectral data. These changes should also be observable for the mono- or heterotrimeric complexes. The absorption maximum of the free ligand (H_2L) at 246 nm is due to a $\pi \rightarrow \pi$ transition of the C=N group and shifts for the mononuclear complexes to lower energy at 272–262 nm in a basic medium due to complexation. The trinuclear complexes in general exhibit two or more absorptions in the region 240–360 nm due to the intraligand $\pi \rightarrow \pi$ and MLCT (metal–ligand charge-transfer) transitions with very high extinction coefficients. For the mononuclear complexes, apart from the ligand band in the abovementioned region, there are new absorptions at 570, 476–475, 398 and 360 nm. Metal-to-ligand charge transfer transitions can occur in these complexes where the unsaturated ligands such as dioximes, which contain empty antibond-

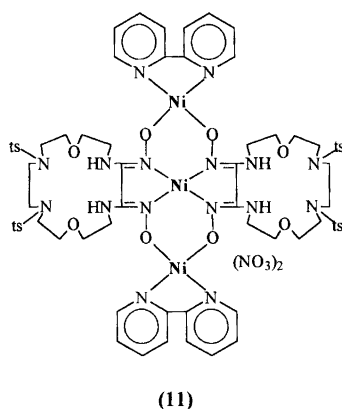
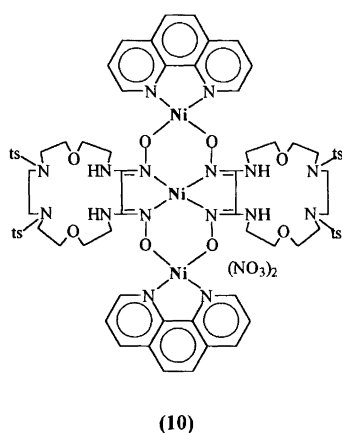
ing π -orbitals, are bonded to another transition metal. Medium strong bands appear at 444 nm for **5** and 556 nm for **6** on the low-energy side of the charge-transfer bands. These transitions are considered to be a spin-allowed d–d transition.^{4,28} The intense absorption band in the region 440–476 nm can be assigned to the ligand-to-metal charge-transfer transition from the binding oximate oxygen nonbonding orbital to the vacant 3d orbital of the metal ion. The fact that this band is lacking in the visible spectrum of mononuclear complexes supports this conclusion.²⁹ Complexes **10** and **11** show four bands at 552, 540, 467 and 461 nm as a shoulder. The latter two bands may be assigned to the d–d transition bands of the planar $N(L)_2^{2-}$ chromophore, but the former absorptions can be attributed to the d–d transition bands of the nickel(II) ions related to end-cap ligands.

Experimental

General. 1H and ^{13}C NMR spectra were recorded on a Bruker ARX400 high-field Fourier transform spectrometer. Mass spectra and metal contents of the complexes were measured on a Kratos MS-50 triple analyzer mass spectrometer and a Unicam 929 AA spectrometer, respectively. IR spectra were recorded on Perkin–Elmer 1600 and Mattson 1000 FTIR spectrophotometers as KBr pellets. UV–VIS spectra and elemental analyses were performed on a Unicam UV2–100 UV–VIS spectrophotometer and on a Hewlett-Packard 185 CHN analyzer, respectively. (*E,E*)-Dichloroglyoxim¹¹ and 1,14-diamino-6,9-bis(toluene-*p*-sulfonyl)-3,12-dioxa-6,9-diazatetradecane¹⁰ were prepared by a reported procedure. Melting points were measured on an Electrothermal apparatus and are uncorrected.

Synthesis of (*E,E*)-dioxime and its complexes.

