Carboxylate Bridging of Amino Acids in Dinuclear Macrocyclic Nickel(II) Complexes

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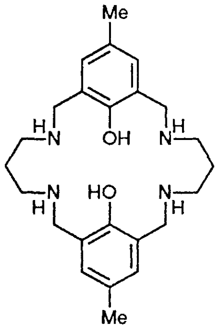
The dinuclear nickel(II) complex $[Ni_2L(MeOH)_2(ClO_4)_2]\cdot 2NEt_3HClO_4$, derived from a tetraazadiphenol macrocyclic ligand H_2L, on reaction with glycine, β-alanine and glycylglycine affords the μ-carboxylato complexes of composition $[Ni_2L(^-O_2C-NH_3^+)(H_2O)_2][ClO_4]_2\cdot nH_2O$. The structure of $[Ni_2L(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$ has been determined: monoclinic, space group C_c, with $a = 17.465(2)$, $b = 21.834(2)$, $c = 11.480(1)$ Å, $\beta = 115.27(2)°$ and $Z = 4$. The structure was solved by direct methods and refined to $R = 0.047$ and $R' = 0.064$.

Amino acids and peptides almost invariably bind metal ions *via* at least one nitrogen atom and a deprotonated carboxyl oxygen atom.[1,2] However, multiply bonded dinuclear ions such as Mo_2^{4+}, Rh_2^{4+} or Cr_2^{4+}, which show a strong tendency to form *syn-syn* carboxylate-bridged complexes, have been found to produce μ-carboxylato species with a few amino acids and glycylglycine in aqueous acidic solution. Crystal structures of the tetrakis complexes of Mo_2^{4+} with glycine, L-isoleucine, L-leucine and glycylglycine,[3] of Rh_2^{4+} with β-alanine,[4] and of Cr_2^{4+} with glycine[5] have been reported. The trimeric iron(III) β-alanine complex $[\{Fe(Ala)_2(H_2O)\}_3O][ClO_4]_7$ has also been structurally characterized.[6] In this compound each pair of Fe atoms in the Fe_3O core is bridged by two alanines through the oxygens of the carboxyl groups.

We have recently reported[7] the structure of a novel dinickel complex $[Ni_2L(MeOH)_2(ClO_4)_2]\cdot 2NEt_3HClO_4$ **1**, derived from the macrocyclic ligand H_2L. Complex **1** exhibits remarkable electrochemistry producing dinickel(III), nickel(II)-nickel(III), nickel(I)nickel(II) and dinickel(I) species in tandem. The stereochemical equilibria of the dinickel(II) complexes in solution involving octahedral and square-pyramidal species have been investigated and their tendency to adopt a square-pyramidal configuration with axially interacting nitrogen donors has been demonstrated by determining the structure of $[Ni_2L(py)_2][ClO_4]_2$[8] (py = pyridine).

We now report the characterization of carboxylate-bridged complexes of the type $[Ni_2L(\mu\text{-}^-O_2C-NH_3^+)(H_2O)_2][ClO_4]_2\cdot nH_2O$, obtained by treating **1** with glycine, β-alanine and glycylglycine. To our knowledge μ-carboxylate binding of amino acids in zwitterionic form is unprecedented in nickel(II) chemistry.



H_2L

Results and Discussion

The complexes $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$ **2**, $[Ni_2L(O_2CCH_2CH_2NH_3)(H_2O)_2][ClO_4]_2$ **3** and $[Ni_2L(O_2CCH_2NHCOCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$ **4** have been obtained as blue crystals in 50, 35 and 30% yield by treating complex **1** directly with the amino acids or glycylglycine in methanol. When these reactions were carried out under alkaline conditions no definite products, however, could be isolated. Branched-chain amino acids such as L-alanine and DL-histidine or the peptide *N*-glycyl-L-α-alanine also failed to produce any isolable product.

