

Copper(II) Simple and Mixed Complexes Containing Tridentate Ligands with O, S, Se Donor Atoms in Aqueous Solution. Spectroscopic Investigations and Thermodynamic Considerations

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Spectroscopic (epr and electronic) investigations have been carried out in solution on the simple and mixed ligand complexes of copper(II) containing oxydiacetate, thiodiacetate or selenodiacetate and 2,2'-bipyridyl or 2,2',2''-terpyridyl. On the ground of the data obtained it is pointed out that the slight differences present along the series of the simple complexes are suppressed in the ternary ones. Pseudo-octahedral geometries are suggested for all these complexes. These results are compared with the thermodynamic parameters previously published.

Introduction

The various factors influencing the formation and stability of mixed ligand metal complexes have been discussed by many workers [1–5]. The effect of the chromophore type around the metal ion on the stability of ternary complexes has been limited to tetra-coordinated compounds, only.

Recently we have determined the thermodynamic properties, in aqueous solutions, of some copper(II) mixed ligand complexes containing 2,2'-bipyridyl (bpy) or 2,2',2''-terpyridyl (tpy) and tridentate ligands with different donor atoms [6–8].

We have now carried out a spectroscopic study (epr and electronic) in solution on the ternary complexes of copper(II) with the above-mentioned bases, by using as second ligands the three dianions (L): oxydiacetate (ODA), thiodiacetate (TDA) and selenodiacetate (SEDA). The prime aim of this work is that of going into the peculiar coordination characteristics of copper(II) ion in these complexes because of the different bonding ability of the donor atoms belonging to group 6B. The experimental data are compared with those of the corresponding simple and parent complexes obtained in the same conditions. The results are discussed together with those drawn out from the thermodynamic investigation

[7], considering the usefulness of this approach in order to obtain a clear picture of geometrical and electronic features of mixed complexes in solution as shown by previous studies [9–11].

Experimental

Chemicals

Oxydiacetic acid (Fluka puriss.), thiodiacetic acid (Fluka purum) and copper(II) nitrate (C. Erba RP) were used without further purification. Selenodiacetic acid previously synthesized by L. D. Pettit *et al.* [12] was kindly supplied by this author, and used as received; its purity was previously verified [7]. 2,2'-bipyridyl (C. Erba RP) and 2,2',2''-terpyridyl were recrystallized from a water–ethanol mixture.

Spectroscopic Measurements

First derivative epr X-band spectra were recorded by means of a Varian E-109 instrument equipped with a standard temperature control unit. All measurements were made at 130 K by using quartz tubes and DPPH as g-marker. The solution of simple and mixed complexes were prepared dissolving the requested amount of the reagents in water, adjusting the pH up to the value of 5–5.5 and diluting the resultant solution ($C_{Cu} = 4 \times 10^{-3} \text{ mol dm}^{-3}$) with methanol in order to obtain a 1:1 water–methanol mixture. Because of the poor coordinating abilities of these dianions, the spectra have been run on solutions containing several ratios of C_L/C_{Cu} . The spectra of simple complexes for ligand to metal ratios ranging from 0.8 to 1.0 showed the presence of two absorbing paramagnetic species, that were attributed to free copper(II) ion and [CuL] complex. The spectra run on solutions containing ratios higher than 1 (up to 10) also showed the presence of two absorbing species that were attributed to [CuL] and

TABLE 1. Spectral (Epr and Visible Absorption) Data of Cu^{II} Simple and Mixed Complexes with Oxydiacetate, Thiodiacetate or Selenodiacetate and 2,2'-bipyridyl or 2,2',2''-terpyridyl.^a