*2,3-Bis(hydroxyimino)-7,16-dioxa-10,13-bis(toluene-*p*-sulfonyl)-1,4,10,13-tetraaza cyclooctadecane, (H_2L).* A solution of (*E,E*)-dichloroglyoxime (**2**) (1.57 g, 10 mmol) in 50 ml of absolute ethanol was added dropwise over 3 h to a solution of 1,14-di-aminobis(toluene-*p*-sulfonyl)-3,12-dioxa-6,9-diazatetradecane (**1**) (5.6 g, 10 mmol) in 400 ml of degassed absolute ethanol under an argon atmosphere containing $NaHCO_3$ (5.0 g) in excess at 40 °C. The reaction mixture was kept at 65 °C for 5 h and then allowed to stand at room temperature and stirred for 12 h. The reaction mixture was evaporated to 25 ml under vacuum, and 400 ml of water which contained 0.5 g of Na_2SO_4 was added in order to prevent colloidal dispersion and stirred until the precipitate appeared. The precipitate was filtered off, washed with water, cold ethanol and diethyl ether, and then dried *in vacuo*. The crude product was crystallized from a mixture of methanol and chloroform (2/1) (5.5 g, 85.0%), m.p. 196–198 °C (dec.). 1H NMR (DMSO- d_6): δ 9.46 (s, 2 OH), 7.45 (d, 4 H, Ar–H), 7.23 (d, 4 H, Ar–H), 5.49 (s, 2 H, NH), 3.20–2.84 (m, 20 H, CH_2), 2.21 (s, 6 H, CH_3). ^{13}C NMR (DMSO- d_6): δ 143.49, 129.94,



126.74, 70.20–69.50, 20.97. IR (KBr): 3371 (N–H), 3216 (O–H), 3062 (Ar–H), 2934–2870 (C–H), 1649 (C=N), 1001 (N–O). cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 290 (3.84), 262 (4.02), 246 (4.15), 242 (4.08). Mass spectrum (FAB positive): $m/z = 627 [M+1]^+$, 608 $[M-\text{OH}_2]^+$. Found: C, 49.98; H, 5.91; N, 13.60. Calc. for $\text{C}_{26}\text{H}_{38}\text{N}_6\text{O}_8\text{S}_2$: C, 49.84; H, 6.07; N, 13.41.

[Ni(HL)₂] (3) and [Cu(HL)₂] (4). A solution of 1.15 mmol of metal salt [$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.27 g) or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.196 g)] in methanol (40 ml) was added to a hot solution of H_2L (1.35 g, 2.2 mmol) in methanol (100 ml) with continuous stirring. A distinct change in colour and a decrease in pH (pH 1.96–2.18) was observed, and the mixture was stirred and heated to 60 °C in a water bath for 2 h while an equivalent amount of methanolic solution of KOH (0.1 M) was added dropwise to maintain a pH value of ca. 5. On cooling to room temperature the solid product precipitated. It was filtered off, washed with water, ethanol and diethyl ether and then dried *in vacuo*.

[Ni(HL)₂] (3). Yield: 1.19 g (77.22%), m.p. 146–147 °C. ¹H NMR (DMSO-*d*₆): δ 17.15 (s, 2 H, O–HO), 7.73 (d, 8 H, Ar–H), 7.35 (m, 8 H, Ar–H), 5.68 (s, 4 H, NH), 3.60–3.31 (m, 40 H, CH₂), 2.46 (s, 12 H, CH₃). ¹³C NMR (DMSO-*d*₆): δ 143.71, 130.28, 127.28, 71.91–71.36, 21.12. IR (KBr): 3310 (N–H), 3051 (Ar–H), 2953–2876 (C–H), 1725 (O–HO), 1626 (C=N), 1010 (N–O) cm^{-1} . UV–VIS (DMSO) ($\log \epsilon$): λ_{max} 475 (3.57), 360 (5.51), 338 (3.49), 290 (3.70), 262 (3.79), 244 (4.06). Mass spectrum (FAB positive): $m/z = 1309 [M+1]^+$. Found: C, 47.31; H, 5.47; N, 12.99 Ni, 4.67. Calc. for $\text{C}_{52}\text{H}_{74}\text{N}_{12}\text{O}_{16}\text{S}_4\text{Ni}$: C, 47.68; H, 5.65; N, 12.83; Ni, 4.48.

