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Synthesis and structure of isocytosine ternary copper(II) complexes †

Angel García-Raso,[a] Juan J. Fiol,*[,a] Bartomeu Adrover,[a] Virtudes Moreno,[b] Elies Molins[c] and Ignasi Mata[c]

[a] *Departament de Química, Universitat de les Illes Balears, 07071 Palma de Mallorca, Spain*
[b] *Departament de Química Inorgànica, Universitat de Barcelona, 08028 Barcelona, Spain*
[c] *Institut de Ciència de Materials de Barcelona (CSIC), Campus de la Universitat Autònoma, 08193 Cerdanyola, Spain*

The ternary complexes (glycylglycinato)(isocytosine)copper(II) dihydrate **1** and (glycylglycinato)(6-methylisocytosine)copper(II) monohydrate **2** have been prepared and characterised by X-ray diffraction, electrochemistry and optical, ESR and IR spectroscopy. The two compounds are slightly distorted square planar, with the four co-ordination sites occupied by the tridentate glycylglycine dianion [O(7), N(13) and N(10)] and N(3) of the pyrimidine base. An additional weak axial interaction exists between an oxygen of a water molecule O(W1) and the copper atom [Cu · · · O(W1) distances 2.74 and 2.70 Å respectively]. Spectroscopic and electrochemical data are in accord with the crystal structures. Although both compounds exhibit irreversible oxidation processes, the oxidation of Cu^{II} to Cu^{III} is best performed with the isocytosine complex.

The copper-containing enzymes and proteins are widely distributed in both animals and plants and the role played by ternary copper(II) complexes in biological systems is well known.[1–3] Copper(II), like other metal ions, destabilises the normal conformation of the DNA double helix but differs in that it helps in the regeneration of the thermally denatured double strand.[4a] Its ability to bind strongly to the heterocyclic nitrogens of the nucleobases, but also less strongly to the oxygens of the phosphodiester group, could be an important feature of the capability of this metal ion in promoting the renaturation of DNA melted in the presence of sufficient solid electrolyte.[4b] It holds the two chains in close enough proximity by binding to the bases during denaturation so that the double helix is regenerated on cooling with addition of salts. Metal ions differ in their preference for the GC- or AT-rich regions of a polynucleotide. Studies in the literature suggest that copper(II) binds primarily to GC-rich regions of DNA.[4c] A considerable number of X-ray crystallographic studies on peptide–copper(II)–cytosine (or cytidine) have been reported and show the N(3) preferential binding mode.[5] The (glycylglycinato)(isocytosine)copper(II) dihydrate complex has been described[6] but X-ray diffraction crystallography studies on copper(II) ternary complexes containing isocytosine or methylisocytosine are not available. On the other hand, isocytosine derivatives are useful chemotherapeutic products, *e.g.* 2-hydrazino-4-hydroxy-6-methylpyrimidine has been reported to be active against *Mycobacterium tuberculosis* (human type H_2-strain).[7] In this work we report on the preparation, spectroscopic characterisation and crystal and molecular structures of the ternary complexes (glycylglycinato)(isocytosine)copper(II) dihydrate [Cu(gg)(isocyt)]·$2H_2O$ **1** and (glycylglycinato)(6-methylisocytosine)copper(II) monohydrate [Cu(gg)(misocyt)]·H_2O **2**.

Experimental

Reagents were used as received from Aldrich (isocytosine and 6-methylisocytosine). The starting binary compound aqua(glycylglycinato)copper(II) was prepared according to Manyak *et al.*[8]

Synthesis of [Cu(gg)(isocyt)]·$2H_2O$ 1 and [Cu(gg)(misocyt)]·H_2O 2

The nucleobase (1 mmol) was added to a warm solution of aqua(glycylglycinato)copper(II) (1 mmol, 0.23 g) in distilled water (15 cm^3). After heating with stirring on a steam-bath for 30 min a blue precipitate was obtained (yield 55% for **1**, 53% for **2**). Each complex was redissolved in distilled water (25 cm^3) and heated to boiling until the volume was reduced to 10 cm^3. The crystals obtained after cooling this concentrated solution were filtered off and air dried.

