ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis and EPR Study of $K_8Cu_2Hg_2As_2W19O67$ (H_2O): Cu (II) Dimer Encapsulated in a Polyoxometalate Lattice

Jeyabalan T*, and Praveen Peter

Department of Chemistry, Sacred Heart College, Tirupattur- 635 601, India

ABSTRACT

EPR studies have been carried out on K8 [Cu2Hg2As2W19O67 (H2O)] in single crystal at 300 K. Single crystal EPR is used to study the dipolar interaction between Cu (II) centers. The appearance of seven lines with intensity ratio 1:2:3:4:3:2:1 clearly shows the interaction between two copper nuclei. The fine structure lines arising from S = 1 ground state are successfully analyzed and the various spin Hamiltonian parameters extracted are, $g_{||} = 2.247$, $g_{\perp} = 2.091$ and $D = 0.0366$ cm^{-1}. The Cu-Cu interaction is mainly dipolar in nature and based on the experimental D value the locations of Cu atoms in the lattice are speculated.

***Corresponding author**

INTRODUCTION

Polyoxometalate complexes are considered to be useful models for metal-oxide catalysts because of their ability to accommodate transition metal ions at specific sites and to undergo multi-electron reduction [1-3]. Since these compounds are structurally rich, they can be used as building blocks for designing molecular based ferromagnets [4,5]. Recently transition ion substituted polyoxometalates have attracted additional interest as model systems for studying exchange interaction in clusters [5]. Additionally these compounds offer ideal structural support to study the interactions between delocalised electron and the paramagnetic metal ion. Because the magnetic clusters of the paramagnetic ions are encapsulated in the diamagnetic, large size polyoxometalate fragments, complications arising from intermolecular interactions become negligible in these compounds. EPR and magnetic susceptibility measurements have been used to study interaction between the paramagnetic metal ions in these centers [6,7]. Most of the EPR studies have been, however, made on mainly powder samples.

In our continued interest to study substituted polyoxometalates, in this paper we report our attempt to synthesise copper clusters by replacing mercury in the polyoxometalate ion, $[Hg4As2W19O67(H2O)]^{10-}$. A dimeric copper center is identified by EPR spectroscopy. The dimeric Cu(II) cluster has been obtained as good crystal and single crystal EPR shows ferromagnetic interaction between the Cu(II) centers. The fine structure lines arising from S = 1 ground state are analyzed to probe the possible geometry of the ‘Cu2Hg2’ moiety. Although EPR of several dimeric Cu(II) complexes are known [8-13], here we report description of a dimeric Cu(II) center encapsulated in a polyoxometalate lattice.

EXPERIMENTAL

Materials

Mercurous nitrate, cupric nitrate, potasium nitrate and diarsenic oxide were obtained from Qualigens fine chemicals, India. Sodium tungstate was received from BDH fine chemicals, India. All the chemicals used were of AR grade and used without further purification.

Preparation of the compounds

K8[Cu2Hg2As2W19O67(H2O)] (I) was prepared based on the literature method [14] employed for the preparation of the parent compound K10[Hg4As2W19O67(H2O)] (II). (Hereafter the compounds (I) and (II) are referred to as PA-Cu2Hg2 and PA-Hg4).

a. Synthesis of PA-Cu2Hg2

Replacing mercurous nitrate in the above procedure by a mixture of copper nitrate and mercurous nitrate in the mole ratio of 2:2 green coloured PA-Cu2Hg2 was obtained. The salted out compound was dissolved in minimum amount of water. On slow evaporation at room temperature, light green coloured needle-shaped crystals were obtained within two weeks.

Found: Cu, 2.34; Hg, 7.41; As, 2.68; W, 60.01; K8[Cu2Hg2As2W19O67(H2O)] requires Cu, 2.30; Hg, 7.29; As, 2.71; W, 59.51 %.

Attempts to prepare trimeric and tetrameric compounds by using required mole ratio of copper nitrate, yielded products which were mainly a mixture of the dimeric and monomeric compounds.

Analytical and physical methods.

Arsenic and tungsten were estimated as pyrophosphate and oxinates. Mercury was estimated spectrophotometrically as mercury thiocyanate [15]. Copper was estimated using Perkin Elmer 380 atomic absorption spectrometer. IR spectra were recorded as KBr disks on a Perkin Elmer 783 spectrometer. EPR spectra were recorded using a Varian E 112 spectrometer equipped with 100 KHz field modulation. DPPH was used as an internal standard. X-band crystal rotation was performed in three mutually perpendicular planes. An insert type Dewar flask was employed to record EPR spectra at 77 K.

