Dinuclear Complexes of M^{II} Thiocyanate (M = Ni and Cu) Containing a Tridentate Schiff-Base Ligand: Synthesis, Structural Diversity and Magnetic Properties

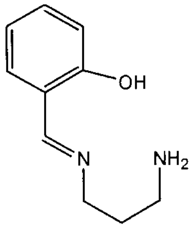
Suparna Banerjee,[a] Michael G. B. Drew,[b] Can-Zhong Lu,[c] Javier Tercero,[d] Carmen Diaz,*[d] and Ashutosh Ghosh*[a]

Keywords: Copper / Nickel / N,N,O ligands / Schiff-base ligands / Magnetic properties / Crystal structures

A dinuclear Ni^{II} complex, $[Ni_2(\mathbf{L})_2(H_2O)(NCS)_2]\cdot3H_2O$ (**1**) in which the metal atoms are bridged by one water molecule and two μ_2-phenolate ions, and a thiocyanato-bridged dimeric Cu^{II} complex, $[Cu(\mathbf{L})NCS]_2$ (**2**) [**L** = tridentate Schiff-base ligand, *N*-(3-aminopropyl)salicylaldimine, derived from 1:1 condensation of salicylaldehyde and 1,3-diaminopropane], have been synthesized and characterized by IR and UV/Vis spectroscopy, cyclic voltammetry and single-crystal X-ray diffraction studies. The structure of **1** consists of dinuclear units with crystallographic C_2 symmetry in which each Ni^{II} atom is in a distorted octahedral environment. The Ni–O distance and the Ni–O–Ni angle, through the bridged water molecule, are 2.240(11) Å and 82.5(5)°, respectively. The structure of **2** consists of dinuclear units bridged asymmetrically by di-$\mu_{1,3}$-NCS ions; each Cu^{II} ion is in a square-pyramidal environment with $\tau = 0.25$. Variable-temperature magnetic susceptibility studies indicate the presence of dominant ferromagnetic exchange coupling in complex **1** with $J = 3.1\ cm^{-1}$, whereas complex **2** exhibits weak antiferromagnetic coupling between the Cu^{II} centers with $J = -1.7\ cm^{-1}$.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

Dinuclear metal complexes and ligands facilitating their formation have been extensively investigated due to their potential applications in many field of chemistry.[1–10] The essential requirements for the formation of these dimeric complexes are an unsaturated coordination environment of the single-coordinated metal ion and the presence of bridging atoms or groups. The bridging abilities of the phenolate oxygen atom[11] and polyatomic moieties[12–15] (e.g. N_3, NCO, NCS, NCSe) have been exploited extensively for the synthesis of dinuclear species. However, it is very difficult to predetermine the structure of the self-assembled species when both types of bridging groups are present. Parameters that should be considered to achieve the desired species in such cases include the nature of the metal ions and their coordination requirement. In order to have an insight into the controlling parameters we have synthesized complexes of Ni^{II} and Cu^{II} with thiocyanate and the tridentate Schiff-base ligand **L** (Scheme 1), prepared by 1:1 condensation of salicylaldehyde and 1,3-propanediamine. We have found that Ni^{II} forms a phenolate-bridged dinuclear complex with thiocyanate acting as terminal ligand, whereas Cu^{II} yields an end-to-end thiocyanato-bridged dinuclear species having phenoxo as the terminal ligand.



Scheme 1. Ligand **L**.

The structural and magnetic properties of dinuclear nickel(II) complexes with bridging ligands have received considerable attention over the past two decades. Magneto-structural correlations have been made and interesting trends have emerged. Among these compounds, the azide group has been predominant due to its versatility as a ligand. When the N_3^- anion acts as bridging ligand, normally the end-to-end 1,3-coordination mode gives antiferromagnetic coupling, while the end-on 1,1-mode gives ferromagnetic coupling, but for very large M–$\mu_{1,3}$-N_3–M bond angles the magnetic coupling may be reversed.[16–19] For the SCN^- anion the bridging mode usually involves a 1,3-coordination mode with both nitrogen and sulfur atom bound to the metal ions. From crystal structures it has been shown

---

[a] Department of Chemistry, University College of Science and Technology, University of Calcutta, 92,
A. P. C. Road, Kolkata 700009, India
[b] School of Chemistry, The University of Reading,
P. O. Box 224, Whiteknights, Reading RG6 6AD, UK
[c] The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences,
Fuzhou, Fujian 350002, P. R. China
[d] Departament de Química Inorgànica,Universitat de Barcelona, Martí I Franquès 1–11, 08028 Barcelona, Spain

DOI: 10.1002/ejic.200500080

experimentally that in Ni^{2+} dinuclear complexes, all dinuclear $[Ni_2(\mu\text{-}NCS)_2]$ cores have approximately the same angles and distances, and they generally show low ferromagnetic behavior, which was explained by Ginsberg et al.[19d] and Duggan et al.[19e] Ferromagnetic interactions have been found, generally, in octahedrally coordinated dimeric nickel(II) complexes with 1,3-thiocyanate[16a,17] and -selenocyanate bridges.[18]

When the phenolate acts as a bridging ligand through the oxygen atom in dinuclear nickel(II) complexes, generally antiferromagnetic behaviour was found;[20–23] only three complexes showing ferromagnetic coupling have been described in the literature.[24] Complex **1**, is, to the best of our knowledge, the first dinuclear complex in which the octahedral Ni^{2+} ions share a face, and it is therefore of considerable interest that its magnetic behavior is ferromagnetic.

The study of polynuclear complexes of Cu^{II} with pseudohalogen bridges has received considerable attention in recent years.[25–29] Again, there are many examples of such complexes in which the azide group acts as a bridge. By contrast the literature available for magneto-structural studies on Cu^{II} complexes containing the bridging thiocyanate groups is scarce, as this ligand is less versatile and also less efficient as a transmitter of magnetic interactions than the azide.[26,27] Most of the previously reported asymmetric end-to-end 1,3-thiocyanate-bridged Cu^{II} compounds have octahedral geometry and exhibit very low values of J or paramagnetic behavior.[26a,28,29] There are only a few examples of double bridged end-to-end thiocyanato dimers in which the Cu^{II} atoms are five-coordinate.[28,30] The design of molecule-based magnets relies on the presence of both intra- and intermolecular coupling. Therefore, the identification of structural features that can be correlated with the strength and sign of this interaction clearly constitutes a necessary step in such design.

