Predicting ESR Peaks in Copper (II) Chelates Having Quadrupolar Coordinating Sites by NMR, ESR and NQR Techniques: A DFT Study

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ABSTRACT

Computational chemistry was helpful in predicting the number of ESR peaks in Cu (II) complexes having a large number of spatially different NMR and ESR active nuclei. The presence of the large Jahn-Teller effect and the high value of spin-orbit coupling constant of the metal ion made the experimental determination of the exact number of ESR peaks quite difficult in such complexes. Fourteen distorted poly-dentate chelating Cu(II) complexes included in this study were of two types such as $[Cu(gly)_2]$, $[Cu(edta)]^{4-}$, $[Cu(tpy)X_2]$ (X= Cl, Br, I, NCS) and $[Cu(en)_2]^{2+}$, $[Cu(teta)]^{2+}$, $Cu(tepa)]^{2+}$, $[Cu(peha)]^{2+}$, $[Cu(deta)X_2]$ (X= Cl, Br, I, NCS). The latter eight complexes belonged to an important class of ligands called *polyethylene polyamines*. Density functional theory implemented in ADF: 2010.02 was applied. Three parameters of both the ESR (A ten) and NQR (NQCC,η) for the Cu(II) and the coordinating atoms of the ligands were obtained from "ESR/EPR program" and two NMR parameters namely the shielding constants (σ) and chemical shifts (δ) were obtained from "NMR/EPR program" after optimization of the complexes. The species having the same values of these 5 parameterswere expected to be spatially equivalent to undergo the same hyperfine interaction with Cu (II).

Key words: Jahn-Teller; Poly-dentate; Chelating; Polyamines; Shielding Constants.

INTRODUCTION

Eight Cu(II) complexes such as $[Cu(en)_2]^{2+}$, $Cu(teta)]^{2+}$, $[Cu(tepa)]^{2+}$, $[Cu(peha)]^{2+}$, $[Cu(deta)X_2]$ (X= Cl, Br, I, NCS) having poly-dentate ligands of a class called polyethylene polyamines (*en*, *deta*, *teta*, *tepa*, *peha)* and six other complexes like $[Cu(gly)_2]$, $[Cu(edta)]^{4-}$, $[Cu (tpy)X_2]$ (X= Cl, Br, I, NCS) with other chelating ligands (*gly*, *edta* and *tpy)* having coordination number 4, 5 and 6 respectivelywere studied.

Enough work had already been reported on (*en*) and (*edta*) complexes[1-7]; only some wok was available on (*tpy*) complexes[8] while a little was known about polyethylene polyamines and five coordinate Cu (II) complexes[9]. This limitation arose from the fact that such complexes with a large number of spatially different NMR and ESR active nuclei were adversely affected by the presence of both the large Jahn-Teller effect and the high value of spin-orbit coupling constant of $\lambda_{Cu (II)}$ (-830.0 cm^{-1})[10-11].

This prompted us to take up this study by using DFT (Density Functional Theory) implemented by ADF (Amsterdam Density Functional) 2010.02 as it allowed us to select the interacting nuclei at our will[12-18]. We selected ^{63}Cu, ^{14}N, ^{35}Cl, ^{79}Br, ^{127}I but omitted ^{1}H. It was primarily due to the reason that all the selected nuclei possessed quadrupole (I > ½) and were directly bonded with Cu(II) while the protons, with no quadrupole were two and more bonds away from the metal ion. This would cause **j-j** coupling to fall and so would be the interaction between the metal ion and the protons.

During the last decade, DFT calculations were often used on small molecule molecules. Although, all electron approaches might be carried out for simpler molecules, yet valence electron approaches considered molecules to be treated without significant loss in either rigor or accuracy. The quasi relativistic and more recent ZORA to Dirac equation approach implemented in ADF represents one such method where relativistic terms treat valence electrons in the field of a frozen core of relativistic atomic wave functions. Also, DFT had enabled us to have a deeper understanding of the relation between the magnetic parameters and electronic and geometrical structures of molecules. As ESR spectra was related to electronic structure and geometry of a system, DFT could provide an alternative to the traditional Hartree-Fock(HF) and post-HF approaches to ESR calculations. Thus, its ability to include the effects of electron correlation had, over the last years, brought DFT to the forefront in the field of calculating ESR parameters.