Complexes **2**–**4** have been characterized by their IR, UV/VIS spectra and room-temperature magnetic moments (Table 1). The 1:2 electrolytic behaviour of the complexes (Λ_M 160–180 S cm^2 mol^{-1} in MeOH) along with their chemical compositions clearly suggest that the amino acids and glycylglycine are present as neutral molecules, that is, zwitterions. In their IR spectra all three complexes exhibit a broad band centred at 3400 cm^{-1} due to the water molecules and a weak but sharp band at 3260 cm^{-1} due to the NH group of the macrocyclic ligand. Complex **2** shows a strong band at 1630 cm^{-1} along with a shoulder at 1610 cm^{-1}, which may be associated to $\nu_{asym}(CO_2^-)$ of glycine and δ(NH) of L^{2-}. For complex **3** these two bands overlap at 1610 cm^{-1}. Similar overlapping also occurs for **4** at 1600 cm^{-1}, but in this case ν(C=O) of glycylglycine (1665 cm^{-1}) preceeds. The $\nu_{sym}(CO_2)^-$ vibration could not be located with certainty due to the presence of four characteristic bands of the macrocyclic ligand at 1470, 1450, 1415 and 1390 cm^{-1}. An interesting feature of the complexes is the occurrence of highly split ν(Cl–O) stretches of the ClO_4^- ions (1145, 1120, 1090 and 1010 cm^{-1}), which provide good evidence of their involvement in hydrogen bonding.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Characterization data for the complexes

Complex	λ_{max}/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})[a]	IR (cm^{-1})	μ_{eff} per Ni^{II}[b]
2	8450(10), 11 150(13), 16 400(12), 27 800 (sh) (65), 34 200(6700), 41 000(13 000)	3400, 3260, 1630, 1610 (sh), 1470, 1455, 1415, 1390, 1145, 1120, 1090, 1010	3.24
3	8600(10), 11 250(14), 16 500(12), 27 800 (sh) (60), 34 000(7000), 42 500(11 700)	3400, 3260, 1610, 1470, 1450, 1420, 1395, 1150, 1120, 1090, 1010	3.18
4	8550(11), 11 300(14), 16 500(13), 27 800 (sh) (65), 34 500(7200), 40 000(11 000)	3400, 3260, 1665, 1600, 1470, 1450, 1415, 1390, 1150, 1115, 1090, 1015	3.25

[a] In MeOH. [b] At 298 K.

Table 2 Crystal data for $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2 \cdot 2H_2O$

Formula	$C_{26}H_{47}Cl_2N_5Ni_2O_{16}$
M	873.88
Crystal system	Monoclinic
Space group	C_c
a/Å	17.465(2)
b/Å	21.834(2)
c/Å	11.480(1)
β/°	115.27(2)
U/Å^3	3959(2)
Z	4
D_c/g cm^{-3}	1.459
λ(Mo-Kα)/Å	0.7107
μ/cm^{-1}	11.58
Transmission (%)	99.96–88.53
Scan type	θ–2θ
Crystal size/mm	0.18 × 0.21 × 0.33

The room-temperature magnetic moments of the complexes, μ_{eff} *ca.* 3.2 per nickel, lie in the range 2.9–3.3 usually observed for octahedral nickel(II) complexes. A variable-temperature (5–300 K) magnetic measurement has been made for complex **2** and preliminary analysis of the data indicates[9] weak ferromagnetic exchange interaction between two $S = 1$ states. Magnetic studies of these and other dinickel(II) complexes of H_2L will be reported elsewhere in detail.

The electronic spectral features of complexes **2**–**4** are quite similar. They exhibit four d–d transitions at about 8500, 11 300, 16 300 and 27 500 cm^{-1}, which are indicative of low-symmetry six-co-ordinate geometries. Indeed, the structural data of **2** (Table 4) reveal that the two Ni^{2+} ions are in a distorted-octahedral environment. The first two bands of the complexes appear to be the split components of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition of regular octahedral complexes and may be assigned, in D_{4h} symmetry, as $^3B_{1g} \longrightarrow {}^3E_g$ and $^3B_{1g} \longrightarrow {}^3B_{2g}$ transitions. On this basis one may extract the following values (cm^{-1}) of the spectrochemical parameters (Dq^{xy}, Dq^z, Dt) for the complexes: **2**, $Dq^{xy} = 1150$, $Dq^z = 540$, $Dt = 350$; **3**, $Dq^{xy} = 1125$, $Dq^z = 590$, $Dt = 310$; **4**, $Dq^{xy} = 1130$, $Dq^z = 580$, $Dt = 315$.