Complex **1** exhibits a mass decrease (Found: 9.37. Calc.: 10.57%) between 31 and 189 °C corresponding to the loss of two water molecules per formula unit (Found: C, 27.62; H, 4.40; N, 20.18. Calc. for $C_8H_{15}CuN_5O_6$: C, 28.17; H, 4.40; N, 20.54%). IR (cm^{-1}): 290m, 551m, 577m, 608vw, 716m, 768w, 825m, 919w, 943w, 1235m, 1294s, 1320w, 1391m, 1416m, 1447m, 1470w, 1498m, 1577s (br), 1634s, 1684s, 3152m, 3256m and 3560m. UV/VIS (water): λ 635 (ε 99), 283 (6.1×10^3) and 261 nm (6.18×10^3 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in water, 20 °C) = 16.0.

Complex **2** exhibits a mass decrease (Found: 5.59. Calc.: 5.35%) between 31 and 205 °C corresponding to the loss of one water molecule per formula unit (Found: C, 32.07; H, 4.47; N, 20.61. Calc. for $C_9H_{15}CuN_5O_5$: C, 32.10; H, 4.46; N, 20.80%). IR (cm^{-1}): 297m, 425w, 391w, 350w, 520m, 549m, 573w, 609m, 658w, 707w, 764w, 798w, 827m, 936w, 1009m, 1032m, 1047w, 1095m, 1116m, 1152m, 1182w, 1262w, 1292m (sp), 1374m, 1386s, 1413m, 1428m, 1453m, 1470m, 1500m, 1568s, 1593s, 1636s, 1692m, 3171s and 3259s (sp). UV/VIS (water): λ 637 (ε 118) and 262 nm (8.9×10^3 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in water, 20 °C) = 19.0.

Physical measurements

Elemental analyses were carried out using a Carlo Erba model 1106 microanalyser. The infrared spectra in the solid state (KBr pellets) were recorded on a PE 683 spectrometer with a PE 1600 infrared data station and electronic spectra on a PE 552 spectrophotometer. Thermogravimetric data in the range from 30 to 700 °C were obtained in a flowing nitrogen atmosphere (heating rate 10 °C min^{-1}) on a PE TGA-2 thermobalance. The ESR spectra were recorded at X-band frequencies with a Bruker ESP-300E spectrometer at 77 and 298 K. Magnetic measurements were carried out on powdered samples with a pendulum-type magnetometer (Manics DSM8). Diamagnetic corrections were estimated from the Pascal tables. The data were also corrected for temperature-independent paramagnetism (taken to be 60×10^{-6} cm^3 mol^{-1}). Cyclic voltammetry for the complexes was carried out under argon at 20 °C using acetonitrile

† *Non-SI units employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Table 1 Crystal data and structure refinement for complexes **1** and **2***

	[Cu(gg)(isocyt)]·2H_2O	[Cu(gg)(misocyt)]·H_2O
Empirical formula	$C_8H_{15}CuN_5O_6$	$C_9H_{15}CuN_5O_5$
Crystal dimensions/mm	0.52 × 0.42 × 0.30	0.58 × 0.50 × 0.04
a/Å	13.565(14)	13.268(1)
b/Å	8.097(6)	8.042(1)
c/Å	13.645(11)	13.628(1)
β/°	118.87(7)	118.07(1)
U/Å^3	1312(2)	1283.1(2)
D_c/g cm^{-3}	1.725	1.749
μ(Mo-Kα)/cm^{-1}	17.0	17.3
T/K	293(2)	294(2)
θ Range/°	4.2–26.3	2.94–30.40
hkl Ranges	−16 to 18, −10 to 0, −14 to 17	−16 to 18, 0–11, −19 to 0
No. reflections measured	2745	4037
No. unique reflections (R_{int})	2635 (0.086)	3887 (0.017)
No. observed reflections, [$I > 2\sigma(I)$]	862	2893
Maximum, minimum transmission	0.9993, 0.9730	0.9994, 0.8094
Weighting scheme, w^{-1}	$\sigma^2(F_o^2)$	$\sigma^2(F_o^2) + (0.0603P)^2 + 0.85P$ $P = [\max(F_o,0) + 2F_o^2]/3$
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0729, 0.0782	0.0336, 0.0914
(all data)	0.3314, 0.1255	0.0685, 0.1071
Largest difference peak, hole/e Å^{-3}	0.612, −0.788	0.474, −0.495

* Details in common: monoclinic, space group $P2_1/n$; $Z = 4$.

(HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) as supporting electrolyte. The half-wave potentials were referred to a Ag–$AgNO_3$ (0.1 mol dm^{-3} in acetonitrile) electrode, separated from the solution by a medium-porosity fritted disc. A platinum-wire auxiliary electrode was used in conjunction with a platinum-disc working electrode (TACUSSEL-EDI, rotatory electrode, 3.14 mm^2). The voltammograms of 10^{-3} mol dm^{-3} solutions of the samples were recorded with a VersaStat EG&G Princeton Applied Research potentiostat. The reference electrodes were checked periodically against the ferrocenium–ferrocene couple in acetonitrile.

Crystallography

X-Ray data from compounds **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ = 0.710 69 Å). The cell parameters and space group were determined from a least-squares refinement of 25 reflections randomly searched. Data collection employed an ω–2θ scan technique.

The MOLEN[9] package was used for applying Lorentz-polarisation correction and ψ-scan empirical absorption corrections. The structures were solved by direct methods using the SHELXS 86[10] program and refined by least squares using SHELXL 93.[11] Hydrogen atoms were placed in calculated positions, except for those of water molecules which were located in Fourier-difference maps. They were isotropically refined with a global thermal parameter in **2**. For **1** two isotropic thermal parameters were defined, one for hydrogens in the complex and the other for those in the water molecules. Details of the data collection and processing are summarised in Table 1.

CCDC reference number 186/866.

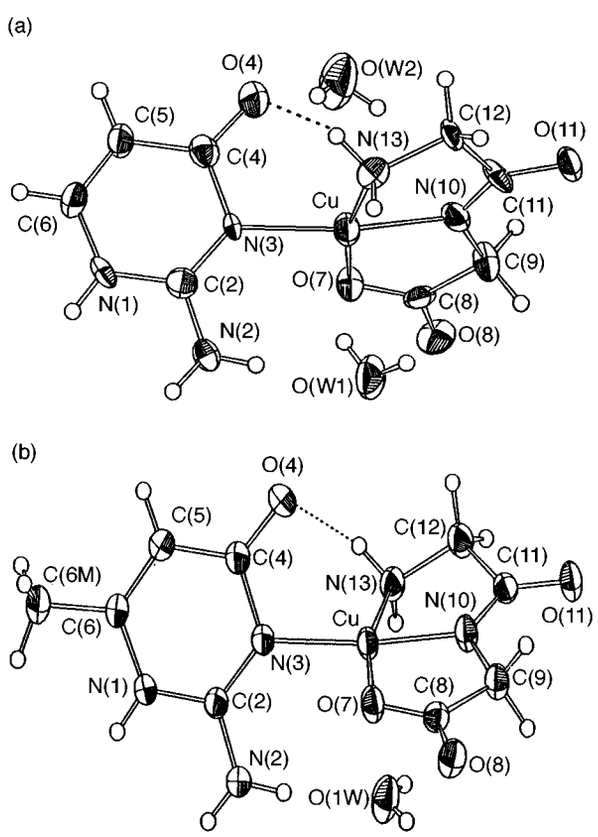

Fig. 1 Crystal structures of (a) [Cu(gg)(isocyt)]·2H_2O **1** and (b) [Cu(gg)(misocyt)]·H_2O **2**. Hydrogen atoms are omitted for clarity

Results and Discussion

Crystal structures

The complexes [Cu(gg)(isocyt)]·2H_2O **1** and [Cu(gg)(misocyt)]·H_2O **2** are slightly distorted square planar, with the four co-ordination sites occupied by the tridentate glycylglycine dianion [O(7), N(13) and N(10)] and the N(3) of the pyrimidine base [Fig. 1(a) and 1(b)]. An additional axial interaction exists between an oxygen of a water molecule O(W1) and the copper atom [Cu···O(W1) 2.74 and 2.70 Å respectively] (Table 2). The previously described compounds with cytosine[5b] and cytidine[5a] show similar primary co-ordination spheres. In all cases an intramolecular interaction between the pyrimidine ligand and the peptide moiety is observed. In both complexes the Cu^{II} is bound to the three co-ordinating atoms of the peptide residue [Cu–N(13) 2.023(8), Cu–N(10) 1.893(8) and Cu–O(7) 2.008(7) Å for **1** and Cu–N(13) 2.045(2), Cu–N(10) 1.893(2) and Cu–O(7) 2.021(2) Å for **2**] as well as to the pyrimidine heterocyclic nitrogen [Cu–N(3) 1.949(7) Å for **1** and 1.987(2) Å for **2**]. The glycylglycine dianions have similar angles as observed in other copper(II) complexes[5b,12] [O(7)–Cu–N(13) 165.6(3), O(7)–Cu–N(10) 83.3(3) and N(13)–Cu–N(10) 82.3(4) for **1**

