Co-ordination Behaviour of N-Protected Amino Acids. Structural and Spectroscopic Study of Complexes of Co^{II}, Ni^{II} and Cu^{II} with *N*-(4-Aminobenzoyl)glycine *

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The structural and spectroscopic properties of complexes of *N*-(4-aminobenzoyl)glycine (HL) with Co^{II}, Ni^{II} and Cu^{II} have been investigated. The complex $[\{CoL_2(H_2O)_2\}_n]\cdot 2nH_2O$ crystallizes in the space group $P\bar{1}$, with a = 8.027(2), b = 8.031(2), c = 10.033(1) Å, α = 96.52(2)°, β = 100.17(2)°, γ = 119.19(2)° and Z = 1; the nickel(II) homologue is isomorphous. The complex $[(CuL_2)_n]\cdot 4nH_2O$ crystallizes in the space group $P2_1/n$, with a = 4.673(1), b = 20.476(1), c = 12.026(1) Å, β = 97.38(2)° and Z = 2. The cobalt(II) co-ordination geometry is tetragonally distorted octahedral with four oxygens from two water molecules and two carboxylate groups in the basal plane and two amino nitrogens in the apical position. The copper(II) complex shows a strongly distorted tetragonal-octahedral geometry with two oxygens and two amino nitrogens of different amino acidate anions in the basal plane and two oxygens in the off-z-axis position. The ligand acts as bidentate bridging giving rise to a polymeric one-dimensional chain in the cobalt(II) complex and two-dimensional layers in the copper(II) one.

A substituent group such as RCO or $R'SO_2$ (R′ = aryl) on the nitrogen atom of an amino acid molecule changes the nitrogen hybridization from sp^3 to sp^2, accompanied by an increase in C–N or S–N bond order, as shown by the considerable shortening in bond distances.[1,2] As a consequence the nitrogen atom tries to maintain planar geometry and metal co-ordination will occur only after proton loss.[3] This reaction is subject to strong competition from metal hydrolysis and can take place if the N-substituent group possesses a strong inductive electrophilic effect such as toluene-*p*-sulphonyl,[4] benzenesulphonyl[5] and 5-dimethylaminonaphthalene-1-sulphonyl[6] with metal ions such as Pd^{2+}, Cu^{2+} and Cd^{2+}; it is ruled out with weak electrophilic groups such as acetyl, benzoyl and benzyloxycarbonyl whatever metal is present.[7] The N-protected amino acid behaves as a N,O-chelating ligand at pH > 5 in the first case[4–6] and as a simple carboxylate ligand in the second.[7]

A 4-aminobenzoyl group should not alter the co-ordination ability of the amide nitrogen with respect to the benzoyl group, but the NH_2 group on the phenyl ring could also, in principle, be involved in metal co-ordination as is suggested by the literature data on 4-aminobenzoic acid which acts either as a monodentate carboxylate or as a N,O-bridging ligand.[8–10]

At the present time no data are available on the co-ordination properties of *N*-(4-aminobenzoyl)glycine, although several studies assign a biological importance to this molecule; it is excreted in the renal metabolism of *p*-aminobenzoic acid and plays a role in the sulphate transport in human neutrophils.[11–13] As we are particularly interested in metal complexes of N-protected amino acids, a structural, spectroscopic and thermal investigation was made on the *N*-(4-aminobenzoyl)glycinates of Co^{II}, Ni^{II} and Cu^{II}.

Experimental

N-(4-Aminobenzoyl)glycine (HL) was purchased from Fluka and recrystallized before use from ethanol.

Preparation of the Complexes $[ML_2]\cdot 4H_2O$ (M = Co^{II}, Ni^{II} *or* Cu^{II}).—A hot (≈60 °C) aqueous solution (0.05 dm^3) of the appropriate metal(II) acetate (0.01 mol dm^{-3}) was added to an aqueous solution (0.05 dm^3) of the amino acid (0.02 mol dm^{-3}). After some hours solid crystalline complexes separated: $[CoL_2(H_2O)_2]\cdot 2H_2O$, yield 70% (Found: C, 41.40; H, 5.10; N, 10.65; H_2O, 14.70. Calc. for $C_{18}H_{26}CoN_4O_{10}$: C, 41.80; H, 5.10; N, 10.80; H_2O, 13.90); $[NiL_2(H_2O)_2]\cdot 2H_2O$, yield 70% (Found: C, 41.70; H, 5.10; N, 10.50; H_2O, 14.85. Calc. for $C_{18}H_{26}N_4NiO_{10}$: C, 41.80; H, 5.10; N, 10.80; H_2O, 13.90%). The copper(II) complex was prepared in the same manner by using methanol as solvent. On cooling the solution an olive-green microcrystalline compound separated, $[CuL_2]\cdot 4H_2O$, yield 90% (Found: C, 41.20; H, 4.80; N, 10.50; H_2O, 14.60. Calc. for $C_{18}H_{26}CuN_4O_{10}$: C, 41.40: H, 5.00; N, 10.70; H_2O, 13.80%).