The cyclic voltammetric behaviour of complex **2** in MeCN solution using a platinum electrode has been studied. The dinickel(II) species undergoes a one-electron oxidation to a nickel(II)nickel(III) species quasireversibly at 0.78 V *vs.* SCE ($\Delta E_p = 160$ mV at $v = 50$ mV s^{-1}). However, further oxidation to the dinickel(III) species occurs irreversibly at 1.0 V. These results may be compared to those for **1** which undergoes stepwise reversible oxidations at 0.94 and 1.08 V. The reduction behaviour of **2** in MeCN is rather featureless, presumably a two-electron irreversible charge-transfer process is involved at *ca.* −1.1 V. By contrast, **1** undergoes successive reduction to nickel(I)nickel(II) and dinickel(I) species in Me$_2$SO solution with a glassy carbon electrode at −1.32 and −1.65 V, respectively. Although the formation of a nickel(II)nickel(III) species from **2** could be detected on the cyclic voltammetric time-scale, it was chemically unstable. Clearly, the carboxylate bridge fails to stabilize the dinickel species both in the higher and lower oxidation states.

Fig. 1(*a*) shows the ORTEP[10] diagram of the $[Ni_2L(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2]^{2+}$ cation along with the atom labelling scheme, while the PLUTO[11] diagram of **2** [shown in Fig. 1(*b*)] gives a projection of the non-CH hydrogen atoms involved in hydrogen bonding. Atomic coordinates, and selected bond lengths and angles are given in Tables 3 and 4, respectively. The structure consists of two distorted nickel(II) centres bridged by two phenoxide oxygens and two carboxylate oxygens of the zwitterionic form of glycine. The co-ordination environment NiN$_2$O$_4$ of each nickel centre is completed by two secondary amine nitrogen donors of the macrocyclic ligand and a water molecule *trans* axially disposed to the carboxylate oxygen. The complex molecule is lacking in symmetry. While the dihedral angle between the basal planes of the two metal centres, *i.e.* Ni(1)O(10)O(31)N(19)N(23) and Ni(5)O(10)O(31)N(34)N(38) is 33.5(3)°, the planes of the two phenyl rings are inclined by 49.3(5)°. The Ni$_2$L unit is of concave shape when viewed down the aminocarboxylate moiety. The metal centres and phenoxide oxygens are displaced below the mean plane Ni(1)Ni(5)O(10)O(31)N(19)N(23)N(34)N(38) as follows: Ni(1), 0.105(1); Ni(5), 0.112(2); O(10), 0.566(7); O(31), 0.525(7) Å. The secondary amine nitrogens, however, are displaced above this plane by 0.28(1)–0.37(3) Å. Significant pyramidal distortions of the low-lying phenoxide oxygens are also evident from deviations of the solid angles (that is, summation of the angles) at these centres, 337.2 and 340.8, from 360°. The 1,3-diaminopropane bridges on both sides of the macrocycle are of puckered configuration and the nitrogen and carbon atoms are alternately displaced above and below the mean planes. Atoms Ni(1)O(10)O(31)Ni(5) form a distorted square plane in which the two metal centres are separated by 3.066(8) Å with Ni–O–Ni bridge angles of 92.6(3) and 95.0(3)°. The oxygen atoms of the carboxylate moiety and co-ordinated water molecules are normal to this plane with angles O(2)Ni(1)O(8) and O(4)Ni(5)O(9) being 177.8(3) and 178.3(4)°, respectively.

The average Ni–N distance in complex **2** [2.085(5) Å] is comparable to those observed in **1** (2.06 Å)[7] and $[Ni_2L(py)_2][ClO_4]_2$ (2.09 Å),[8] and is close to the mean distance 2.11 Å reported[12] for a large number of high-spin secondary amine nickel(II) complexes. By contrast, the Ni–O (phenolate) distances, which lie between 2.076(8) and 2.124(7) Å, are significantly longer than those observed in **1** (2.027 Å), $[Ni_2L(py)_2][ClO_4]_2$ (2.011 Å) and the range 1.93–2.01 Å reported for various Ni–O(phenolate) bonds.[13–17] These exceptionally long Ni–O distances, however, are comparable to the other Ni–O distances in **2** due to the carboxylate [Ni(1)–O(2) 2.081(6), Ni(5)–O(4) 2.073(7) Å] and water [Ni(1)–O(8) 2.134(7), Ni(5)–O(9) 2.147(8) Å]. It appears that the metal–donor distances in **2** are strongly influenced by the shape of the molecule and the stereochemistry of the metal ions.

