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Structural, spectroscopic and potentiometric investigation on the coordination properties of 4-NO_2-hippuric acid towards Cu(II) in binary and ternary systems

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Abstract

The solid state and aqueous solution study on the binary and ternary system copper(II)–4-NO_2-hippuric acid is reported. The binary complex separated in the solid state is $[Cu(4\text{-}NO_2\text{-hip})_2(H_2O)_2]_2 \cdot 4H_2O$ and the crystal structure has been determined. The compound is monoclinic, space group $P2_1/a$, with cell dimensions $a=7.289(3)$, $b=44.25(1)$, $c=7.344(7)$ Å, $\beta=102.05(6)°$, $Z=2$, $R=0.055$ and $R'=0.053$. The structure consists of dimeric penta-coordinated $[Cu(4\text{-}NO_2\text{-hip})_2(H_2O)_2]_2$ units and lattice water molecules. The copper atom is coordinated by two 4-NO_2-hip anions acting as carboxylate ligands and two water molecules. One 4-NO_2-hip anion acts as monodentate ligand and the second acts as monodentate bridging ligand through one carboxylic oxygen which is an equatorial ligand for one copper atom and is the apical ligand for the second copper atom. In the ternary system with 2,2′-bipyridine (bpy) we separated mono-amine and bis-amine species, in that with 1,10-phenanthroline (ophen) only the mono-amine species was obtained. For the compound $[Cu(bpy)_2(4\text{-}NO_2\text{-hip})] \cdot NO_3 \cdot H_2O$ the crystal and molecular structure was determined. The crystal is triclinic, space group $P\bar{1}$, with cell dimensions: $a=10.162(2)$, $b=10.953(5)$, $c=13.651(2)$ Å, $\alpha=96.76(3)$, $\beta=100.40(1)$, $\gamma=96.19(3)°$, $Z=2$, $R=0.043$ and $R'=0.048$. The copper atom is coordinated by the two bpy molecules and by the 4-NO_2-hip anion which acts as an asymmetrically bidentate ligand through the carboxyl group. The Cu–O(1) bond distance is normal, while the Cu–O(2) one is significantly longer (2.646(3) Å), so the geometry can be represented as $(4+1+1^*)$. On the basis of the ESR spectrum the copper(II) ground state is established as $d_{x^2-y^2}$. In solution the prevailing species are $[CuL_2]$ in the binary system, $[CuAL_2]$ and $[CuAL(OH)]$ in the ternary system.

Keywords: Crystal structures; Copper complexes; Hippuric acid complexes

1. Introduction

Among R–CO–N-protected amino acids the hippuric acid–metal(II) systems have been extensively investigated because they form very original structures [1–3]. The Cu(II) complex shows a dimeric structure with a carboxylate oxygen as a monoatomic bridge; in the Co(II), Ni(II) and Fe(II) complexes the metal ions are linked to each other in infinite chains by a bridging water molecule giving rise to complexes with peculiar magnetic properties; while the Zn(II) complex is monomeric with a square pyramidal geometry [4,5a,6].

In aqueous solution hippuric acid acts as a simple carboxylate ligand, and with Cu(II) and Zn(II) ions gives rise to very weak complex species [7]. The $[Cu(hip)_2 \cdot (H_2O)_2]_2 \cdot 4H_2O$ complex reacts easily with amines to form mixed complexes [7].

We have recently investigated the coordination properties of 4-amino-hippuric acid which acts as a bidentate bridging ligand through the carboxylate and amino groups despite the low basicity of its amino nitrogen ($pK_{NH_3^+}=2.83(1)$). The ligand gives rise to a one-dimensional polymeric chain with Co(II) and Ni(II) and two-dimensional layers with Cu(II). The coordination of the amino nitrogen with the metal ion is favoured with respect to the coordination of water molecules, despite the high degree of hydration, and prevents the separation of mixed-amine complexes [8].

We have now decided to investigate the 4-nitrohippuric acid–copper(II) binary and ternary systems, with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (ophen), both in the solid state and in aqueous solution, in order to compare the effect of the electrophilic nitro

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group to that of the electron-donating amino group on the coordination behaviour of the hippuric acid derivatives.

2. Experimental

4-Nitro-hippuric acid (4-NO_2-hipH) was purchased from Janssen and used as received.

2.1. Preparation of the complexes

$[Cu(4\text{-}NO_2\text{-hip})_2(H_2O)_2]_2 \cdot 4H_2O$ (**1**) was prepared by adding 0.025 dm^3 of an aqueous solution (0.04 mol dm^{-3}) of copper(II) acetate monohydrate to 0.030 dm^3 of a hot ethanolic solution of the acid (0.066 mol dm^{-3}). On cooling the solution a pale blue crystalline compound separated. By dissolving this compound in H_2O/MeOH 1/1 vol/vol. medium, suitable crystals for X-ray analysis were obtained. *Anal.* Found: C, 37.70; H, 3.05; N, 8.70; H_2O, 12.70. Calc. for $C_{36}H_{44}Cu_2N_8O_{28}$: C, 37.10; H, 3.80; N, 9.60; H_2O, 12.40%.