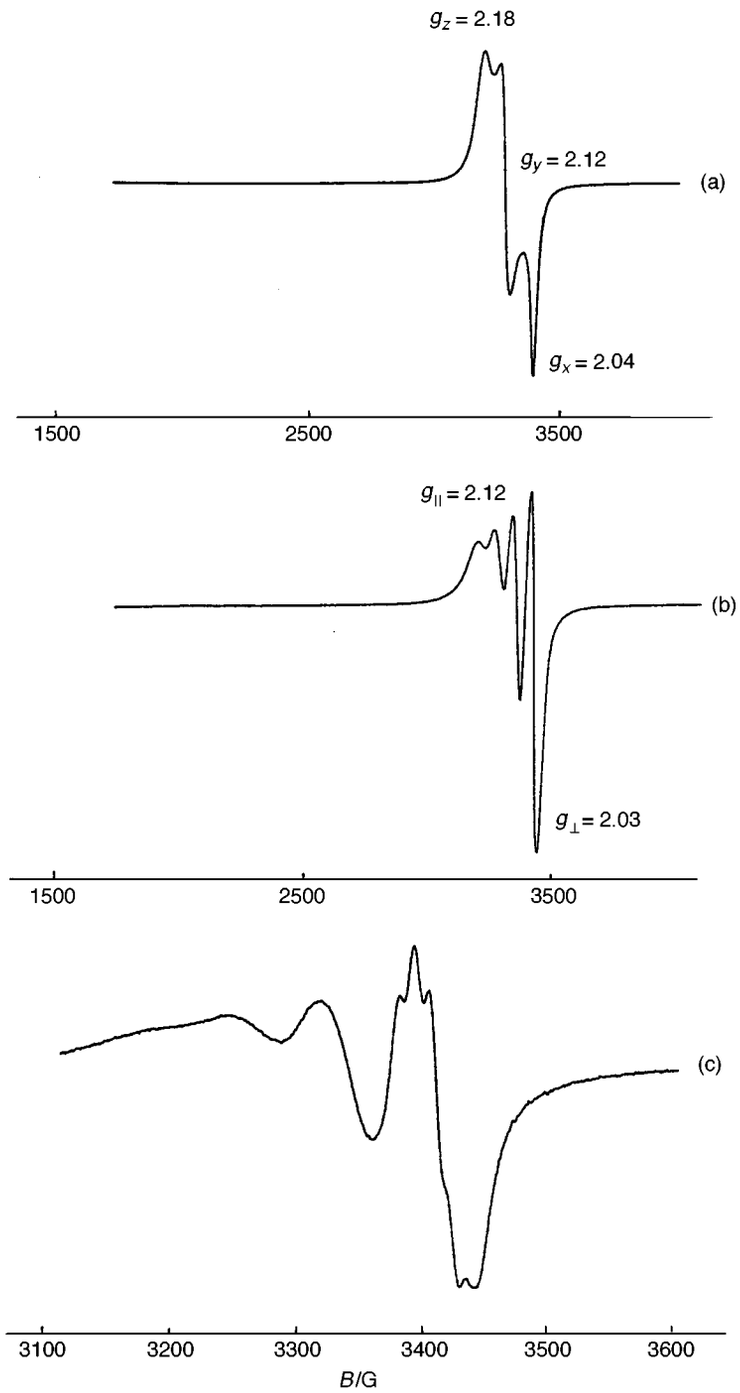

Fig. 2 The ESR spectra of complex **1**: (a) polycrystalline powder at 298 K, (b) in dmso at 298 K and (c) in dmso at 298 K (500 G expansion display)

and O(7)–Cu–N(13) 164.27(7), O(7)–Cu–N(10) 82.61(7) and N(13)–Cu–N(10) 81.86(8)° for **2**]. A hydrogen bond N(13)(gg)–H · · · O(4)=C (pyrimidine) at 2.87 Å (**1**) and 2.80 Å (**2**) is observed.