Complex	g_z	g_y	g_x	A_z	A_y	A_x	A_{\parallel}^N	A_{\perp}^N	Electronic spectra (10^3 cm^{-1}) ^c
[Cu(ODA)]	2.385(1)	2.067(2)	2.067(2)	133(1)	13(2)	13(2)	—	—	12.5(42)
[Cu(ODA) ₂] ²⁻	2.335(1)	2.068(2)	2.068(2)	156(1)	8(2)	8(2)	—	—	23.0(32)
[Cu(bpy)(ODA)]	2.293(1)	2.069(5)	2.060(5)	174(1)	3(3)	6(2)	15(2)	10(2)	14.9(69)
[Cu(bpy)(ODA)] + py	2.255(1)	2.063(5)	2.058(5)	186(1)	6(3)	5(3)	15(2)	10(2)	15.1(104)
[Cu(tpy)(ODA)]	2.254(1)	2.065(5)	2.055(5)	176(1)	8(3)	10(3)	—	—	14.8(110)
[Cu(TDA)]	2.381(1)	2.071(5)	2.065(5)	136(1)	3(3)	5(3)	—	—	13.0(40)
[Cu(TDA) ₂] ²⁻	2.315(1)	2.042(2)	2.042(2)	143(1)	8(3)	8(3)	—	—	14.3(56)
[Cu(bpy)(TDA)]	2.290(1)	2.065(5)	2.054(5)	171(1)	3(3)	6(3)	14(2)	10(2)	15.0(69); 11.4(31)
[Cu(bpy)(TDA)] + py	2.259(1)	2.069(5)	2.062(5)	181(1)	8(3)	5(3)	15(2)	10(2)	14.7(92); 11.7(54)
[Cu(tpy)(TDA)]	2.253(1)	2.070(5)	2.064(5)	175(1)	8(3)	5(3)	—	—	14.6(143)
[Cu(SEDA)]	2.381(1)	2.073(5)	2.065(5)	137(1)	4(3)	5(3)	—	—	13.2(50)
[Cu(SEDA) ₂] ²⁻	2.314(1)	2.041(2)	2.041(2)	140(1)	10(3)	10(3)	—	—	14.6(64)
[Cu(bpy)(SEDA)]	2.292(1)	2.068(5)	2.055(5)	172(1)	3(3)	6(3)	14(2)	10(2)	15.3(110); 11.7(63)
[Cu(bpy)(SEDA)] + py	2.257(1)	2.065(5)	2.059(5)	180(1)	8(3)	3(3)	15(2)	10(2)	15.1(128); 11.6(73)
[Cu(tpy)(SEDA)]	2.250(1)	2.062(5)	2.056(5)	175(1)	8(3)	7(3)	—	—	15.0(164)
[Cu(bpy)] ^{2+ b}	2.308(4)	2.068(4)	2.068(4)	166(2)	7(2)	7(2)	14	10	—
[Cu(tpy)] ²⁺	2.270(1)	2.064(2)	2.064(2)	175(1)	15(3)	15(3)	14(2)	10(2)	14.7(80)
[Cu(tpy)(OH)] ⁺	2.259(1)	2.063(2)	2.063(2)	157(1)	16(3)	16(3)	14(2)	10(2)	—

^aThe values in parentheses are the presumed errors on the last decimal figure. All hyperfine coupling constants are in 10^4 cm^{-1} .

^bF. A. Walker, J. H. Sigel and D. B. McCormick, *Inorg. Chem.*, **11**, 2576 (1972). ^cThe values in parentheses are the molar absorption coefficients in $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

[Cu(L)₂]²⁻ complexes. This procedure was shown to be particularly useful to distinguish among several species present in the spectra. The spectra of ternary complexes were recorded from solutions containing copper(II) ion and bpy or tpy in the same molar ratio, while an excess of the dianions (up to 10) was used in order to promote the mixed species formation. The spectra showed only one absorbing species that was attributed to [Cu(B)(L)] (B = 2,2'-bipyridyl or 2,2',2''-terpyridyl) even if this species can be sometimes accompanied by the mono-complex [CuL]. The [Cu(bpy)(L)] solution spectra were also recorded from solutions after the addition of free pyridine (ranging from 2% to 30%) and they were consistent with a single set of bands. The solution spectra of Cu-tpy system were also examined, fixing the ratio $C_{\text{tpy}}/C_{\text{Cu}}$ equal to 1 and adjusting the solution acidity to pH = 3 and pH = 8. At these values two different singlet sets of bands characteristic of monomer species were found; they were attributed to the complexes [Cu(tpy)]²⁺ and [Cu(tpy)(OH)]⁺ respectively on the basis of the distribution diagram previously obtained [13].