X-Ray Data Collection and Structure Determination.—Crystal data and other crystallographic details are reported in Table 1.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, at room temperature, by using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) with the ω–2θ scan technique, θ ranging from 2.5 to 25°. Three standard reflections, monitored at 4 h intervals, showed no significant change. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.[14]

The structures were solved by conventional Patterson and Fourier techniques, and refined through full-matrix least-squares calculation with $\Sigma w(|F_o| - |F_c|)^2$ minimized. All non-hydrogen atoms were located on a Fourier difference map, then treated as fixed contributors with isotropic thermal parameters 1.0 Å^2 higher than those of the atoms to which they are bonded. Final refinement of this model led to R = 0.031, R' = 0.032 for $[\{CoL_2(H_2O)_2\}_n]\cdot 2nH_2O$ **1** and R = 0.031, R' = 0.028 for $[(CuL_2)_n]\cdot 4nH_2O$ **2**. Unit weights were used at all stages, and no trend in $\Sigma w(|F_o| - |F_c|)^2$ *vs.* $|F_o|$, sin θ, or Miller indices was observed.

The final difference map was featureless, with no peaks higher than 0.2 e Å^{-3}. There was no evidence of secondary extinction.

Complex neutral-atom scattering factors were taken from ref. 15. Major calculations were performed on a Vax-6310 computer by the SHELX 76 system of programs,[16] distances, angles and mean planes by PARST[17] and drawings by

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

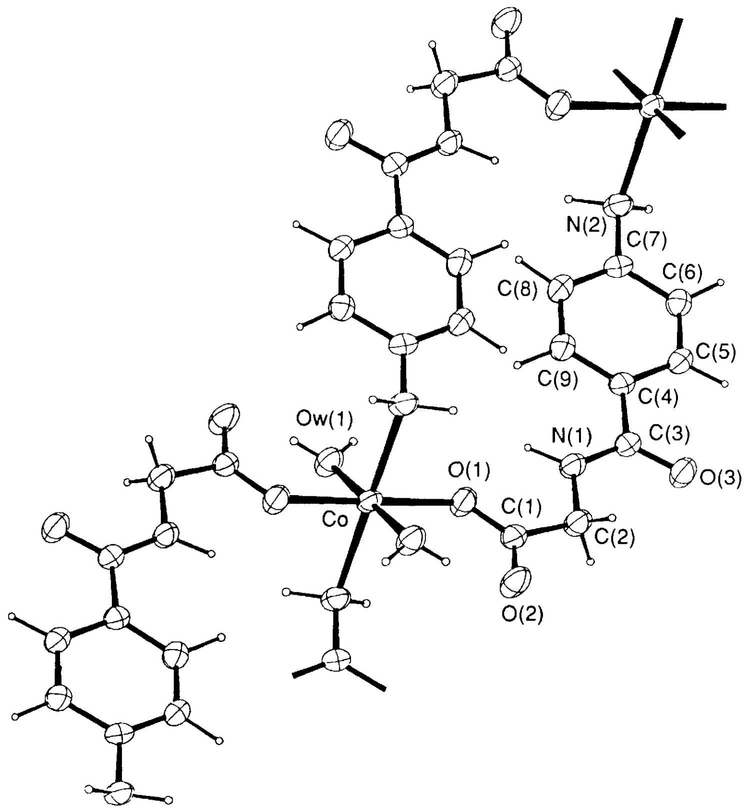

Fig. 1 An ORTEP view of the $[\{CoL_2(H_2O)_2\}_n]$ moiety showing the atom numbering and thermal ellipsoids (40%) for the non-hydrogen atoms. The H atoms are represented as spheres of arbitrary radius

