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EPR and Magnetic Studies of Copper Amino Carboxylates

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Abstract

Metal complexes of N-substituted amino acids provide simple but appropriate model compounds for the understanding of metal protein interactions. Seven complexes of copper *viz.* Cu(II) N-acetyl glycinate mono-hydrate, Cu(II) N-acetyl methioninate, Cu(II) N-acetyl alaninate, Cu(II) N-acetyl valinate, Cu(II) N-acetyl glutamate, Cu(II) cyanoacetate, and Cu(II) thio-dipropionate, have been investigated by EPR measurements. The spectra appear to arise from dimeric coppers ($s = 1$) coupled by anti-ferromagnetic exchange. The exchange coupling constant '$2J$' and the –Cu–Cu– separation 'r' have been evaluated from the spectral data. Although the existence of bridged structure is confirmed, super-exchange via the ligands appears to be the dominant mechanism. All of these complexes exist as monomers in strongly coordinating solvents.

Introduction

The role of magnetic exchange in cluster complexes of 3d [1–9] metal ions has been emphasized in reviews by Kato [1], Ginsberg [2] and Owen and Harris [3]. Considerable information about structure (both X-ray and magnetic) can be obtained by studying transition metal complexes using magnetic resonance and magnetic susceptibility techniques. Structural studies [4] of 3d ions like Cu, Ni, Cr, Fe with simple amino acids ligands are useful as model compounds in simulating the properties of corresponding metal proteins. The role of copper [5] in particular in biological systems is of much interest. Metal complexes of N-substituted amino acids provide simple but appropriate compounds for the understanding of metal-protein interactions.

Unlike higher amino acids, small peptides such as N-acetyl glycine [6, 7], N-benzyl glycine [8], N-acetyl alanine [9], N-acetyl-DL-tryptophan [10] do not coordinate Cu(II) ions through the peptide nitrogen atom. They act as simple carboxylic acids causing strong antiferromagnetic coupling between the Cu^{2+} ions within the pairs. In view of the earlier discussion, seven complexes of copper(II) have been investigated, *viz.*

(1) Cu(II) N-acetyl glycinate mono-hydrate
(2) Cu(II) N-acetyl methioninate
(3) Cu(II) N-acetyl alaninate
(4) Cu(II) N-acetyl valinate
(5) Cu(II) N-acetyl glutamate
(6) Cu(II) cyanoacetate
(7) Cu(II) thiodipropionate

Experimental

The EPR spectra were recorded in the X-band (9 Ghz) on VARIAN E4 EPR spectrometer and AEG-EPR spectrometer. The sample temperatures were varied from 100 K to 300 K. The accuracy in g values is ±0.005 and the magnetic field homogenity is ±30 mG over the effective sample volume. The complexes were prepared following standard procedures [11]. The complexes were characterized by recording IR, FIR, and optical spectra; the assigned bands are listed in Table I and Table II.

Results and Discussion

The powder EPR X-band spectra recorded at various temperatures for complex (3) are shown in Fig. 1. The spectra appear to arise from triplet states, in the presence of zero field splitting arising from binuclear species. They are thus characteristic of dimeric copper complexes governed by antiferromagnetic exchange [12], analogous to the copper acetate monohydrate and other similar dimeric carboxylates [13, 14a]. The X-band spectrum, as seen in Fig. 1, is spread over a range of 0–7000 gauss along with zero field splitting (D). The spectrum is axially symmetric, and the perpendicular components (Z) occur at extreme ends of the spectrum. The component around 3000 gauss is due to the monomeric impurity present. This spectrum is typical

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TABLE I. Principal Bands Assigned IR and FIR Spectra.

Complex	COO(asym) (cm^{-1})	COO(sym) (cm^{-1})	N–H (cm^{-1})	Cu–O (cm^{-1})
1	1710	1270	2890 3390	450,410,310 285,260
2	1730	1280	2900 3370	580,450,305 210
3	1650 1600	1375 1310	3360	586,443,230
4	1660 1595	1270 1285	3320 3230	570,430,210
5	1680 1540	1240 1295	3340 3460	550,485,310
6	1710	1270 1230	2890 3320	385,410,520
7	1590 1510	1285 1230	2920 2960	389,425

TABLE II. Principal Bands, Optical Spectra.

