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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF COPPER(II) TERNARY COMPLEXES OF 4-AMINOBENZOIC ACID AND PHENANTHROLINES

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Abstract—Solid state and solution EPR, and electronic spectroscopy, conductivity and magnetic susceptibility studies were carried out on a series of copper(II) complexes with different substituted phenanthrolines and 4-aminobenzoic acid. The ternary complexes were obtained as monomers of the type [Cu(pAb)₂(phen)] [pAbH = 4-aminobenzoic acid, phen = unsubstituted phenanthroline (1) or 4,7-dimethyl- (2), 2,9-dimethyl- (3), 5-nitro-(4), 3,4,7,8-tetramethylphenanthroline (5)] or dimers of the type [Cu(pAb)(phen) (H₂O)]₂(NO₃)₂ [phen = 4,7-dimethyl- (6), 5-nitro- (7), 4,7-diphenylphenanthroline (8)] as a function of the condition of the reaction, as well as a function of the position of the substituents on the phenanthroline ligand. The formation of aromatic ring stacking interaction is a function of the geometry of the coordination sphere, as well as of the substituents on the phenanthroline ligand.

4-Aminobenzoic acid is involved in the biosynthesis of folic acid, which is a constituent of the vitamin B complex and is found in animal and plant tissues. 4-Aminobenzoic acid has been shown to be a growth factor in certain microorganisms,¹ particularly Enterococci and Lactobacilli, and it is well known as an inhibitor of the bacteriostatic action of sulphonamide.²

Pursuing our interest in the study of ternary metal complexes of molecules of biological importance containing a copper(II)–phenanthroline core,^{3–5} we examined copper(II) ternary complexes of 4-aminobenzoic acid (pAbH) with some substituted phenanthrolines, such as 2,9-dimethyl- (2,9-phen), 4,7-dimethyl- (4,7-phen), 5-nitro- (5-NO₂-phen),

3,4,7,8-tetramethyl- (3,4,7,8-phen) and 4,7diphenylphenanthroline (4,7-dph).

These compounds were synthesized with the aim of inducing electronic and structural changes in derivatives retaining the copper(II)-phenanthroline core. The main goal was to ascertain whether the position of different substituents on the aromatic ring of phenanthrolines can be related to structural variety in these new ternary complexes with the 4-aminobenzoate anion. In addition, we discuss the possibility of obtaining a binuclear structure through an intramolecular stack between phenanthroline ligands.

Among intramolecular ligand-ligand non-covalent interactions occurring in ternary metal complexes, the stacking interactions between suitable aromatic rings of the two coordinated ligands are of great interest with regard to biological systems. In fact, intramolecular stacks are known

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to occur in a number of mixed-ligand complexes of biological interest.^{6,7}

The ternary complexes were obtained as monomers of the type $[Cu(pAb)_2(phen)]$, in which exchange interaction between metal ions can be excluded, as well as dimers of the type [Cu(pAb) $(phen)(H_2O)]_2(NO_3)_2$, in which antiferromagnetic coupling between copper(II) ions is present, as a function of the condition of the reaction, as well as a function of the nature of the substituents and their position on the phenanthroline rings.

The compounds were characterized in the solid state and in solution by means of conductivity and magnetic measurements, IR, EPR and UV-vis spectroscopy.

EXPERIMENTAL

Materials

4-Aminobenzoic acid was purchased from Fluka; 4,7-dimethyl-, 2,9-dimethyl-, 5-nitro-, 3,4,7,8-tetramethyl- and 4,7-diphenylphenanthrolines were purchased from Aldrich; $Cu(NO_3)_2$. $3H_2O$ was from Fluka. The binary $[Cu(pAb)_2]$ complex was prepared as reported by us in a previous work,⁸ and used as a starting material in the synthesis of the monomer ternary complexes. Solvents and chemicals were of high purity grade.

Physical measurements

Elemental analyses were carried out on a Perkin– Elmer 240 B instrument; thermogravimetric determinations were made under an air flow on a Perkin– Elmer TGS-2 instrument using a heating rate of 5°C min⁻¹ in the 25–850°C range. Electronic (solution) spectra were recorded on a Jasco Uvidec 610 spectrophotometer equipped with a reflectance unit. Magnetic susceptibilities were measured at room temperature using the Faraday method on a Bruker B-MB4 electrobalance with Hg[Co(SCN)₄] as a calibrant and correcting for diamagnetism with the appropriate Pascal constants. IR spectra were recorded as KBr pellets (4000–400 cm⁻¹) using a Perkin–Elmer 983 spectrophotometer.