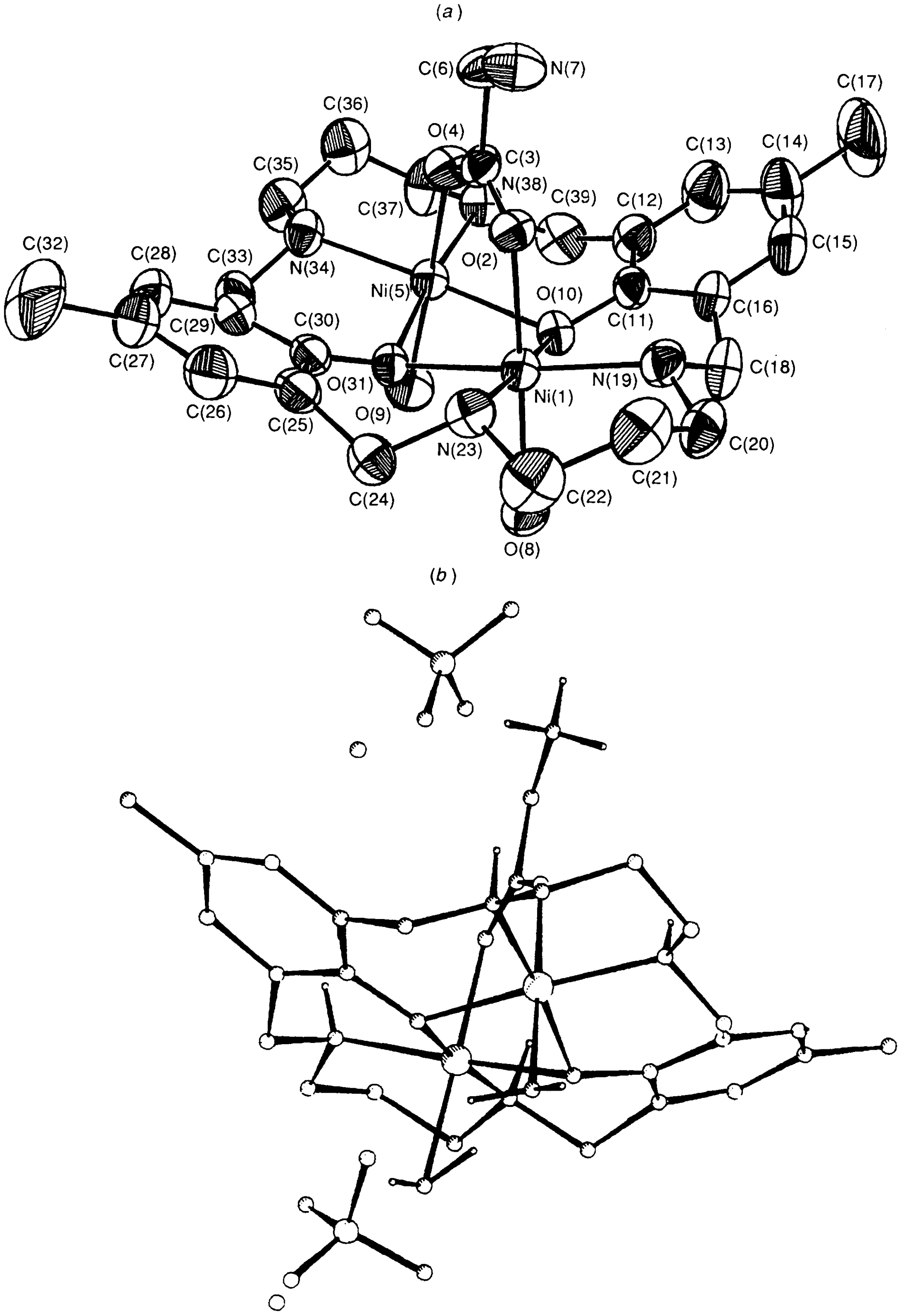


Fig. 1 (*a*) An ORTEP diagram and atom labelling scheme of the cation $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2]^{2+}$ showing 50% probability thermal ellipsoids. (*b*) Perspective view showing the projection of non-CH hydrogen atoms involved in hydrogen bonding

A comparison of the bond distances and angles of glycine[18] with that of the zwitterion in complex **2** (Table 5) reveals that the configuration of the amino acid remains practically unchanged on complexation and is in accord with previous observations.[3-5] An important aspect of the structure of **2** is that 15 non-CH hydrogen atoms in the molecule are involved in an elaborate network of intra- and inter-molecular hydrogen bonding. Table 6 lists twenty such D–H···A (D = donor, A = acceptor) distances which are less than 3.3 Å. It is noteworthy that a tight web of hydrogen bonding so effectively locks the perchlorate ions that they have unusually low thermal parameters. The packing diagram of **2** viewed down the '*b*' axis is shown in Fig. 2. The perchlorate ions as well as the uncoordinated water molecules are wedged between the cationic macrocyclic channels and are oriented parallel to the '*ac*' direction of the unit cell.

