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FULL PAPER

Ferromagnetic exchange interaction of the Cu–Cu dimer $[Cu_2(picditn)(CH_3CO_2)(H_2O)_2Cl][ZnCl_4]\cdot 0.5H_2O$ [picditn = 1,11-bis(2-pyridyl)-2,6,10-triazaundecane] ‡

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Elemental analysis, IR and UV/VIS spectroscopy, magnetic susceptibility at room temperature and ESR at X- and Q-band at 300 and 77 K were carried out on the complex of formula $C_{20}H_{36}Cl_5Cu_2N_5O_{4.5}Zn$. Based on the elemental analysis, IR and UV/VIS results a bimetallic molecular structure is proposed where the acetate and the 1,11-bis(2-pyridyl)-2,6,10-triazaundecane groups bridge the copper(II) ions that locally have a square-based distorted pyramid geometry obeying approximately C_{4v} molecular symmetry or lower. The d–d transitions are tentatively assigned. From the measured magnetic moment, $\mu = 2.55\ \mu_B$, the calculated exchange interaction $J = +76\ cm^{-1}$, indicating an interaction of ferromagnetic character which is interpreted as being due to the accidental orthogonality of the bridged magnetic orbitals. The X- and Q-band spectra at 300 and 77 K show a single rather narrow resonance at $g = 2.058$, quite atypical of copper(II) monomeric species. The spectral features and their temperature behavior are fully rationalized in terms of a spin Hamiltonian with exchange, Zeeman and crystal-field interactions. The magnetic moment value and all the ESR features at 300 and 77 K are fully consistent with an exchange interaction of ferromagnetic character, $J > 0$, present in the Cu^{II}–Cu^{II} compound, and hence with the proposed mixed bridged dimeric molecular structure.

Synthetic copper(II)–copper(II) co-ordination dimers that are magnetically diluted and that experience magnetic exchange interaction, J, between the copper ions have been profusely studied.[1–3] The ground state for each copper(II) ion with spin $S_1 = S_2 = \frac{1}{2}$ consists of a Kramers doublet[4,5] when the exchange interaction, J, is zero or negligible. When the exchange interaction for each copper(II) pair becomes appreciable, then the spin states split into a singlet and a triplet state.[3,4,6] The value of the exchange constant J measures the difference in energy between the triplet and the singlet state.

A binuclear complex is in the triplet ground state for $J > 0$, in which case the exchange interaction is ferromagnetic in nature and for $J < 0$ the ground state is the spin singlet and the exchange interaction is antiferromagnetic. Both interactions are present simultaneously in any interacting system,[7–9] however, depending on the orbital disposition of the system, one or other will be the predominant one.[7–9] Both types of exchange interaction are electrostatic in nature.[7–9] The ferromagnetic interaction, $J > 0$, comes from the two-electron orbital exchange integral and the antiferromagnetic one comes from the overlap integral. The number of dinuclear copper(II) complexes studied with antiferromagnetic exchange interaction is large compared to those that show ferromagnetic character.[8]

The presence of these type of magnetic complexes in biological systems such as enzymes and other protein systems, is well documented. For example: the mimosine–copper(II) complex presents binding of mimosine to a binuclear copper site of derivatives of the binuclear active site of met-tyrosinase; also hemerythrin, an iron dinuclear protein found in some marine phyla, may reversibly bind oxygen to form oxyhemerythrin.[10–12] It has been established that the presence of these bimetallic complexes is vital to the function of such systems. For these reasons, they have attracted much attention in order to further their characterization and deepen the knowledge of their structural and magnetic properties. In particular, the scanty amount of ferromagnetic Cu–Cu systems studied, makes it relevant to synthesize dimeric Cu–Cu complexes that show ferromagnetic exchange interaction, in order to study them with techniques such as magnetic susceptibility, ESR and UV/VIS spectroscopy.[2,6,8]

In this work, the synthesis, elemental analysis, infrared spectroscopy, UV/VIS, ESR and magnetic moment characterization of the binuclear complex $[Cu_2(picditn)(CH_3CO_2)(H_2O)_2Cl][ZnCl_4]\cdot 0.5H_2O$ **1** is presented. Complex **1** yielded a mixed bridged ferromagnetic exchange interaction with an effective magnetic moment of 2.55 μ_B and an exchange interaction $J = +76\ cm^{-1}$. The results of its elemental analysis, IR, UV/VIS, ESR and magnetic moment studies are presented.