EPR spectra at 298 and 115 K were obtained in the solid state and in DMF or DMSO solution using a Bruker ER 220D-SRC spectrometer (Xband). The microwave frequency was calibrated against powder diphenylpicrylhydrazyl (dpph; g = 2.0036). Spin Hamiltonian parameters were obtained by simulating EPR spectra by means of a revised version of the Monoclin program.⁹ Synthesis

Complexes of the type $[Cu(pAb)_2(phen)]$ (1), $[Cu(pAb)_2(4,7\text{-phen})]$ (2), $[Cu(pAb)_2(2,9\text{-phen})]$ (3), $[Cu(pAb)_2(5\text{-NO}_2\text{-phen})]$ (4) and $[Cu(pAb)_2$ (3,4,7,8-phen)] (5) were prepared using the binary $[Cu(pAb)_2]$ complex as a starting material, by adding a MeOH solution of the proper phenanthroline to an aqueous solution of the binary $[Cu(pAb)_2]$ complex in the molar ratio 1:1. After magnetic stirring, the powdered precipitates separated.

The synthesis of complexes of the type $[Cu(pAb) (4,7-phen)(H_2O)]_2(NO_3)_2$ (6), $[Cu(pAb)(5-NO_2-phen)(H_2O)]_2(NO_3)_2$ (7) and $[Cu(pAb)(4,7-dph) (H_2O)]_2(NO_3)_2$ (8) was carried out by adding a MeOH solution of the proper phenantroline to an aqueous solution of 4-aminobenzoic acid. Then, an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ was added. The respective molar ratio in the reaction mixture was 1:1:1. Small crystals of the compounds separated and were air dried.

RESULTS AND DISCUSSION

The elemental analysis and the conductivity measurements at 5×10^{-4} M concentration in DMF resulted in agreement with the formulation $[Cu(pAb)_2(phen)] \cdot nH_2O$ [Cu(pAb)(phen) or $(H_2O)]_2(NO_3)_2 \cdot nH_2O$, where n is different for the different compounds (n = 2-3.5). Thermogravimetric analysis was used to monitor the solvent content. Thermal gravimetry showed that loss of the solvent molecules is complete at about 80°C for the first type of solvated compound. The second type of compound lost solvent molecules from 50 to 150-200°C in a process that seems to involve overlapping steps, as expected for complexes where water molecules are coordinated or not.

Magnetic susceptibility measurements at 290 K of the compounds gave μ_{eff} values in the 1.6–1.7 μ_B range. They seem to exclude exchange interaction between metal ions for all the compounds. In fact, they were no lower than those usually found for mononuclear copper(II) compounds. On the contrary, they were different from those found for complexes where an antiferromagnetically coupled pair of copper(II) ions was present.

The EPR spectra of polycrystalline samples were of isotropic type for 2 and 4 and of axial type for 1 and 5, with g_{\parallel} in the range 2.23–2.40 and g_{\perp} in the range 2.05–2.07, and of rhombic type for 3, with $g_1 = 2.15, g_2 = 2.08$ and $g_3 = 2.04$, suggesting that when the 2,9-dimethylphenanthroline ligand is

involved, a pronounced distortion from planar symmetry is present.

In addition, the unusually narrow resonances that we found for these compounds could indicate magnetic exchange trasmitted via 4-aminobenzoate bridges in polymeric chains, as we found previously for the binary $[Cu(pAb)_2]$ compound.⁸

The EPR spectra of frozen solutions (DMF, DMSO or MeOH, 115 K) of these compounds were of axial type, except for compound 3. The g_{\parallel} values found were in the 2.26–2.29 range and g_{\perp} in the 2.05–2.06 range, with $g_{\parallel} > g_{\perp} > 2.040$, suggesting a $d_{x^2-y^2}$ (or d_{xy}) ground state, characteristic of a square planar, square-based pyramidal or octahedral stereochemistry.¹⁰ The best resolved frozen solution EPR spectrum was recorded on compound 4. Its frozen DMF solution EPR paired with the corresponding simulated spectrum is reported in Fig. 1(a). In the perpendicular region of the EPR spectrum, a splitting is visible due to a superhyperfine structure that is attributable to the interaction between the unpaired electron of copper and nitrogen atoms of the ligands. The number of the lines suggests the presence of two nitrogen atoms coordinated to the copper(II) ion. The simulation which gives the best fit allows a precise evaluation of the magnetic parameters: $g_{\parallel} = 2.289, g_{\perp} = 2.049,$ $A_{\parallel,\mathrm{Cu}} = 158 \mathrm{G}, A_{\mathrm{N}} = 14.3 \mathrm{G}.$