ORTEP.[18] Final fractional coordinates for non-hydrogen atoms are given in Tables 2 and 3 for complexes **1** and **2** respectively. For the analogous complex $[NiL_2]\cdot 4H_2O$ the cell parameters were: $a = 7.99(1)$, $b = 8.03(2)$, $c = 9.98(1)$ Å, $\alpha = 96.5(1)$, $\beta = 100.0(1)$, $\gamma = 119.2(1)^\circ$ and $Z = 1$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Physical Measurements.—Solid-state electronic spectra were obtained with a Beckman Acta MIV spectrophotometer, IR spectra as KBr (4000–500 cm^{-1}) or Polythene pellets (500–50 cm^{-1}) with a Bruker FT-IR 113v spectrophotometer. The room-temperature ESR spectrum was recorded with a Varian E-9 spectrometer with diphenylpicrylhydrazyl as standard field marker.

Spectrophotometric and pH-metric titrations employed a Perkin-Elmer 551 spectrophotometer and a fully automatic ORION 960 autochemistry system with a Ross 8102 SC combined electrode at constant ionic strength ($I = 0.1$ mol dm^{-3}, $NaClO_4$) and using carbonate-free standardized 0.1 mol dm^{-3} NaOH as titrant. The data were processed with the SUPERQUAD computer program.[19]

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 by using a Carlo Erba model 1106 elemental analyser by Mr. G. Goldoni.

Results and Discussion

N-(4-Aminobenzoyl)glycine.—The amino acid molecule possesses two pH-dependent dissociation equilibria (1) and (2).

$$NH_3{}^+C_6H_4NHCOCH_2CO_2H \xrightleftharpoons{pK_{1a}} NH_2C_6H_4NHCOCH_2CO_2H + H^+ \quad (1)$$

$$NH_2C_6H_4NHCOCH_2CO_2H \xrightleftharpoons{pK_{2a}} NH_2C_6H_4NHCOCH_2CO_2{}^- + H^+ \quad (2)$$

The pK_{1a} value determined spectrophotometrically in aqueous solution is 2.77 ± 0.08, the potentiometric value of pK_{2a} is 3.70 ± 0.01 and the simultaneous refinement from potentiometric titration leads to values of 2.83 ± 0.01 and 3.56 ± 0.01 for pK_{1a} and pK_{2a} respectively. The pK_{1a} value is slightly greater than that of 4-aminobenzoic acid (2.501)[20] and is comparable to that of 4-(*p*-aminobenzoyl)aniline (2.93),[20] so that the amino nitrogen of *N*-(4-aminobenzoyl)glycine should possess almost the same donor ability as that of 4-aminobenzoic acid. As expected, pK_{2a} is similar to that of *N*-benzoylglycine (3.80)[20] because the NH_2 group on the phenyl ring exerts no effect on the dissociation equilibrium of CO_2H.

Description of the Structures.—Drawings showing the labelling schemes are given in Figs. 1 and 2 for complexes **1** and **2** respectively. Selected bond distances and angles are reported in Table 4.

$[\{CoL_2(H_2O)_2\}_n]\cdot 2nH_2O$. The structure is built up of polymeric ribbons, generated by applying the transformation $-x + 1, -y + 1, -z + 1$, and of lattice water molecules. The metal lies on the symmetry centre and exhibits an elongated octahedral co-ordination geometry with four oxygen atoms in the basal plane and two nitrogens at the apex of the bipyramid. The equatorial O atoms are derived from two water molecules and two carboxylate oxygens. Each ligand anion bridges two Co atoms through the amino nitrogen and one carboxylate oxygen atom.

The $Co-O_{carboxy}$ bond distance [2.079(2) Å] is in the range observed (2.06–2.10 Å) for other structurally known cobalt(II) complexes of N-protected amino acids,[21] whereas the Co–N distance is longer than those of complexes with simple amino acids, in line with the low basicity of the aniline nitrogen.