Results and Discussion

The elemental analysis (Found: C, 30.41; N, 8.76; H, 4.11. $C_{20}H_{36}Cl_5Cu_2N_5O_{4.5}Zn$ requires C, 30.48; N, 8.46; H, 4.59%) agrees very well with the calculated values.

The IR spectroscopy of the KBr pellets of **1**, gives characteristic bands for aromatic group vibrations at 1610 and 768 cm^{-1}; acetate group bands at 1660 and 1446 cm^{-1}, indicating the presence of the acetate in the complex; a symmetric N–H elongation band at 3200 cm^{-1},[13] as is shown in Fig. 1. These vibrations along with the NH's of the pentadentate ligand and the presence of the acetate group allow us to propose a binuclear complex with a double bridge between the two copper(II) ions. The proposed structure is shown in Fig. 2. Each Cu^{II} ion shows a five-co-ordination with inequivalent ligand spheres. Two types of chromophores are present: CuN_3OO' (Cu^1) and CuN_2OClO' (Cu^2); these asymmetric chromophores in dinuclear copper(II) complexes are common.[14] The proposed local geometry around each Cu^{II} ion is a square-based pyramid slightly distorted with four strong bonds to N_3, O, (Cu^1) and N_2,

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‡ *Non-SI units employed*: $\mu_B \approx 9.274 \times 10^{-4}\ J\ T^{-1}$; $G = 10^{-4}\ T$.

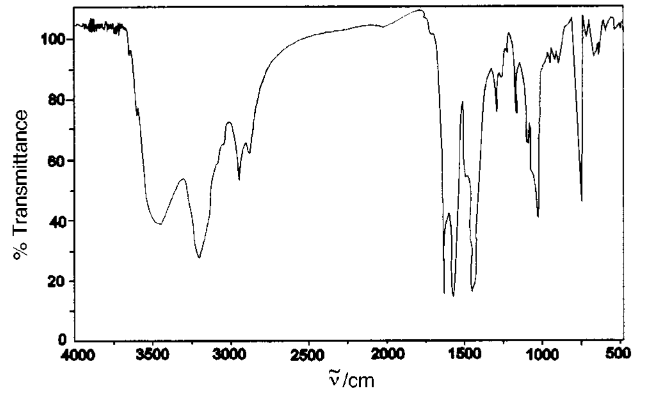

Fig. 1 Infrared spectrum of compound **1**

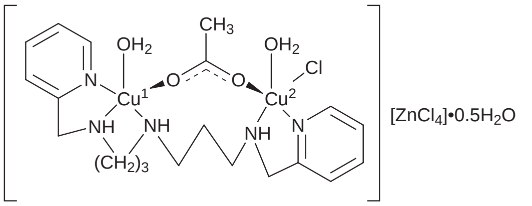

Fig. 2 Molecular structure proposed for the copper(II) compound **1**

O, Cl (Cu^2) atoms in the equatorial positions and an O′ atom from a water molecule co-ordinated in the axial position. The distances Cu^{II}–X with X = N, O or Cl, are commonly shorter than the distance $Cu^{II}–OH_2$ in accord with the strength of the ligand field.[14] For a dinuclear Cu^{II} complex with similar chromophores, in general, the distances between the copper centers and the co-ordinated atoms are different.[15]

The cation $[Cu_2(picditn)(CH_3CO_2)(H_2O)_2Cl]^{2+}$ is a binuclear structure where the copper centers are doubly bridged. On one hand the oxygens of the acetate group form the bridge Cu–OC-(CH_3)O–Cu, and on the other, the NH groups of the picditn ligand form the second bridge, Cu–NH(CH_2)$_3$HN–Cu. These two asymmetric bridges provide exchange interaction trajectories between the Cu^{II} ions, and both should contribute to the total interaction.[12,16,17]