Figure 1(b) shows the EPR spectrum obtained for the same compound in DMF solution at 298 K. Although magnetic anisotropies are averaged out by Brownian fast motion, $g_{iso} = 2.132$ is consistent with the average value calculated for the polycrystalline state and, from the spectrum in Fig. 1(a), $g_{\rm m} = 2.129$. Three of the four components predictable for a typical copper(II) complex in solution are clearly distinguishable in Fig. 1(b), allowing a precise evaluation of the copper hyperfine coupling constants ($A_{\parallel,Cu} = 53.57$ G). The correlation between g_{iso} and g_m , calculated from the isotropic and from the anisotropic spectra respectively, suggests that no changes in the coordination around copper(II) occur by passing from room temperature DMF, DMSO or MeOH solution to the frozen state.

The electronic spectra gave λ_{max} in the range 670–700 nm for compounds 1, 2, 4 and 5, but for 3 it was in the 750–760 nm range.

The electronic and EPR spectra are consistent with a tetragonal environment involving oxygen and nitrogen donor atoms and a Cu—N₂O₂-based chromophore for 1, 2, 4 and 5. For 3, the frozen solution EPR spectrum shows a splitting in the g_{\perp} signal into lines g_{xx} and g_{yy} , confirming the presence of a distortion of the coordination sphere around the copper(II) ion. Contrary to the magnetic susceptibility results, for the compounds of the type [Cu(pAb) $(phen)(H_2O)]_2(NO_3)_2$, EPR spectra of polycrystalline samples are clearly indicative of dimeric species and reveal features typical of a randomly oriented triplet state with S = 1. In fact, the EPR spectra are very similar for all the compounds and very similar to that obtained for binuclear copper(II) complexes in which quadruple bridges of bidentate neutral adenine and adenine anionic ligand bind through the N(3) and N(9) ring nitrogens¹¹⁻¹³ to the two copper(II) ions.

The X-band radiation spectra of a polycrystalline sample at room temperature and at 115 K (Fig. 2(a) and (b), respectively) raise a moderately strong absorption at about 1420 G, a weak absorption at about 3200 G, and strong absorptions at about 2560 and 3870 G.

Using the measured positions and the approach reported by Wasserman et al.¹⁴ for the spectra of randomly oriented organic triplets, we assigned the pair of bands at about 2560 and 3870 G to the $\Delta m = 1$ transitions H_{xy1} and H_{xy2} . From these positions we obtained $g_{xy} = 2.03-2.04$ and the zerofield splitting parameter D = 0.11 - 0.125 cm⁻¹. For comparison, the g_{xy} and D values found for copper acetate dimer in which four bridging carboxylic groups are involved are 2.08 and 0.34 cm^{-1} , respectively. These results are in agreement with those found for the binuclear copper(II) complex for which the crystal structure was determined,¹⁵ in which each copper atom is surrounded by two carboxylic oxygens, two nitrogens belonging to a phenanthroline ligand at the base of a square pyramid and by a water molecule at the apical position, as shown in Scheme 1.

The EPR spectra of these last compounds are temperature-dependent. The intensity of the triplet signals decreases with decreasing temperature; the monomer signal increases at the same time, as can clearly be seen from the EPR frozen DMF solution of 6 (Fig. 3). Even if there is more monomer present,



RCOO = 4-aminobenzoate anion

Scheme 1.

(a)



Fig. 1(a).

it was possible to observe triplet signals showing that the binuclear structure is, at least partially, preserved in this solvent. In fact, only monomer signals are present in the solution room temperature EPR spectra.

These results are typical for dimeric systems with a singlet ground state and a thermally accessible triplet excited state. At 115 K, the absorption at about 3200 G was used to calculate $g_{\parallel} = 2.30$ and $g_{\perp} = 2.07$ for the magnetic dilute copper(II) impurity, S = 1/2 species. Proof that this line is not part of the triplet state is demonstrated by the fact that it shows, in the g_{\parallel} region, four hyperfine coupling lines with one copper nucleus, I = 3/2, giving $A_{\parallel} = 164$ G. There is no evidence of hyperfine splitting in the triplet signals. As reported in the literature,¹⁶⁻¹⁸ following the temperature variation of the EPR lines over the range 77–298 K, we found that the triplet state lies in the range 300 ± 60 cm⁻¹ above the singlet ground state.

In conclusion, as reported in the literature for similar compounds, ^{19,20} the stability of the bridged structure is due to an intramolecular stack, but not all of the individual ternary complexes exist in this form, and in solution an intramolecular equilibrium between an "open" and a "stacked" form, which is responsible for the S = 1 species, is hypothesized.