$Cu(A)(4\text{-}NO_2\text{-hip})_2 \cdot 3H_2O$ (A = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (ophen)). These compounds were prepared by dissolving 0.5 mmol of **1** in 0.03 dm^3 of a 1:2 vol/vol. mixture of H_2O and CH_3OH and mixing in 0.010 dm^3 of a methanolic solution (0.05 mol dm^{-3}) of bpy or ophen. After some hours the solid blue crystalline complexes separated out. $Cu(bpy)(4\text{-}NO_2\text{-hip})_2 \cdot 3H_2O$: *Anal.* Found: C, 46.20; H, 4.00; N, 11.20; H_2O, 8.00. Calc. for $C_{28}H_{28}CuN_6O_{13}$: C, 46.70; H, 3.90; N, 11.70; H_2O, 7.50%; $Cu(ophen)(4\text{-}NO_2\text{-hip})_2 \cdot 3H_2O$: *Anal.* Found: C, 48.35; H, 3.50; N, 11.30; H_2O, 7.50. Calc. for $C_{30}H_{28}CuN_6O_{13}$: C, 48.40; H, 3.80; N, 11.30; H_2O, 7.30%.

$[Cu(bpy)_2(4\text{-}NO_2\text{-hip})] \cdot NO_3 \cdot H_2O$ (**2**). By slow evaporation at 25 °C of the titrated solutions in the Cu:4-NO_2-hipH:bpy molar ratio of 1:2:1, blue crystals, suitable for X-ray analysis, separated out. *Anal.* Found: C, 51.30; H, 3.60; N, 14.40; H_2O, 2.40. Calc. for $C_{29}H_{25}CuN_7O_9$: C, 51.25; H, 3.70; N, 14.45; H_2O, 2.60%.

2.2. Physical measurements

The diffuse reflectance electronic spectra were obtained with a Perkin-Elmer Lamba 19 spectrophotometer; IR spectra, as KBr pellets (4000–400 cm^{-1}), with a Bruker FT-IR 113v spectrometer. The X-band ESR spectra were recorded with a Bruker ER200-SRC spectrometer. The thermogravimetric measurements were made using a Mettler TA 3000 instrument at a rate of 10 °C min^{-1}. Carbon, nitrogen and hydrogen were determined using a C. Erba model 1106 elemental analyser. The spectrophotometric titrations were performed with a Perkin-Elmer Lamba 19 spectrophotometer. For the Cu/4-NO_2-hipH/bpy system, the solution was prepared by dissolving complex **2** in H_2O (10^{-2} mol dm^{-3}).

2.3. Potentiometry

$Cu(NO_3)_2 \cdot 3H_2O$ of analytical grade was from C. ERBA and standardized with EDTA. Solutions of bpy and ophen (0.005 mol dm^{-3}) (C. ERBA) were standardised potentiometrically with 0.1 mol dm^{-3} HNO_3. The NaOH solution (C. ERBA) was standardised with potassium hydrogen phthalate (N.B.S.). Potentiometric measurements were performed at 25 ± 0.1 °C, with the fully automatic ORION 960 Autochemistry system using a Sure Flow ORION reference electrode and a glass ORION electrode. All the titrations were carried out at constant ionic strength (0.1 mol dm^{-3}) adjusted with solid $NaNO_3$. The standard electrode potential $E°$ was determined before and after each experiment by titration of a known amount of HNO_3 (0.1 mol dm^{-3}) with a standard NaOH solution. The ionic product K_w was calculated in the alkaline region of each calibration curve. The liquid-junction potentials were found reproducible and rather small as compared to the potential of the cell (about 2%), consequently they were neglected in the calculations. All the experiments were carried out under nitrogen atmosphere, determining the equivalent point by the first derivative technique with constant cm^3 or mV increments. For determination of the protonation constant of 4-NO_2-hipH eight titrations were performed and the concentration of the solution varied in the range 0.005–0.007 mol dm^{-3}, the data processed being 130. The Cu(II):4-NO_2-hip binary system was investigated in the 1:2, 1:4, 1:6, 1:8 molar ratios with the 4-NO_2-hipH concentration ranging from 3.3×10^{-3} to 1.32×10^{-2} mol dm^{-3}. The data processed were 86. The ternary systems were investigated with Cu(II) concentrations 3×10^{-3} and 0.75×10^{-3} mol dm^{-3} and Cu(II):A:4-NO_2-hipH molar ratios of 1:1:2, 1:1:4, 1:1:6 and 1:1:8, 1:2:1, 1:2:2. The data processed were 330 and 256 for A = bpy and ophen, respectively. The stability constants were obtained by using thc SUPERQUAD program [9]. During refinements $\sigma_E = 0.2$ (mV error) and $\sigma_V = 0.01$ (volume error) were employed. The protonation and stability constants β_{pqrs} are defined as follows:

$$pM + qA + rL + sH = = M_pA_qL_rH_s$$

$$\beta_{pqrs} = [M_pA_qL_rH_s]/[M]^p[A]^q[L]^r[H]^s$$

where M = metal, L = 4-NO_2-hipH, A = bpy or ophen.

2.4. X-ray data collection and structure refinement

For both compounds the structure was determined on an Enraf Nonius CAD4 single crystal diffractometer. Lattice constants were determined by least-squares