Results and Discussion

Synthesis

The monocondensed ligand *N*-(3-aminopropyl)salicylaldimine (**L**) was prepared as [Ni**L**$_2$] by the reaction of Ni^{II} nitrate, salicylaldehyde and 1,3-propanediamine (see Exp. Sect.). [Ni**L**$_2$] reacted readily with $Ni(SCN)_2$ in a 1:1 molar ratio in methanolic solution to produce the μ_2-phenolato- and aqua-bridged complex $[Ni_2(\mathbf{L})_2(H_2O)(NCS)_2]\cdot 3H_2O$ (**1**). The free ligand (**L**) which was isolated by removing nickel as bis(dimethylglyoximato)nickel(II) from [Ni**L**$_2$], on reaction with the methanolic solution of copper acetate followed by ammonium thiocyanate yielded the thiocyanato-bridged dinuclear complex $[Cu(\mathbf{L})NCS]_2$ (**2**).

IR Spectra

In the IR spectrum of complex **1**, a strong band at 2091 cm^{-1} is due to ν(CN) of the *N*-bonded thiocyanate and a band at 1626 cm^{-1} is due to ν(CO) of the phenolato-bridged ligand. The broad band in the range 3391–3340 cm^{-1} is assigned to the O–H stretching vibrations of uncoordinated and bridged water molecules.

In complex **2**, only one ν(CN) vibration at 2094 cm^{-1} is observed, due to the presence of bridging thiocyanato ligands and the ν(CS) is assigned at 782 cm^{-1}. The C=N stretch of the phenolate ligand is observed near 1630 cm^{-1} in both complexes. The two primary NH_2 stretching modes are clearly seen in **2** near 3310 and 3185 cm^{-1} for the asymmetric and symmetric vibrations respectively.

Description of Structure 1

The molecular structure of **1** is shown in Figure 1. Selected bond lengths and angles are summarized in Table 1. The dimeric structure shows a crystallographic two-fold

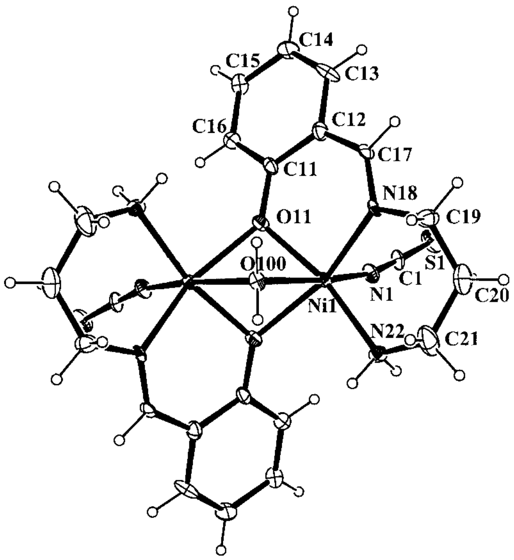


Figure 1. Perspective view of the complex **1** (30% thermal probability ellipsoids, for clarity hydrogen atoms and uncoordinated water molecules are omitted).

Table 1. Selected bond lengths [Å] and angles [°] for compound $[Ni_2(\mathbf{L})_2(H_2O)(NCS)_2]\cdot 3H_2O$ (**1**).

Ni1–O11	1.990(10)	Ni1–O11A	2.131(9)
Ni1–N18	2.035(10)	Ni1–O100	2.240(11)
Ni1–N1	2.039(12)	Ni1–Ni1A	2.953(4)
Ni1–N22	2.085(11)		
O11–Ni1–N18	91.5(4)	O11A-Ni1–O100	75.5(3)
O11–Ni1–N1	92.6(4)	N18–Ni1–N1	91.3(5)
O11–Ni1–N22	167.8(4)	N18–Ni1–N22	98.6(5)
N1–Ni1–N22	93.9(5)	O11A-Ni1–O11	76.3(4)
N18–Ni1–O11A[a]	163.8(4)	C11–O11–Ni1	124.8(8)
N1–Ni1–O11A	99.7(4)	C11–O11–Ni1A	141.2(8)
N22–Ni1–O11A	92.5(4)	Ni1–O11–Ni1A	91.5(4)
O11–Ni1–O100	78.3(3)	N18–Ni1–O100	91.8(4)
N1–Ni1–O100	170.5(4)	N22–Ni1–O100	94.5(4)
Ni1–O100–Ni1A	82.2(5)		

[a] A represents symmetry element –*x*, *y*, 0.5 – *z*.

axis through the bridging water molecule O100. The dinuclear unit is formed by two $\mathrm{Ni^{II}}$ atoms labeled Ni1 and Ni1A, bridged by this water molecule and by the two μ_2-phenolato oxygen atoms O11 and O11A of the Schiff-base ligands. The two equivalent nickel atoms have distorted octahedral environments. The basal plane $\mathrm{Ni_2N_2O_2}$ is formed by the two nitrogen atoms N18 and N22 and the two oxygen atoms O11 and O11A of the bridging phenoxo ligands. The N1 atom of the thiocyanato terminal ligand and the O100 atom of the bridging aqua ligand occupy the axial positions. The two Ni atoms are separated by 2.953(4) Å with two Ni–O11–Ni bridge angles of 91.5(4)° and one Ni–O100–Ni bridge angle of 82.5(5)°. The basal bond lengths around the Ni atom are in the range of 1.990(10)–2.131(9) Å. The apical bond lengths are Ni1–N1 2.039(12) Å and Ni1–O100 2.240(11) Å, the bond angle being O100–Ni1–N1 170.5(4)°. The Ni–NCS distance, 2.039(12) Å, is as expected. However, the Ni–$\mathrm{OH_2}$ distance, 2.240(11) Å, although comparable to those found in some aqua-bridged dinuclear $\mathrm{Ni^{II}}$ complexes,[31] is much longer than the range 2.09–2.16 Å reported for few other known examples of water bridges in $\mathrm{Ni^{II}}$ structures.[32] Some of this bond lengthening can be accounted for by the involvement of the bridging water molecule in hydrogen bonds to another water molecule O101. Another water molecule O102 is also hydrogen-bonded to the nitrogen atom of the thiocyanato ligand (Figure 2). The *cis* angles in the nickel polyhedra are all within 15° of 90° (Table 1). These distortions can be rationalized as resulting from the ligand constraints in the molecule, particularly in the bridging system.