RESULTS AND DISCUSSION

Crystal structure of K10[Hg4As2W19O67(H2O)]

Single crystal X-ray diffraction study [14] of PA-Hg4 shows the polyoxoanion to crystallise in triclinic form with α = 78.49, ⍰ = 84.36 and ⍰ = 78.25°. The lattice parameters are a = 28.99, b = 18.82 and c = 16.88 Å and Z = 4. The structure of the anion [14] is given in Figure 1. The unit cell contains two asymmetrical AsW9O33 units in which the arsenic atoms are in the apex of the AsO3 pyramids. The two AsW9O33 units are linked by a WO6 octahedron. Of the six oxygen atoms in WO6, four atoms are shared with two AsW9O33 units, and the other two lie in a *trans* position at the vertices of the WO6 octahedron. The four mercury atoms in the anion form a rectangle whose sides are 2.49 and 3.73 Å. The two AsW9O33 units face each other, but are turned 90° with respect to each other. As a result the eight mercury atoms form a distorted cube [14] shown in Figure 2. The various Hg-Hg distances are listed in Table 1. Knowledge of the dispositions of Hg atoms helps to speculate the probable site for the Cu (II) (*vide infra*).

IR study

IR spectra of the compounds PA-Cu2Hg2 and PA-Hg4 are given in Figure 3. In general the compound PA-Cu2Hg2 shows absorption pattern similar to PA-Hg4, indicating that the two compounds possess similar heteropoly anion structure. The bands observed at the spectral region 960 and 890 cm^{-1} may be due to W-O terminal and W-O-W edge-sharing vibrations respectively [16].

Table 1: Distances between the various mercury atoms of the distorted cube of the anion*, [Hg4As2W19O67(H2O)]$^{10-}$

Atoms	Distance (Å)	Atoms in the triangle (Δ)	Chord distance (Å)
Hg1-Hg2	2.496	Hg2-Hg3 (Δ123)	4.543
Hg1-Hg5	3.303	Hg2-Hg3 (Δ234)	4.485
Hg1-Hg3	3.796	Hg7-Hg6 (Δ567)	4.461
Hg2-Hg4	3.760	Hg7-Hg6 (Δ678)	4.503
Hg2-Hg7	3.340	Hg7-Hg1 (Δ721)	4.169
Hg3-Hg4	2.440	Hg7-Hg1 (Δ715)	4.933
Hg3-Hg6	3.267	Hg8-Hg3 (Δ863)	4.965
Hg4-Hg8	3.732	Hg8-Hg3 (Δ843)	4.087
Hg5-Hg6	2.545	Hg7-Hg4 (Δ724)	5.029
Hg5-Hg7	3.664	Hg7-Hg4 (Δ784)	4.132
Hg6-Hg8	3.732	Hg1-Hg6 (Δ516)	5.031
Hg7-Hg8	2.521	Hg1-Hg6 (Δ563)	4.141

* From reference (14)

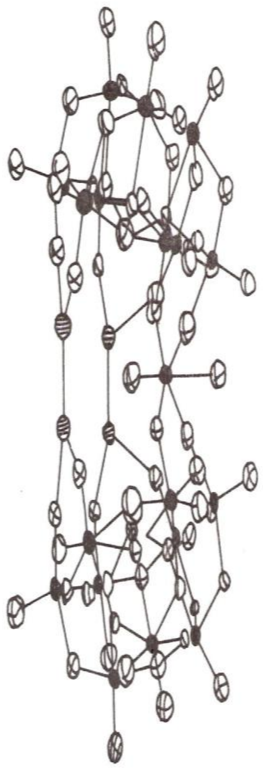

Figure 1 : The crystal structure of the anion $[As_2Hg_4W_{19}O_{67}(H_2O)]^{10-}$: black circles, tungsten atoms; striped circles, mercury atoms ; spotted circles, arsenic atoms.