In Cu^{II} five-co-ordinate model complexes with mixed bridges,[12] the reported Cu–Cu distances are 3.615(3) Å. The equatorial Cu–N and the axial O–Cu distances, are 1.94–2.06 and 2.11(1) Å, respectively, see also ref. 17 and refs. therein. McKee *et al.*[12] report for the stable bridged 1,3-azide, a Cu–Cu distance of 3.6 Å. Some other Cu^{II} bridged complexes have been reported with Cu–Cu distances of 2.61–3.6 Å.[18–21] Based on the above and the elemental analysis and IR data of complex **1**, it is reasonable to expect exchange interaction between the Cu^{II} ions. Such interaction is indeed observed and calculated from the effective magnetic moment and the ESR measurements as is described in the sections below.

The UV/VIS of complex **1** presents a broad asymmetric band as shown in Fig. 3. Its maximum is at 622 nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 192.5) with a shoulder at 791 nm.

The interpretations of the UV/VIS spectra for $Cu^{II}–Cu^{II}$ complexes follows the extensive work of Hathaway, Solomon and McKee. For many dicopper(II) complexes there have been reported bands centered at 700 nm which are assigned as d–d transitions.[10,12,21,22] Tomlinson and Hathaway have reported three bands for the electronic spectrum in the compound $[Cu(en)_2NH_3]X_2$, with a tetragonal distorted symmetry and a square-based pyramid in a close C_{4v} group, and they are assigned to the transitions: $^2B_1 \longrightarrow {}^2E_1$, $^2B_1 \longrightarrow {}^2B_2$ and $^2B_1 \longrightarrow {}^2A_1$, respectively.[23] Similar assignments are made for $[Cu(en)_2]X_2$ complexes.[24] In accord with Hathaway, this kind of broad band is characteristic of a square-based pyramidal geometry around the Cu^{II} ion.[25] Along these lines, complex **1** is proposed to be five-co-ordinated with an approximate C_{4v} symmetry, other symmetries cannot be ruled out completely. The UV/VIS spectrum of **1** was fitted and the best fit gives three Gaussians at: 560, 650 and 780 nm, that are tentatively assigned to the d–d transitions: $^2B_1 \longrightarrow {}^2E_1$, $^2B_1 \longrightarrow {}^2B_2$ and $^2B_1 \longrightarrow {}^2A_1$, respectively,[25–29] as shown in Fig. 4.

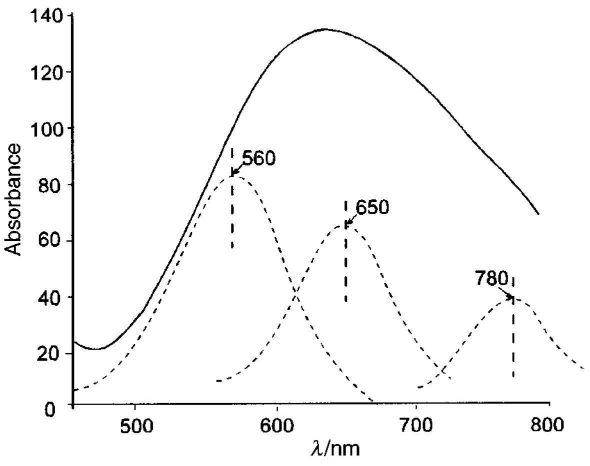

Fig. 3 The UV/VIS spectrum for compound **1** and the best fit to three Gaussians

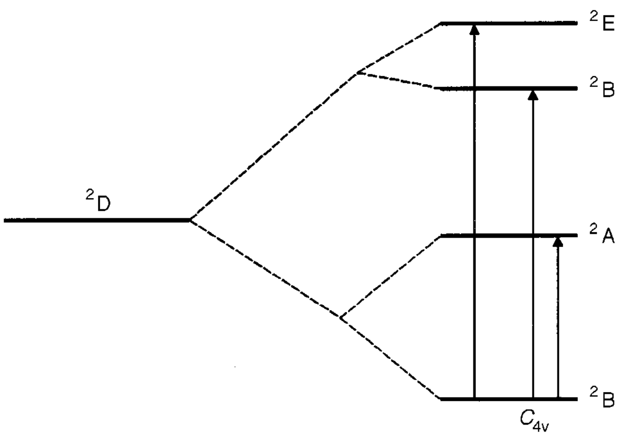

Fig. 4 Energy level diagram for the copper(II) ion in a square-based pyramidal ligand field (C_{4v})