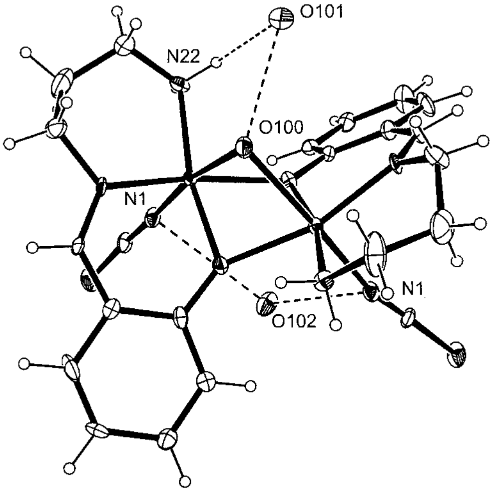


Figure 2. Hydrogen bonding in complex **1** involving uncoordinated water molecules (30% thermal probability ellipsoids, water molecules uninvolved in hydrogen bonding are omitted for clarity).

Description of Structure 2

Figure 3 shows an NCS-bridged copper dimer $[\mathrm{Cu_2}(\mathbf{L})_2(\mu\text{-NCS})_2]$, in which the asymmetric units are related by a centre of inversion. Selected bond lengths and angles are summarized in Table 2. The intradimer Cu–Cu distance is 5.863 Å. The copper atoms are located in a distorted square-pyramidal environment as revealed by the trigonal index, $\tau = 0.25$. The value of τ is defined as the difference between the two largest donor–metal–donor angles divided by 60, a value which is 0 for the ideal square pyramid and 1 for the trigonal bipyramid[33] In the present case τ is calculated as $(176.8 - 161.4)/60 = 0.25$. The elongated square-pyramidal (4 + 1) geometry of the copper(II) centers is constructed from a basal plane containing three ligating atoms, O, N2, N3 of the tridentate Schiff-base ligand and a nitrogen atom, N1 from the thiocyanate group. In addition, the elongated apical position is occupied by the weakly bonded sulfur donor atom S′ from the other centrosymmetrically related thiocyanato bridge at a distance of 2.952(1) Å (symmetry operation: $^1/_2 - x$, $^1/_2 - y$, $1 - z$); the bond angle at the axially coordinated Cu–S′–C1′ being 102.6(1)°. The metal–nitrogen and metal–oxygen distances involving the equatorial plane ($\mathrm{CuON_3}$) agree well with those generally found in five-coordinate $\mathrm{Cu^{II}}$ complexes.[26a,30] The metal atom is 0.064 Å above the basal plane in the direction of the apex, which is usual for square-pyramidal geometry. The dimeric units are related by translation along the *y* axis to form extended chains by strong interdimer hydrogen bonding between the amine nitrogen atom of one dimeric unit and the phenolate oxygen atom of the adjacent dimeric unit (N2A···O = 2.938 Å, H2A···O = 2.067 Å, ∠N2–H2A···O′ = 162.67°) (Figure 4). The shortest interdinuclear $\mathrm{Cu^{II}}$–$\mathrm{Cu^{II}}$ distance between the two H-bonded units is

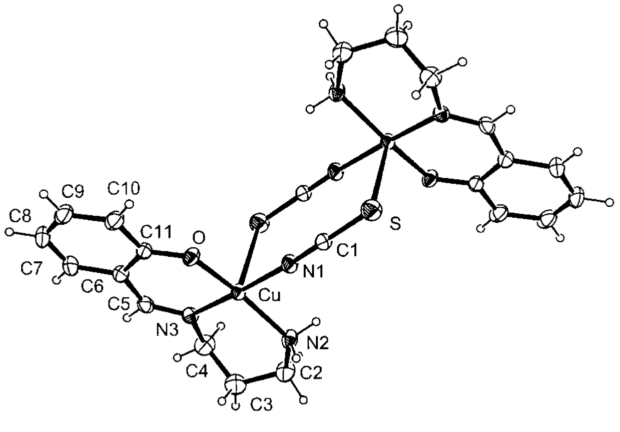


Figure 3. Perspective view of complex **2** (30% thermal probability ellipsoids).

Table 2. Selected bond lengths [Å] and angles [°] for compound $[\mathrm{Cu}(\mathbf{L})\mathrm{NCS}]_2$ (**2**).

Cu–O	1.910(2)	Cu–N2	2.019(3)
Cu–N3	1.964(3)	Cu–S′[a]	2.952(1)
Cu–N1	1.995(3)		
O–Cu–N3	93.33(11)	N1–Cu–N2	85.04(12)
O–Cu–N1	86.57(11)	S′–Cu–N1	92.15(10)
N3–Cu–N1	176.77(12)	S′–Cu–O	101.08(8)
O–Cu–N2	161.37(12)	S′–Cu–N3	84.70(9)
N3–Cu–N2	95.97(12)	S–Cu–N2	95.8310)

[a] The primes (′) refer to atoms related by the symmetry operation: $^1/_2 - x$, $^1/_2 - y$, $1 - z$.

3.571 Å. Numerous (thiocyanato)Cu^{II} complexes have been described in the literature; however, it is worth noting that most of them are made up of dinucleear entities and have octahedral coordination around Cu^{II} containing di-$\mu_{1,3}$-NCS bridges[17] whereas in the present complex end-to-end thiocyanato-bridged dimer the Cu^{II} atoms are five-coordinate.

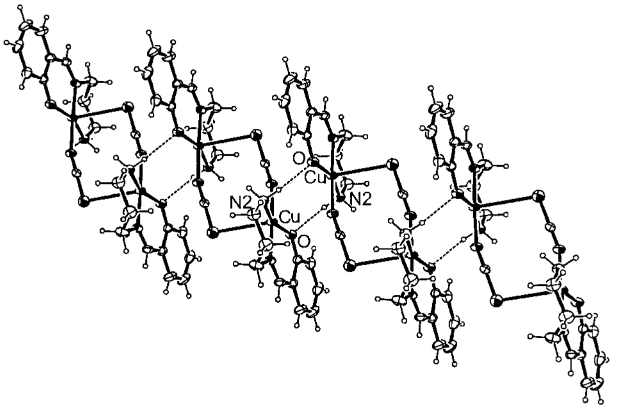


Figure 4. Molecular packing view of **2** along the *y* direction; the intermolecular hydrogen bonds are shown as dashed lines.

Electronic Spectra

The peaks in the electronic spectrum, taken in the solid state (Nujol mull) and in acetonitrile solution are similar in the two complexes.

The dinickel complex **1** exhibits two distinct bands at 610 and 874 nm and a weaker band near 773 nm. The first two bands can be assigned to the spin-allowed d-d transition $^3T_2 \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$, respectively, and the weaker band to the spin-forbidden transition $^1E_g \leftarrow {}^3A_{2g}$. These values are in agreement with the literature values for octahedral Ni^{II} compounds.[34]

The dicopper complex **2** shows a d-d transition around 612 nm. The UV absorption band observed at 358 nm can be assigned to the charge transfer transition. Strong absorption bands in the region 280 nm are clearly also due to charge transfer.