Complex	λ (d–d) (nm)	λ (nm)
1	510	345
2	525	380
3	625	358
4	625	365
5	650	369
6	780	370
7	650	340

of $s = 1/2$ Cu^{2+} ions. This is confirmed by studying the temperature variation of the spectra from room to liquid nitrogen temperature. The intensity of lines due to monomeric impurity is governed by Curie susceptibility; there is increase of intensity with temperature. The intensities of the lines from dimeric coppers is governed by HDVV eqn. 1.

$$\chi_M = \tfrac{2}{3}Ng^2\beta^2/kT(1 + (1/3)\exp(-2J/kT))^{-1} + N\alpha \quad (1)$$

χ_M is the molar susceptibility; the other constants are known [13]. The intensities show a maximum around a particular temperature and then decrease progressively as the temperature is lowered to 77 K (shown in Fig. 2a). This behaviour is understood in terms of a singlet–triplet level scheme formed by copper–copper interaction due to anti-ferromagnetic exchange. In the systems being studied, we have a singlet ground state and a triplet excited state separated by $2J$, where J is the exchange coupling constant. $2J$ being of the order of kT, the triplet population is dependent on temperature and is governed by kT. At very low temperatures ($E < kT$) all the spins are in the singlet ground state, with the

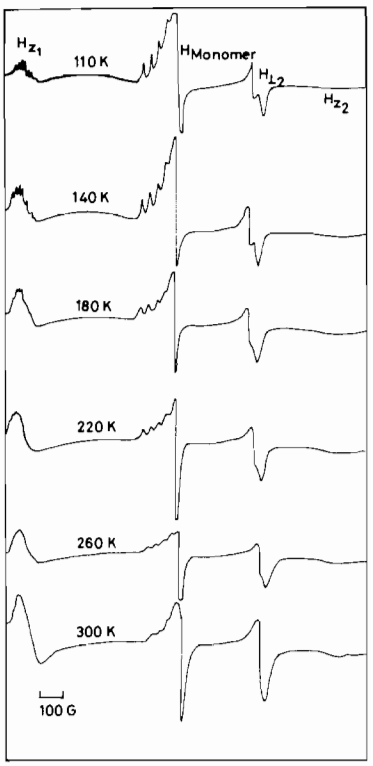

Fig. 1. Powder EPR X-band spectra recorded at various temperatures for Cu(II) N-acetyl alaninate.

triplet state completely depopulated. The magnetic susceptibility (bulk) and the EPR transitions of the dimeric coppers arise only from the unpaired spins in the triplet state. The susceptibility and intensity of EPR lines increase with temperature until all the levels are singly occupied ($E \approx kT$). Any further addition of spins to the triplet results in pairing ($E > kT$) so that the net susceptibility drops, as evident from Figs. 2a and 2b. This model of strongly-coupled exchange pairs in terms of the HDVV Hamiltonian (eqn. 2)

$$\mathcal{H} = -2J\, s_1 \times s_2 \quad (2)$$

forms the basis for understanding the magnetic behaviour of most copper carboxylates having dimeric bridged structures. This explains the temperature variation of the spectra obtained. The susceptibility observed here is basically of the Curie type, *i.e.* paramagnetic susceptibility modulated by the exchange interaction.

The seven line hyperfine pattern with ratio 1:2:3:4:3:2:1 in Fig. 1 confirms that the spectra arise from $s = 1$. Two Cu^{2+} $s = 1/2$ ions are coupled by antiferromagnetic exchange to give an effective spin of 1. The average hyperfine constant measured from the spectra is 63 gauss and is consistent with the values for other similar dimeric copper complexes [14b]. This conforms with the dimeric nature of (Cu–Cu–) pairs in the complex.