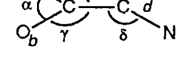
Table 3 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	0.500(0)	0.225 93(6)	0.250(0)	C(3)	0.396 2(6)	0.208 2(5)	−0.034(1)
Ni(5)	0.575 69(9)	0.168 21(6)	0.079 1(2)	C(6)	0.312 1(7)	0.217 2(7)	−0.152(1)
Cl(40)	0.250 4(2)	0.406 4(2)	0.045 5(4)	C(11)	0.580 9(7)	0.307 8(5)	0.114(1)
Cl(45)	0.178 7(2)	0.151 3(2)	0.170 8(3)	C(12)	0.611 1(8)	0.314 8(6)	0.022(1)
O(2)	0.397 9(4)	0.225 7(3)	0.069 2(7)	C(13)	0.598(1)	0.368 4(7)	−0.044(2)
O(4)	0.454 0(4)	0.186 7(4)	−0.057 6(7)	C(14)	0.559(1)	0.417 9(6)	−0.023(2)
O(8)	0.602 5(5)	0.223 3(4)	0.437 5(8)	C(15)	0.535(1)	0.413 2(6)	0.076(1)
O(9)	0.702 3(5)	0.147 4(4)	0.216 6(8)	C(16)	0.546 0(8)	0.359 2(5)	0.146(1)
O(10)	0.587 0(4)	0.253 0(3)	0.176 0(7)	C(17)	0.548(2)	0.477 5(8)	−0.097(2)
O(1)	0.268(1)	0.094(1)	−0.073(2)	C(18)	0.530 4(8)	0.359 6(5)	0.263(1)
O(3)	0.825(2)	0.046(1)	0.933(3)	C(20)	0.438 8(8)	0.334 6(6)	0.364(1)
O(31)	0.538 0(4)	0.139 6(3)	0.219 9(7)	C(21)	0.373 0(8)	0.293 2(6)	0.373(1)
O(41)	0.225 2(8)	0.435 3(6)	−0.076(1)	C(22)	0.405 1(9)	0.226 6(7)	0.423(1)
O(42)	0.289 3(8)	0.350 8(5)	0.038(1)	C(24)	0.443 7(7)	0.128 6(5)	0.373(1)
O(43)	0.176 4(9)	0.392 7(8)	0.064(2)	C(25)	0.437 6(7)	0.083 9(5)	0.272(1)
O(44)	0.302(10)	0.444 3(7)	0.143(1)	C(26)	0.383 8(8)	0.034 0(6)	0.250(1)
O(45)	0.223 6(8)	0.168 1(9)	0.100(1)	C(27)	0.382(1)	−0.012 5(6)	0.169(1)
O(47)	0.235 8(6)	0.139 5(6)	0.298(1)	C(28)	0.441 0(9)	−0.010 8(6)	0.116(1)
O(48)	0.122 7(8)	0.199 7(7)	0.161(1)	C(29)	0.495 9(8)	0.039 2(5)	0.136(1)
O(49)	0.134(1)	0.101 4(6)	0.118(2)	C(30)	0.491 9(7)	0.089 1(5)	0.207(1)
N(7)	0.245 1(6)	0.232 1(5)	−0.115(1)	C(32)	0.326(1)	−0.068 3(9)	0.146(2)
N(19)	0.466 2(6)	0.316 5(4)	0.262 7(9)	C(33)	0.563 3(8)	0.033 7(5)	0.088(1)
N(23)	0.418 6(6)	0.191 6(4)	0.324 2(9)	C(35)	0.608 5(9)	0.064 3(6)	−0.076(1)
N(34)	0.557 7(6)	0.082 3(4)	−0.006 4(9)	C(36)	0.610(1)	0.111 0(7)	−0.171(1)
N(38)	0.612 3(6)	0.207 3(4)	−0.055 8(9)	C(37)	0.659 0(9)	0.168 6(6)	−0.111(1)
				C(39)	0.660 9(8)	0.264 7(6)	0.003(1)