Electrochemical Study

The cyclovoltammogram of complex **1** in acetonitrile solution (Pt electrode) under nitrogen displays a electrochemically irreversible (ΔE_p = 120 mV) oxidative response attributed to the Ni^{II}/Ni^{III} couple at +0.70 V vs. SCE.

The cyclovoltammogram of the copper complex **2** recorded in dry acetonitrile solution (vs. SCE) at ambient temperature exhibits a reversible signal at +1.1 V (ΔE_p = 80 mV). The redox process is assigned to Cu^{2+}/Cu^{3+} oxidation. No reductive response of either Cu^{2+}/Cu^{1+} or Cu^{2+}/Cu was observed in the cathode sweep.

To ascertain the stoichiometry of the redox couple of the Cu^{II} complex **2** we performed constant potential exhaustive electrolysis at +1.25 V under ambient conditions. The coulomb count of the experiment revealed one electron oxidative transfer from Cu^{2+} resulting in the formation of Cu^{III} analogs. The oxidized Cu^{III} compound, however, is not isolable at room temperature but stable enough for EPR study at 77 K (toluene/acetonitrile mixture) to determine the metal valence. The oxidized compound is EPR-inactive under frozen glass conditions (77 K), thereby confirming the formation of a diamagnetic Cu^{III} species.

The other possibility of ligand oxidation has been far outweighed from this experimental observation, which otherwise would have resulted in an odd electron paramagnetic species (s = 1/2), sensitive towards EPR measurement. Therefore, it is justified to conclude the oxidative response at +1.1 V to be associated with a Cu^{II}/Cu^{III} oxidation instead of an energetically unfavourable phenolate moiety based ligand oxidation event.

Magnetic Properties

The variable-temperature magnetic properties $\chi_M T$ vs. T of **1** and **2** are illustrated in Figures 5 and 6, respectively.

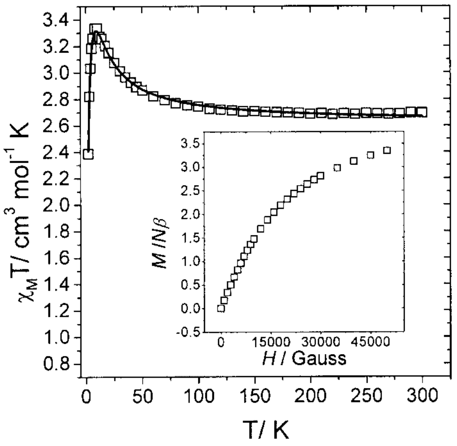


Figure 5. Plot of $\chi_M T$ [cm^3 mol^{-1} K] vs. T [K] in the range 2–300 K for **1**. The solid line is generated from the best-fit magnetic parameters. Inset: Plot of $M/N\beta$ vs. H for complex **1**.

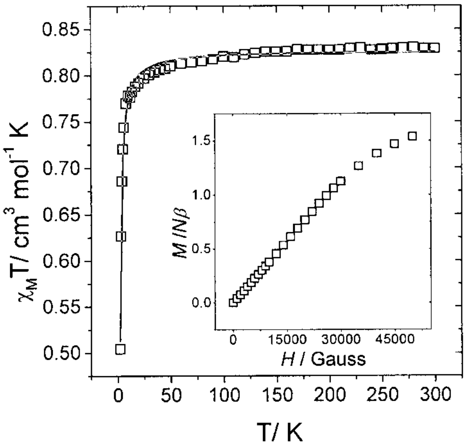


Figure 6. Plot of $\chi_M T$ [cm^3 mol^{-1} K] vs. T [K] in the range 2–300 K for **2**. The solid line is generated from the best-fit magnetic parameters. Inset: plot of $M/N\beta$ vs. H for complex **2**.

In complex **1** the $\chi_M T$ values (χ_M is the molar susceptibility for two Ni^{II} ions) show a gradual increase from a room-temperature value of 2.70 cm^{-1} mol^{-1} K to 3.25cm^{-1} mol^{-1} K at 6 K, followed by a drop at lower temperature. This behavior is typical of a system exhibiting dominant intramolecular ferromagnetic exchange coupling. The $\chi_M T$ vs. temperature curve for **1** was least-squares-fitted {by minimizing the function $R = \Sigma[(\chi_M T)_{exp.} - (\chi_M T)_{calcd.}]^2/\Sigma(\chi_M T)_{exp.}{}^2$} to the theoretical expression of magnetic susceptibility of Ginsberg et al.,[35] from the Hamiltonian

$$H = -2JS_1S_2 - D(S_{1Z}{}^2 + S_{2Z}{}^2) - g\beta H(S_1 + S_2) - Z'J'S\langle S\rangle$$

in which J is the intradimer exchange parameter, D the single-ion zero-field splitting, and $Z'J'$ the parameter for effective interdimer exchange; it is assumed that $g_x = g_y = g_z = g$. The resulting χ_M expression is:

$$\chi_M = 2Ng^2\beta^2/3k[F_1/(T - 4Z'J'F_1) + 2F'/(1 - 4Z'J'F')$$

F_1 and F' being complicated functions of temperature, zero-field splitting, and the intradimer exchange parameter J.

The best-fitting parameters obtained are J = 3.1(1) cm^{-1}, g = 2.29(1), D = 1.8(1) cm^{-1}, $Z'J'$ = –0.2(1) cm^{-1} with $R = 1.8\times10^{-5}$. These values should be considered with caution because, although the Ginsberg expression gives accurate values of J and g, the parameters D and $Z'J'$ are not well determined from magnetic susceptibility data.[35b,35c] The value of the reduced molar magnetization is 3.55 $N\beta$ when the field is 5 T (inset, Figure 5). This small value can be explained by the presence of either parameter D or antiferromagnetic interdimer interactions or by a combination of the two.