[Cu(HL)₂] (4). Yield: 0.74 g (52.25%), m.p. 185 °C. IR (KBr): 3314 (N–H), 3059 (Ar–H), 2955–2881 (C–H), 1716 (O–HO), 1621 (C=N), 1012 (N–O) cm^{-1} . UV–VIS (DMSO) ($\log \epsilon$): λ_{max} 570 (3.39), 486 (3.57), 398 (3.78), 280 (4.19), 272 (4.20), 244 (3.56). Mass spectrum (FAB positive): $m/z = 1313 [M]^+$. Found: C, 47.38; H, 5.70; N, 12.92; Cu, 4.65. Calc. for $\text{C}_{52}\text{H}_{74}\text{N}_{12}\text{O}_{16}\text{S}_4$ Cu: C, 47.50; H, 5.63; N, 12.79; Cu, 4.83.

[Cu(L)₂Cu₂(phen)₂](NO₃)₂ (5) and [Cu(L)₂Cu₂(dpy)₂](NO₃)₂ (6). A solution of Lewis base [1,10-phenanthroline (0.07 g, 0.35 mmol) or 2,2'-bipyridine (0.05 g, 0.35 mmol)] in dry THF (15 ml) and a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.09 g, 0.35 mmol) in dry THF (15 ml) was added dropwise to a boiling solution of the [Cu(HL)₂] complex as an end-cap ligand (0.19 g, 0.15 mmol) in dry THF (40 ml). The reaction mixture was stirred and refluxed for 5 h and cooled to room temperature after which the mixture was filtered off, and washed with dry THF. The volume of the filtrate was reduced to 12 ml under reduced pressure, and diethyl ether was added dropwise with continuous stirring to this solution until the complex precipitated. The complex

was filtered off, washed with water, cold ethanol and diethyl ether, and then dried *in vacuo*.

[Cu(L)₂Cu₂(phen)₂](NO₃)₂ (5). Yield: 0.084 g (30.21%), m.p. 231–233 °C. IR (KBr): 3336 (N–H), 3061 (Ar–H), 2955–2878 (C–H), 1634 (C=N), 1370 (N–O), 1012 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 615 (3.03), 444 (3.16), 374 (3.72), 350 (3.70), 268 (3.65), 250 (3.71), 238 (3.50). Mass spectrum (FAB positive): $m/z = 1967 [M+2.5\text{H}_2\text{O}+1]^+$, 1561 $[M-2\text{phen}]^+$. Found: C, 47.59; H, 4.73; N, 13.23; Cu, 10.11. Calc. for $\text{C}_{76}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4\text{Cu}_3$: C, 47.43; H, 4.57; N, 13.10; Cu, 9.90.

[Cu(L)₂Cu₂(dpy)₂](NO₃)₂ (6). Yield: 0.096 g (35.34%), m.p. 197–199 °C. IR (KBr): 3330 (N–H), 3063 (Ar–H), 2933–2908 (C–H), 1636 (C=N), 1382 (N–O), 1009 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 626 (3.24), 556 (3.17), 580 (3.11), 476 (3.17), 394 (3.23), 290 (3.52), 266 (3.68), 240 (4.05). Mass spectrum (FAB positive): $m/z = 1882 [M+0.5\text{H}_2\text{O}]^+$. Found: C, 45.91; H, 4.53; N, 13.61; Cu, 10.01. Calc. for $\text{C}_{72}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4\text{Cu}_3$: C, 46.09; H, 4.69; N, 13.44; Cu, 10.16.