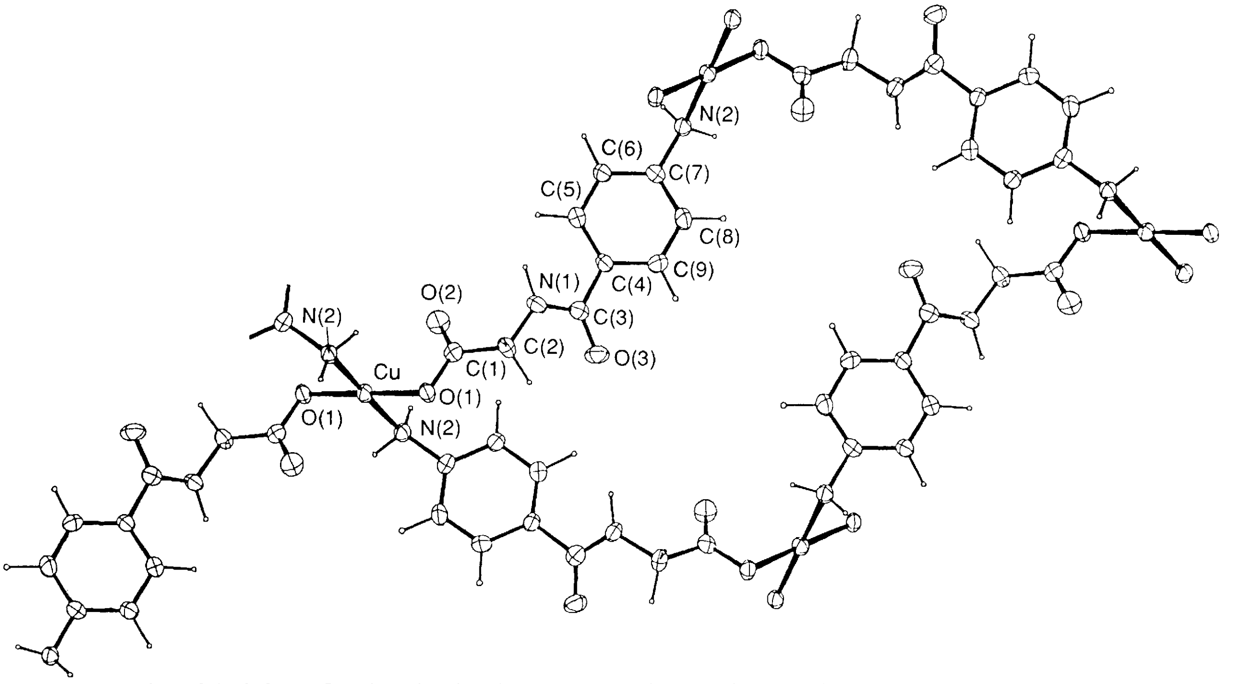

Fig. 2 An ORTEP view of the $[(CuL_2)_n]$ moiety showing the atom numbering and thermal ellipsoids (40%) for the non-hydrogen atoms. The H atoms are represented as spheres of arbitrary radius

Table 1 Experimental data for the crystallographic analyses

Compound	**1**	**2**
Formula	$C_{18}H_{26}CoN_4O_{10}$	$C_{18}H_{26}CuN_4O_{10}$
M	517.17	521.78
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.027(2)	4.673(1)
b/Å	8.031(2)	20.476(3)
c/Å	10.033(1)	12.026(1)
α/°	96.52(2)	
β/°	100.17(2)	97.38(2)
γ/°	119.19(2)	
U/Å^3	540.6(3)	1141.3(3)
Z	1	2
F(000)	269	542
D_c/g cm^{-3}	1.59	1.52
D_m/g cm^{-3}	1.60	1.48
Colour	Pink	Olive-green
Crystal size/mm	0.40 × 0.30 × 0.25	0.60 × 0.30 × 0.12
μ(Mo-Kα)	8.51	10.15
h,k,l ranges	−9 to 9, −9 to 9, 0–11	−5 to 5, 0–24, 0–14
Scan width	1.0 + 0.35 tanθ	0.6 + 0.35 tanθ
Scan speed/° min^{-1}	2.34–8.2	1.03–8.24
No. reflections measured	2039	2190
No. reflections used [$I > 2\sigma(I)$]	1895	1314
Transmission coefficient	0.94 < *T* < 0.99	0.89 < *T* < 0.99
R	0.031	0.031
R'	0.032	0.028
Minimum, maximum height in the final Δ*F* map, Δρ/e Å^{-3}	−0.38, 0.46	−0.42, 0.47

Cell constants were determined by least-squares refinement of diffractometer angles for 25 automatically centred reflections.