While the discussion on NMR of transition metal complexes encircled around ligand field theory, in the late 70s, a number of review articles were collected on small molecules[19-20]. De Brouchere

(1978) published a100 page review containing 289 references[21]. But till then no calculations on nuclear shielding and spin-spin coupling parameters was carried out. **H F** approach, given by Nakatsuzi did present a paper on calculation of NMR parameters of complexes[22],but it was found lacking in high oxidation states d^{10} systems[23]. In 80s, NMR shielding codes based on **HFS**or X α method were developed. It was later called DFT[23-25]. In 1993, Kohn-Sham DFT employed **IGLO** method to calculate nuclear shielding[26-27]. **LORG** approach[28] as improved upon by **GIAODFT**[29-30] and **CSGT** methods[31] was employed. The spin-spin coupling constants of the metal complexes were first of all calculated by Malkin et al.[32]. In 1996, Dickson and Zieglar [33] calculated **FC** term[34] by finite-perturbation approach. Later on, **SD** term[35-36] was also included in spin-spin coupling values.

The software gave both the ESR [(Hyperfine coupling Constant (A $_{ten}$)], NQR parameters [Nuclear Quadrupole Coupling Constant (NQCC) and asymmetric constant (η)]from its "ESR/EPR Program" while Shielding constants (σ) and Chemical shifts (δ) of copper(II) and the Coordinating Atoms (CA) of ligands were calculated by another program called "NMR/EPR Program".

Theoretical Basis of Prediction of ESR Peaks

Method evolved to theoretically predict the exact number of ESR peaks in chelating Cu(II) complexes which, hitherto, was not attempted had been summarized as follows:

I. The unpaired electron of ^{63}Cu(II) may undergo hyperfine interaction with coordinating ^{14}N and X= ^{35}Cl, ^{79}Br, ^{127}Iof ligands as all have appreciable natural abundances.

II. The presence of a large Jahn-Teller effect generally allowed hyperfine interaction. Therefore, peaks should arise both from ^{63}Cu(II) and ^{14}N, ^{35}Cl, ^{79}Br, ^{127}Iof ligands.

III. ^{63}Cu(II)(I=3/2) would always give a quartet according to the relation:

$$(2 I_M +1) \qquad ...(a)$$

IV. The five parameters such as A $_{ten}$, NQCC, η, σ, δ were obtained from the software. If these parameters possessed the same values for the [CA], then ligands would be spatially equivalent otherwise non equivalent.

Knowing spatial nature of ligands, the number of peaks was predicted as follows:

(a) Suppose I_{CA} was the nuclear spin of coordinating atoms of ligands and all the **n** ligands were spatially equivalent then the number of lines obtained were:

$$(2\,n\,I_{CA}+1) \qquad ...(b)$$

(b) When n_1 ligands were spatially of one type; n_2 are of the other type and so on, then number of lines observed were:

$$(2\,n_1\,I_{CA}+1)(2n_2\,I_{CA}+1)(2\,n_3\,I_{CA}+1) \qquad ...(c)$$

(c) All **n** spatially nonequivalent ligands would show the lines equal to:

$$(2\,I_{CA}+1)^n \qquad ... (d)$$

As there was a considerable overlapping of ESR lines due to different reasons, the experimentally observed number of lines might be less than theoretically predicted lines. Also, when the predicted number of lines was large and A_{ten} values of species undergoing hyperfine interaction were very small, they may merge to give a continuum.

Further, if A_{ten} of Cu(II) was of higher value than those of CA of ligands, then first a large quartet from Cu(II) should be considered .This might, further, split into a number of lines by CA of ligands if a hyperfine interaction was possible. Conversely, if the CA of ligands possessed higher A_{ten} value/s, then, we should first calculate number of lines obtained from the ligands. Each line of the ligands, may, then split into a quartet from Cu(II) due to hyperfine interaction between Cu(II) and ligands.
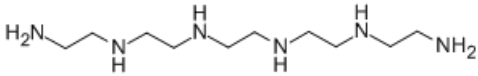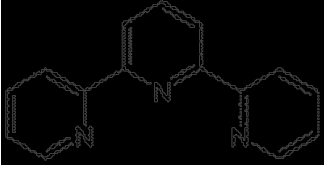
Methodology
Obtaining ESR and NQR parameters

After *optimization* of complexes, the software was run by *Single Point, LDA, Default, Spin Orbit, Unrestricted, None*, *Collinear* commands using *DZ* or *TPZBasis sets* with *No sym*symmetry in its "ESR/EPR Program" to obtain ESR (A_{ten}) and NQR (NQCC,η) parameters for the Cu(II) and the coordinating atoms (^{14}N, ^{35}Cl, ^{89}Br, ^{127}I) of the ligands[37-40].