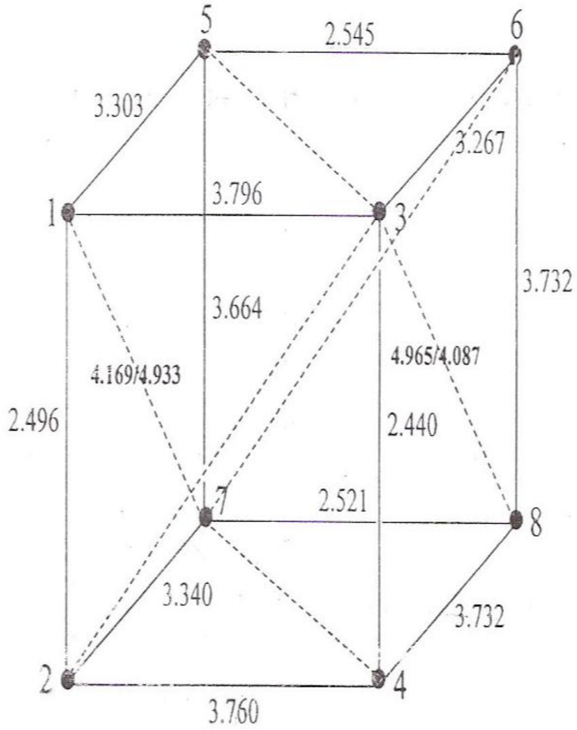

Fig. 2. The structure of the distorted cube of the anion $[As_2Hg_4W_{19}O_{67}(H_2O)]^{10-}$ Intra-atomic distances of mercury atoms are listed in Table 1.

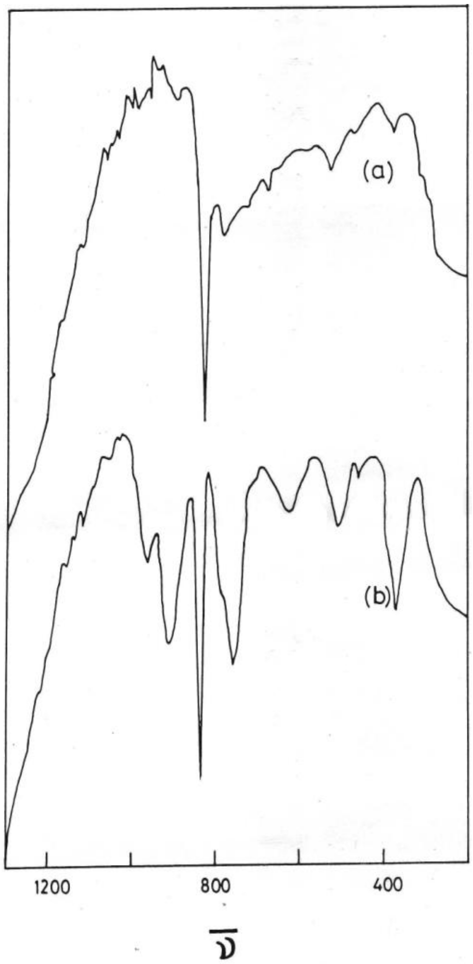

Figure.3. IR spectra of (a) $[As_2Hg_4W_{19}O_{67}(H_2O)]^{10-}$ and (b) $[Cu_2Hg_2W_{19}As_2O_{67}(H_2O)]^{8-}$ as KBr disks.

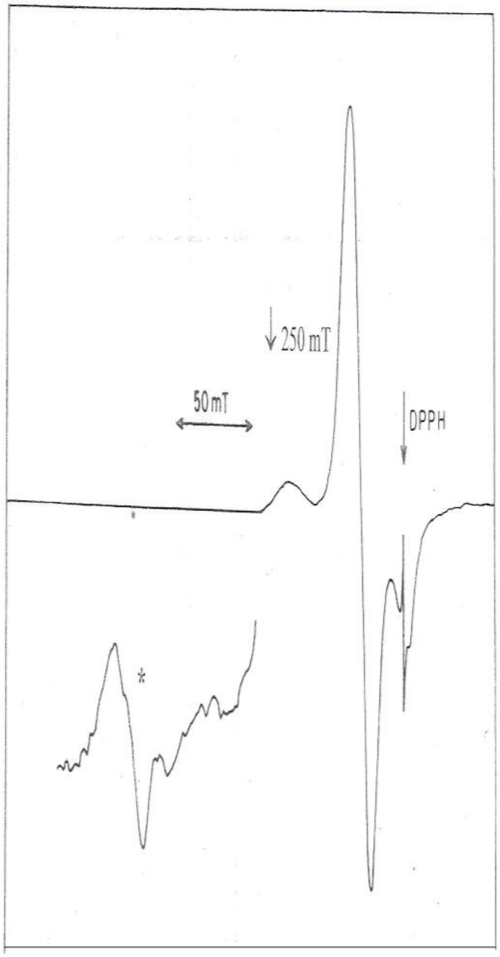

Figure. 4. Polycrystalline X-band EPR spectrum of $[As_2Cu_2Hg_2W_{19}O_{67}(H_2O)]^{8-}$ at 300 K. The $\Delta M_s = \pm 2$ transition is indicated by *.