The crystal packing is dominated by three principal features: (i) interaction between two ternary complexes *via* water molecules; (ii) a zigzag array *via* interaction between the CO_2 (peptide moiety) and H_2N–C–NH (pyrimidine ring) of different ternary complexes‡ (an additional hydrogen bond between alternating complex units stabilises the crystal packing for the isocytosine complex but is absent for the methylisocytosine one); (iii) stacking is present between pyrimidine moieties. Similar crystal packings occur for the two complexes.

‡ In both complexes two characteristic intermolecular interactions are observed between the gg moiety and the pyrimidine base: N(1)–H · · · O=CO(gg) 1.79 Å for **1** and 1.83 Å for **2** and HN(2)–H · · · OC=O(gg) 2.15 Å for **1** and **2**.

Infrared spectra

The IR spectra of the complexes were recorded down to the far-IR region of 200 cm^{-1} and compared with those of the free nucleobases.

[Cu(gg)(isocyt)]·2H_2O 1. Tentative band assignments (cm^{-1}) for isocytosine according to the literature[13–17] are: $\nu_{sym}(NH_2)$ 3141s (br); ν[C(2)=O] 1679vs; ν(C=C) + ν(C=N) + $\delta(NH_2)$ 1610s, 1570w (sh); ν(ring), ν(C–C) + ν(C=N), ν(C–N), ν(N–H) 1518m, 1476s; ν(ring) 1374m, 1209s; ring-breathing mode ν(ring) 810s. The strong band at 1679 cm^{-1} remains unchanged (only 5 cm^{-1} shift) upon complexation, ruling out direct O(2) binding of isocytosine to the metal ion.[18] The bands related to

Table 2 Bond lengths (Å) and angles (°) for complexes **1** and **2**

	[Cu(gg)(isocyt)]·2H_2O	[Cu(gg)(misocyt)]·H_2O
Cu–N(10)	1.893(8)	1.893(2)
Cu–N(3)	1.949(7)	1.987(2)
Cu–O(7)	2.008(7)	2.021(2)
Cu–N(13)	2.023(8)	2.045(2)
Cu···O(W1)	2.736(9)	2.697(2)
C(2)–N(3)	1.318(12)	1.342(3)
C(4)–O(4)	1.240(11)	1.242(3)
O(7)–C(8)	1.278(11)	1.273(3)
C(8)–O(8)	1.250(12)	1.247(3)
C(9)–N(10)	1.454(11)	1.439(3)
N(10)–C(11)	1.293(12)	1.307(3)
C(11)–O(11)	1.256(10)	1.256(3)
N(10)–Cu–N(3)	169.5(4)	171.85(9)
N(10)–Cu–O(7)	83.3(3)	82.61(7)
N(3)–Cu–O(7)	94.0(3)	96.27(7)
N(10)–Cu–N(13)	82.3(4)	81.86(8)
N(3)–Cu–N(13)	100.3(3)	99.46(8)
O(7)–Cu–N(13)	165.6(3)	164.27(7)
C(2)–N(3)–Cu	130.8(8)	129.7(2)
C(4)–N(3)–Cu	110.5(7)	110.24(14)
C(8)–O(7)–Cu	113.2(7)	113.35(14)
C(11)–N(10)–C(9)	124.8(8)	122.9(2)
C(11)–N(10)–Cu	120.4(8)	120.7(2)
C(9)–N(10)–Cu	114.5(6)	116.32(14)
C(12)–N(13)–Cu	109.0(6)	107.95(14)

the glycylglycinatocopper(II) system at 1620 [ν(C=O)] and 1593 cm^{-1} [$\nu_{asym}(CO_2)$] exhibit significant shifts in their frequency overlapping with the 1610s and 1570w cm^{-1} peaks of the isocytosine ring. The bands at 1518 and 1476 cm^{-1} of the isocytosine moiety shift to lower wavenumber, consistent with binding between the copper and the heterocyclic N(3) of the isocytosine. The intensity of the band at 1476 cm^{-1} is changed noticeably and the bands related to the isocytosine ring torsion (1374m, 1209s cm^{-1}) disappear. In the lower-frequency region a new band at 290 cm^{-1} is tentatively assigned to ν(Cu–N).[19] All this infers tridentate bonding of the glycylglycinate system and an additional binding between the copper and N(3) of the isocytosine.