Electronic absorption spectra in solution were recorded at room temperature with an Optica CF 4 NI double beam spectrophotometer in 1 cm silica cells. In the case of simple complexes the spectra were recorded on solutions containing different ratios of C_L/C_{Cu} to draw out the absorption pattern of each species.

Calculations

The analysis of epr spectra has been carried out using a simulation program originally due to Pilbrow *et al.* [14] and slightly modified to perform calculations over more than one absorbing species. It was assumed that g and hyperfine coupling tensors had the same principal axis system. The epr data collected in Table I are the best spin hamiltonian parameters that fitted closely enough the experimental spectra. The analysis of electronic absorption spectra of simple complexes has been performed by using the EQUIL program [15] in order to work out exactly the concentrations of the two predominant species CuL and [Cu(L)₂]²⁻. The experimental conditions we have chosen for the measurements and

TABLE II. Experimental Conditions for Calculation of Molar Extinction Coefficients.

System	$[\text{Cu}^{2+}]_{\text{Tot}}$ 10^2 mol dm^{-3}	$[\text{L}]_{\text{Tot}}$ 10^2 mol dm^{-3}	$[\text{Cu}^{2+}]$ 10^3 mol dm^{-3}	$[\text{CuL}]$ 10^3 mol dm^{-3}	$[\text{Cu}(\text{L})_2]^{2-}$ 10^3 mol dm^{-3}	pH
Cu-ODA	1	1	1.4	7.7	—	3.61
	1	9	—	2.6	7.4	4.40
Cu-TDA	0.8	0.8	1.3	6.0	—	3.54
	1	9	—	0.45	9.5	4.59
Cu-SEDA	0.53	0.6	1.7	2.6	—	3.78
	0.56	6	—	1.8	3.8	5.37

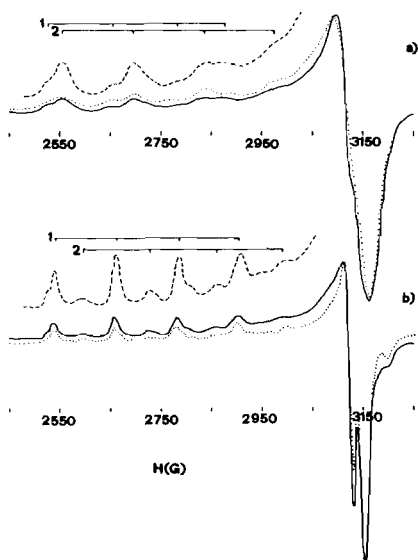


Fig. 1. Frozen-solution epr spectra of copper(II)-oxidiacetate system a) $[\text{Cu}(\text{ODA})]$ 1., $[\text{Cu}(\text{ODA})_2]^{2-}$ 2.; and copper(II)-thiodiacetate system b) $[\text{Cu}(\text{TDA})]$ 1., $[\text{Cu}(\text{TDA})_2]^{2-}$ in water-methanol mixture with $[\text{Cu}] = 2-3 \times 10^{-3} \text{ mol dm}^{-3}$ and $C_{\text{ODA}}/C_{\text{Cu}} = C_{\text{TDA}}/C_{\text{Cu}} = 10$ at 130 K. Dotted lines are the simulated spectra obtained using the spin hamiltonian parameters reported in Table I.

calculation of molar extinction coefficients are presented in Table II.

Results and Discussion

Simple Complexes

As one can see from Table I, the spin Hamiltonian parameters of these species are not quite different even if slight differences between $[\text{Cu}(\text{ODA})]$ or $[\text{Cu}(\text{ODA})_2]^{2-}$ and $[\text{Cu}(\text{TDA})]$, $[\text{Cu}(\text{SEDA})]$ or $[\text{Cu}(\text{TDA})_2]^{2-}$, $[\text{Cu}(\text{SEDA})_2]^{2-}$ might be taken into account in order to estimate the probable stereochemistry of these complexes. In Fig. 1 the epr

spectra of the systems $[\text{Cu}(\text{ODA})]$ - $[\text{Cu}(\text{ODA})_2]^{2-}$ and $[\text{Cu}(\text{TDA})]$ - $[\text{Cu}(\text{TDA})_2]^{2-}$ are reported together with their best simulation.