Obtaining NMR Parameters

The σ and δ values of Cu (II) and ^{14}N, ^{35}Cl, ^{89}Br, ^{127}I of ligands were obtained from "NMR/EPR Program" by the above commands except for replacing *Spin Orbit* by *None*[29,41-42].

Table 1: Abbreviations, acronyms and their expanded forms

Abbreviation	Expanded Forms	Acronyms	Expanded Forms
	Diamine NH_2-CH_2-CH_2-NH_2	ZORA	Zeroth-Order Regular Approximation
	Diethylenetriamine $HN(CH_2CH_2NH_2)_2$	H F	Hartree- Fock
Or Trien	Triethylenetetramine $[CH_2NHCH_2CH_2NH_2]_2$	HFS	Hartree-Fock-Dickson-Slater)
	Tetraethylenepentamine	IGLO	Independent or Individual Gauge of Localized Orbitals
	Pentaethylenehexamine	LORG	Localized Orbitals Resonance Gauge
		GIAO	Gauge Including Atomic Orbitals
		CSGT	Continuous Set of Gauge Transformations
		SD	Spin-dipole
		FC	Fermi-contact
		LDA	Local Density Approximation
	Terpyridine		
	Glycinato -O(CO)-CH2-NH2	DZ	Double Zeta
	Ethylenediaminetetraacetato $[(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2]^{4-}$	TPZ Nysom	Triple Zeta Normalized or True

RESULTS

Table: 1 and 2 gave expanded forms of the names of the ligands, acronyms used , optimization parametersgiving the bonding energies, the total energies (Xc) including their LDA components consisting of Exchange and Correlation parts [43-44]. Tables: 3-4 contained values of A $_{ten}$, NQCC, η, σ, δ of Cu(II) and the CA along with the spatial nature of ligands for the fourteen Cu(II)complexes.

DISCUSSION

No doubt, ESR of Cu (II) complexes had been extensively studied at room temperature, but the experimental determination of number of its ESR peaks having a large number of spatially different ESR active nuclei was cumbersome.

Table for ESR, NQR and NMR Parameters of Cu (II) and N of Copper (II) Polyethylene polyamines Complexes

Table: 3 contained A $_{ten}$, NQCC, η , σ , δ values of the parameters of Cu(II) and the Coordinating Atoms(CA) of the ligands for [Cu(gly)$_2$], [Cu(edta)]$^{4-}$ and [Cu(L)]$^{2+}$ (L=*en, teta, tepa*and*peha*).Their ESR discussion was divided into four parts:

Number of ESR Peaks in [Cu (gly)$_2$] and[Cu(edta)]$^{4-}$

Table 2: Optimization Parameters of Copper (II) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy :X c [kJ mol^{-1}] LDA(Exchange; Correlation)
[Cu(gly)$_2$]	C$_2$	11.0	-10851.04	-338936.63 -319322.20; -19614.43
Cu(edta)] $^{4-}$	C$_2$	10.3	-19296.54	-497280.87 -465641.17; -31639.70
[Cu(en)$_2$]$^{2+}$	C$_1$	1.4	-11461.20	-294532.08 -277441.03; -17091.06
[Cu(teta)]$^{2+}$	C$_1$	3.0	-14070.64	-320541.62 -301291.69; -19249.94
[Cu(tepa)]$^{2+}$	C$_1$	2.2	-18061.38	-364494.57 -341574.58; -22920.00
Cu(peha)] $^{2+}$	C$_1$	2.2	-19850.46	-408474.95-381881.65; -26593.31
[Cu(deta)Cl$_2$]	C$_s$	13.3	-11681.36	-417048.89 -394474.78; -22574.11
[Cu(deta)Br$_2$]	C$_s$	13.3	-12168.69	-743708.66 -711425.03; -32283.63
[Cu(deta)I$_2$]	C$_s$	13.2	-23777.60	-1202228.22 -1159801.77; -42426.45
Cu(deta)(NCS)$_2$	C$_s$	12.5	469.66	-460842.42 -434423.66; -26418.76
[Cu(tpy)Cl$_2$]	C$_{2v}$	8.04	-20756.01	-552275.99 -519159.50; -33116.50
[Cu(tpy)Br$_2$	C$_{2v}$	7.9	-21266.37	-878917.74 -836093.81; -42823.93
[Cu(tpy)I$_2$]	C$_1$	7.4	-32800.17	-1337425.22 -1284459.56; -52965.66
[Cu(tpy)(NCS)$_2$]	C$_s$	4.5	-8767.54	-596097.26 -559133.50; -36963.76