For complex **2** the value of $\chi_M T$ at 300 K is 0.83, which is expected for two magnetically quasi-isolated spin doublets ($g > 2.00$). This value remains practically constant upon cooling and then decreases sharply in the low-temperature region attaining a value of 0.50 at 2 K; no maximum of the magnetic susceptibility (χ_M vs. T) is observed. These observed features are characteristic of very weak antiferromagnetic interactions between copper(II) ions. We have analyzed the magnetic data through a simple Bleaney–Bowers expression for a copper(II) dimer,[36] derived through the isotropic Hamiltonian $H = -JS_1S_2$, where J is the exchange coupling parameter and $S_1 = S_2 = 1/2$ (interacting local spins). Least-squares fitting leads to the following parameters: J = –1.71(1) cm^{-1}, g = 2.10(1), and $R = 3\times10^{-5}$ {R is the agreement factor defined as: $R = \Sigma[(\chi_M T)_{exp.} - (\chi_M T)_{calcd.}]^2/\Sigma(\chi_M T)_{exp.}{}^2$}. Considering that in complex **2** the dinuclear entities are linked by structurally strong hydrogen bonds, the fit of the magnetic data has been carried out, too, by the Bleaney–Bowers expression taking into account the J' intermolecular parameter. The best-fit parameter obtained was J = –1.8 cm^{-1}, J' = 0.10 cm^{-1}, g = 2.10 and the same R value. The small positive J' value indicates that the hydrogen intermolecular interactions could be ferromagnetic. The value of the reduced molar magnetization is 1.55 $N\beta$ when the field is 5 T (inset in Figure 6). The shape of the curve formed by the experimental points does not follow the Brillouin formula. This feature is also indicative of the small antiferromagnetic coupling.

Discussion

Complex 1

The demonstration of a linear dependence of the exchange coupling constant (J) with the Cu–O–Cu bridge angle in planar dihydroxy-bridged dicopper(II) complexes has turned out to be one of the most useful and best known magneto-structural correlations.[37] Unlike hydroxo- and alkoxo-bridged Cu^{II} dinuclear complexes[38] structural modeling and magneto-structural correlations are scarce in nickel(II) complexes, due to fewer number of known complexes and to the large number of structural parameters that affect the superexchange mechanism in these systems. Dinuclear nickel(II) complexes in which one or two phenolate groups act as bridges are generally found to be antiferromagnetic.[20–23] Ferromagnetic behavior has been found in only three complexes[24] of which one has not been structurally characterized,[24a] while the other two have one of the nickel ions in a five-coordinate, trigonal-bipyramidal coordination environment. Correlations of the superexchange coupling in centrosymmetric Ni–O–Ni dinuclear nickel(II) complexes made by Nanda et al.,[21] and a quantumchemical ab initio study by Wang el al.,[39] show that the value of the exchange coupling constants is directly proportional to the Ni–O–Ni bridge angles or Ni···Ni distance. The results (at least qualitatively) are in very good agreement with nearly all measurements on such complexes: Thus, for Ni–O–Ni angles in the region of 90° the coupling is ferromagnetic with J values in the order of 10 cm^{-1}. The magnetic properties of **1**, which contain a distorted octahedral geometry around the Ni^{2+} ions and with a noncentrosymmetric structure, are interpreted in terms of two different bridges, the phenolate and the H_2O. The Ni–O–Ni′ bridge angle through the phenolato ligand is 91.5(4)° and the Ni···Ni distance is 2.953(4) Å. The Ni–O100–Ni′ bridge angle through the oxygen atom of the water molecule is 82.2(4)° and the Ni–O100 distance is 2.240(11) Å. Taking into account the small Ni···Ni distance and the small angles in the bridges, it is reasonable to assume a ferromagnetic exchange through the two kinds of bridges.

Complex 2

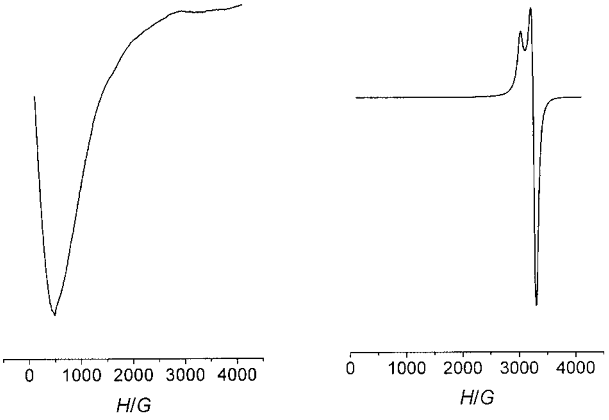
A weak but significant interaction between the copper(II) centers is observed through the end-to-end thiocyanato intrametallic bridges. Complex **2** shows the following features: (a) the copper(II) centers are bridged by two thiocyanate ions in an asymmetric end-to-end fashion, (b) the copper(II) ions are five-coordinated, (c) the nitrogen atom of the SCN bridge ligand lies in the equatorial plane and the sulfur ligand occupies the axial position. Few complexes with these characteristics are reported in the literature.[30]

The majority of the complexes described in the literature with NCS^--bridged ligand(s) with an N(basal)–S(apical) disposition, exhibit either very low values of J or paramagnetic behavior.[26a,28,29] This behaviour is characteristic of all complexes and does not seem to depend on either the topology of the copper(II) centers (usually octahedral) or the existence of single or double μ-NCS bridges.

EPR Measurements

The X-band EPR spectra of complexes **1** and **2** were recorded on microcrystalline powders at temperatures from 280 to 4 K.

It is of interest to note that in complex **1** the spectrum, recorded at low temperature, shows only one absorption at very low field (Figure 7a). For an axial integer $S = 2$ spin system, the zero-field interaction (D parameter) splits the m_s levels into two doublets $m_s = |\pm 2\rangle$ and $|\pm 1\rangle$ and one $m_s = 0$ state. Transitions between these Kramer doublets are not possible due to the D value expected for the nickel(II) ion. For a rhombic distortion, the E parameter splits the $m_s = |\pm 2\rangle$ and $m_s = |\pm 1\rangle$ Kramer doublets giving a Δ_2 and Δ_1 gap at zero field. The value of Δ_1 is strongly dependent on E and is usually much greater than the $g\beta H$ energy of an X-band measurement. In contrast, the Δ_2 increases as a function of E^2/D and the ±2 transition usually lies in the low-field region of the spectra.[40] This type of EPR spectrum is similar to that previously reported for manganese(III), iron(IV), and tetranuclear cobalt(II) spectra.[24b,41]



a) b)

Figure 7. EPR spectra of polycrystalline complexes **1** (a) and **2** (b) at 4 K.

The X-band EPR spectra of complex **2** shown in Figure 7b shows absorption features of axial symmetry with $g_{\parallel} = 2.22$ and $g_{\perp} = 2.08$. The observed g inequality ($g_{\parallel} > g_{\perp}$) is consistent with the square-pyramidal geometry of complex **2** with the unpaired electron residing in the $3d_{x^2-y^2}$ orbital thereby making $^2B_{1g}$ the ground state.