Table 1
Experimental data for the crystallographic analysis

Compound	$[Cu(4\text{-}NO_2\text{-}hip)_2(H_2O)]_2 \cdot 4H_2O$	$[Cu(bpy)_2(4\text{-}NO_2\text{-}hip)] \cdot NO_3 \cdot H_2O$
Formula	$C_{36}Cu_2H_{44}N_8O_{28}$	$C_{29}CuH_{25}N_7O_9$
M	1163.88	679.10
Crystal system	monoclinic	triclinic
Space group	$P2_1/a$	$P\bar{1}$
a (Å)	7.289(3)	10.162(2)
b (Å)	44.25(1)	10.953(5)
c (Å)	7.344(7)	13.651(2)
α (°)		96.76(3)
β (°)	102.05(6)	100.40(1)
γ (°)		96.19(3)
U (Å^3)	2316(2)	1471.0(8)
Z	2	2
D_c (g cm^{-3})	1.67	1.53
D_m (g cm^{-3})	1.75	1.50
$F(000)$	1196	698
h, k, l Range	−8 8, 0 50, 0 8	−11 11, −12 12, 0 15
Crystal size (mm)	0.06×0.3×0.06	0.3×0.32×0.2
Colour	pale blue	blue
μ (Mo Kα) (cm^{-1})	10.21	7.55
Scan width (°)	$0.8+0.35\text{tg}\theta$	$0.5+0.35\text{tg}\theta$
Scan speed (° min^{-1})	9.2–1.3	8.2–0.9
No. reflections measured	4019	4938
No. reflections used in the refinement ($I > 2\sigma(I)$)	1222	3168
Transmission coefficient	$0.95 < T < 1.00$	$0.94 < T < 1.00$
R	0.055	0.043
R'	0.053	0.048
Min., max. height in the ΔF map, $\Delta\rho$ (e Å^{-3})	−0.43, 0.41	−0.43, 0.41

refinements of the angular setting of 25 reflections. Crystal data details are summarized in Table 1. Intensity data were collected by using Mo Kα radiation ($\lambda = 0.71069$ Å) with the ω–2θ scan technique in the θ range 2.5–24°. All data were corrected for Lorentz and polarisation effects and absorption correction based on ψ scan [10] was applied. The structures were solved by conventional Patterson and Fourier techniques and refined through full-matrix least-squares calculations with $\Sigma w(|F_o| - |F_c|)^2$ being minimised. For **1**, Cu, N and O atoms were refined anisotropically, whereas carbon atoms were refined isotropically. For **2**, anisotropic refinement was carried out for all non-hydrogen atoms.

The subsequent ΔF map for both the structures provides the position of all hydrogen atoms, except those belonging to H_2O molecules. The former were then treated as fixed contributors in the final refinement. The R index for **1** was 0.055 and $R' = 0.053$ using the weighting scheme $w = 1.6250/(\sigma^2 F_o + 0.0005 F_o^2)$, while for complex **2** R was 0.043 and $R' = 0.048$ using unit weights. Complex neutral-atom scattering factors were used throughout [11]; all calculations were carried out on a VAX6310 computer of the Centro Interdipartimentale di Calcolo Automatico of the University of Modena using SHELX76 [12], PARST [13] and ORTEP [14] programs.

The final fractional coordinates for the non-hydrogen atoms of **1** and **2** are listed in Tables 2 and 3, respectively.

3. Results and discussion

The logarithm of the acid protonation constant and overall stability constants of the complexes are reported in Table 4 and species distribution curves are given in Fig. 1. The titration of 4-NO_2-hipH in the 3–12 pH range revealed only one equivalent point corresponding to the dissociation of carboxyl. The pK_a value is similar to that of hippuric (3.80) [16] and 4-NH_2-hippuric (3.56) [8] acids. The spectrophotometric titration does not reveal any additional equivalent point up to pH ≈ 12. This indicates that the substituent on the phenyl ring does not significantly affect the dissociation of the carboxyl and amide groups. Also the titration curves of the binary system reveal only one equivalent point corresponding to the dissociation of the carboxyl, followed by the precipitation of copper(II) hydroxide at pH ≈ 6. This suggests that the only active binding site is the carboxyl which is known as a weak coordinating group. This behaviour is the one normally found with R–CO–N amino acids, irrespective of the R group, and the values of log β are similar to those of the above

Table 2
Final positional parameters for complex **1**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.6210(2)	0.49164(4)	0.7124(2)
O(1)	0.755(1)	0.4557(2)	0.820(1)
O(2)	0.843(1)	0.4814(2)	1.082(1)
C(1)	0.846(2)	0.4584(3)	0.986(2)
C(2)	0.968(2)	0.4317(3)	1.069(2)
N(1)	0.963(1)	0.4059(3)	0.951(1)
C(3)	0.818(2)	0.3871(3)	0.927(2)
O(3)	0.691(1)	0.3902(3)	1.012(1)
C(4)	0.816(2)	0.3620(3)	0.791(2)
C(5)	0.730(2)	0.3353(4)	0.818(2)
C(6)	0.718(2)	0.3117(4)	0.692(2)
C(7)	0.783(2)	0.3164(4)	0.531(2)
C(8)	0.871(2)	0.3437(3)	0.504(2)
C(9)	0.890(2)	0.3657(3)	0.633(2)
N(2)	0.759(3)	0.2922(4)	0.386(3)
O(4)	0.692(3)	0.2695(4)	0.425(2)
O(5)	0.801(2)	0.2990(4)	0.245(2)
O(6)	0.492(1)	0.5272(2)	0.589(1)
O(7)	0.569(1)	0.5521(2)	0.859(1)
C(10)	0.510(2)	0.5515(3)	0.689(2)
C(11)	0.445(2)	0.5799(3)	0.579(2)
N(3)	0.504(2)	0.6073(2)	0.685(1)
C(12)	0.614(2)	0.6282(3)	0.633(2)
O(8)	0.669(2)	0.6263(2)	0.484(2)
C(13)	0.663(2)	0.6546(3)	0.754(2)
C(14)	0.672(2)	0.6526(3)	0.942(2)
C(15)	0.733(2)	0.6766(4)	1.062(2)
C(16)	0.782(2)	0.7028(4)	0.987(2)
C(17)	0.773(2)	0.7062(4)	0.803(2)
C(18)	0.716(2)	0.6814(4)	0.683(2)
N(4)	0.850(2)	0.7284(4)	1.113(3)
O(9)	0.846(3)	0.7257(3)	1.280(3)
O(10)	0.911(2)	0.7506(3)	1.050(2)
Ow(1)	0.404(1)	0.4803(2)	0.821(1)
Ow(2)	0.858(1)	0.5064(2)	0.650(1)
Ow(3)	0.303(1)	0.4110(2)	0.793(1)
Ow(4)	1.052(1)	0.4481(2)	0.553(1)