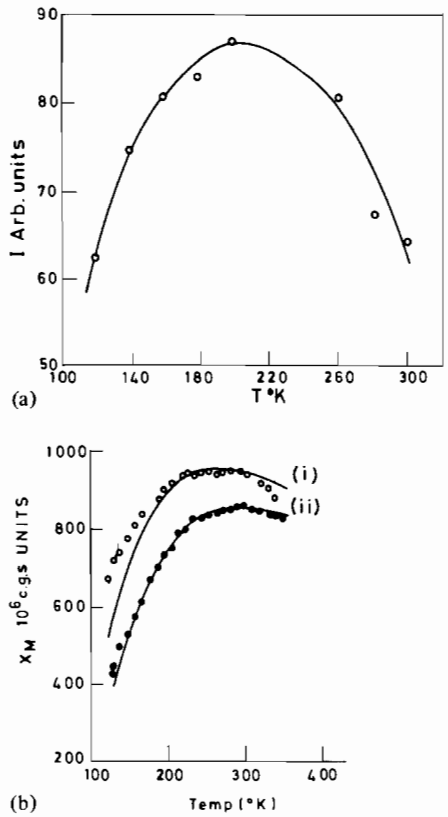

Fig. 2. (a) Plot of EPR intensity *vs.* temperature for Cu(II) N-acetyl alaninate (experimental). (b) Plot of magnetic susceptibility *vs.* temperature [25] for Cu(II) N-acetyl alaninate (i) monohydrate, (ii) anhydrous.

In the case of the binuclear species, two Cu^{2+} ions coupled by magnetic exchange interaction result in a triplet state with $s = 1$, unlike $s = 1/2$ for a normal Cu^{2+} ion. The resulting EPR spectrum gives two transitions instead of one, governed by a zero field splitting with a fine structure. This, being an orthorhombic case, will give three components. Therefore we get two components in each transition, which gives six transitions in all, separated by the zero field parameter D. The spectrum is thus spread over a range of 6000 gauss. Six simultaneous equations are set up, corresponding to the six transitions, based on the Hamiltonian for a binuclear ($s = 1$) ion [14b] as given below for the case of axial symmetry,

$$\mathcal{H} = g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y) + D(S_z^2 - (1/3)S(S+1)) + E(S_x^2 - S_y^2) \quad (3)$$

for the magnetic field along x, y, z axes respectively.

$$H_{x1}^2 = (g_e/g_x)^2((H_o - D' + E')(H_o + 2E')) \quad (3a)$$

$$H_{x2}^2 = (g_e/g_x)^2((H_o + D' - E')(H_o - 2E')) \quad (3b)$$

$$H_{y1}^2 = (g_e/g_y)^2((H_o - D' - E')(H_o - 2E')) \quad (3c)$$

$$H_{y2}^2 = (g_e/g_y)^2((H_o + D' + E')(H_o + 2E')) \quad (3d)$$

$$H_{z1}^2 = (g_e/g_z)^2((H_o - D')^2 - E'^2) \quad (3e)$$

$$H_{z2}^2 = (g_e/g_z)^2((H_o + D')^2 - E'^2)) \quad (3f)$$

where $H_o = h\nu/g_e\beta$, $D' = D/g_e\beta$, $E' = E/g_e\beta$, H_{x1} and H_{x2} are the $\Delta m = \pm 1$ resonance fields when the microcrystallites are in the x direction; the other fields are correspondingly in the y and z directions. g_e is the free electron g value.

In a powder sample it is not possible to align the magnetic field along a given direction. The observed spectrum is a sum over all possible orientations. Sharp discontinuities occur at the values of the magnetic field given by eqns. 3a–f; thus even in a powder sample the axial resonance field may be obtained and the parameters g_x, g_y, g_z, D, E can be calculated. In addition to the six resonances given by eqns. 3a–f, a resonance line will occur corresponding to $\Delta m = \pm 2$. This will appear as an additional spectral line in the powder spectrum when $D < h\nu$. When $D > h\nu$, which is usually the case in compounds containing copper dimers; H_x, H_y, and $\Delta m = \pm 2$ transitions can no longer be observed. The powder spectrum will therefore consist of only four resonance lines. Further, in these complexes the inplane anisotropy is small ($E < 0.01$ cm^{-1}), so that eqns. 3a–f reduce to only three *viz.*,

$$H_{\perp 2}^2 = (g_e/g_\perp)^2(H_o(H_o + D')) \quad (4a)$$

$$H_{z1} = (g_e/g_z)^2(H_o - D') \quad (4b)$$

$$H_{z2} = (g_e/g_z)^2(H_o + D') \quad (4c)$$

Only three transitions appear in the powder spectra of these complexes. The parameters g_{11}, $g_\perp$, and D can be calculated with the field positions $H_{\perp 2}, H_{z1}, H_{z2}$ from the spectra using the eqns. 4a–c. The spin Hamiltonian parameters calculated are shown in Table III. The nature and order of g values obtained for the dimeric species of the complexes are consistent with those reported in literature for analogous systems [15]. The $g_{average}$ values obtained for the monomeric species present as inseparable impurities are about the same in all compounds, showing that the nature of the monomeric impurity is the same. The spectra of complex **2** can be understood in terms of the monomeric species of copper, as can be seen from Fig. 3. The observed spectrum is only from Cu^{2+}, with $s = 1/2$ present as monomeric impurity. The spectra recorded at temperatures ranging from 77 K to 300 K (Fig. 3) show the intensity of the components increasing with decreasing temperature. This behaviour is evidently of the Curie type. The magnetic moments measured using the Guoy balance give a value of 1.39 BM (Table IV), which is subnormal and thus indicates the presence

TABLE III. Spin Hamiltonian Parameters and X-Band Powder Spectra.