EPR spectra

a. Powder spectrum

Line shape analysis of powder EPR spectra, has been extensively used to evaluate the zero-field parameters of S = 1 systems. Powder EPR spectrum of PA-Cu2Hg2, measured at 300 K, given in Figure 4, exhibits resonance lines at 307.5, 262.5 and 335 mT corresponding to ΔMs = ± 1 transitions. In addition to the ΔMs = ± 1 transitions, the forbidden ΔMs = ± 2 lines is also clearly visible around 155 mT. The intensities of the ΔMs = ± 1 and ΔMs = ± 2 signals follow the expected ratio, 1: $(D/B)^2$ where D is the zero-field splitting parameter. The field position of the half-field transition can be related to the average g value and the zero-field parameter by expression [17]

$$D^* = (D^2 + 3E^2)^{1/2} = \sqrt{3}/2\ [(g\square B0)^2 - (2g\square Bmin)^2]^{1/2} \qquad (1)$$

The spin Hamiltonian parameters obtained from the powder spectrum are given in Table 2.

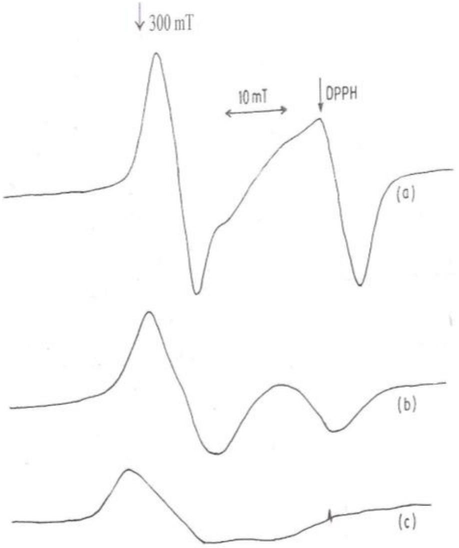

Figure. 5. Typical X-band single crystal EPR spectra of the anion $[As_2Cu_2Hg_2W_{18}O_{67}(H_2O)]^{8-}$ at 300 K.

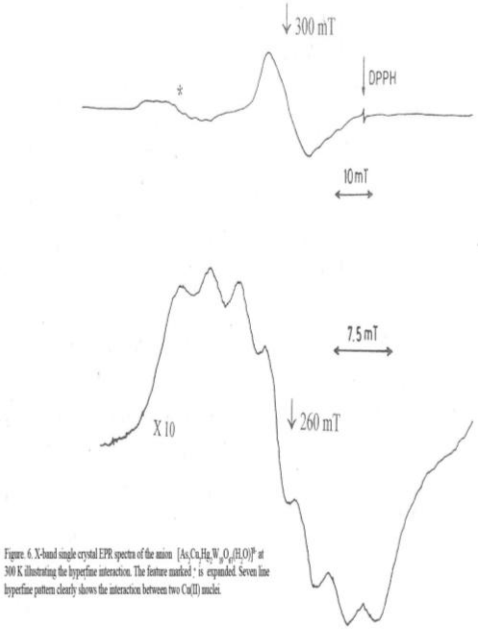

Figure. 6. X-band single crystal EPR spectra of the anion $[As_2Cu_2Hg_2W_{18}O_{67}(H_2O)]^{8-}$ at 300 K illustrating the hyperfine interaction. The feature marked * is expanded. Seven line hyperfine pattern clearly shows the interaction between two Cu(II) nuclei.

b. Single crystal EPR spectra

Due to the needle shaped nature of the crystals, the crystal was first rotated about the needle axis. Typical spectra recorded for rotation about needle axis are shown in Figure 5. As seen from the spectra, generally two resonances are observed. These two lines correspond to the expected ΔMs = ± 1 lines. The line widths vary from 5 to 8 mT.

Additionally, the hyperfine splitting due to copper nucleus is observed at certain orientations especially on the ΔMs = ± 2 line. This is shown in Figure 6. The ΔMs = ± 2 line could be clearly seen on high gain as shown in Figure 6. The seven line pattern follows the expected ratio for two equivalent copper nuclei *viz.,* 1:2:3:4:3:2:1. This observation supports the formation of copper dimer. The appearance of well resolved zero-field lines and the ΔMs = ± 2 line suggest the present system conform to case *i.e.* Hzee > HDip + HHF >> Hex.