Table 3
Final positional parameters for complex **2**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.24876(6)	0.42374(6)	0.21098(4)
N(1)	0.2861(4)	0.4388(4)	0.3606(3)
C(1)	0.2379(5)	0.5201(5)	0.4217(4)
C(2)	0.2663(5)	0.5227(5)	0.5252(4)
C(3)	0.3471(5)	0.4421(5)	0.5658(4)
C(4)	0.3987(5)	0.3575(5)	0.5038(4)
C(5)	0.3650(5)	0.3577(4)	0.4002(4)
N(2)	0.3537(4)	0.2774(3)	0.2288(3)
C(6)	0.4103(4)	0.2718(4)	0.3255(3)
C(7)	0.5036(5)	0.1919(5)	0.3508(4)
C(8)	0.5377(5)	0.1138(5)	0.2751(4)
C(9)	0.4758(6)	0.1159(5)	0.1769(4)
C(10)	0.3839(6)	0.1972(5)	0.1561(4)
N(3)	0.2124(4)	0.3973(4)	0.0598(3)
C(11)	0.3100(5)	0.4122(5)	0.0067(4)
C(12)	0.2854(6)	0.3915(6)	−0.0965(4)
C(13)	0.1531(6)	0.3559(6)	−0.1469(4)
C(14)	0.0524(5)	0.3433(5)	−0.0936(4)
C(15)	0.0842(5)	0.3618(4)	0.0116(3)
N(4)	0.0319(4)	0.3642(4)	0.1759(3)
C(16)	−0.0160(5)	0.3443(4)	0.0759(4)
C(17)	−0.1533(5)	0.3056(6)	0.0376(4)
C(18)	−0.2404(6)	0.2893(7)	0.1027(5)
C(19)	−0.1897(6)	0.3077(7)	0.2044(5)
C(20)	−0.0536(6)	0.3492(6)	0.2386(4)
O(1)	0.2493(3)	0.6083(3)	0.2157(2)
O(2)	0.4631(3)	0.5858(3)	0.2146(3)
C(21)	0.3710(5)	0.6507(5)	0.2177(3)
C(22)	0.4035(5)	0.7888(5)	0.2192(4)
N(5)	0.3115(4)	0.8642(4)	0.2580(3)
C(23)	0.3193(5)	0.8864(5)	0.3577(4)
O(3)	0.3991(4)	0.8399(4)	0.4161(3)
C(24)	0.2296(5)	0.9729(4)	0.3956(4)
C(25)	0.2699(5)	1.0325(5)	0.4945(4)
C(26)	0.1948(6)	1.1147(5)	0.5341(4)
C(27)	0.0785(5)	1.1387(5)	0.4733(4)
C(28)	0.0345(5)	1.0795(5)	0.3758(4)
C(29)	0.1096(5)	0.9952(5)	0.3382(4)
N(6)	−0.0004(6)	1.2300(5)	0.5144(4)
O(4)	−0.1043(5)	1.2472(5)	0.4594(4)
O(5)	0.0391(5)	1.2834(5)	0.5989(4)
N(7)	0.7628(6)	0.9418(5)	0.1250(4)
O(6)	0.7708(6)	0.9364(6)	0.2129(4)
O(7)	0.6513(6)	0.9248(6)	0.0706(4)
O(8)	0.8583(6)	0.9546(8)	0.0853(6)
Ow	0.1377(4)	0.9593(5)	0.0992(3)

cited Cu(II)–R–CO–N amino acid systems [7]. In the data treatment the species $[\mathrm{CuL}]^+$ and $[\mathrm{CuL_2}]$ were taken into account, but the better convergence was reached by considering only the latter species.

The ternary system with bpy presents titration curves which deviate from that of free 4-NO_2-hipH acid also at pH ≈ 3 and two equivalent points are observed: the first corresponds to the complete dissociation of the carboxyl and the second requires a number of base equivalents corresponding to those of Cu(II). The spectrophotometric titration shows at pH = 5.7 two absorption maxima at 900 and 740 nm. By increasing the pH, the maximum at 740 nm shifts to higher energy until 615 nm at pH ≈ 11, with the formation of an isosbestic point. The same trend is also observed for the Cu(II):bpy = 1:1 system, and so the species formed with increasing pH must be due to the deprotonation of a metal coordinated H_2O molecule. This finding suggests that the magnitude of the electron-withdrawing effect of the NO_2 group is not enough to lower the $\mathrm{p}K_{\mathrm{NH}}$ to a value appropriate to prevent metal hydroxide precipitation through the deprotonated nitrogen coordination.