[Cu(L)₂Ni₂(phen)₂](NO₃)₂ (7). A mixture of 1,10-phenanthroline (0.07 g, 0.35 mmol) in dry THF (15 ml) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.102 g, 0.35 mmol) in dry THF (15 ml) solution was added dropwise to a solution of [Cu(HL)₂] (0.19 g, 0.15 mmol) in dry THF (40 ml). The reaction mixture was stirred and heated at reflux and the reaction conditions were kept at reflux temperature for 6 h. At the end of refluxing, the mixture was cooled to room temperature and filtered off, and then washed with dry THF. The filtrate was reduced to 15 ml under vacuum, and a small amount of diethyl ether was added dropwise to complete the precipitation. This was filtered off, washed with water, cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.08 g (28.90%), m.p. 172–174 °C. IR (KBr): 3368 (N–H), 3045 (Ar–H), 2929–2856 (C–H), 1630 (C=N), 1338 (N–O), 993 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 527 (3.11), 422 (3.23), 342 (3.36), 302 (3.48), 290 (3.54), 262 (3.76), 244 (4.09). Mass spectrum (FAB positive): $m/z = 1912 [M+1]^+$, 1733 $[M-\text{phen}+2]^+$, 1669 $[M-\text{phen}-\text{NO}_3]^+$. Found: C, 47.80; H, 4.75; N, 13.02; Cu, 3.19; Ni, 6.29. Calc. for $\text{C}_{76}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4$ CuNi₂: C, 47.67; H, 4.60; N, 13.17; Cu, 3.31; Ni, 6.13.

[Ni(L)₂Cu₂(phen)₂](NO₃)₂ (8) and [Ni(L)₂Cu₂(dpy)₂](NO₃)₂ (9). A solution of 0.35 mmol of Lewis base [phenanthroline (0.07 g) or 2,2'-bipyridine (0.05 g)] in dry THF (15 ml) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.09 g, 0.35 mmol) in dry THF (15 ml) was added to a solution of [Ni(HL)₂] (0.20 g, 0.15 mmol) in dry THF (40 ml) at reflux temperature. The mixture was kept at this reflux condition for 5 h after which the reaction mixture was cooled to room temperature and filtered off, and washed with THF. The volume of the filtrate was reduced to 10 ml under reduced pressure and diethyl ether was added dropwise with continuous stirring to the cloudy

mixture. This reaction mixture was allowed to stand in a refrigerator at -18°C overnight. Then the product was filtered off, washed with water, cold ethanol and diethyl ether, and dried *in vacuo*.

$[\text{Ni}(\text{L})_2\text{Cu}_2(\text{phen})_2](\text{NO}_3)_2$ (**8**). Yield: 0.112 g (38.22%), m.p. 247–249 $^{\circ}\text{C}$. IR (KBr): 3325 (N–H), 3055 (Ar–H), 2985–2864 (C–H), 1638 (C=N), 1380 (N–O), 1018 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 533 (3.39), 470 (3.24), 406 (3.02), 356 (3.19), 290 (3.63), 254 (4.03), 248 (4.05), 244 (4.03). Mass spectrum (FAB positive): $m/z=1917 [M+1]^+$, 1944 $[M+1.5\text{H}_2\text{O}+1]^+$, 1737 $[M-\text{phen}+1]^+$. Found: 47.69; H, 4.71; N, 13.30; Ni, 2.91; Cu, 6.40. Calc. for $\text{C}_{76}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4\text{NiCu}_2$: C, 47.55; H, 4.58; N, 13.14; Ni, 3.06; Cu, 6.62.

$[\text{Ni}(\text{L})_2\text{Cu}_2(\text{dpy})_2](\text{NO}_3)_2$ (**9**). Yield: 0.10 g (34.93%), m.p. 212–214 $^{\circ}\text{C}$. IR (KBr): 3326 (N–H), 3064 (Ar–H), 2923–2872 (C–H), 1640 (C=N), 1374 (N–O), 992 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 5.12 (3.22), 450 (3.37), 368 (3.56), 302 (3.99), 272 (4.07). Mass spectrum (FAB positive): $m/z=1870 [M+2]^+$, 1557 $[M-2\text{dipy}+1]^+$. Found: 46.50; H, 4.85; N, 13.64; Ni, 3.00; Cu, 6.93. Calc. for $\text{C}_{72}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4\text{NiCu}_2$: C, 46.21; H, 4.70; N, 13.47; Ni, 3.14; Cu, 6.79.