Table 3: ESR, NQR and NMR Parameters of Cu (II) and N

Complex	5 Parameters of Cu(II)			Total Number of N and their 5 Parameters						Spatial nature of N
	A_{ten} [NQCC][h]	σ	δ	No	A_{ten}	NQCC	η	σ	δ	
$[Cu(gly)_2]$	171.21 [-79.56](0.661)	-5476.3	5476.3	2	49.96	-2.77	0.24	259.5	-259.5	Both N are equivalent
$[Cu(edta)]^{4-}$	119.787 [22.952](0.847)	-13517.1	13517.1	-do-	129.46	-3.77	0.19	259.1	-259.1	-do-
					-do-	-do-	-do-	-do-	-do-	
$[Cu(en)_2]^{2+}$	-31.04 [-63.18]	-1951.7	1951.7	4	87.1	-2.08	0.17	218.4	-218.4	All N are nonequivalent
					51.1	-2.09	0.29	223.1	-223.1	
					33.6	-2.33	0.29	228.7	-228.7	
					33.8	-2.09	0.30	241.9	-241.9	
$[Cu(teta)]^{2+}$	1.61 [58.382] (0.679)	-1525.7	1525.7	-do-	34.8	-2.23	0.03	240.1	-240.1	-do-
					89.4	-2.51	0.31	162.6	-162.6	
					66.3	-2.22	0.18	186.7	-186.7	
					32.7	-2.52	0.33	239.9	-239.9	
$[Cu(tepa)]^{2+}$	141.90 [-48.95] (0.418)	-17252.2	17252.2	5	71.43	-3.02	0.07	262.3	-262.3	-do-
					186.26	-2.63	0.10	171.5	-171.5	
					91.98	-2.49	0.03	269.4	-269.4	
					83.93	-3.64	0.06	288.6	-288.6	
					72.98	-2.82	0.53	234.0	-234.0	
$[Cu(peha)]^{2+}$	-14.91 [-44.05] (0.688)	-1950.7	1950.7	6	108.5	-4.72	0.56	198.7	-198.7	-do-
					186.2	-2.68	0.45	225.5	-225.5	
					32.5	-3.45	0.22	166.7	-166.7	
					1.75	-3.57	0.15	224.1	-224.1	
					-2.13	-3.46	0.13	140.2	-140.2	
					14.29	-3.41	0.14	226.7	-226.7	

In [Cu(gly)$_2$] and [Cu(edta)]$^{4-}$, both the coordinating N possessed same values of the five parameters respectively to confirm their spatial equivalence. In [Cu(gly)$_2$] each line of a *quartet* of Cu(II)with higher A$_{ten}$ split into a *quintet* from two equivalents N having lower A$_{ten}$ values.Conversely, in [Cu (e d t a)]$^{4-}$ each line of the *quintet* from the two

equivalents N with higher A$_{ten}$ split into a *quartet* from Cu (II)with smaller A$_{ten.}$

Number of ESR Peaks in [Cu(en)$_2$]$^{2+}$ and [Cu(teta)]$^{2+}$

In [Cu(en)$_2$]$^{2+}$ and [Cu(teta)]$^{2+}$, all the four coordinating N were spatiallynon equivalent as all

Table 4: ESR and NMR Parameters of Cu (II), N and X (Cl, Br, I, NCS)