Complex	g_{II}	g_I	g_o	D (cm^{-1})	$2J$ (cm^{-1})	r (A)	$g_{(monomer)}$[a]
1	2.419	2.080	2.193	0.289	211.04 (292.00)[b]	2.677 (2.666)[c]	2.160
2	2.158	2.050	2.090				
3	2.428	2.090	2.202	0.363	221.88 (285.00)[b]	2.805 (2.613)[c]	2.110
4	2.441	2.086	2.204	0.365	219.20	2.604	2.230
5	2.265	2.104	2.157	0.260	303.26	2.998	2.180
6	2.385	2.120	2.200	0.380	362.00	2.959	2.140
7	2.989	2.106	2.167	0.271	212.22	2.821	2.190

[a]g value from monomeric species ($S = 1/2$). [b]Obtained from magnetic susceptibility data. [c]Value reported from X-ray data.

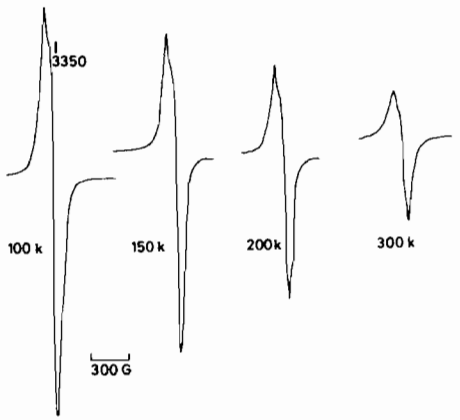

Fig. 3. Temperature variation of EPR spectra for Cu(II) N-acetyl methioninate.

TABLE IV. Room temperature Magnetic Moments from Guoy Balance Measurements.

Complex	μ_{eff} (BM)
1	1.42
2	1.39
3	1.47
4	1.32
5	1.53
6	1.29
7	1.56

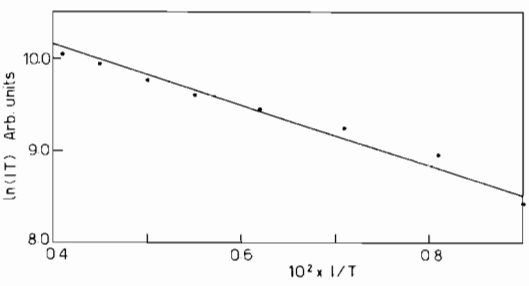

Fig. 4. Plot of ln (intensity × temperature) *vs.* 1/temperature.

of exchange. This suggests that the dimeric Cu–Cu– pairs have a different structure compared to the other complexes studied.

Spectral data from the temperature variation of EPR has been used to evaluate the exchange coupling constant $2J$. The quantity ln(intensity × temperature) *vs.* 1/(temperature) has been plotted for the various complexes, one of which is shown in Fig. 4. $2J$ can be evaluated from the slope of the plot, as is evident from eqn. 1. This is explained by the fact that susceptibility is proportional to I, the signal intensity; therefore, the plot will show the same behaviour as χ. Thc zero field splitting D observed in these complexes comes from the magnetic dipolar interaction between the two ions as well as magnetic exchange interaction. The spectra are the resultant of the two. The exchange part of the dipolar arises when the spin orbit coupling is comparable in magnitude to the exchange interaction. This is represented by

$$D_{ex} = -1/8J(1/4)(g_{11} - 2)^2 - (g_\perp - 2)^2) \quad (5)$$

while the net resultant dipolar part is given by

$$D = D_{ex} - (g_{11}^2 + \tfrac{1}{2}g_\perp^2)(\beta^2/r^3) \quad (6)$$

Thus, it is not possible to distinguish between the contributions to the D from these interactions. However, when the crystal structure is known, the r value can be used to compute the value of $2J$. When structural data is not known, r can be estimated from these measurements using eqns. 5 and 6. The values of $2J$ and D so computed are shown in Table III and agree reasonably well with other analogues [15].