When the crystal rotated about an axis perpendicular to the needle axis, the spectra showed similar behaviour. But the separation between fine structure lines was found to be maximum in this plane. Typical spectra recorded in this plane are shown in Figure 7. Further it is also noticed that around 300 mT, in addition to the S =1 resonance, features corresponding to S = 1/2 species were also seen. These spectra are due to mononuclear impurities and are believed to originate from defective sites in the lattices [18]. The variation of fine structure lines in this plane was followed for every ten degree and it is shown in Figure 8.

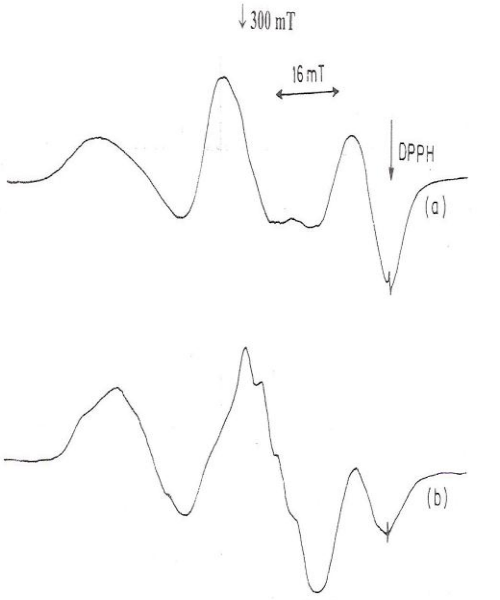

Figure. 7. X-band single crystal EPR spectra of the anion $[As_2Cu_2Hg_2W_{19}O_{67}(H_2O)]^{8-}$ at 300 K for the orientations corresponding to (a) maximum spread and (b) 90° away from the maximum spread. The features around 300 mT correspond to S = 1/2 species

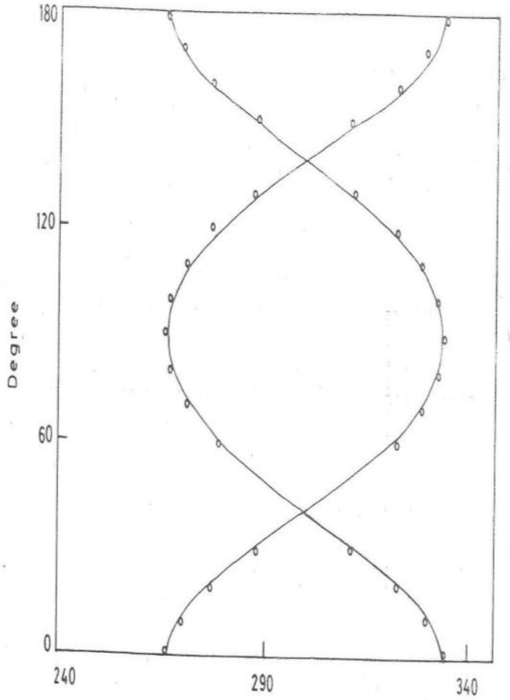

Fig. 8. The angular variation of the resonance lines at 300 K for the single crystal of the compound $[As_2Cu_2Hg_2W_{19}O_{67}(H_2O)]^{8-}$. The circles represent experimental points and solid lines correspond to calculated values.

The EPR spectra can be interpreted by the following spin Hamiltonian [19]

$$H = \square SgB + D[Sz^2 - S(S+1)/3] + E(Sx^2 - Sy^2) \qquad (2)$$

The EPR transitions derived from this Hamiltonian are given by the equation

$$h\nu = EM - EM-1 = g\square\ \square + (M - 1/2)\ [D\ (3g||^2\cos^2\theta\ /g^2-1) + 3E\ Cos\ 2\varphi\ (1-g||^2\cos^2\theta/g^2-1)] \qquad (3)$$

Where $B = h\nu/g\square$

$g^2\square\ \square g\square^2\sin^2\theta + g||^2\cos^2\theta$

$g\perp^2 = gx^2\ \cos 2\varphi + gy^2\sin 2\varphi$

Based on these equations the angular variation in this plane can be simulated successfully using the spin Hamiltonian parameters (given in Table 2). Figure 8, shows that there is good agreement between the experimental and the calculated angular variation of the $\Delta Ms = \pm 1$ transitions.