$[\text{Ni}(\text{L})_2\text{Ni}_2(\text{phen})_2](\text{NO}_3)_2$ (**10**) and $[\text{Ni}(\text{L})_2\text{Ni}_2(\text{dpy})_2](\text{NO}_3)_2$ (**11**). A solution of 0.35 mmol of Lewis base [1,10-phenanthroline (0.07 g) or 2,2'-bipyridine (0.05 g)] in THF (15 ml) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.102 g, 0.35 mmol) in THF (15 ml) was added dropwise to a boiling solution of $[\text{Ni}(\text{HL})_2]$ (0.20 g, 0.15 mmol) in THF (40 ml) with continuously stirring and reflux was maintained for another 5 h. The end of the period, the reaction mixture was cooled to room temperature, filtered off, and washed with THF. After filtration, the filtrate was evaporated to 10 ml under reduced pressure, and a small amount of diethyl ether was added dropwise until the precipitation appeared. This mixture was allowed to stand in a refrigerator overnight at -18°C . The reaction mixture was filtered off, washed with water, cold ethanol and diethyl ether, and then dried *in vacuo*.

$[\text{Ni}(\text{L})_2\text{Ni}_2(\text{phen})_2](\text{NO}_3)_2$ (**10**). Yield: 0.135 g (46.28%), m.p. 226–228 $^{\circ}\text{C}$. IR (KBr): 3315 (N–H), 3093 (Ar–H), 2922–2865 (C–H), 1642 (C=N), 1339 (N–O), 991 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 552 (3.51), 461 (3.34), 366 (3.74), 350 (3.71), 324 (3.74), 294 (3.89), 278 (4.02), 252 (3.55). Mass spectrum (FAB positive): $m/z=1942 [M+2\text{H}_2\text{O}]^+$, 1980 $[M+4\text{H}_2\text{O}+2]^+$, 1664 $[M-\text{phen}-\text{NO}_3]^-$. Found: C, 47.63; H, 4.76; N, 13.35; Ni, 9.04. Calc. for $\text{C}_{76}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4\text{Ni}_3$: C, 47.79; H, 4.61; N, 13.20; Ni, 9.23.

$[\text{Ni}(\text{L})_2\text{Ni}_2(\text{dpy})_2](\text{NO}_3)_2$ (**11**). Yield: 0.11 g (38.6%), m.p. 238–241 $^{\circ}\text{C}$. IR (KBr): 3306 (N–H), 3087 (Ar–H), 2920–2870 (C–H), 1645 (C=N), 1340 (N–O), 998 (N–O) cm^{-1} . UV–VIS (THF) ($\log \epsilon$): λ_{max} 540 (3.28), 467 (3.52), 368 (3.47), 336 (3.49), 306 (3.62), 292 (3.66), 276 (3.66), 246 (4.03). Mass spectrum (FAB positive):

$m/z=1876 [M+\text{H}_2\text{O}]^+$, 1640 $[M-\text{dipy}-\text{NO}_3]^-$, 1422 $[M-2\text{dipy}-2\text{NO}_3]^-$. Found: C, 46.31; H, 4.51; N, 13.29; Ni, 9.65. Calc. for $\text{C}_{72}\text{H}_{88}\text{N}_{18}\text{O}_{22}\text{S}_4\text{Ni}_3$: C, 46.44; C, 4.73; N, 13.54; Ni, 9.46.

Acknowledgements. Support for this research was used by The Research Fund of Karadeniz Technical University (Trabzon, Turkey). S.Z.Y. thanks the Scientific and Research Council of Turkey (Ankara, Turkey). We are also indebted to Professor C. C. Leznoff (York University, Canada) for assistance with the NMR and MS spectral data.