The ternary ophen containing system parallels the pattern observed with bpy and the treatment of data took into account the species $[\mathrm{CuAL_2}]$ and $[\mathrm{CuAL(OH)}]$. We also calculated $\Delta\log\beta$ ($\Delta\log\beta = \log\beta^{\mathrm{Cu}}_{[\mathrm{CuAL_2}]} - \log\beta^{\mathrm{Cu}}_{[\mathrm{CuA}]}$) which is positive for both bpy and ophen complexes. This confirms that these amines exert an important selective effect toward the coordination of a carboxylate ligand [17]; this effect is clearly shown

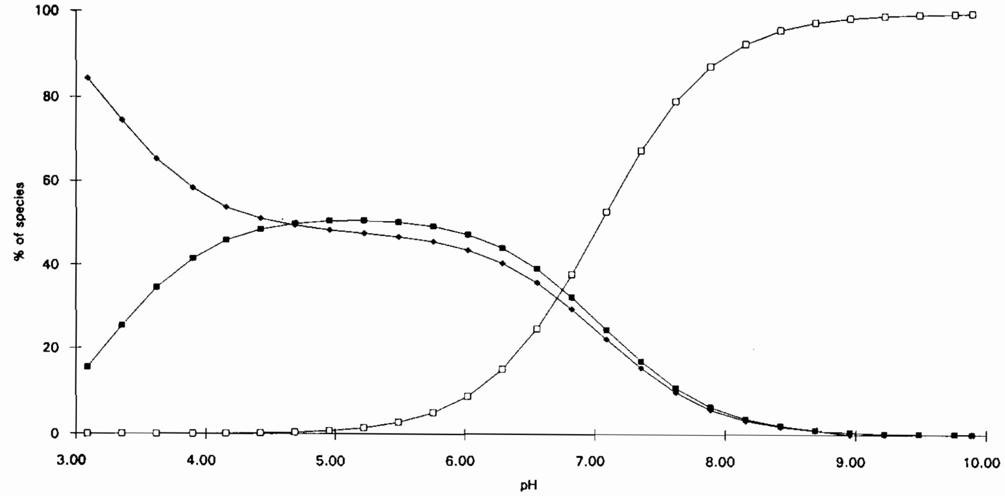

Fig. 1. Species distribution curves for the ternary system Cu^{2+}–bpy–L in a 1:1:4 molar ratio. ◆ $[Cu(bpy)]^{2+}$; ■ $[Cu(bpy)L_2]$; □ $[Cu(bpy)L(OH)]$; $[Cu^{2+}] = [bpy] = 1.8 \times 10^{-3}$, $[L] = 7.2 \times 10^{-3}$.

Table 4
Logarithm of protonation constant of 4-NO_2-hippuric acid and log β of the complexes at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$) with e.s.d.s in parentheses

LH	log β_{0011}	3.41(4)	
$[CuL]^+$	log β_{1010}	1.90(5)	
$[CuL_2]$	log β_{1020}	3.70(2)	
		A = bpy	A = ophen
$[CuAL_2]$	log β_{1120}	12.54(3)	13.8(1)
$[CuAL(OH)]$	log $\beta_{111\text{-}1}$	3.59(2)	4.7(1)
$[CuA]^{2+}$	log β_{1100}	8.00[a]	9.25[a]
	log K[b]	4.54	4.55
	Δlog K[c]	0.84	0.86

[a] Values taken from Ref. [15].
[b] log $K = \log \beta_{1210} - \log \beta_{1010}$.
[c] Δlog $K = \log K - \log \beta_{1200}$.

because an increase of pH only allows the substitution of one L ligand for one OH group and the precipitation of $Cu(OH)_2$ is prevented.

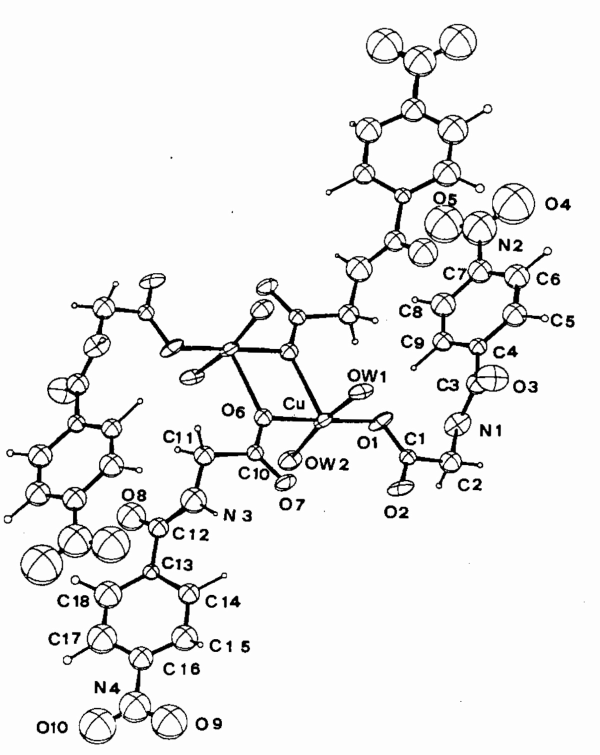

Fig. 2. ORTEP view of the $[Cu(4\text{-}NO_2\text{-}hip)_2(H_2O)_2]_2$ moiety with the thermal ellipsoids (40%) for the non-hydrogen atoms. The H atoms are represented as spheres of arbitrary radius.

3.1. Description of the structure of $[Cu(4\text{-}NO_2\text{-}hip)_2(H_2O)_2]_2 \cdot 4H_2O$

The ORTEP view of the complex molecule with the atom numbering scheme is reported in Fig. 2; selected bond distances and angles are given in Table 5. The unit cell contains dimers of formula $[Cu(4\text{-}NO_2\text{-}hip)_2(H_2O)_2]_2$ and lattice water molecules. In the dimer each Cu(II) atom displays a distorted square-pyramidal geometry; the in-plane coordinated atoms are two water oxygens and two carboxylate oxygens from two 4-NO_2-hip anions, and the fifth position is occupied by a carboxylate oxygen which is an equatorial ligand for the second Cu(II). So the centrosymmetrically related Cu(II) atoms are connected by a monoatomic bridge forming a perfectly planar Cu_2O_2 ring. The equatorial coordination plane deviates from planarity and the deviations of the atoms from the mean plane are ±0.12 Å, while the Cu(II) is 0.07 Å out of the plane toward the apex of the pyramid. This coordination geometry is closely similar to that observed in $[Cu(hip)_2(H_2O)_2]_2 \cdot 4H_2O$ [2]; this indicates that the presence of the NO_2 group on the phenyl ring does not affect the binding mode of hippuric acid. The