The effective magnetic moment measured at room temperature was $\mu = 2.55\ \mu_B$. This value is 15% higher than the maximum expected value (2.20) for a spin ($S = \frac{1}{2}$) only system.[2,6] This is also higher than the magnetic moments of antiferromagnetically coupled $Cu^{II}–Cu^{II}$ complexes.[30] Hence, this value of 2.55 μ_B strongly suggests the presence of a ferromagnetic ($J > 0$) exchange interaction in compound **1**.[8,9]

Starting from Van Vleck's theory of magnetic susceptibility χ, the molar susceptibility for a system composed by $Cu^{II}–Cu^{II}$ dimer is obtained as[1,2,18] given in equations (1) and (2) where N,

$$\chi_m = \frac{N\beta^2}{kT}\mu^2 \qquad (1)$$

$$\mu^2 = \frac{2g^2}{3 + exp(-J/kT)} \qquad (2)$$

β, k and g have their usual meaning. Substituting $\mu = 2.55\ \mu_B$ and $g = 2.058$, into equation (2) and solving for J, we obtain a ferromagnetic exchange constant of $J = +76 \pm 15.2\ cm^{-1}$. The rather large $\pm 15.2\ cm^{-1}$ standard deviation comes from theory.[31] The value of J determines the separation between the spin-triplet ground state and the excited singlet state.

Kahn *et al.*[32] indicated that values of $\chi_m T \cong 1.0\ cm^3\ K\ mol^{-1}$ are characteristic of ferromagnetically coupled copper ion systems. Indeed, Comarmond *et al.*[31] reported for the binuclear Cu^{II}–[24]aneN_2O_6 ([24]aneN_2O_6 = 1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane) complex, a value of $\chi_m T = 1.10$ cm^3 K mol^{-1} at $T = 30$ K and $\chi_m T = 0.95$ cm^3 K mol^{-1} at $T = 18$ K. From equation (2) we obtain for compound **1** $\chi_m T = 1.06$ cm^3 K mol^{-1} at $T = 300$ K, pointing out the ferromagnetic exchange interaction for this complex.

The exchange coupling between the metallic centers sets in *via* the metal magnetic orbitals and the orbitals of the bridging atoms through the overlap and exchange integrals,[8,33,34] and so, J is written as $J = J_F + J_{AF}$ where $J_F = 2C$ and $J_{AF} = -2\Delta S$ where C is the two-electron exchange integral of magnetic orbitals, S the overlap integral and Δ is the energy separation between molecular magnetic orbitals occupied by the unpaired electrons. Given that the experimental value of J is $+76$ cm^{-1}, then J_F is the dominant term and hence the exchange integral C must be large. For C to be large, there must be a considerable closeness and favorable magnetic orbital orientations of the Cu^{II} interacting ions.[16,35,36]

The magnitude of J_F is determined by the strict or accidental orthogonality of the magnetic orbitals. In Cu^{II} complexes, strict orthogonality does not occur,[17,31–33] hence the value of J_F is due to accidental orthogonality of the magnetic orbitals involved; also a polarization effect can be active.[37] The π orbitals of O and N certainly interact with the metal orbitals; electron delocalization from the π orbitals into the $d_{x^2-y^2}$ orbital of copper 1 deposits some unpaired spin density of the same net orientation as that in copper 1 onto the bridging atoms. Then, coupling of the unpaired spins in orthogonal orbitals, π and $d_{x^2-y^2}$ of copper 2, produces the triplet ground state.[16,40]

The X-band ESR spectra of compound **1** were registered at 300 and 77 K and that recorded at 300 K is shown in Fig. 5(a). The ESR spectrum at 300 K shows an unresolved, asymmetric resonance at $g = 2.058$ with a rather narrow line width of 170 G. It also shows a shoulder at 3065 G. When the temperature is lowered to 77 K, this resonance remains at $g = 2.058$ and preserves its narrow width suggesting exchange interaction.[6,14] This narrow line width is quite atypical of powdered monomeric Cu^{II} complexes.[21,37,39] No hyperfine lines appear, indicating that the hyperfine splitting (hfs) remains unresolved.