Table 4 Selected bond distances (Å) and angles (°) for $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$

Ni(1)–N(19)	2.09(1)	Ni(5)–N(38)	2.09(1)
Ni(1)–N(23)	2.08(1)	Ni(5)–N(34)	2.077(9)
Ni(1)–O(2)	2.081(6)	Ni(5)–O(4)	2.073(7)
Ni(1)–O(8)	2.134(7)	Ni(5)–O(9)	2.147(8)
Ni(1)–O(10)	2.118(9)	Ni(5)–O(10)	2.124(7)
Ni(1)–O(31)	2.076(8)	Ni(5)–O(31)	2.086(9)
Ni(1) ··· Ni(5)	3.066(8)		
N(19)–Ni(1)–N(23)	92.8(4)	N(34)–Ni(5)–N(38)	92.9(4)
O(10)–Ni(1)–O(31)	81.4(3)	O(10)–Ni(5)–O(31)	81.0(4)
O(10)–Ni(1)–N(19)	92.1(4)	O(10)–Ni(5)–N(38)	92.4(3)
O(31)–Ni(1)–N(23)	93.7(4)	O(31)–Ni(5)–N(34)	93.6(4)
Ni(1)–O(10)–Ni(5)	92.6(3)	Ni(5)–O(31)–Ni(1)	95.0(3)
O(2)–Ni(1)–O(8)	177.8(3)	O(4)–Ni(5)–O(9)	178.3(4)
O(10)–Ni(1)–N(23)	175.0(3)	O(10)–Ni(5)–N(34)	174.4(4)
O(31)–Ni(1)–N(19)	172.9(5)	O(31)–Ni(5)–N(38)	173.3(3)
C(11)–O(10)–Ni(1)	122.9(7)	C(11)–O(10)–Ni(5)	121.1(7)
C(30)–O(31)–Ni(1)	123.1(7)	C(30)–O(31)–Ni(5)	122.7(7)

Table 5 Comparison of bond lengths (Å) and angles (°) of the zwitterion in $[Ni_2L(^-O_2CCH_2NH_3{}^+)(H_2O)_2][ClO_4]_2\cdot 2H_2O$ with that of glycine



	Glycine	**2**
a	1.250(1)	1.25(2)
b	1.251(1)	1.23(1)
c	1.526(1)	1.53(1)
d	1.476(1)	1.44(2)
α	125.45(8)	129.7(8)
β	117.46(16)	115(2)
γ	117.09(7)	116(2)
δ	111.85(5)	111(2)

Experimental

Complexes **2**–**4** were prepared in the same way. A methanol solution (20 cm^3) of complex **1** [7] (1.19 g, 1 mmol) was treated with glycine, β-alanine or glycylglycine (2 mmol) and a few drops of water. The wine-red solution changed to sky blue on stirring and was filtered after 0.5 h. The filtrate on slow evaporation deposited blue crystals, which were collected by filtration and washed with small portions of cold ethanol and water. The complexes may be recrystallized from methanol–water (Found: C, 35.9; H, 5.5; N, 7.95. $C_{26}H_{47}Cl_2N_5Ni_2O_6$ **2** requires C, 35.75; H, 5.4; N, 8.0. Found: C, 38.1; H, 5.4; N, 8.4. $C_{27}H_{45}Cl_2N_5Ni_2O_{14}$ **3** requires C, 38.05; H, 5.3; N, 8.2. Found: C, 35.8; H, 5.2; N, 8.8. $C_{28}H_{50}Cl_2N_6Ni_2O_7$ **4** requires C, 36.1; H, 5.35; N, 9.05%).

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer using KBr discs, electronic spectra on a Hitachi U3400 or JASCO 7850 spectrophotometer over the UV/VIS and near-IR regions. Room-temperature magnetic susceptibility was measured on a EG&G PAR 155 vibrating-sample magnetometer using $Hg[Co(NCS)_4]$ as the calibrant. Susceptibility data were corrected for diamagnetism using Pascal constants. Conductivity measurements were carried out using a Philips PR 9500 conductivity bridge. Carbon, H and N analyses were performed on a Perkin-Elmer 240C elemental analyser.