Table 5
Selected bond distances (Å) and angles (°) for complex **1**

Cu–O(1)	1.946(8)	Cu–O(6)	1.955(8)
Cu–Ow(1)	1.981(9)	Cu–O(6)′	2.345(8)
Cu–Ow(2)	1.989(9)	Cu...Cu′	3.331(4)
O(1)–C(1)	1.27(1)	O(6)–C(10)	1.30(2)
O(2)–C(1)	1.24(1)	O(7)–C(10)	1.23(2)
C(1)–C(2)	1.53(2)	C(10)–C(11)	1.51(2)
C(2)–N(1)	1.43(2)	C(11)–N(3)	1.46(2)
N(1)–C(3)	1.33(2)	N(3)–C(12)	1.32(2)
C(3)–O(3)	1.23(2)	C(12)–O(8)	1.26(2)
C(7)–N(2)	1.49(2)	C(16)–N(4)	1.48(2)
N(2)–O(4)	1.18(3)	N(4)–O(9)	1.24(3)
N(2)–O(5)	1.18(3)	N(4)–O(10)	1.21(3)
Ow(1)–Cu–Ow(2)	169.3(4)	O(6)–Cu–Ow(2)	89.2(4)
O(1)–Cu–Ow(2)	88.7(4)	O(6)–Cu–Ow(1)	92.5(4)
O(1)–Cu–Ow(1)	90.1(4)	O(6)–Cu–O(1)	176.3(4)
O(6)–Cu–O(6)′	78.9(4)		
Cu–O(1)–C(1)	115.6(8)	Cu–O(6)–C(10)	115.1(8)
O(1)–C(1)–O(2)	124(1)	O(6)–C(10)–O(7)	124(1)
O(2)–C(1)–C(2)	119(1)	O(7)–C(10)–C(11)	122(1)
O(1)–C(1)–C(2)	117(1)	O(6)–C(10)–C(11)	114(1)
C(1)–C(2)–N(1)	116(1)	C(10)–C(11)–N(3)	112(1)
C(2)–N(1)–C(3)	120(1)	C(11)–N(3)–C(12)	124(1)
N(1)–C(3)–C(4)	117(1)	N(3)–C(12)–C(13)	118(1)
N(1)–C(3)–O(3)	122(1)	N(3)–C(12)–O(8)	122(1)
O(3)–C(3)–C(4)	122(2)	O(8)–C(12)–C(13)	120(1)
C(7)–N(2)–O(5)	116(2)	C(16)–N(4)–O(9)	118(2)
C(7)–N(2)–O(4)	115(2)	C(16)–N(4)–O(10)	120(2)
O(4)–N(2)–O(5)	129(2)	O(9)–N(4)–O(10)	123(2)

corresponding bond distances and angles at the metal are similar in both complexes and the Cu···Cu separation and Cu–O–Cu′ angle in the Cu_2O_2 ring are exactly the same. In the present complex the carboxylic, amidic and nitro groups are planar and the dimensions of the two nitrohippurate anions are comparable. Bond distances and angles in the NO_2 groups are comparable with those in diaquabis(nitrophenylaceturate)copper(II) [18], where the N–O distances are 1.199 and 1.225 Å, and the angles at the N atom fall in the range 117.0–123.9°. In the unit cell intra- and intermolecular contacts in the range 2.66–3.00 Å are present, involving both coordinated and lattice water molecules. In particular Ow(4) forms only one short contact and the other water oxygens form two short contacts.

The d–d band maximum position and ESR parameters of our compound (Table 6) compare well with those of the hippurate compound (d–d max. = 14 700, 11 400(sh) cm^{-1} [2b]; $g_{\parallel}=2.356$, $g_{\perp}=2.068$ [5]). The ESR spectrum is characteristic of monomeric species as found for all such dimeric complexes, in view of the very small magnetic interaction [5]. The differential thermogravimetric analysis shows two well resolved peaks corresponding to a weight loss of 3.2 and 9.5% in agreement with a loss of two and six water molecules, respectively. The different number of contacts involving Ow(4) as compared to the other water molecules suggests that the first peak is due to Ow(4).

3.2. Description of the structure of [Cu(bpy)$_2$(4-NO$_2$-hip)]·NO$_3$·H$_2$O

The ORTEP drawing of the $[Cu(bpy)_2(4\text{-}NO_2\text{-hip})]^+$ moiety with numbering scheme is reported in Fig. 3; selected bond distances and angles are given in Table 7. The ternary complex consists of monomeric $[Cu(bpy)_2(4\text{-}NO_2\text{-hip})]^+$ cations, NO_3^- anions and lattice water molecules. The cations structure may be discussed in terms of a penta-coordinated stereochemistry, with the atom donor set CuN_4O. The 4-NO_2-hippurate anion is linked to the Cu(II) atom through one carboxylic oxygen; the second occupies the sixth position, 2.646(3) Å from Cu(II), also suggesting a (4+1+1*) geometry. This type of stereochemistry was previously observed in several ternary bpy-containing complexes with poorly coordinating carboxylate ligands such as $[Cu(bpy)_2(CH_3COO)]\cdot X\cdot H_2O$ where $X=ClO_4^-$ (**I**), BF_4^- (**II**) [19], $[Cu(bpy)_2(HCOO)]\cdot BF_4\cdot 0.5H_2O$ (**III**) [20] and $[Cu(bpy)_2(acasp)]\cdot C_2H_5OH\cdot 4H_2O$ (**IV**) [21] (acasp = *N*-acetylaspartate dianion). The CuN_4O group shows a strongly distorted geometry intermediate between the square-pyramidal and the distorted trigonal-bipyramidal geometry, commonly observed in $[Cu(bpy)_2(OCO)]Y$ complexes.