[Cu(gg)(misocyt)]·H_2O 2. The band at 1677 cm^{-1} assigned to ν[C(2)=O] of the isocytosine ligand[13–17] is displaced to higher frequencies for the ternary complex by about 5 cm^{-1}, ruling out direct O(2) binding of methylisocytosine to the metal ion,[18] as observed for the isocytosine complex **1**. The three strong bands in the 1640–1550 cm^{-1} region can be assigned to ν(C=O) + ν(C–N) + $\nu_{asym}(CO_2)$ of the peptide. The broad and strong bands at 1516, 1505, 1486 cm^{-1} and the shoulder at 1476 cm^{-1} assigned to ν(ring) of the free pyrimidine become sharper in the spectrum of the complex and decrease noticeably in frequency and intensity (1500m and 1470m cm^{-1}). These bands are related to vibration modes involving the heterocyclic N and the changes indicate participation of the N atom in the bonding to Cu^{II}. The band at 297 cm^{-1} present in the spectrum of the complex is assignable to ν(Cu–N).[19]

Electronic spectra

The compounds yield blue solutions in water. The d–d transitions show broad bands centred at 635 (ε = 99) and 637 nm (ε = 118 dm^3 mol^{-1} cm^{-1}) for the isocytosine (**1**) and methylisocytosine (**2**) complexes respectively suggestive of approximate square-pyramidal geometry about Cu as observed in other copper(II) peptide complexes.[12,20] This is consistent with the structure found in the crystal, although a stronger axial water interaction seems to occur in solution. The π–π* transition bands corresponding to the pyrimidine ring of the isocytosine [263 (sh), ε = 3.7 × 10^3; 284 nm, ε = 4.49 × 10^3 dm^3 mol^{-1} cm^{-1}] exhibit some changes in intensity and slight shifts to higher

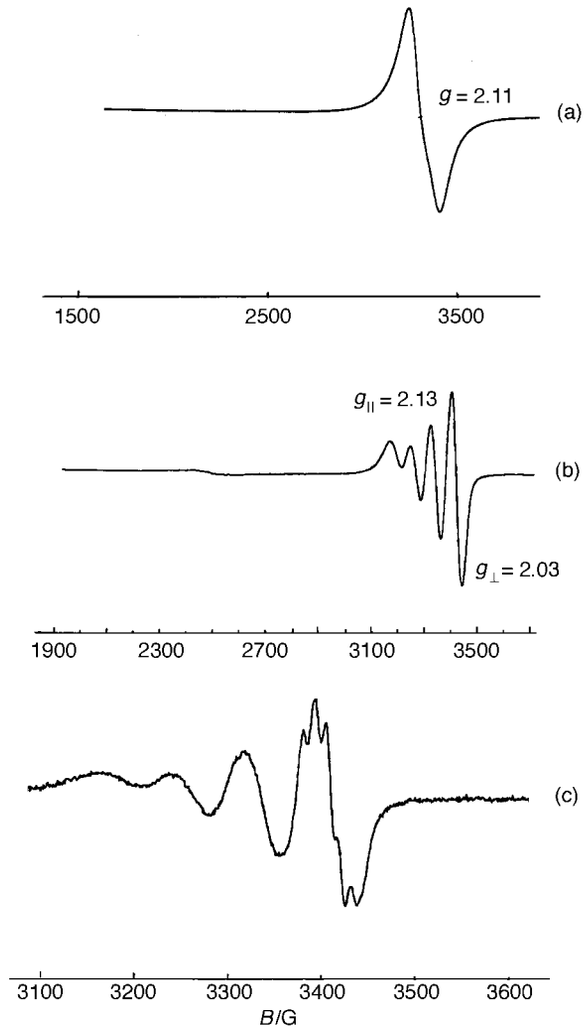

Fig. 3 The ESR spectra of complex **2**; details as in Fig. 2

energies on complexation (261, ε = 6.18 × 10^3; 283 nm, ε = 6.10 × 10^3 dm^3 mol^{-1} cm^{-1}). The corresponding band of methylisocytosine (266 nm, ε = 5.10 × 10^3 dm^3 mol^{-1} cm^{-1}) is displaced to higher energies (262 nm, ε = 8.9 × 10^3 dm^3 mol^{-1} cm^{-1}) increasing its relative intensity. The differences observed between the spectra of complexes **1** and **2** can be related to the inductive effect of the methyl group at position 6 of the ligand ring. The Λ_M (10^{-3} mol dm^{-3}) values in water at 20 °C (16.0 and 19.0 Ω^{-1} cm^2 mol^{-1} respectively) imply the presence of non-electrolyte species.[21]