References

1. Kahn, O. *Angew. Chem., Int. Ed. Engl.* 24 (1985) 834.
2. Ginsberg, A. P. *Inorg. Chim. Acta Rev.* 5 (1971) 45; Gatteschi, D., Kahn, O. and Willett, R. D., Eds., *Magneto Structural Correlations in Exchange Coupled Systems*. D. Reidel, Dordrecht 1984.
3. Solomon, E. I. In: Que, L. Jr., Ed., *Metal Cluster in Proteins*, American Chemical Society, Washington, DC 1988, p. 116.
4. Birkelbach, F., Winter, M., Flörke, U., Haupt, H.-J., Butzlaff, C., Lengen, M., Bill, E., Trautwein, A. X., Wieghardt, K and Chaudhuri, P. *Inorg. Chem.* 33 (1994) 3990; Kahn, O. *Molecular Magnetism*, VCH Verlagsgesellschaft, Weinheim 1993; Chaudhuri, P., Winter, M., Della Vedova, B. P. C., Fleisshauer, P., Haase, W., Flörke, U and Haupt, H. J. *Inorg. Chem.* 30 (1991) 4291; Gatteschi, D., Kahn, O., Miller, J. S. and Palacio, F., Eds., *Magnetic Molecular Materials*, NATO ASI Series E, Vol. 198, Kluwer Academic, Dordrecht 1990.
5. Ruiz, R., Lloret, F., Julve, M., Munoz, M. C. and Bois, C. *Inorg. Chim. Acta.* 219 (1994) 179; Ruiz, R., Lloret, F., Julve, M., Faus, J., Munoz, M. C. and Solans, X. *ibid.* 213 (1993) 261.
6. Ruiz, R., Sanz, J., Cervera, B., Lloret, F., Julve, M., Bois, C., Faus, J. and Munoz, M. C. *J. Chem. Soc., Dalton Trans.* (1993) 1523; Luneau, D., Oshio, H., Okawa, H., Koikawa, M and Kida, S. *Bull. Chem. Soc. Jpn.* 63 (1990) 2212; Verdager, M., Julve, M., Michalowicz, A. and Kahn, O. *Inorg. Chem.* 22 (1983) 2524; Pei, Y., Journaux, Y. and Kahn, O. *ibid.* 28 (1989) 100; Sinn, E. In: Karlin, K. D. and Zubieta, J., Eds., *Biological and Inorganic Copper Chemistry*, Adenine Press, New York 1985.
7. Chakravorty, A. *Coord. Chem. Rev.* 13 (1974) 1; Mohanty, J. G., Baral, S., Singh, R. P. and Chakravorty, A. *Inorg. Nucl. Chem. Lett.* 10 (1974) 655; Baral, S. and Chakravorty, A. *Inorg. Chim. Acta.* 39 (1980) 1; Nichalson, G. A. Lazarus, C. R. and McCromick, B. J. *Inorg. Chem.* 19 (1980) 192.
8. Lloret, F., Ruiz, R., Julve, M., Faus, J., Journaux, Y., Castro, I. and Verdager, M. *Chem. Mater.* 4 (1992) 1150; Okawa, H., Koikawa, M., Kida, S., Luneau, D. and Oshio, H. *J. Chem. Soc., Dalton Trans.* (1990) 469.
9. Gok, Y. and Kantekin, H. accepted for publications in *J. Coord. Chem.* 1997; Bilgin, A., Karaböcek, S. and Gok, Y. *Trans. Met. Chem.* 22 (1997) 420.
10. Shimada, T., Kodera, M., Kawa, H. and Kida, S. *J. Chem. Soc., Dalton Trans.* (1992) 1121.
11. Lance, K. A., Goldsby, K. A. and Busch, D. H. *Inorg. Chem.* 29 (1990) 4437.
12. Erbaş, M., Ahsen, V., Gül, A. and Bekaroglu, O. *J. Organomet. Chem.* 335 (1987) 105.
13. Gordon, M. S., Sujka, S. A. and Krause, J. G. *J. Org.*