The CuN_4O group can be described as a distorted trigonal bipyramid with N(1), N(4), O(1) atoms in the equatorial plane, N(1) and N(3) in the apical positions, with an N(1)–Cu–N(3) angle of 176.4(2)°, compared to the ideal value of 180°. The Cu(II) atom is 0.029 Å out of this basal plane. The most important deviations from a trigonal-bipyramidal geometry, as observed in **I**, **II** and **III**, concern the angles α_1, α_2 and α_3 [20], whose values, 149.0, 99.6 and 111.3°, significantly differ from the ideal values of 120°. As the large O(1)–Cu–N(2) angle is opposite the elongated Cu–N(4) bond, it represents the basal angle of the square pyramid. Nevertheless the square-pyramidal stereochemistry is strongly distorted because the four equatorial ligands show root-mean square deviations of 0.267 Å from this plane. The distortion modes of the $[Cu(bpy)_2(OXO)]Y$ system were extensively discussed by Fitzgerald and Hathaway [20] and involve two alternative modes of coordination C and D. Route D, which describes the situation from symmetrical *cis*-distorted octahedral to a (4+1+1*) coordination involving a very asymmetrically OXO^- anion and a long Cu–N(4) distance, can be satisfactorily assigned to the present complex, as it was previously assigned to the structurally similar **I**, **II** and **III** complexes. The good fitting of the $\Delta N=0.146$ Å and $\Delta O=0.631$ Å values to the linear relationship between the differences in the Cu–O_{eq} bond lengths (ΔO) and the differences in the Cu–N_{eq} bond lengths (ΔN) [22] supports the proposed distortion mode.

The coordination mode of 4-NO_2-hipH, in the present compound, indicates that the nitro group reduces the

Table 6
Room temperature electronic and IR spectral data, ESR parameters, dehydration temperature and decomposition

	$[CuL_2(H_2O)_2]_2 \cdot 4H_2O$	$[Cu(bpy)L_2] \cdot 3H_2O$	$[Cu(ophen)L_2] \cdot 3H_2O$	$[Cu(bpy)_2L] \cdot NO_3 \cdot H_2O$
$g_{\parallel}$	2.369	2.309	2.447	$g_3 = 2.254$
$g_{\perp}$	2.112	2.089	2.089	$g_2 = 2.121$ $g_1 = 2.034$
d–d_{max} (cm^{-1})	14580, 11560	15500	13980	13660, 10360
T range (°C)	40–170	57–150	33–160	100–180
T dec. (°C)	200	220	220	220
ν(OH)	3560s, 3500s	3540b	3500b	3550b
ν(NH)	3330s, 3297s	3425ms, 3305s	3427ms, 3278ms	3411ms, 3258ms
$\nu(CO)_{ket}$	1653vs	1662vs	1656vs	1651vs
$\nu(COO)_{asym}$	1630sh, 1615vs	1632vs	1620vs	1608vs
$\nu(NO_2)_{asym}$	1540vs, 1520vs	1529vs	1524vs	1518s
$\nu(COO)_{sym}$	1438s	1445s	1429s	1450vs
$\nu(NO_2)_{sym}$	1352vs, 1323vs	1350vs, 1319s	1349s, 1328m	1347s, 1319s
$\nu_3(NO_3^-)$				1378vs
$\nu_1(NO_3^-)$				790s

Abbreviations: s = strong, b = broad, m = medium, v = very, sh = shoulder.

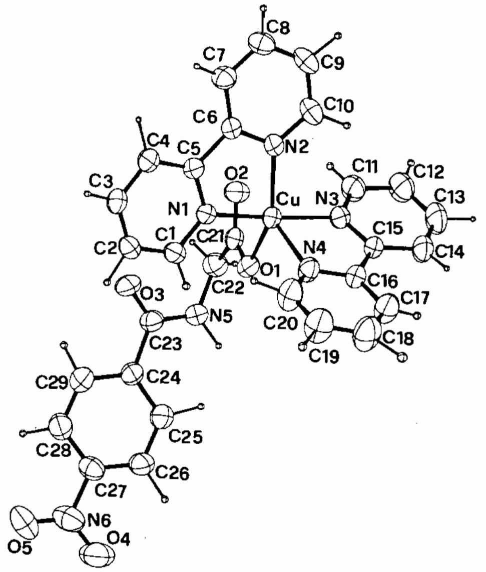

Fig. 3. ORTEP view of the $[Cu(bpy)_2(4\text{-}NO_2\text{-}hip)]^+$ moiety with the thermal ellipsoids (40%). The H atoms are represented as spheres of arbitrary radius.

binding ability of the hippurate residue and the formation of mixed-amine species is further favoured. This is confirmed by comparison with the coordination behaviour of 4-NH_2-hip, which coordinates through the NH_2 group and does not form mixed-amine species.