ESR spectra and magnetic properties

The effective magnetic moments μ_{eff} of 1.78 (complex **1**) and 1.74 μ_B (**2**) at room temperature are normal for magnetically diluted d^9 systems. The X-band ESR spectra of a polycrystalline powder of **1** recorded at room temperature (frequency = 9.785 545 0 GHz, power 5.02 × 10^{-1} mW, modulation amplitude = 3.199 G) and 77 K (frequency = 9.393 875 0 GHz, power = 3.17 × 10^{-2} mW, modulation amplitude = 3.199 G) are identical and do not show any hyperfine splitting. The three different principal values of g observed, $g_x = 2.18 \pm 0.01$, $g_y = 2.12 \pm 0.01$ and $g_z = 2.04 \pm 0.01$, are indicative of a rhombically distorted ligand field [Fig. 2(a)]. The room-temperature dmso solution ESR spectrum of **1** shows hyperfine splitting due to copper ($I = \frac{3}{2}$, four lines; $A_\parallel = 70.38 \pm 0.01$ G) with the estimation of $g_\parallel = 2.12 \pm 0.01$ and $g_\perp = 2.03 \pm 0.01$ [Fig. 2(b)]. Simulated spectra obtained by using the Bruker WINEPR program gave good agreement with the experimental g and A values. The value of $A_\parallel$ seems to be quite low in comparison with those of other copper(II) complexes.[22] In addition, the 500 G expansion