$[\text{Cu}(\text{ODA})]$ and $[\text{Cu}(\text{ODA})_2]^{2-}$ give an axial-type spectrum, the parameters of which show a noteworthy ionic bonding situation around the copper(II) ion. The values of g_z and A_z for the complex $[\text{Cu}(\text{ODA})_2]^{2-}$, lower and higher than the relative ones for the mono-complex respectively, can be ascribed to the fact that we are dealing with a negative charged compound [16]. Previous diffractometric and Raman spectroscopic solution studies [17, 18] on the compound $\text{Cu}(\text{ODA}) \cdot 6\text{H}_2\text{O}$ have shown that the chelation of ODA ligand occurs in such a way as to make the metal ion and the three oxygen donor atoms lie in the same plane. Actually one can assert that the epr parameters just reflect this situation giving rise to two pseudo-octahedral compounds; three water molecules are supposed to be linked to $[\text{Cu}(\text{ODA})]$ in order to achieve the coordination number of six. It is interesting to note the similarity between the $g_{x,y}$ values of $[\text{Cu}(\text{ODA})]$ and $[\text{Cu}(\text{ODA})_2]^{2-}$ species; it reflects the point that the bonding situation is not very different: after all $[\text{Cu}(\text{ODA})]$ and $[\text{Cu}(\text{ODA})_2]^{2-}$ can be considered as having CuO_6 chromophore in a tetragonally distorted octahedral geometries.

$[\text{Cu}(\text{TDA})]$ and $[\text{Cu}(\text{SEDA})]$ show a quite similar pattern in their g_z and A_z values, whilst their perpendicular part of the spectrum is characterized by the appearance of a well resolved slight rhombic component. This particular behaviour could also be explained considering an extra-peak appearance in the high field region of the spectrum, taking into account the high anisotropy of both g and A tensors [19]. But the presence of different donor atoms in the equatorial plane strengthens the conclusion of a rhombic component. Also in this case both bis-complexes $[\text{Cu}(\text{TDA})_2]^{2-}$ and $[\text{Cu}(\text{SEDA})_2]^{2-}$ have lower g_z and higher A_z , furthermore their $g_{x,y}$ strongly decrease up to 2.04 (an axial symmetry was assumed to overcome the difficulties arising from a

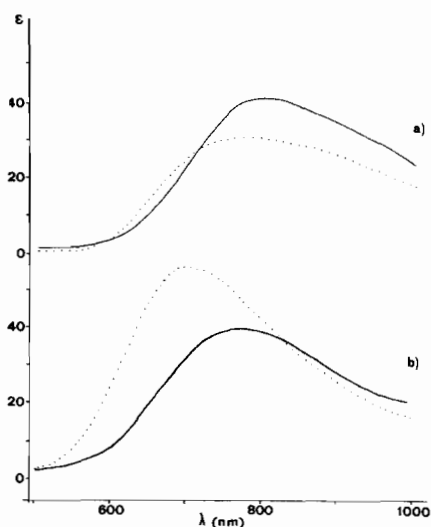


Fig. 2. Visible absorption spectra of $[\text{Cu}(\text{ODA})]$ (—) and $[\text{Cu}(\text{ODA})_2]^{2-}$ (.....) a), $[\text{Cu}(\text{TDA})]$ (—) and $[\text{Cu}(\text{TDA})_2]^{2-}$ (.....) in aqueous solutions, at room temperature. The experimental conditions are reported in Table II.