- Chem.* 91 (1969) 4694; Gok, Y. and Kantekin, H. *Acta Chem. Scand.* 51 (1997) 664.
14. Gök, Y. and Kantekin, H. *Chem. Ber.* 123 (1990) 1479; Gök, Y. and Kantekin, H. *N. J. Chem.* 19 (1995) 461.
 15. Nakamura, A., N;Konishi, A. and Otsuka, S. *J. Chem. Soc., Dalton Trans.* (1979) 488.
 16. Pedersen, S. B. and Larsen, E. *Acta Chem. Scand.* 27 (1973) 3291; Ma, M. S. and Angelici, R. J. *Inorg. Chem.* 19 (1980) 363; Nakamura, A., Konishi, A. and Otsuka, S. *J. Chem. Soc., Dalton Trans.* (1979) 488.
 17. Lance, K. A., Goldsby, K. A. and Busch, D. H. *Inorg. Chem.* 29 (1990) 4537; Abusamleh, A. S., Chmielewski, P. J., Warburton, P. R., Morales, L., Stephenson, N. A. and Busch, D. H. *J. Coord. Chem.* 23 (1991) 91.
 18. Gül, A. and Bekaroglu, O. *J. Chem. Soc., Dalton Trans.* (1983) 2537; Gok, Y. and Bekaroglu, O. *Synth. React. Inorg. Met.-Org. Chem.* 11 (1981) 621; Serin, S. and Bekaroglu, O. *Z. Anorg. All. Chem.* 496 (1983) 197; Gok, Y., Ertepinar, H. and Yıldız, S. *Z. Spect. Lett.* 23 (1990) 713.
 19. Ramanujam, V. V. and Alexander, V. *Inorg. Chem.* 26 (1987) 3124; Alexander, V. *Inorg. Chim. Acta.* 163 (1989) 25.
 20. Szczepura, L. F., Muller, J. G., Bessel, C. A., See, R. F., Janik, T. S., Churchill, M. R. and Takeuchi, K. *Inorg. Chem.* 31 (1992) 856; Gök, Y. and Kantekin, H. *Polyhedron.* 16 (1997) 2413; Gök, Y. and Kantekin, H. *Acta Chem. Scand.* 51 (1997) 664.
 21. Blinc, R. and Hadzi, D. *J. Chem. Soc.* (1958) 4536; Caton, J. E. and Banks, C. V. *Inorg. Chem.* 6 (1967) 1670; Ruiz, R., Sanz, J., Cervera, B., Lloret, F., Julve, M., Bois, C., Faus, J. and Munoz, M. C. *J. Chem. Soc., Dalton Trans.* (1993) 1623.
 22. Hamuryudan, E. and Bakaroglu, Ö. *Chem. Ber.* 127 (1994) 2483; Nakamoto, K., *Infrared and Raman of Inorganic and Coordination Compounds*, 3rd Edn., Wiley, New York 1978, p. 244.
 23. Zhong, Z. J., Okawa, H., Marsumoto, N., Sakiyama, H. and Kida, S. *J. Chem. Soc., Dalton Trans.* (1991) 497; Coucouvanis, D. *J. Am. Chem. Soc.* 92 (1970) 707; O'Bryan, N. B., Maier, T. O., Paul, I. C. and Drago, R. S. *ibid.* 95 (1973) 6640.
 24. Luneau, D., Oshio, H., Okawa, H. and Kida, S. *J. Chem. Soc., Dalton Trans.* (1990) 2283.
 25. Burger, K., Ruff, I. and Ruff, F. *Inorg. Nucl. Chem.* 27 (1965) 179.
 26. Luneau, D., Oshio, H., Okawa, H., Koikawa, M. and Kida, S. *Bull. Chem. Soc. Jpn.* 63 (1990) 2212.
 27. McKenzie, E. D. *Coord. Chem. Rev.* 6 (1971) 187; Okawa, H., Koikawa, M., Kida, S., Luneau, D. and Oshio, H. *J. Chem. Soc., Dalton Trans.* (1990) 469.
 28. Nishida, Y., Hayashida, K., Sumita, A. and Kida, S. *Inorg. Chim. Acta* 31 (1978) 19.
 29. Handa, M., Idehara, T., Nakano, K., Kasuga, K., Mikuriya, M., Matsumoto, N., Kodera, M. and Kida, S. *Bull. Chem. Soc. Jpn.* 65 (1992) 3241; Ruiz, R., Sanz, J., Lloret, F., Julve, M., Faus, J., Bois, C. and Munoz, C. *J. Chem. Soc., Dalton Trans.* (1993) 3035.

Received July 18, 1997.