The complexes studied have been chosen to help understand the dimeric nature underlying the exchange mechanism and to correlate structural data with magnetic studies. The values of $2J$ as measured from magnetic susceptibility [6, 9, 16] for complexes **1**, **3**, and **6** compare reasonably well with the experimental values obtained from the spectral data. The Cu–Cu– separation calculated based on the spectral data also compares reasonably well with

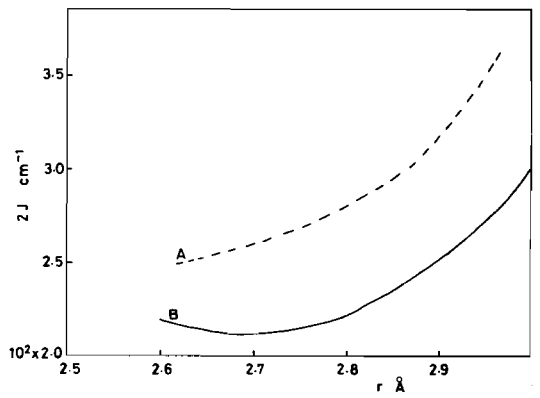

Fig. 5. Plot of Cu–Cu separation '*r*' *vs.* exchange coupling constant '2*J*', (A) Values from ref. 13; (B) Values obtained from present investigation.

the X-ray data previously reported for complexes **1** and **3** reported in parentheses (Table III). The X-ray data for other complexes are not available; thus the computed values of *r* predict the possible Cu–Cu– separation based on EPR data.

A plot of '2*J*' *vs.* '*r*' in Fig. 5 shows 2*J* increasing with Cu–Cu– separation. Since, the basic carboxylate bridged structure is the same, the value of *r* seems to vary with substitution of different amino acid groups. Some values of *r* and 2*J* reported in the literature for similar complexes are shown in the plot for comparison. This variation is understood in terms of the basic mechanism of exchange. The antiferromagnetic exchange which governs the dimeric behaviour can arise from a direct overlap of the $d_{x^2-y^2}$ orbitals of the two copper atoms. This is made possible by the bridged structure and the bridging ligands. In this case the magnitude of the exchange coupling constant 2*J* is strongly dependent on the *r* value, *i.e.* Cu–Cu– separation. The bridging ligand acts as a pathway via the bonds. This is referred to as super exchange, in contrast with direct exchange. The exchange integral or 2*J* in such a case varies with the nature of the bridging ligands and the pathways. There is a correspondingly weak dependence on the relative Cu–Cu– separation. In most complexes where the bridged structure exists, both mechanisms are present. The bridging ligands and the structure bring the two copper atoms close enough for an orbital overlap to occur. However, depending on the nature of the bridging ligands, one of the mechanisms is predominant. In complexes with polymeric structures but, no bridging, the two coppers are far apart (>3 Å) and the super exchange mechanism alone prevails. In our case the increase of 2*J* with *r* suggests that, in spite of the bridged structure, the superexchange via the ligands governs the magnitude of exchange. The literature values shown also have a common bridged structure with different ligands. Except for complex **1**, these complexes are all anhydrous. This being common, the coordinating amino acid group alone governs the magnitude and nature of the exchange. The *r* values (computed) are greater than 2.7 Å in the complexes **5**, **6**, and **7**. The possibility of direct overlap of d orbitals is less when the relative separation is more than 2.6 Å to 2.7 Å. In other words, the δ bond formed in this exchange due to direct overlap would be very weak. Further, the optical spectra gives bands in the region of 350–370 nm (Table I). This indicates the presence of exchange and the existence of a δ bond between the two coppers. These observations show that the exchange interaction observed in these complexes is predominantly of superexchange type, which takes place via the bridging ligands.