perpendicular part poorly resolved). These results can be taken as an acceptable evidence of the coordination of a sulphur or a selenium atom which are greater than an oxygen one, thus destroying the square symmetry of the plane. The lower g_z and $g_{x,y}$ values found in the case of the bis-complexes $[\text{Cu}(\text{TDA})_2]^{2-}$ and $[\text{Cu}(\text{SEDA})_2]^{2-}$ with respect to the analogous species $[\text{Cu}(\text{ODA})_2]^{2-}$ account for a more covalent situation. This different behaviour agrees with the spectral pattern shown by these complexes. In Figure 2 the electronic absorption spectra of $[\text{Cu}(\text{ODA})]$, $[\text{Cu}(\text{ODA})_2]^{2-}$, $[\text{Cu}(\text{TDA})]$ and $[\text{Cu}(\text{TDA})_2]^{2-}$ systems are reported in the region 400–1000 nm. The trend shown by the $[\text{Cu}(\text{SEDA})]$, $[\text{Cu}(\text{SEDA})_2]^{2-}$ system ($[\text{Cu}(\text{SEDA})_2]^{2-}$ overall formation constant was estimated to be $\log \beta_2 = 5.2 \pm 0.2$) is very similar to the copper(II) thiodiacetate one. This trend is the expected one for an increase of covalency around the copper(II) ion [20, 21] on going from CuO_6 to CuSO_5 and CuS_2O_4 or CuSeO_5 and CuSe_2O_4 chromophores. $[\text{Cu}(\text{tpy})]^{2+}$ and $[\text{Cu}(\text{tpy})(\text{OH})]^+$ epr spectra can be fitted by an axial spin hamiltonian. It is interesting to observe the shift undergone by the g_z , $g_{x,y}$, and A_z , when an hydroxyl group substitutes a water molecule. The shift of g_z and $g_{x,y}$ is the theoretical one [22, 23] predicted for an increased covalency in the equatorial plane, but the A_z decrease does not agree with this hypothesis. Probably the shift of g_z and $g_{x,y}$ is to be ascribed to a partial neutralization of the double charge present in $[\text{Cu}(\text{tpy})]^{2+}$ while the less A_z is indicative of a tetrahedral distortion [24].

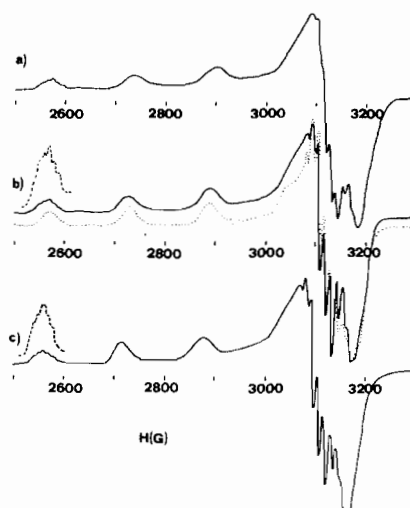


Fig. 3. Frozen-solution epr spectra of $[\text{Cu}(\text{bpy})(\text{ODA})]$ a), $[\text{Cu}(\text{bpy})(\text{TDA})]$ b), and $[\text{Cu}(\text{bpy})(\text{SEDA})]$ c) in water-methanol mixture $[\text{Cu}] = [\text{bpy}] = 2-3 \times 10^{-3} \text{ mol dm}^{-3}$ and $C_{\text{ODA}}/C_{\text{Cu}} = C_{\text{TDA}}/C_{\text{Cu}} = 1.5$, $C_{\text{SEDA}}/C_{\text{Cu}} = 2.5$ at 130 K. Dotted lines represent the simulated spectrum obtained for $[\text{Cu}(\text{bpy})(\text{TDA})]$ using the spin hamiltonian parameters reported in Table I.