For compound 7, in which an electron-withdrawing nitro group is present on the phenanthroline rings, only weak signals of the S = 1species are visible in the EPR spectrum.

For these last compounds λ_{max} is in the 640–650 nm range; a shoulder at about 400 nm is visible, which is attributable to a charge-transfer band, as





(a) (a) 500 G

Fig. 2. EPR spectra of polycrystalline sample at (a) room temperature (298 K) and (b) 115 K of $[Cu(pAb)(4,7-phen)(H_2O)]_2(NO_3)_2$ (6).

Fig. 1. EPR frozen solution (115 K) spectrum (a) paired with the corresponding simulated and solution EPR room temperature (298 K) spectrum (b) of [Cu(pAb)₂(5-NO₂phen)] (4).

expected when π - π interactions between aromatic systems are present.

IR carboxylate bands were assigned based on data available in the literature.²¹⁻²³ The mode of coordination of carboxylate groups has often been deduced from the magnitude of the observed separation Δ between $v_{as}(OCO)$ and $v_{s}(OCO)$, as well as from the position of the symmetric carboxylate stretching vibration $v_s(OCO)$, which is connected with the oxygen atom bound to the metal ion. $v_{s}(OCO)$ appears at about 1380 cm⁻¹ for the monomers, in which the carboxylate groups act as monodentate. Even if some difficulties arise with the identification of $v_s(OCO)$ because of the presence (at about 1410 cm^{-1}) of the very strong band from the ionic NO_3^- group, $v_s(OCO)$ was tentatively assigned at 1420 cm^{-1} for the dimers, in which the carboxylate groups act as "bridging" bidentate. $v_{as}(OCO)$ was more easily assigned in the 1600-1580 cm⁻¹ range for both types of compounds obtained. The Δ separation was in the 200 cm⁻¹ range, as expected for similar compounds.

The broad band at about $3300-3400 \text{ cm}^{-1}$ can be



Fig. 3. EPR frozen solution (115 K) spectrum of $[Cu(pAb)(4,7-phen)(H_2O)]_2(NO_3)_2$ (6).

attributed to v(OH) of water; the band at 3280 to the $v_{as}(NH_2)$ of the amino group in the benzoate ligand.

In conclusion, all physical measurements carried out in this study suggest that we can obtain the two types of compounds. (1) Monomers such as $[Cu(pAb)_2(phen)]$ in which there are no exchange interaction between metal ions: in this case EPR spectra are typical of magnetically dilute copper(II) complexes, suggesting the absence of conducting bridges between the copper(II) centres. The coordination sphere can be described as in Scheme 2. (2) Dimers such as $[Cu(pAb)(phen)(H_2O)]_2(NO_3)_2$ $(phen = 4,7-phen; 5-NO_2-phen; 4,7-dph)$ in which a binuclear structure results from the bridging of two pAb molecules by bidentate carboxylic groups : the EPR results for the latter compounds show that intramolecular stacking contacts between the phenanthroline ligands is very important to determine the dimeric structure (Scheme 1).

The peculiar behaviour is a property of the 2,9dimethylphenanthroline ligand, since in this case it was not possible to obtain the dimer. This fact suggests that a pronounced distortion in the sphere of coordination precludes the possibility of obtaining an intramolecular stack between phenanthroline ligands and then obtaining the binuclear structure.

Our ternary complexes can therefore be obtained as monomers or dimers as a function of the condition of reaction, except for the phenanthroline ligand dimethyl substituted in the 2 and 9 positions close to the nitrogen donor atoms; in this case only the monomer compound was obtained.

The influence of the geometry of the coordination sphere of the bridging metal ion is fundamental in obtaining the binuclear structure; the metal ion may impose certain steric restrictions and influence the orientation of the phenanthroline moieties forming the intramolecular stack.

This confirms that the steric hindrance caused by the presence of methyl groups in the 2 and 9 pos-



RCOO = 4-aminobenzoate anion

Scheme 2.

itions on the aromatic ring close to the coordination sites plays an essential role in the coordination behaviour of the ligands. Methyl groups in the 4 and 7 positions have no effect on the coordination when compared to the complex with unsubstituted phenanthroline.

In addition, since the formation of stacking adducts is usually connected with π - π interactions between the aromatic systems forming the stack,²⁴⁻²⁶ it is noteworthy that the substituents which alter the electron density on the phenanthroline ligand can influence the degree of stack and therefore the stability of the Cu²⁺-bridged stacking adducts. This is significant when an electron-withdrawing nitro group is present on the phenanthroline ligands. In this case only rather weak dimeric signals occur in the EPR spectrum.

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