Table 2 Final positional parameters for $[\{CoL_2(H_2O)_2\}_n]\cdot 2nH_2O$

Atom	*X/a*	*Y/b*	*Z/c*
Co	0.0	0.0	0.0
O(1)	0.0834(2)	−0.0488(2)	0.1930(2)
O(2)	−0.1863(3)	−0.3356(2)	0.1818(2)
C(1)	−0.0203(3)	−0.1894(3)	0.2436(3)
C(2)	0.0609(4)	−0.1813(3)	0.3926(3)
N(1)	0.2456(3)	0.0010(3)	0.4611(2)
C(3)	0.3286(3)	0.0370(3)	0.5962(2)
O(3)	0.2510(3)	−0.0867(2)	0.6637(2)
C(4)	0.5144(3)	0.2285(3)	0.6647(2)
C(5)	0.5963(4)	0.2623(3)	0.8058(3)
C(6)	0.7646(4)	0.4379(3)	0.8777(3)
C(7)	0.8570(3)	0.5839(3)	0.8080(3)
C(8)	0.7767(4)	0.5519(3)	0.6678(3)
C(9)	0.6060(4)	0.3758(4)	0.5962(3)
N(2)	1.0285(3)	0.7671(3)	0.8828(2)
Ow(1)	0.2958(2)	0.1740(2)	0.0146(2)
Ow(2)	0.5859(3)	0.3205(3)	0.2518(2)

$[(CuL_2)_n]\cdot 4nH_2O$. The Cu atom lies on the symmetry centre and is co-ordinated by two carboxylate oxygens and two amino nitrogens; the second carboxylic oxygen [O(2)] is 2.627(3) Å from the copper in an 'out-of-plane' position. As a consequence of the angle between the Cu–O(2) vector and the normal to the equatorial plane [34.9(1)°], which reduces the degree of metal–ligand orbital overlap, the Cu···O(2) distance must be considered as a weak bonding interaction giving rise to a 4 + 2* co-ordination;[22] lattice water molecules complete the cell content. Each ligand molecule is bidentate toward two metal ions, giving rise to a polymeric network arrangement. The Cu–O distance is normal for those to N-protected amino acids[23] and, as expected, the Cu–N distance is longer with respect to that found with simple amino acids.[24]

In all these complexes the *N*-(4-aminobenzoyl)glycine co-ordinates through the carboxylate oxygen and amino nitrogen, although the high degree of hydration of the complexes would particularly favour a O_6 donor set as found in $[Co(4\text{-}NH_2\text{-}C_6H_4CO_2)_2(H_2O)_4]$ or a O_4 donor set as suggested for $[Cu(4\text{-}NH_2C_6H_4CO_2)_2(H_2O)_2]$.[9] Some differences among the present copper(II) and cobalt(II) complexes are observed, the bond angles at O(1) and N(2) being 105.7(2), 110.8(2)° for the former and 126.9(2), 120.7(1)° for the latter; the strong Cu–O bond significantly affects the C(1)–O distances, taking them toward the values typical of a neutral carboxyl.[1]

Table 3 Final positional parameters for $[(CuL_2)_n]\cdot 4nH_2O$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.0	0.0	0.0
O(1)	−0.2650(5)	0.0737(1)	0.0023(2)
O(2)	0.1175(5)	0.1086(1)	0.1131(2)
C(1)	−0.1255(7)	0.1175(2)	0.0638(3)
C(2)	−0.2824(7)	0.1820(2)	0.0685(3)
N(1)	−0.1090(6)	0.2310(1)	0.1330(2)
C(3)	−0.0039(7)	0.2828(2)	0.0863(3)
O(3)	−0.0583(5)	0.2948(1)	−0.0164(2)
C(4)	0.1842(7)	0.3276(2)	0.1607(3)
C(5)	0.3635(7)	0.3054(2)	0.2539(3)
C(6)	0.5369(7)	0.3487(2)	0.3208(3)
C(7)	0.5276(7)	0.4151(2)	0.2959(3)
C(8)	0.3501(8)	0.4374(2)	0.2031(3)
C(9)	0.1830(8)	0.3941(2)	0.1350(3)
N(2)	0.6892(6)	0.4604(1)	0.3699(2)
Ow(1)	0.8942(5)	0.1809(1)	0.3608(2)
Ow(2)	0.5960(6)	0.0635(1)	0.2724(3)

Table 4 Selected bond distances (Å) and angles (°)