The X-band ESR spectra at 300 and 77 K do not show any additional line at any gain at zero field or any other field. Hence, $\Delta Ms = \pm 2$ (Ms = double quantum spin flip), and zero-field transitions do not occur in this system.[31,41]

Looking for hfs resolution, the Q-band spectra were taken at 300 and 77 K. They are identical to each other except that the 300 K spectrum has a higher noise-to-signal ratio than does the 77 K spectrum. Fig. 5(b) shows this spectrum which consists of a single resonance line centered at $g = 2.058$ with a width of 311 G. No extra signals at any field between zero and 14 000 G are detected at any gain of the spectrometer.[41,42] No shoulder is detected at Q-band indicating that its presence at X-band is not due to hyperfine splitting.

All the experimental characteristics of the X- and Q-band spectra along with their very slight dependence on temperature indicate that the species responsible for such spectra are far from monomeric Cu^{II} species.[21,37,39] Rather a ferromagnetically coupled species fits well these spectral features as the spin Hamiltonian treatment shows below.

A spin Hamiltonian that includes the Zeeman terms, an exchange interaction and the crystal field term is written as in equation (3) where g_1 and g_2 are the isotropic spectroscopic

$$H = \beta\vec{H}\cdot\vec{g}_1\cdot\vec{S}_1 + \beta\vec{H}\cdot\vec{g}_2\cdot\vec{S}_2 - J\vec{S}_1\cdot\vec{S}_2 + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \quad (3)$$

factors of the ions, respectively; J is the exchange interaction constant, D and E are the axial and rhombic crystalline field parameters, S_x, S_y and S_z are the components for the total spin $\vec{S} = \vec{S}_1 + \vec{S}_2$. The other parameters have their usual meaning.

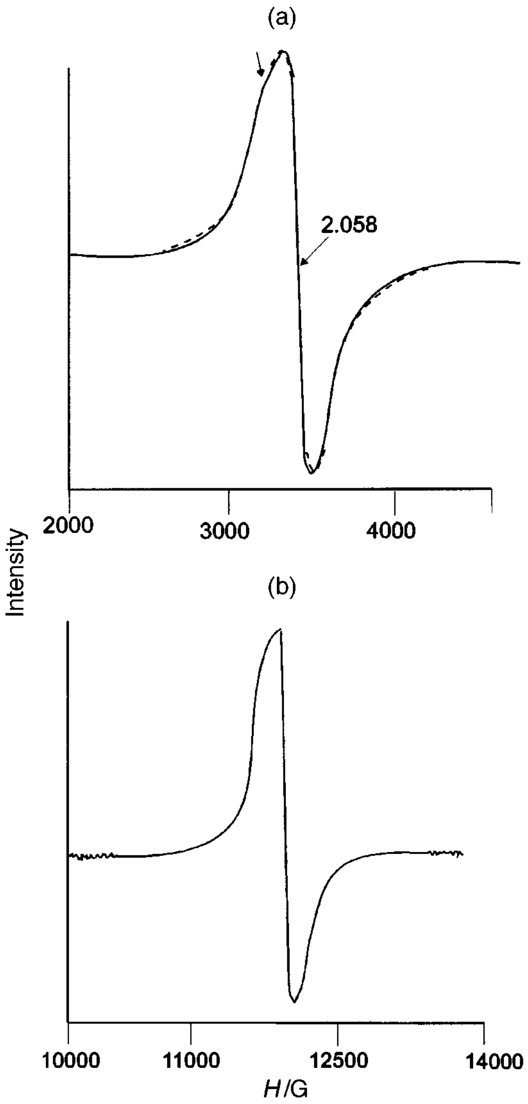

Fig. 5 (a) The X-band ESR spectrum at 300 K and (b) Q-band ESR spectrum at 300 K, both for compound **1**

Taking $J = +76$ cm^{-1}, as calculated above from the magnetic moment measurement, the exchange term in equation (3) is orders of magnitude larger than the Zeeman and the crystal field. Hence, to first order in perturbation theory the solution gives the four eigen energies split into a ground triplet state and a singlet one with an energy difference equal to $J = 76$ cm^{-1}.