Conclusions

Two new complexes of Ni^{II} and Cu^{II} thiocyanate have been synthesized using an N,N,O-donor Schiff-base ligand. The tridentate ligand is chelated and the thiocyanate ion is coordinated to metal centers through the nitrogen atom in both complexes, as expected. However, the construction of the dinuclear entities occurs in very different ways. In complex **1** two Ni ions are bridged through the phenolate oxygen atom, and a water molecule acts as an additional bridge to complete the hexacoordination around the nickel ion. On the other hand, the sulfur atom of the *N*-bonded thiocyanato ligand coordinates axially to bridge the two copper atoms in complex **2**. The weak axial coordination and consequently the square-pyramidal geometry around Cu^{II} is probably dictated by the active Jahn–Teller effect of the d^9 system. Thus, the nature of the metal ion plays a very important role in the self-assembly of the mononuclear units into the dinuclear complex. From the magnetic point of view complex **1** is the first example where dinucluear Ni^{II}, simultaneously bridged by phenolato and aqua ligands, exhibits ferromagnetic behaviour.

Experimental Section

Starting Materials: Salicylaldehyde, 1,3-diaminopropane, $Cu(OAc)_2 \cdot H_2O$, ammonium thiocyanate and Ni^{II} salts were purchased from commercial sources and used as received. HPLC grade acetonitrile, was used for electrochemical and UV/Vis measurements and all other solvents were of reagent grade and were used without further purification.

Physical Measurements: Spectral measurements were carried out using the following equipments: UV/Vis (both in acetonitrile solution and solid), Hitachi-U 3501 Spectrophotometer. IR (KBr disc), Perkin–Elmer RXI FT-IR spectrometer and Nicolet Magna IR 750 Series II. A Perkin–Elmer 240C elemental analyzer was used for microanalysis (C, H, N). The magnetic measurements were carried out in the "Servei de Magnetoquimica (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL susceptometer in the temperature range of 2–300 K and the magnetic field was 1 T. Magnetization measurements were carried out in the same instrument at 2 K. EPR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer, varying the temperature between 4 and 300 K. Electrochemical measurements were performed under nitrogen using a PAR model Versastat-2 electrochemical analyzer, with a platinum working electrode under dry nitrogen. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the potentials are referenced to the saturated calomel electrode (SCE) without junction correction.

***N*-(3-Aminopropyl)salicylaldimine (L):** The complex bis(3-aminopropylsalicylideneiminato)nickel(II) ($C_{20}H_{26}N_4Ni$) was prepared by the method of Elder.[42] A solution of the ligand (10 mmol) was obtained by refluxing the Ni^{II} complex (2.06 g, 5 mmol) with 2 equiv. of DMG (1.16 g, 10 mmol) in methanol (20 mL) for 2 h and filtering the precipitated bis(dimethylglyoximato)nickel(II) according to the procedure of Burke and McMillin.[43]

$[Ni_2(L)_2(H_2O)(NCS)_2] \cdot 3H_2O$ (1): $Ni(SCN)_2$ (0.351 g, 1.5 mmol), dissolved in 10 mL of hot methanol, was added to a methanolic solution (10 mL) of bis(3-aminopropylsalicylideneiminato)nickel(II)

(0.619 g, 1.5 mmol) and stirred for 10 min. The colour of the solution turned to light green. The resulting solution, on keeping at room temperature for several hours, yielded a dark green crystalline solid. It was filtered and dissolved in a minimum volume of acetonitrile and kept in a refrigerator. Upon slow evaporation of the solvent, dark green crystals of complex **1,** suitable for X-ray analysis appeared after 2 d. Yield: 0.529 g (86%). $C_{22}H_{34}N_6Ni_2O_6S_2$ (660.06): calcd. C 40.03, H 5.19, N 12.73; found C 39.90, H 5.14, N 12.72.

[Cu(L)NCS]$_2$ (2): To a solution of **L** (0.534 g, 3 mmol) in methanol (10 mL), $Cu(OAc)_2 \cdot H_2O$ (0.598 g, 3 mmol), dissolved in a minimum volume of hot methanol, was added and stirred for 30 min. To the resulting solution, a methanolic solution of NH_4SCN (456 mg, 6 mmol) was added. The blue solution yielded needle-shaped crystals on keeping at room temperature for 24 h. Yield: 0.824 g (92%). $C_{11}H_{13}CuN_3OS$ (298.02): calcd. C 44.21, H 4.38, N 14.06; found C 44.15, H 4.30, N 14.51.

X-ray Crystallography: Data for both crystals were measured with Mo-K_α radiation (λ = 0.71073 Å) using a MARresearch Image Plate System for **1** and a Siemens SMART CCD diffractometer for **2**. For **1** the crystals were positioned at 70 mm from the image plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis for **1** was carried out with the XDS program[44] and for **2** with the SHELXAL$^{\text{TM}}$ V.5.03 program.[45] The structures were solved by direct methods (SHELX-86 program for **1**[46] and SHELXTL for **2**). Absorption corrections were carried out using DIFABS[47] for **1** and SADABS for **2**[48] The structures were then refined to convergence on F^2 using SHELXL for **1**[49] and SHELXTL for **2**. The non-hydrogen atoms were refined with anisotropic thermal parameters in all cases. For **1** the hydrogen atoms bonded to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they are attached. All calculations were carried out using SHELX-86, SHELXL-93, PLATON-99 for **1** and Siemens SHELXTL, Bruker SHELXTL for **2**. Selected bond lengths and bond angles of the crystals are presented in Tables 1 and 2. while selected crystallographic data for the two complexes are summarized in Table 3. Repeated recrystallization from acetonitrile failed to produce good-quality crystals of **1**. The poor quality of the crystals of **1** gave rise to misshapen large spots in the diffraction pattern which in turn led to high *R* values. CCDC-256766 (**1**) and -256767 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{22}H_{34}N_6Ni_2O_6S_2$	$C_{11}H_{13}CuN_3OS$
M	660.09	298.84
System	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a [Å]	8.735(11)	20.5473(10)
b [Å]	15.950(17)	7.2149(3)
c [Å]	21.31(2)	18.0073(7)
β [°]	100.807(10)	108.0170(10)
V [Å^3]	2916(6)	2538.62(19)
Z	4	8
D [mg m^{-3}]	1.503	1.564
T [K]	293(2)	293(2)
μ [mm^{-1}]	1.480	1.871
Independent reflections	2438	2216
R_{int}	0.0796	0.0166
Collected reflections	6483	3888
[$I > 2\sigma(I)$], R_1, wR_2	0.1423, 0.3010	0.0425, 0.1078

Acknowledgments

This work was supported by the University Grants Commission (UGC), India (Fellowship for S. B., Sanction No. UGC/548/jr. Fellow Sc 2001/2002). We like to thank the Spanish government (Grant BQU2003-00539) and EPSRC, the University of Reading for funds for the image plate system. We are thankful to Dr. S. Chaudhuri, RSIC, Bose Institute, Kolkata, India, for useful discussion on crystallography.