	Complex **1** M = Co	Complex **2** M = Cu
M–O(1)	2.079(2)	1.954(2)
M–N(2′)*	2.224(2)	2.060(3)
M–Ow(1)	2.051(2)	—
O(1)–C(1)	1.260(3)	1.286(4)
O(2)–C(1)	1.247(2)	1.225(4)
C(1)–C(2)	1.502(3)	1.515(5)
C(2)–N(1)	1.452(2)	1.451(4)
N(1)–C(3)	1.330(3)	1.323(5)
C(3)–O(3)	1.238(3)	1.253(4)
N(2)–C(7)	1.425(2)	1.432(4)
Ow(1)–M–N(2′)	95.9(1)	—
O(1)–M–N(2′)	86.1(1)	87.6(1)
O(1)–M–Ow(1)	87.4(1)	—
M–O(1)–C(1)	126.9(2)	105.7(2)
M–N(2′)–C(7′)	120.7(1)	110.8(2)
O(1)–C(1)–O(2)	126.1(2)	123.0(3)
O(2)–C(1)–C(2)	116.3(2)	122.3(3)
O(1)–C(1)–C(2)	117.6(2)	114.7(3)
C(1)–C(2)–N(1)	113.0(2)	112.5(3)
C(2)–N(1)–C(3)	120.3(2)	122.6(3)
N(1)–C(3)–C(4)	119.0(2)	117.5(3)
N(1)–C(3)–O(3)	120.1(2)	122.4(3)

* The symmetry transformation is $-x + 1, -y + 1, -z + 1$ for Co and $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ for Cu.

The ligand conformation may be described by the torsion angles O(1)–C(1)–C(2)–N(1) and C(1)–C(2)–N(1)–C(3) which are 4.81(4) and 174.9(2)° for Co^{II} and −176.3(3) and 110.1(4)° respectively for Cu^{II}. As a consequence the whole ligand molecule is fairly planar in the cobalt complex, which deviations ranging from −0.0971 to 0.0927 Å and atom O(2) is 0.1639 Å below the plane. In the copper complex the carboxylate and peptide groups are nearly planar but the dihedral angle formed by these planes is 67.3(1)° and that formed by the peptide group with the phenyl ring is 32.3(1)°.

In both complexes the crystal packing is due to hydrogen bonds which in the cobalt(II) complex are abundant and particularly strong (Table 5).

Table 5 Possible hydrogen bonds (Å) and angles (°)

(*a*) Complex **1**

O(2) ··· Ow(2′)	2.726(3)	O(3) ··· Ow(2″)	2.885(3)
Ow(2′)–H(12′)	0.922(3)	Ow(2″)–H(13″)	0.814(2)
O(2) ··· H(12′)	1.839(2)	O(3) ··· H(13″)	2.077(2)
Ow(2′)–H(12′) ··· O(2)	160.4(1)	Ow(2″)–H(13″) ··· O(3)	171.7(1)
O(3) ··· N(2′)	3.054(2)	Ow(1) ··· Ow(2)	2.684(2)
N(2′)–H(8′)	1.053(3)	Ow(1)–H(10)	0.874(3)
O(3) ··· H(8′)	2.005(3)	Ow(2) ··· H(10)	1.815(3)
N(2′)–H(8′) ··· O(3)	173.6(1)	Ow(1)–H(10) ··· Ow(2)	172.3(1)

Symmetry transformations: ′ $x - 1, y - 1, z$; ″ $-x + 1, -y, -z + 1$.

(*b*) Complex **2**

Ow(2) ··· O(2)	2.903(4)	Ow(1) ··· O(3′)	2.775(4)
Ow(2)–H(13)	0.986(3)	Ow(1)–H(9)	1.051(3)
O(2) ··· H(13)	1.936(2)	O(3′) ··· H(9)	1.751(3)
Ow(2)–H(13) ··· O(2)	166.2(2)	Ow(1)–H(9) ··· O(3′)	163.8(2)

Symmetry transformation: ′ $x - 1, y, z$.