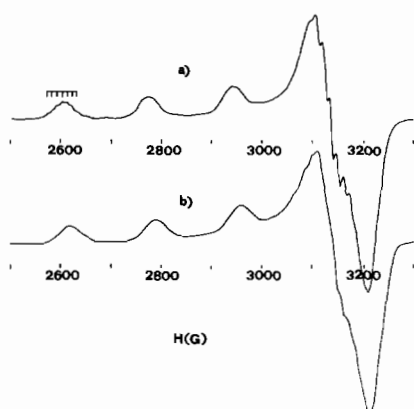
Mixed Complexes

In the case of the mixed complexes $[\text{Cu}(\text{bpy})(\text{L})]$ or $[\text{Cu}(\text{tpy})(\text{L})]$ the differences between their spectral parameters become less evident. It is convenient to examine first the mixed complexes with tpy because there is no possibility of other coordination from a chelation of the two ligands in perpendicular planes; this condition is assured by the obvious planarity of tpy molecule. In fact, both epr and electronic results show that these compounds behave in the same way, as one can see from a careful inspection of Table I. Only a difference in the visible absorption extinction coefficients can be observed, but it increases along the series O, S, Se owing to the formation of more covalent bonds [21]. The slight rhombicity shown by these systems is to be ascribed to distorted octahedral geometries because of the steric conditions imposed by the coordination of tpy. In these mixed complexes with tpy the TDA and SEDDA dianions are probably forced to occupy the free positions after the coordination of the tpy molecule occurred.

Within the series of the complexes $[\text{Cu}(\text{bpy})(\text{L})]$ the epr parameters are not very different. The bpy molecule coordinates in the equatorial plane as it is possible to see from the superhyperfine structure due to two nitrogens that appears in all these spectra. In Fig. 3 the epr spectra for the systems $[\text{Cu}(\text{bpy})(\text{ODA})]$, $[\text{Cu}(\text{bpy})(\text{TDA})]$ and $[\text{Cu}(\text{bpy})(\text{SEDA})]$ are presented. Also in this case these complexes seem to give rise to distorted octahedral geometries (the six position being occupied by a water mole-

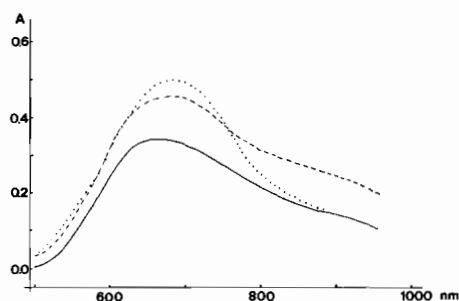
TABLE III. Enthalpic Changes of Mixed Complexes of Copper(II) Containing Oxidiacetate, Thiodiacetate or Selenodiacetate and 2,2'-Bipyridyl in Aqueous Solution at 25 °C and $I = 0.1 \text{ mol dm}^{-3}$ (KNO_3).^a

Equilibrium	ΔH° (kJ mol ⁻¹)
$\text{Cu}^{2+} + \text{bpy} + \text{ODA}^{2-} \rightleftharpoons [\text{Cu}(\text{bpy})(\text{ODA})]$	-29.9
$[\text{Cu}(\text{ODA})] + \text{bpy} \rightleftharpoons [\text{Cu}(\text{bpy})(\text{ODA})]$	-44.8
$\text{Cu}^{2+} + \text{bpy} + \text{TDA}^{2-} \rightleftharpoons [\text{Cu}(\text{bpy})(\text{TDA})]$	-40.6
$[\text{Cu}(\text{TDA})] + \text{bpy} \rightleftharpoons [\text{Cu}(\text{bpy})(\text{TDA})]$	-44.7
$\text{Cu}^{2+} + \text{bpy} + \text{SEDA} \rightleftharpoons [\text{Cu}(\text{bpy})(\text{SEDA})]$	-35.9
$[\text{Cu}(\text{SEDA})] + \text{bpy} \rightleftharpoons [\text{Cu}(\text{bpy})(\text{SEDA})]$	-46.0

^aRef. 7.Fig. 4. Frozen-solution epr spectra of $[\text{Cu}(\text{bpy})(\text{SEDA})]$ + pyridine system a) and $[\text{Cu}(\text{tpy})(\text{SEDA})]$ b) in water-methanol mixture at 130 K.

cule), even if in the case of $[\text{Cu}(\text{bpy})(\text{TDA})]$ and $[\text{Cu}(\text{bpy})(\text{SEDA})]$ the additional shoulder centered at about 830–910 nm (it is absent in the electronic spectrum of $[\text{Cu}(\text{bpy})(\text{ODA})]$) might lead one to think that a square-pyramidal arrangement can be achieved [25, 26].