---

[1] P. Dapporto, M. Formica, V. Fusi, L. Giothi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi, *Inorg. Chem.* **2001**, *40*, 6186.

[2] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017.

[3] J. M. Lehn, *Pure Appl. Chem.* **1977**, *49*, 857.

[4] D. J. Gam, J. M. Gam, *Science* **1984**, *183*, 4127.

[5] J. M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89.

[6] P. Guerriero, S. Tamburini, P. A. Vigato, *Coord. Chem. Rev.* **1993**, *110*, 17.

[7] C. Bazzsicalupi, A. Bencini, V. Fusi, C. Giorgi, P. Paoletti, B. Vattacoli, *Inorg. Chem.* **1998**, *37*, 941 and references cited therein.

[8] D. A. Nation, A. E. Martell, R. I. Carroll, A. Clearfield, *Inorg. Chem.* **1996**, *35*, 7246.

[9] T. Koike, M. Inoue, E. Kimura, M. Shiro, *J. Am. Chem. Soc.* **1996**, *118*, 3091.

[10] a) C. Bazzsicalupi, A. Bencini, A. Bianchi, V. Fusi, E. Gracia-Espana, C. Giorgi, M. J. Llinares, J. A. Ramirez, B. Valtancoli, *Inorg. Chem.* **1999**, *38*, 620 and references cited therein; b) A. Bianchi, K. James-Bowman, E. Garcia-Espana, *Supramolecular Chemistry of Anions*, Wiley-VCH, New York, **1997**.

[11] a) A. S. Hay, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 505; b) H. Higashimura, M. Kubota, A. Shiga, K. Fujisawa, Y. Morooka, H. Uyama, S. Kobayashi, *Macromolecules* **2000**, *33*, 1986 and refercences therein; c) B. A. Jazdzewski, W. B. Tolman, *Coord. Chem. Rev.* **2000**, *200–202*, 633.

[12] a) J. Ribas, M. Monfort, I. Resino, X. Solans, P. Rabu, F. Maingot, M. Drillan, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2520; b) G. De Munno, M. Julve, G. Viau, F. Lloret, J. Faus, D. Viterbo, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1807.

[13] a) E. A. Mauro, I. S. Klein, A. C. Saldana, D. Simone, J. Zukerman-Schpector, E. E. Castellano, *Polyhedron* **1990**, *9*, 2937; b) R. Vicente, A. Escuer, E. Penalba, X. Solans, M. Font-Badia, *J. Chem. Soc., Dalton Trans.* **1994**, 3005.

[14] a) M. Monfort, J. Ribas, X. Solans, *Inorg. Chem.* **1994**, *33*, 4271; b) R. Vicente, A. Escuer, J. Ribas, X. Solans, *J. Chem. Soc., Dalton Trans.* **1994**, 259.

[15] a) J. Ribas, C. Diaz, X. Solans, M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* **1997**, 35; b) J. Ribas, C. Diaz, R. Costa, X. Tercero, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1998**, *37*, 233.

[16] a) R. Cortes, T. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M. I. Arriortua, *J. Chem. Soc., Dalton Trans.* **1992**, 2723; b) M. I. Arriortua, R. Cortes, L. Lezama, T. Rojo, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta* **1990**, *174*, 263.

[17] M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo, G. Villenueve, *Transition Met. Chem. (Weinheim, Ger.)* **1988**, *13*, 371.

[18] a) M. D. Duggan, D. N. Hendrickson, *Inorg. Chem.* **1974**, *13*, 2929; b) A. E. Shrelashvili, M. A. Porii-Koshits, A. S. Antsyshkina, *J. Struct. Chem. (Engl. Transl.)* **1969**, *10*, 552; c) T. Rojo, R. Cortes, L. Lezama, I. M. Arriortua, G. Villenueve, *J. Chem. Soc., Dalton Trans.* **1991**, 1779.

[19] a) C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, E. K. Barefield, R. L. Martin, *Inorg. Chem.* **1975**, *14*, 604; b) P. Chaudhuri, M. Gottmann, D. Ventur, K. Wieghardt,

B. Nuber, J. Weiss, *J. Chem. Soc., Chem. Commun.* **1985**, 1618; c) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–195*, 1027–1068; d) A. P. Ginsberg, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* **1972**, *11*, 2884; e) D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* **1974**, *13*, 2929.

[20] a) S. L. Lambert, D. N. Hendrickson, *Inorg. Chem.* **1979**, *18*, 2683; b) C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne, D. N. Hendrickson, *Inorg. Chem.* **1981**, *20*, 1229.

[21] a) K. K. Nanda, L. K. Thompson, J. N. Bridson, K. Nag, *J. Chem. Soc., Chem. Commun.* **1994**, 1337; b) K. K. Nanda, R. Das, K. Venkatsubramanium, P. Paul, K. Nag, *Inorg. Chem.* **1994**, *33*, 1188 and references cited therein.

[22] E. Berti, A. Caneschi, C. Daiguebonne, P. Dapporto, M. Formica, V. Fusi, L. Giorgi, A. Guerri, M. Micheloni, P. Paoli, R. Pontelli, P. Rossi, *Inorg. Chem.* **2003**, *42*, 348.

[23] a) T. Koga, H. Furutachi, T. Nakamura, N. Fukita, M. Ohba, K. Takahaski, H. Okawa, *Inorg. Chem.* **1998**, *37*, 989; b) S. K. Dey, N. Mondal, M. S. El Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardia, V. Gramlich, S. Mitra, *Inorg. Chem.* **2004**, *43*, 2427.

[24] a) K. K. Nanda, A. W. Addison, N. Paterson, E. Sinn, L. K. Thompson, U. Sakaguchi, *Inorg. Chem.* **1998**, *37*, 1028; b) D. Volkmer, B. Hammerich, K. Griesar, W. Haase, B. Krebs, *Inorg. Chem.* **1996**, *35*, 3792.