Table 2: Spin Hamiltonian parameters for PA-Hg2Cu2

PA-Hg2Cu2	g||	g⊥	D (cm^{-1})	E (cm^{-1})
Powder				
300 K	2.247	2.091	0.0366	0.0057
77 K	2.241	2.089	0.0361	0.0054
Single crystal 300 K	2.244	2.090	0.0364	0.0056

c. Zero-field splitting parameter

The experimentally observed zero-field splitting parameter may arise from a combination of two important interactions [20] namely

i) magnetic dipole-dipole interactions
ii) anisotropic exchange interactions
i.e. Dexptl = Ddd + Dex

Assuming that the contribution from the exchange interaction is not very siginificant Cu(II) - Cu(II) distance can be arrived from the experimentally observed zero-field splitting parameter. The dipole-dipole interaction is inversely proportional to the third power of the metal-metal distance. When the zero-field splitting is predominantly due to the dipolar interaction between the copper ions, the following equation [21], based on a point-dipole model, gives the copper-copper distance,

$$r = (0.650\ gav^2/D)^{1/3} \qquad (4)$$

Using gav (2.14) and D (0.0366) given in Table 6.2, r is approximately estimated to be 4.039 Å. As discussed in previous section, the eight mercury atoms in $[Hg_4As_2W_{19}O_{67}(H_2O)]^{10-}$ form distorted cube (Figure 2). The mercury-mercury distances are given in Table 1. The estimated mercury-mercury distance of 4.309 Å matches fairly with the length of the face diagonal *viz.,* 4.503 Å. Hence we speculate that the copper atoms have replaced the diagonally opposite mercury atoms of the faces of the cube. Thus in this paper it is shown that the location of the paramagnetic impurities in a polyoxometalate can be approximately estimated using EPR as a tool.

ACKNOWLEDGEMENTS

We thank RSIC, IIT, Chennai for EPR measurements. Thanks are due to UGC, New Delhi for financial support

REFERENCES

[1] Pastor NC, Serra JB, Coronado E, Baker LCW. J Am Chem Soc 1992; 114: 10380.

[2] Jeyabalan T. J Chem & Chem Sci 2011; 103:1.

[3] Pope MT. Heteropoly and Isopolyoxometalates; Springer, Verlag 1983.

[4] Mano JG, Song L, Ying X, Hang JS. Polyhedron 1997; 16: 963.

[5] Li JY, Zou JZ, Xu Z, You XA. Polyhedron 1996; 15: 3325.

[6] Gracia CJ, Coronado E, Romero PG, Pastor NC. Inorg Chem 1993; 32: 3378.

[7] Muller A, Peters F, Pope MT, Gatteschi D. Chem Rev 1998; 98:239.

[8] Koolhass GJA, Drissen WL, Reedijk J, Vanderplas JL, De graff RAG. Inorg Chem 1996; 35:1509.

[9] Gatteschi D, Goslar J, Hilezer W, Hoffman SK, Zanchini C. Inorg Chem 1996; 35:1148.

[10] Samantha R, Pal AK. Phys Stat Sol 1993; 179:195.

[11] Cheruiyot LL, Thompson LK, Greedan JE, Liu G. Can J Chem 1995; 73: 573.

[12] Hilezer W, Goslar J, Trit-Goc, Hoffman SK. Inorg Chem 1995; 34:1852.

[13] Cheng P, Bai L, Liao D, Yan S, Jiang Z, Wang G. Polyhedron 1995; 14: 2519.

[14] Martin-Frere J, Jeannin Y. Inorg Chem 1984; 23:3394.

[15] Vogel AI. A Text book of Quantitative Inorganic Analysis, ELBS, Fourth Edn. London 1978.

[16] Thouvenot R, Fournier M, Franck R, Deltcheff CR. Inorg Chem 1984; 23: 598.

[17] Sreehari N, Manoharan PT. Mol Phys 1988; 63: 1077.

[18] Bencini A, Gatteschi D. Electron Paramagnetic Resonance of Exchange Coupled Systems, Springer-Verlag 1990.

[19] Cho Y, So H. Bull Korean Chem Soc 1995; 16: 243.

[20] Felthouse TR, Hendrickson DN. Inorg Chem 1978; 17: 444.

[21] Yokoi H, Chikra M. J Am Chem Soc 1975; 14: 3975.