The EPR X-band spectra of some of these complexes have been recorded in different coordinating solvents at room temperature and liquid nitrogen temperatures to understand the stability of bridged structure and the dimeric nature of the complexes. Typical powder, solution and frozen solution spectra are shown in Fig. 6 (a–d) and the corresponding spin Hamiltonian parameters are shown in Table V. The spectra obtained are typical of monomeric copper with $s = 1/2$. The solution spectra give a single isotropic line, while the frozen solution spectra show near axial symmetry with parallel and perpendicular components. The hyperfine separation observed is generally greater in the case of solvents with lone pair nitrogens, as seen from Table V. Additional hyperfine splittings of the order of 15 gauss are observed

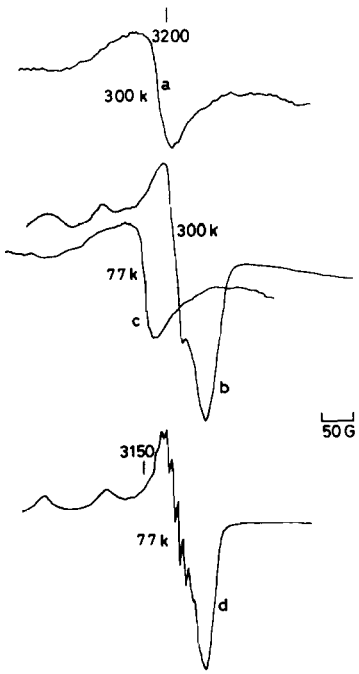

Fig. 6. Solution and frozen solution spectra of complex **2** (a) DMF, (b) 300 K (DMSO), (c) 77 K (DMSO), (d) pyridine.

TABLE V. Spin Hamiltonian Parameters in Solution and Glass States.

Complex	Solvents	Solution	Frozen solution								
		g_o	g_{II}	g_I	g_o	g_1	g_2	g_3	g_o	A_{II} (gauss)	a (gauss)
1	DMSO	2.13	2.35	2.06	2.15					136.6	
	DMF					2.34	2.07	2.05	2.15	138.3	
	Ammonia	2.23	2.02	2.09						172.5	
	β-Picoline	2.28	2.03	2.11						157.5	
	Morphiline					2.23	2.04	2.00	2.09	160.0	
	EDC					2.19	2.05	2.03	2.09	185.0	
	Pyridine		2.25	2.05	2.11					175.0	16
2	DMSO	2.07				2.32	2.07	2.02	2.13	145.0	
	DMF	2.07				2.29	2.06	2.04	2.13	167.5	
	Dioxan		2.33	2.05	2.14					143.3	
	Ammonia		2.23	2.06	2.11					175.0	
	β-Picoline		2.27	2.05	2.12					165.0	
	Morphiline					2.20	2.05	1.99	2.08	182.5	
	EDC					2.19	2.03	1.99	2.07	182.5	
	Pyridine		2.24	2.03	2.10					172.5	15
6	DMSO					2.32	2.08	2.04	2.14	135.0	
	Ammonia		2.23	2.09	2.14					170.0	
	β-Picoline		2.27	2.05	2.12					160.0	16
	Morphiline		2.24	2.03	2.10					162.5	
	EDC		2.20	2.06	2.01						
	Pyridine		2.26	2.03	2.11						

due to the lone pair nitrogens in these cases. The g values suggest that the Cu^{2+} ion is in the $d_{x^2-y^2}$ ground state.

Conclusions

The N-protected amino acid groups, when complexed with copper, coordinate through the carboxylate oxygens forming a dimeric bridged structure. They behave as simple carboxylates similar to copper acetate. The peptide nitrogen is bonded with the N-acetyl group and does not take part in coordination with copper. We find that thiodipropionate cyanoacetate also behaves like copper acetate when complexed with copper. Cu(II) N-acetyl methioninate indicates presence of exchange, but does not show any EPR dimeric spectra. This suggests that Cu–Cu– pairs are in a polymeric form of chain structure; the dimeric Cu–Cu– pairs are thus EPR-inactive by the absence of net unpaired spin density. A similar polymeric structure is proposed for Cu(II) cyanoacetate based on earlier study [16]. From the construction of a model for Cu(II) thiodipropionate, we also find that only one of the propionates contributes carboxylate oxygens to the bridge and the sulphur does not play a role in bridging. Such non-detectable copper is present in proteins which, due to polymeric structure, is EPR inactive for the dimeric coppers. The super exchange mechanism is predominant, being modulated by the amino acid groups. These complexes have a monomeric structure in coordinating solvents. In addition we demonstrate that in the absence of data from other techniques, carefully performed EPR studies can furnish information regarding exchange mechanism, structure and magnetic properties. N-Acetyl substituted monopeptides form very good model compounds to understand metal protein interactions, as evident from our investigations.

Acknowledgments

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