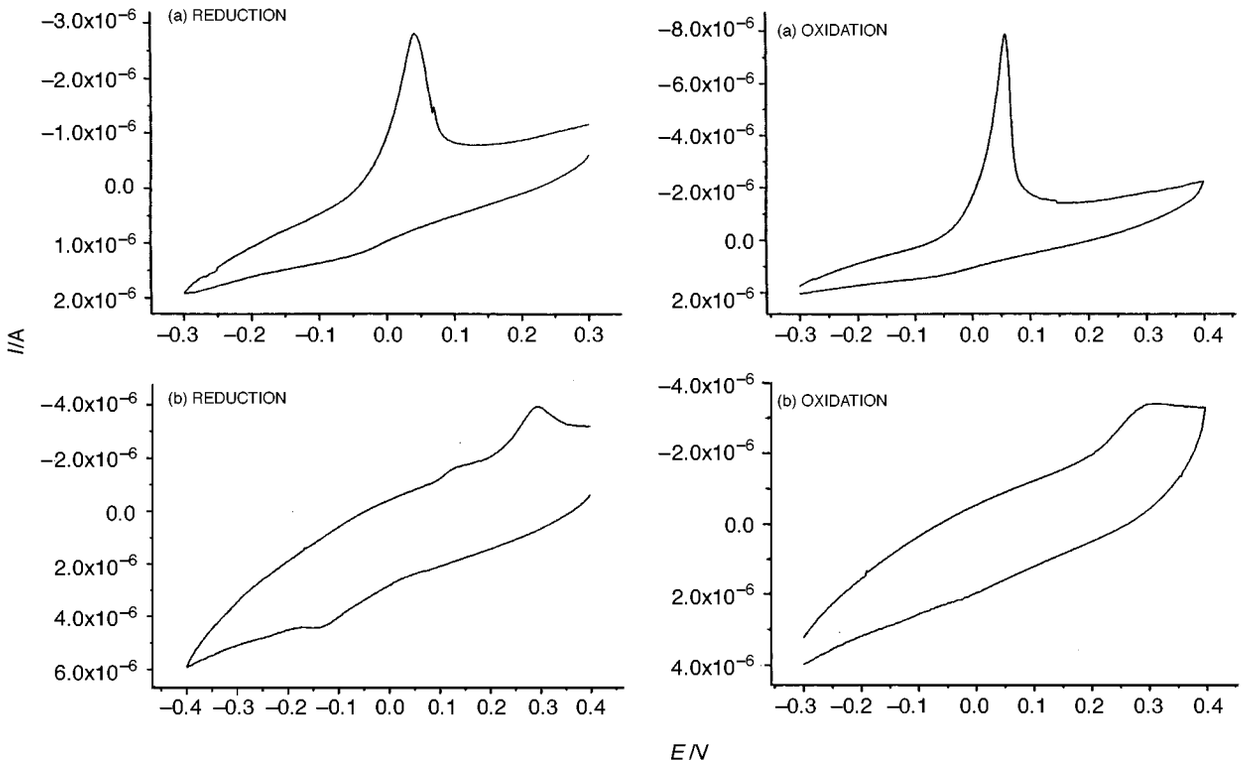

Fig. 4 Cyclic voltammetry of complexes **1** (a) and **2** (b). Experiments beginning with the reduction and oxidation processes are shown

displayed superfine splitting due probably to the co-ordinated N(3) nitrogen ($A_{\|} = 11.74 \pm 0.01$ G) [Fig. 2(c)]. The change from solid state to solution seems to affect the copper environment probably by axial interaction with dmso molecules. The X-band ESR spectra of a polycrystalline powder of **2** recorded at room temperature (frequency = 9.786 103 0 GHz, power = 2.51×10^{-1} mW, modulation amplitude = 3.199 G) and 77 K (frequency = 9.400 347 0 GHz, power = 3.17×10^{-2} mW, modulation amplitude = 3.199 G) exhibit only a quasi-symmetric signal centred at $g = 2.11 \pm 0.01$ [Fig. 3(a)]. The room-temperature dmso solution ESR spectrum shows hyperfine splitting due to copper ($I = \frac{3}{2}$, four lines; $A_{\|} = 76.73 \pm 0.01$ G) with $g_{\|} = 2.13 \pm 0.01$ and $g_{\perp} = 2.03 \pm 0.01$ [Fig. 3(b)]. Simulated spectra gave good agreement with the experimental g and A values. The value of $A_{\|}$ seems to be quite low in comparison with those of other copper(II) complexes.[22] As in the case of complex **1**, the 500 G expansion displays superfine splitting due probably to the co-ordinated N(3) ($A = 12.12 \pm 0.01$ G) [Fig. 3(c)]. The change from solid state to solution seems also to affect the copper environment probably by axial interaction with dmso molecules.

Electrochemical behaviour

The cyclic voltammetric behaviour of complex **1** at $\nu = 0.20$ V s^{-1} in the potential range +0.4 to −0.3 V exhibits an anodic peak at −0.042 V corresponding to the irreversible oxidation of Cu^{II} to Cu^{III}, suggesting that a substantial structural change occurs on oxidation. In the reduction experiment a very weak cathodic peak was observed at −0.0436 V which is assigned to the Cu^{II}–Cu^{I} couple. On the return scan only a strong peak was observed which corresponds basically to the oxidation of Cu^{II} to Cu^{III} masked by the peak due to Cu^{I}–Cu^{II} reoxidation. The voltammetric behaviour of complex **2** shows important differences with respect to that of **1**. A very weak reduction peak at $E_{pc} = -0.1236$ V is observed corresponding to the Cu^{II}–Cu^{I} redox change. On reversal of the scan the complex exhibits a weak peak at $E_{pa} = 0.036$ V attributable to the reoxidation of Cu^{I} to Cu^{II} and a second peak at 0.206 V assigned to the irreversible oxidation of Cu^{II} to Cu^{III} (Fig. 4). Both compounds exhibit irreversible processes and the oxidation of Cu^{II} to Cu^{III} is best performed with the isocytosine complex. Several studies have demonstrated that deprotonated oligopeptide complexes of Cu^{III} are reasonably stable in neutral aqueous solution[23] and the copper(III) state was shown to occur in the galactose oxidase active cycle and other enzyme reactions. The reason that large numbers of copper(III) complexes have not been characterised is not because the Cu^{III}–Cu^{II} oxidation–reduction potential is high, but rather that most copper(III) complexes are kinetically unstable.[24]

Acknowledgements

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