Spectroscopic and Thermogravimetric Data.—Although the site symmetry is lower than O_h, because of the tetragonal distortion along the Co–N bond, the electronic spectrum pattern is satisfactorily interpreted in terms of O_h symmetry and the bands are then assigned as follows: 8330, ν_1, $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$; 19 200 (sh), 21 050, 22 400 (sh) cm^{-1}, ν_3, $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$; Dq = 951 cm^{-1} and B = 927 cm^{-1} calculated from ν_1 and ν_3.[25] For the nickel(II) complex the O_h symmetry leads to the following assignments: 9520, ν_1, $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$; 13 700, $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$; 16 000, ν_2, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$; 27 550 cm^{-1}, ν_3, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$; Dq = 952 cm^{-1} and B = 996 cm^{-1} calculated by using ν_1, ν_2, ν_3,[25] or Dq = 972 cm^{-1} and B = 959 cm^{-1} calculated from ν_2 and ν_3.[26]

On the basis of the chemical formula, cell parameters and spectroscopic properties the complexes of Ni^{II} and Co^{II} are isomorphous and isostructural.

The d–d band position and crystal-field parameters of the nickel(II) complex fall in the ranges for an O_4N_2 donor atom set,[27] while for the cobalt(II) complex the data are near to those of octahedral MO_6 as found for cobalt(II) and nickel(II) complexes of *N*-benzoyl-,[28] *N*-acetyl- and *N*-(arenesulphonyl)-glycine, -α- and -β-alanine[21] confirming that the bound amino nitrogen possesses only a weak donor ability. This finding reflects the pK_a value for the NH_2 group which is lower than that of the CO_2H group.

Nevertheless co-ordination of the amino nitrogen to the metal, instead of a water molecule, is preferred in all the complexes investigated because it gives rise to a polymeric arrangement which enhances the crystal-packing stability.

The d–d band transitions (14 800, 18 150 cm^{-1}) and ESR parameters (g_1 = 2.21, g_2 = 2.09, g_3 = 2.05) for the copper(II) complex are close to the values reported for the structurally similar $[Cu(NH_3)_2(CH_3CO_2)_2]$ and are consistent with a stereochemistry intermediate between square planar and tetragonal octahedral due to the inability of the carboxylate oxygen to co-ordinate effectively along the z axis.[29]

A correct assignment of the infrared bands is difficult because of the great number of vibrations falling in the 3500–3100 and 1650–1400 cm^{-1} spectral regions but two points may be emphasized: (*i*) the spectra of the isomorphous complexes of Co^{II} and Ni^{II} are superimposable and this fact indicates also for the latter a co-ordination through NH_2 and CO_2^- groups; (*ii*) the spectrum of the copper(II) complex below 1300 cm^{-1} shows some new bands with respect to the cobalt(II) complex and this may be related to the observed differences in the torsion angles of the ligand.

The far-IR spectra enable us tentatively to assign the M–O and M–N vibrations by comparison with the free ligand and sodium salt. The M–N stretching vibration is assigned at 365 and 370 cm^{-1} for Co^{II} and Ni^{II} respectively and the M–O stretching vibration at 243 cm^{-1} for Co^{II} and 247 cm^{-1} for Ni^{II};[10,30] the copper(II) complex shows two bands assignable to the Cu–N vibration (476, 407 cm^{-1}) and two to the Cu–O vibration (334, 282 cm^{-1}).[31]

The thermogravimetric analysis shows a sharp weight loss in the temperature ranges 90–230 and 120–230 °C for the complexes of Co^{II} and Ni^{II} respectively, which correspond to the complete loss of co-ordinated and lattice water molecules without decomposition. For the copper(II) complex two peaks are present (45–90, 113–170 °C), each corresponding to the loss of two water molecules, and decomposition begins above 250 °C, as is observed for the cobalt(II) and nickel(II) species.

Conclusion

The bonding mode of *N*-(4-aminobenzoyl)glycine is different from that of *N*-benzoylglycine which was found to act as O-monodentate (in complexes of Co^{II}, Ni^{II} and Fe^{II})[28] or O-monodentate and O-bidentate bridging through a monoatomic bridge [in the copper(II) complex].[32]

To the slight increase in basicity of the NH$_2$ group of *N*-(4-aminobenzoyl)glycine, compared to 4-aminobenzoic acid (pK_a for NH$_2$ = 2.83 *vs.* 2.50) corresponds a marked reduction in pK_a for the carboxyl of the first ligand with respect to the second one (3.56 *vs.* 4.87). However, the NH$_2$ group of *N*-(4-aminobenzoyl)glycine is invariably an active binding site and the ligand acts as N,O-bidentate bridging forming a polymeric arrangement which allows a peculiar stability for the crystal packing.

The stability of the polymer makes further reaction with strong donor ligands such as 2,2′-bipyridine or imidazoles very difficult and no solid complexes are obtained.

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