In the 4-NO_2-hippurate anion bond distances and angles are normal and comparable to those in the binary complex. The carboxylate group is nearly planar, the angle Cu–O(2)–O(1) is 54.7(4)° and far from the z axis of the square pyramid, so the long Cu–O(2) distance should be considered only a weak interaction. Bond distances and angles in the bpy molecules are normal; the dihedral angles formed by the pyridine rings are 8.6(2) and 3.1(2)° for molecules N(1)/N(2) and N(3)/N(4), respectively. The nitrate ion does not interact with the cation and forms a short contact with the lattice water molecule. The crystal packing (Fig. 4) is mainly due to short stacking interactions between bpy rings belonging to different cations giving rise to a mono-dimensional polymeric arrangement. The room temperature ESR spectrum (Table 6) is clearly rhombic and the lowest g value of 2.036 is indicative of an approximate d_{z^2} ground state for the CuN_4O group, but, notwithstanding this finding, $g_3 - g_2 > g_2 - g_1$ substantiates a $d_{x^2-y^2}$ ground state [20] in agreement with the clear (D) type distortion towards square-pyramidal. Its electronic spectrum (Table 6) shows two well resolved bands, of comparable intensity, separated by ~4000 cm^{-1}, the position of which is near the ranges

Table 7
Selected bond distances (Å) and angles (°) for complex **2**

Cu–N(1)	1.992(4)	Cu–N(2)	2.033(4)
Cu–N(3)	2.011(4)	Cu–N(4)	2.179(4)
Cu–O(1)	2.015(3)	Cu–O(2)	2.646(3)
O(1)–C(21)	1.267(6)	O(2)–C(21)	1.239(6)
C(21)–C(22)	1.510(7)	C(22)–N(5)	1.442(7)
N(5)–C(23)	1.340(7)	C(23)–O(3)	1.227(6)
C(27)–N(6)	1.470(8)	N(6)–O(5)	1.207(7)
N(6)–O(4)	1.226(7)		
N(4)–Cu–O(1)	99.6(2)	N(3)–Cu–O(1)	92.0(2)
N(3)–Cu–N(4)	78.6(2)	N(2)–Cu–O(1)	149.0(2)
N(2)–Cu–N(4)	111.3(2)	N(2)–Cu–N(3)	96.0(2)
N(1)–Cu–O(1)	91.6(2)	N(1)–Cu–N(4)	101.2(2)
N(1)–Cu–N(3)	176.4(2)	N(1)–Cu–N(2)	80.7(2)
Cu–N(1)–C(5)	115.3(3)	Cu–N(1)–C(1)	125.0(3)
Cu–N(2)–C(10)	127.4(3)	Cu–N(2)–C(6)	113.8(3)
Cu–N(3)–C(15)	117.5(3)	Cu–N(3)–C(11)	122.8(3)
Cu–N(4)–C(20)	129.0(3)	Cu–N(4)–C(16)	111.6(3)
O(2)–C(21)–C(22)	118.3(5)	O(1)–C(21)–O(2)	124.3(5)
O(1)–C(21)–C(22)	117.4(5)	C(21)–C(22)–N(5)	115.8(4)
C(22)–N(5)–C(23)	119.1(4)	N(5)–C(23)–C(24)	117.6(4)
C(27)–N(6)–O(5)	119.3(5)	C(27)–N(6)–O(4)	117.0(5)
O(4)–N(6)–O(5)	123.7(6)	O(7)–N(7)–O(8)	117.3(6)

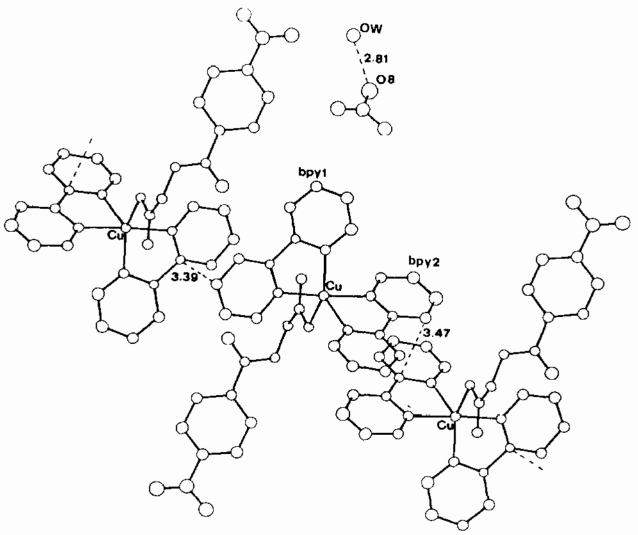

Fig. 4. Crystal packing of the $[Cu(bpy)_2(4\text{-}NO_2\text{-hip})]\cdot NO_3\cdot H_2O$ complex.

9990–10 860, 13 880–15 150 cm^{-1} observed for compounds **I**, **II** and **III** and is consistent with a $d_{x^2-y^2}$ ground state that was assigned to **I**, **II** and **III**.

The monoamine ternary complexes show ESR parameters and d–d band maximum position in agreement with a distorted square-pyramidal or distorted octahedral geometry with a CuN_2O_3 or CuN_2O_4 atom donor set as normally observed in almost all copper(II) complexes with these amines [23].

3.3. IR spectroscopy

The more relevant IR bands and their tentative assignment are reported in Table 6. For the monoamine complexes the metal coordination of the peptide group can be excluded because the stretching frequencies of the NH and CO groups are almost unchanged with respect to the structurally known complexes. The splitting of $\nu(COO)_{asym}$ in the binary complex can be ascribed to the presence of two ligand molecules involved in different coordination modes.

4. Supplementary material

Lists of anisotropic thermal parameters, hydrogen atom parameters, complete bond distances and angles, least-squares planes, possible hydrogen bonds, and observed and calculated structure factors (37 pp.) are available from the authors on request.

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