Crystal Structure Determination and Refinement.—Diffraction data for complex **2** were collected with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The unit-cell parameters were obtained by least-squares refinement of the scattering angles of 25 arbitrarily chosen higher-order reflections. Crystal data and the details of the data collection are given in Table 2. A total of 3417 reflections (+*h*, +*k*, ±*l*) were collected in the range $4 < 2\theta < 48°$, of which 3217 with $I > 3\sigma(I)$ were used in the structure analysis. The intensity data were corrected for Lorentz and polarization effects and for absorption by the empirical method of North *et al.*[19] The structure was solved by direct and Fourier difference methods using the program MULTAN 82[20] and the SDP package[21] for the PDP-11/73 system. The positions of the hydrogen atoms were all located from difference maps. A mixed mode of refinement with all the non-hydrogens varying

Table 6 Inter- and intra-molecular hydrogen-bond distances (Å) and angles (°) for $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$

D	H	A	D···A	D–H···A	Symmetry[a]
O(1)[b]	H(11)	O(45)	2.992	143.4	
O(1)[b]	H(12)	N(7)	3.062	143.0	
O(3)[b]	H(31)	O(41)	2.961	175.6	
O(3)[b]	H(32)	O(44)	3.181	180.0	I
O(8)	H(81)	O(43)	2.930	146.1	I
O(8)	H(81)	O(31)	2.983	108.6	*c*
O(8)	H(82)	O(48)	2.956	160.5	II
O(9)	H(91)	O(41)	2.874	163.4	II
O(9)	H(92)	O(10)	2.963	168.5	
N(7)	H(71)	O(10)	2.798	173.6	II
N(7)	H(71)	O(9)	3.158	106.9	*c*
N(7)	H(72)	O(45)	2.995	149.0	
N(7)	H(72)	O(2)	2.605	92.1	*c*
N(7)	H(73)	O(42)	3.040	176.5	
N(19)	H(19)	O(2)	2.833	113.5	
N(19)	H(19)	O(42)	3.157	152.2	*c*
N(23)	H(23)	O(2)	2.889	105.8	
N(23)	H(23)	O(45)	3.317	160.6	*c*
N(34)	H(34)	O(4)	2.812	92.8	
N(38)	H(38)	O(4)	2.792	95.8	

[a] Symmetry of A with respect to D when not x,y,z: I $\frac{1}{2}+x, y-\frac{1}{2}, \frac{1}{2}+z$; II $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$. [b] Lattice water. [c] Probably a bifurcated hydrogen bond or an additional weak hydrogen bond to reinforce packing.

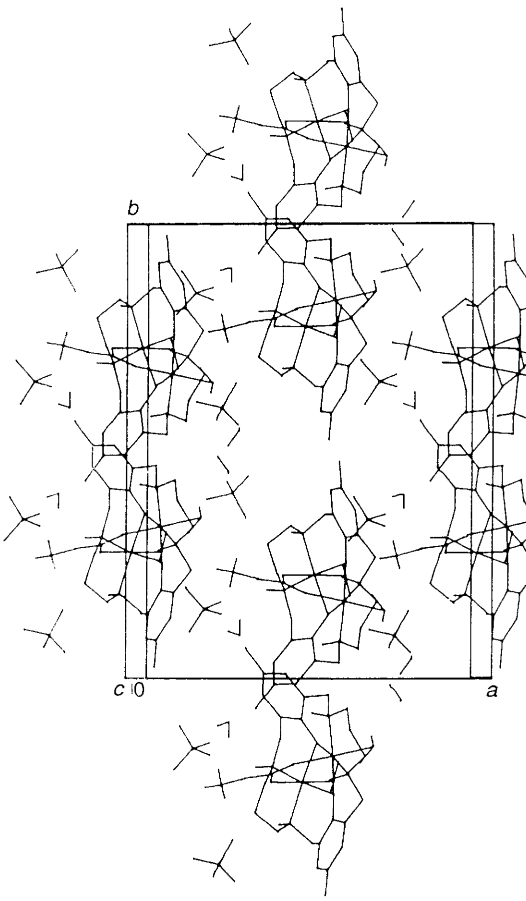


Fig. 2 Packing diagram of complex **2** in the unit cell

anisotropically, except for those of disordered lattice water, and a unit weighting scheme with a Dunitz–Seiler factor,[22] resulted in final residuals $R = 0.047$ and $R' = 0.064$. The scattering factors used were those given in ref. 23.

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

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