meter	Cu (deta)Cl$_2$	Cu (deta)Br$_2$	Cu (deta)I$_2$	[Cu (deta)(NCS)$_2$]	Cu (tpy)Cl$_2$	Cu (tpy)Br$_2$	Cu(tpy)I$_2$	[Cu(typ) (NCS)$_2$]
A$_{ten\,Cu(II)}$	-22.29	-20.26	-17.54	-74.21	-25.98	51.92	-74.11	44.33
NQCC Cu(II)	78.85	57.53	-35.80	32.24	69.76	65.08	-41.29	-96.51
η Cu(II)	0.392	0.636	0.644	0.251	0.985	0.920	0.590	0.464
σ$_{Cu(II)}$	-2648.9	-2385.0	-1761.5	676.9	-1647.9	-1238.2	-737.8	610.53
δ$_{Cu(II)}$	2648.9	2385.0	1761.5	-676.9	1647.9	1238.2	737.8	-610.53
A$_{ten\,N}$	81.13	69.73	57.18	-10.5	-149.5	146.6	35.84	47.5
	68.15	58.38	43.61	0.6	32.2	30.5	51.30	0.9
	81.13	69.73	57.18	-10.5	-149.5	146.6	40.92	47.5
				-11.5				-3.8
				-7.7				21.5
NQCC$_N$	-2.73	-2.89	-3.77	-3.8	-2.51	-2.51	-2.79	-3.0
	-3.56	-3.61	-296	-3.9	-3.15	-3.13	-2.96	-2.6
	-2.73	-2.89	-3.77	-3.8	-2.51	-2.51	-2.76	-3.0
				5.3				5.3
				5.4				5.6
η$_N$	0.445	0.403	0.130	0.25	0.223	0.211	0.147	0.38
	0.128	0.033	0.387	0.16	0.142	0.162	0.102	0.55
	0.445	0.403	0.130	0.25	0.223	0.211	0.171	0.38
				0.04				0.07
				0.03				0.2
σ$_N$	219.4	218.0	214.5	210.3	-33.6	-29.9	-14.4	9.8
	196.5	196.9	200.5	204.7	28.3	-40.5	-107.1	41.9
	219.4	218.0	214.5	210.3	-33.6	-29.9	12.2	9.8
				57.6				72.0
				52.0				-34.4
δ$_N$	-219.4	-218.0	-214.5	-210.3	33.6	29.9	14.4	-9.8
	-196.5	-196.9	-200.5	-204.7	-28.3	40.5	107.1	-41.9
	-219.4	-218.0	-214.5	-210.3	33.6	29.9	-12.2	-9.8
				-57.6				-72.0
				-52.0				34.4
A$_{ten\,X}$	5.81	41.77	153.09	----	3.40	548.08	297.38	----
	37.46	159.22	424.53		3. 40	548. 08	224.26	
NQCC$_X$	-15.53	102.8	-280.8	----	-37.28	288.7	-885.1	-----
	36.0	270.53	-768.6		-37.28	288.7	1045.9	
η$_X$	0.168	0.221	0.952	----	0.039	0.044	0.219	-----
	0.071	0.005	0.169		0.039	0.044	0.438	
σ$_X$	466.9	1299.9	2672.9	----	223.1	539.9	2324.2	-----
	-262.9	-425.8	431.9		223.1	539.9	558.6	
δ$_X$	-466.9	1299.9	2672.9	----	-223.1	-539.9	-2324.2	-----
	262.9	-425.8	431.9		-223.1	-539.9	-558.6	
Spatial nature of ligands	I .N of two types; first having I N and other having 2 N. II. Both Cl different	I. Two types Of N; first having one N and other having two N. II. Both Br different	I.N of two types; one having I N and other with two N. II. Both I different	N of 4 types;2 of one type and other three of 3 different types	I.N of 2 types; two of 1st and one of 2nd II. Both Cl same type	1,N of 2 types; two of 1st and one of 2nd II .Both Br same type	I. All three N of different types II Both I different	N of 4 types;2 of one type and other three of 3 different types

the five parameters of each N differ from one another. Again, in both the complexes, A_{ten} values of all the four N atoms were higher than that of Cu(II).So ESR spectrum of eachgives 81 lines[c]; each line splitting into a quartet from Cu (II).

Number of ESR Peaks in [Cu (tepa)]$^{2+}$

In [Cu (tepa)]$^{2+}$,one N of highest A_{ten} gave a *triplet* with each line further splitting into a quartet from Cu(II) to give three quartets whose each line was then split into 81 lines [c] from remaining four non equivalents N having lower A_{ten} values.

Number of ESR Peaks in [Cu (peha)] $^{2+}$

In [Cu(peha)]$^{2+}$, the three nonequivalent N withhighest A_{ten} values gave 27[c] lines with each line further splitting into a quartet from Cu (II) to give 27 quartets. Each line of these quartets again split into 27 lines[c] from the remaining three non equivalents N having smallerA_{ten} than Cu (II).