[25] a) A. H. Norbury, A. I. P. Q. Sinha, *Rev. Chem. Soc.* **1970**, *24*, 69; b) O. Kahn, Y. Pei, Y. Journaux, in: *Inorganic Materials*, 2nd ed. (Eds.: W. Q. Bruce, D. O'Hare), John Wiley, Chichester, U. K. **1997.**

[26] a) M. Julve, M. Verdaguer, G. De Munno, J. A. Real, G. Bruno, *Inorg. Chem.* **1993**, *32*, 795; b) M. Cannas, G. Carta, G. Marongis, *J. Chem. Soc., Dalton Trans.* **1973**, 556; c) M. Kabesova, M. Dunaj-Jurco, J. Soldanova, *Inorg. Chim. Acta* **1987**, *130*, 105; d) L. Walz, W. Haase, *J. Chem. Soc., Dalton Trans.* **1985**, 1243.

[27] a) J. G. Haasnoot, W. L. Driessen, J. Reedijk, *Inorg. Chem.* **1984**, *23*, 2803; b) C. Harding, D. Mc Dowell, J. Nelson, S. Raghunathan, C. Stevenson, M. G. B. Drew, P. C. Yates, *J. Chem. Soc., Dalton Trans.* **1990**, 2521.

[28] a) N. N. Karan, S. Mitra, T. Matsushita, V. Gramlich, G. Rosair, *Inorg. Chim. Acta* **2002**, *332*, 87; b) P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi, G. predieri, *J. Chem. Soc., Dalton Trans.* **1975**, 2357; c) J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quiros, E. R. T. Tickink, *Inorg. Chem.* **1997**, *36*, 4988; d) P. Gomez-Saiz, J. Garcia-Tojal, F. J. Arnaiz, M. A. Maestro, L. Lezama, T. Rojo, *Inorg. Chem. Commun.* **2003**, *6*, 558; e) R. Vicente, A. Escuer, E. Penalba, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta* **1997**, *7*, 255.

[29] a) S. Ferlay, G. Francese, H. W. Schamalle, S. Decurtis, *Inorg. Chim. Acta* **1999**, *286*, 108; b) C. Diaz, J. Ribas, N. Sanz, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta* **1999**, *286*, 169; c) H. Grove, M. Julve, F. Lloret, P. E. Kruger, K. W. Tornroos, J. Sletten, *Inorg. Chim. Acta* **2001**, *325*, 115; d) Z. E. Serna, R. Cotes, M. K. Urtiaga, M. G. Barandika, L. Lezama, M. I. Arriortua, T. Rojo, *Eur. J. Inorg. Chem.* **2001**, 865; e) M. Soibinet, I. Dechamps-Oliver, E. Goillon, J. P. Barbier, M. Aplicourt, F. Chuburu, M. Le Baccen, H. Handel, *Eur. J. Inorg. Chem.* **2003**, 1984; f) P. G. Saiz, J. Garcia-Tojal, F. J. Arnaiz, M. A. Maestro, L. Lezama, T. Rojo, *Inorg. Chim. Acta* **2003**, *6*, 558.

[30] a) M. B. Cingi, A. M. Manotti Lanfredi, A. Tiripicchio, J. G. Haasnoot, J. Reedijk, *Inorg. Chim. Acta* **1983**, *72*, 81; b) R. Vicente, A. Escuer, E. Penalba, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta* **1997**, *255*, 7; c) J. G. Haasnoot, W. L. Driessen, J. Reedijk, *Inorg. Chem.* **1984**, *23*, 2803.

[31] a) E. D. Mckenzie, *Inorg. Chim. Acta* **1979**, *32*, 253; b) D. Volkmer, B. Hommerich, K. Griesar, W. Haase, B. Krebs, *Inorg. Chem.* **1996**, *35*, 3792; c) A. M. Barrios, S. J. Lippard, *J. Am. Chem. Soc.* **1999**, *121*, 11751.

[32] a) U. Turpeinen, *Finn. Chem. Lett.* **1976**, 173; U. Turpeinen, *Finn. Chem. Lett.* **1977**, 36; U. Turpeinen, *Finn. Chem. Lett.* **1977**, 123; b) M. Ahlgren, R. Hamalainen, U. Turpeinen, *Cryst. Struct. Commun.* **1977**, *6*, 829.

[33] A. W. Addison, T. Nageswara Rao, J. Reedijk, J. Vanrijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

[34] a) W. Henke, D. Reinen, *Z. Anorg. Allg. Chem.* **1977**, *436*, 187; b) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1986**.

[35] a) A. P. Ginsberg, *Inorg. Chim. Acta* **1971**, *5*, 45; b) M. D. Duggan, E. K. Barefield, D. N. Hendrickson, *Inorg. Chem.* **1973**, *12*, 985; c) L. P. Battaglia, A. Bianchi, A. Bonamartini-Corradi, E. Garcia-Espana, M. Micheloni, M. Julve, *Inorg. Chem.* **1988**, *27*, 4174.

[36] B. Bleaney, K. D. Bowers, *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

[37] a) V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, W. E. Hatfield, *Inorg. Chem.* **1976**, *15*, 2107; b) D. J. Hodgson, *Prog. Inorg. Chem.* **1975**, *19*, 173.

[38] a) E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *Inorg. Chem.* **1997**, *36*, 3683; b) E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297.

[39] C. Wang, K. Fink, V. Staemmler, *Chem. Phys.* **1995**, *192*, 25.

[40] A. Abragam, B. Bleaney, in: *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, New York, **1986**, pp. 209–216.

[41] a) S. L. Dexheimer, J. W. Gohdes, K. S. Hagen, W. H. Amstrong, M. P. Klein, *J. Am. Chem. Soc.* **1989**, *111*, 8923; b) K. L. Kostka, B. G. Fox, M. P. Hendrich, T. J. Collins, C. E. F. Rickard, L. J. Wright, E. Munch, *J. Am. Chem. Soc.* **1993**, *115*, 6746; c) G. S. Papaefstathiou, A. Escuer, C. P. Raptopoulou, A. Terzis, S. P. Perlepes, R. Vicente, *Eur. J. Inorg. Chem.* **2001**, 1567.

[42] R. C. Elder, *Aust. J. Chem.* **1978**, *31*, 35.

[43] P. J. Burke, D. R. Mcmillin, *J. Chem. Soc., Dalton Trans.* **1980**, 1794.

[44] W. Kabsch, *J. Appl. Crystallogr.* **1988**, *21*, 916.

[45] G. M. Sheldrick, *SHELXTL*™, V.5.03, Bruker Analytical X-ray Systems, Madison, WI, USA, **1994**.

[46] *SHELX86*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[47] *DIFABS*: N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

[48] G. M. Sheldrick, *SADABS, Aborption Correction Program*, University of Göttingen, Germany, **1996**.

[49] G. M. Sheldrick, *SHELXL, program for crystal structure refinement*, University of Göttingen, **1993**.

Received: January 25, 2005