For the purpose of an ESR experiment in which the excitation microwave energy is $hv = |g\beta H| \approx 0.31$ cm^{-1}, only transitions among the ground triplet state levels are taken into account. This triplet subsystem is characterized by the reduced spin Hamiltonian (4), with the effective spin $S = 1$, g its spectroscopic value, and D and E are the crystal field terms that

$$\boldsymbol{H} = \beta\vec{H}\cdot\vec{g}\cdot\vec{S} + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \quad (4)$$

experience the spin $S = 1$. The eigen energies of this subsystem under a weak axial crystal field ($D \neq 0$, $E = 0$) are given in Fig. 6(a), where in addition, the vertical lines indicate all the possible ESR transitions: t_1, t_2, t_3 and t_4. This eigen energies diagram is sufficient to rationalize all the ESR features observed at X-band.

From the experimental ESR spectra and the eigen energies diagram, it is seen that the absence of zero-field transitions, t_4, indicates that $D \neq 0.31$ cm^{-1}. Furthermore, the absence of transitions at fields larger than $H_0 = 3336$ G is indicative that if a D

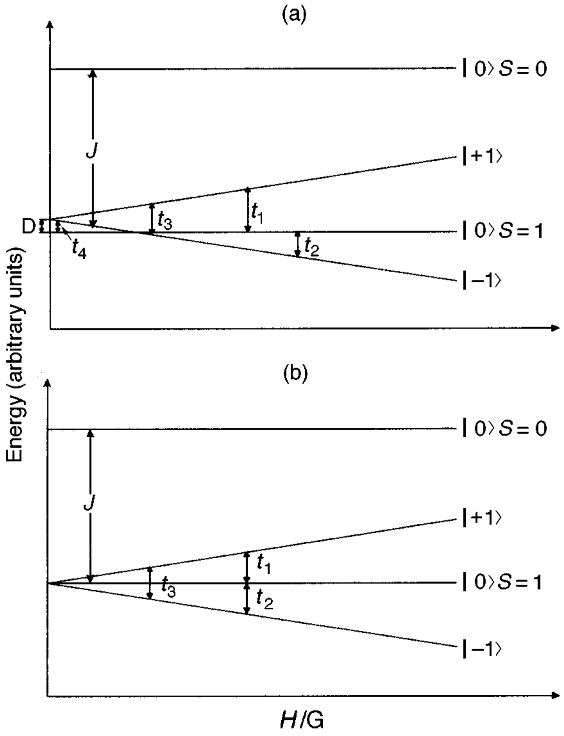

Fig. 6 Eigen energy diagrams for the Hamiltonian in equation (4) for (a) $D \neq 0$ and $E = 0$ and (b) $D = 0$ and $E = 0$; see text

term exists, it cannot be larger than 0.31 cm^{-1}, hence D should be $0 < |D| < 0.31$ cm^{-1}. The presence of the main line and a shoulder in the X-band ESR spectrum in Fig. 5(a) is interpreted as being due to the transitions: t_1, $|0\rangle \longleftrightarrow |+1\rangle$ and t_2, $|0\rangle \longleftrightarrow |-1\rangle$ indicated in the eigen energies diagram in Fig. 6(b), where t_1 and t_2 have become slightly different by an amount of $D \leqslant 200$ $G = 0.02$ cm^{-1}. Under these circumstances $D \ll$ Zeeman term.