Table for ESR and NMR Parameters of Cu (II), N and X (Cl, Br, I, NCS) of [Cu (deta) X$_2$] Complexes

Table: 4 gave A_{ten}, NQCC, η, σ, δ values of the parameters of Cu(II) and the CA for [Cu (deta) X$_2$] (X= Cl, Br, I, NCS).All these complexes had the same symmetry symbol (C$_s$). Their ESR discussion was divided into four parts:

Number of ESR Peaks in [Cu (deta) Cl$_2$]

In [Cu (deta) Cl$_2$], the relative order of A_{ten} values was observed as:

Two types of the three N › First Cl › Cu (II)› Second Cl

The two types of the three N gave 15 lines [b] with each line splitting into a quartet from first Cl to give 15 quartets. Each line of these quartets again split into another quartet from Cu (II)whose each line would further split into another quartet from the second Cl.

Number of ESR Peaks in [Cu (deta) Br$_2$]

In [Cu (deta) Br$_2$], the relative order of A_{ten} values was:
a)   One Br › Two types of the three N › Second Br› Cu(II)

b)   One Br gave a quartet with each line splitting into15 linesfrom two types of three N [b] to give 15 quartets. Each line of these quartets split into another quartet from the other Br to give sixty quartets. Each line of these quartets again split into a quartet from Cu(II).

Number of ESR Peaks in [Cu (deta) I$_2$]

In [Cu (deta) I$_2$], the relative order of A$_{ten}$ values was:

Both I › Two types of the three N › Cu (II)

Two non equivalents I gave 36 lines [c] with each line splitting into 15 lines from two types of three non equivalentsN;with each line further splitting into a quartet from Cu(II).

Number of ESR Peaks in [Cu (d e t a) (NCS) $_2$]

In [Cu (d e t a) (NCS) $_2$], the relative order of A $_{ten}$ values was given as:

Cu (II) ›Four types five N; two of one type and remaining three of three different types. Here, Cu (II) gave a quartet with each line splitting into 135 lines from two types of a total of five N [(2.2.1+1)(2.1+1)^3][b , c,] .

Table for ESR and NMR Parameters of Cu (II), N and X (Cl, Br, I, NCS) of [Cu (tpy) X$_2$] Complexes

Table: 4 contained A $_{ten}$, NQCC, η, σ, δ values of the parameters of Cu(II) and the CA of complexes [Cu (tpy) X$_2$] (X= Cl, Br, I, NCS) with X=Cl, Br having symmetry symbols (C$_{2v}$) while the complexes (X=I, NCS) possessed C$_1$ and C$_s$ symbols respectively Their ESR discussion is divided into four parts:

Number of ESR Peaks in [Cu (t py) Cl$_2$]

In [Cu (t py) Cl$_2$] the relative order of A$_{ten}$ values was:
a)   Two types of the three N› Cu(II)› Both the Cl
b)   Two types of the three N gave15 lines [b];each line splitting into a quartet from Cu (II) to give 15 quartets. Each line would again split into a septet from two equivalents Cl.

Number of ESR Peaks in [Cu (t py) Br$_2$]

In [Cu (t p y) Br$_2$], the observed relative order of A $_{ten}$ values was:

a)   Two Br › Two N of same type › Cu (II)› Third N of different type

b)   Both the equivalents Br would give a septet [a] with each line split into a quintet from two equivalents N to give 35 lines [b]. Then each line split into a quartet from Cu (II) whose each line would further split into a triplet from the third N.

Number of ESR Peaks in [Cu (t py) I$_2$]

In [Cu (t p y) I$_2$], the relative order of A$_{ten}$ values was observed to be:

a)   Both I of two different types› Cu (II) › Three N of three different types

b)   The two non equivalents I would give 36 lines [c] with each line splitting into a quartet from Cu(II).Then, each line should split into 27 lines from three non equivalents N.

Number of ESR Peaks in [Cu (t p y) (NCS) $_2$]

In [Cu (t p y) (NCS) $_2$], the relative order of A$_{ten}$ values was:

a)   Two N of same type › Cu(II)› Three N of three different types

b)   Two spatially equivalents N gave a quintet [a] with each line splitting into a quartet from Cu(II). Then each line again would split into 27 lines [c] from three spatially different N.

CONCLUSION

The originality, the relevance, the objective of present work and how it moved the bodyof scientific knowledge forward would lay in the fact that we were able to theoretically predict the number of ESR peaks even in these highly distortedcopper (II)complexes.

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