Electronic and epr spectra have also been run after some free pyridine was added to the solutions of $[\text{Cu}(\text{bpy})(\text{L})]$ complexes, in order to ascertain the position that the water molecule occupies in the copper(II) coordination polyhedron. In Fig. 4 the epr spectra of $[\text{Cu}(\text{bpy})(\text{SEDA})]$ + pyridine and $[\text{Cu}(\text{tpy})(\text{SEDA})]$ are reported, while in Fig. 5 the features of electronic spectra of $[\text{Cu}(\text{bpy})(\text{TDA})]$, $[\text{Cu}(\text{bpy})(\text{TDA})]$ + pyridine and $[\text{Cu}(\text{tpy})(\text{TDA})]$ are shown in order to make a comparison among them. The addition of pyridine causes an opposite shift in the values of g_z and A_z ; moreover the super-hyperfine nitrogen structure appearing in the parallel part of their spectra can be attributed to the presence of three quasi-equivalent nitrogens in the equatorial plane. This addition also makes the electronic band

Fig. 5. Visible absorption spectra of $[\text{Cu}(\text{bpy})(\text{TDA})]$ (—), $[\text{Cu}(\text{bpy})(\text{TDA})]$ + pyridine (-----) and $[\text{Cu}(\text{tpy})(\text{TDA})]$ (.....) at room temperature. The concentration of $[\text{Cu}(\text{bpy})(\text{TDA})]$ is $5 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{Cu}(\text{tpy})(\text{TDA})]$ is $3.3 \times 10^{-3} \text{ mol dm}^{-3}$.

become more symmetric, increasing ϵ_{max} and slightly shifting ν_{max} only. The values of g tensors are similar to those found in the mixed complexes with tpy. The higher A_z values mean that no distortion is involved when bpy and pyridine chelate on the same plane.

Tridentate ligands bonded to the copper(II) ion through the donor atom sets O_3 , O_2S and O_2Se do not give rise to peculiar differences in the coordination polyhedron (substantially octahedral), only causing small distortions in the geometry of these complexes because of the different covalent character of the group 6B atoms. This behaviour is in agreement with the thermodynamic results previously obtained [7] and reported in Table III. As one can see the enthalpic changes (they are apparently different if the overall equilibrium is considered) result to be similar among them and approximately equal to the enthalpic change for the simple reaction $\text{Cu}^{2+} + \text{bpy} \rightleftharpoons [\text{Cu}(\text{bpy})]^{2+}$ ($-44.6 \text{ kJ mol}^{-1}$) [27].

The results of this spectroscopic study seem to confirm not only the preceding assertion upon the levelling effect of the heterocyclic diimine in copper(II) ternary complexes [10, 11] (extending such an effect to tridentate ligands containing different

chromophore group), but they point out that an analogous effect is obtained in the ternary complexes with tpy. This means that varying the coordination level of copper(II) ion, from a tetra-coordination in the complexes $[\text{Cu}(\text{bpy})(\text{L}')]$ ($\text{L}' =$ dicarboxylate dianion) [9, 10] to an hexa-coordination in the complexes $[\text{Cu}(\text{bpy})(\text{L})]$ here reported, the influence of nitrogen donor atoms in suppressing the differences found along the series of the simple complexes, remains constant. These results agree with previous conclusions [11, 28] about the fact that the geometric and electronic characteristics of the 'strongest' ligand bonded to the metal ion are the driving forces for the chelation of the second. In fact both the $\log K_{\text{Cu}(\text{bpy})}^{\text{Cu}}$ and $\log K_{\text{Cu}(\text{tpy})}^{\text{Cu}}$ values are always higher than $\log K_{\text{CuL}}^{\text{Cu}}$ ones ($\log K_{\text{Cu}(\text{bpy})}^{\text{Cu}} = 8.11$, $\log K_{\text{Cu}(\text{tpy})}^{\text{Cu}} = 12.29$, $\log K_{\text{Cu}(\text{ODA})}^{\text{Cu}} = 4.17$, $\log K_{\text{Cu}(\text{TDA})}^{\text{Cu}} = 4.43$ and $\log K_{\text{Cu}(\text{SEDA})}^{\text{Cu}} = 3.54$).

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