The slight increased intensity of the narrow resonance when the temperature is decreased to 77 K is consistent with a triplet spin ground state and a singlet excited state,[3,5,31,38] in which case the thermal population of these states and hence the ESR integral of the ESR line is little affected when the temperature drops from 300 to 77 K. This temperature behavior would be drastically different if the exchange coupling were antiferromagnetic ($J < 0$) with the spin triplet state as the excited state or if the system were paramagnetic, where the Boltzmann population factor indicates a T^{-1} intensity dependence with temperature.[18,40]

For the Q-band ESR experiment, the Zeeman term increases 3.8 times with respect to the X-band experiment while the crystal field term remains constant, hence the inequality: Zeeman energy $\gg D$ holds even better than in the X-band experiment, and the transitions $|0\rangle \longleftrightarrow |+1\rangle$ and $|0\rangle \longleftrightarrow |-1\rangle$ become practically identical as is shown in Fig. 6(b), and only one transition centered at $g = 2.058$ is detected and resolved. The absence of zero-field and high-field transitions confirms the smallness of the crystal-field term.[21,31] The line intensity behavior with temperature is similar to that at X-band and is rationalized in the same way. The constancy of the linewidth with temperature, both at X- and Q-band is taken as a result of the balance of the spin relaxation mechanisms: spin–lattice (T_2) and spin–spin (T_1) of similar importance, hence cancelling out the temperature dependence of the linewidth.[6]

On the other hand, the Q-band linewidth of 311 G of the resonance is about two times larger than the X-band linewidth of 170 G. This linewidth increase with increased frequency of the ESR experiment, is thought to be due to a slight g factor anisotropy which tends to split the spectrum by a factor of 3.8 when going from ≈9.4 to ≈35 GHz.

Experimental

The 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (picditn) ligand was prepared by the reaction of 2-pyridinecarbaldehyde (1 mol) and 2,6,10-triazaundecane (0.5 mol) in a 2 : 1 molar ratio, in a reducing medium containing zinc (400 g) and acetic acid (400 ml). It was purified prior to use in the synthesis of the co-ordinated compound. This method of synthesis is similar to that used for 1,9-bis(2-pyridyl)-2,5,8-triazanonane reported somewhere else.[43,44] The copper complex was prepared by adding $CuCl_2 \cdot 2H_2O$ to the ligand in a 1 : 1 ratio in ethanol, obtaining the dimeric copper(II) complex $[Cu_2(picditn)(CH_3CO_2)(H_2O)_2Cl][ZnCl_4] \cdot 0.5H_2O$, by crystallization (yield 85%). Compound **1** is a blue polycrystalline powder with fusion point in the range 151–153 °C.[43,44] Many attempts to crystallize the compound have been made and they have been unsuccessful so far.

The elemental analysis was obtained using a Perkin-Elmer 240-B microanalyzer at Butterworth Ltd., UK. The IR spectra were recorded on Perkin-Elmer 599-B and 283-B spectrometers. Visible and ultraviolet spectra were recorded at room temperature on a Cary 5E-UV/VIS-NIR spectrophotometer. The effective magnetic moment was measured at room temperature with a Cahn 2000 electrobalance and a 6685 model electrometer. The diamagnetic corrections were made using Pascal's constants.[2,16] The setup was calibrated with $HgCo(SCN)_4$ as standard. The ESR spectra for the polycrystalline powder were recorded with a JEOL JES-RE3X spectrometer with 100 KHz modulation, for X- (9.45 GHz) and Q-band (35 GHz) at temperatures of 300 and 77 K.

Conclusion

The elemental analysis, IR, and UV/VIS characterization along with the magnetic moment and ESR studies on compound **1** allow us to propose a dimeric molecular structure for the compound bridged by acetate and picditn groups, where each Cu^{II} ion is five-co-ordinate with a local geometry of a distorted square-based pyramid with approximate C_{4v} or lower symmetry[45] and the metal orbital $d_{x^2-y^2}$ as the ground state.

The magnetic moment and the ESR studies are fully consistent with an exchange interaction of ferromagnetic character, $J > 0$, present in the Cu^{II}–Cu^{II} compound, and hence with the mixed bridged dimeric molecular structure.[46,47]

Acknowledgements

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