H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.012$
Absolute structure: Flack (1983)
Flack parameter = −0.010 (8)

Table 1. *Selected geometric parameters (Å, °)*

C1—O1	1.203 (9)	Cl3—Pt	2.323 (2)
C1—O2	1.317 (9)	Pt—S	2.215 (2)
C1—C2	1.521 (10)	O3—O12^{i}	2.966 (11)
C2—N	1.484 (8)	O11—O2	2.561 (9)
C2—C3	1.517 (10)	O11—O12	2.768 (12)
C3—C4	1.534 (8)	N—O5*A*	2.97 (2)
C4—S	1.781 (7)	N—O7*A*	3.03 (3)
C5—S	1.777 (7)	N—O9*A*	2.93 (2)
O3—S	1.450 (6)	N—O5*B*	2.98 (2)
Cl1—Pt	2.321 (3)	N—O7*B*	2.88 (3)
Cl2—Pt	2.263 (3)	N—O9*B*	2.81 (2)
O1—C1—O2	125.6 (7)	Cl2—Pt—Cl1	176.65 (12)
O1—C1—C2	123.2 (7)	O3—S—C5	109.0 (4)
O2—C1—C2	111.1 (6)	O3—S—C4	106.7 (4)
S—Pt—Cl1	90.48 (9)	C5—S—C4	101.9 (3)
S—Pt—Cl2	91.76 (10)	O3—S—Pt	119.8 (3)
S—Pt—Cl3	178.26 (9)	C5—S—Pt	108.2 (3)
Cl2—Pt—Cl3	89.81 (12)	C4—S—Pt	109.7 (2)
Cl1—Pt—Cl3	87.98 (10)		

Symmetry code: (i) $2 - x, \frac{1}{2} + y, 1 - z$.

Data collection: *IPDS Software* (Stoe & Cie, 1996*a*). Cell refinement: *IPDS Software*. Data reduction: *IPDS Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*93.

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged, as is the loan of chemicals by Degussa (Hanau).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1320). Services for accessing these data are described at the back of the journal.

References

Albert, A. & Mootz, D. (1997). *Z. Naturforsch. Teil B*, **52**, 615–619.
Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jeffrey, G. A. & Saenger, A. (1994). *Hydrogen Bonding in Biological Structures*, p. 29. Berlin: Springer.
Keppler, B. K. (1993). Editor. *Metal Complexes in Cancer Chemotherapy*. Weinheim: VCH.
Maverick, E., Seiler, P., Schweizer, W. B. & Dunitz, J. D. (1980). *Acta Cryst.* B**36**, 615–620.
Mootz, D., Albert, A., Schaefgen, S. & Stäben, D. (1994). *J. Am. Chem. Soc.* **116**, 12045–12046.
Reedijk, J. (1992). *Inorg. Chim. Acta*, **198–200**, 873–881.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Steinborn, D., Gravenhorst, O., Hartung, H. & Baumeister, U. (1997). *Inorg. Chem.* **36**, 2195–2199.
Steinborn, D., Gravenhorst, O., Junicke, H. & Heinemann, F. W. (1998). *Z. Naturforsch. Teil B*, **53**, 581–586.
Steinborn, D., Junicke, H. & Heinemann, F. W. (1997). *Inorg. Chim. Acta*, **256**, 87–92.
Stoe & Cie (1996*a*). *IPDS Software*. Version 2.86 (Stoe publication 4805–017). Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1996*b*). *XRED. Data Reduction Program*. Version 1.07. Stoe & Cie, Darmstadt, Germany.
Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., pp. 563–566. Oxford University Press.

Acta Cryst. (1999). C**55**, 1257–1260

Intramolecular C—H···O and intermolecular N—H···O and C—H···O interactions in *N*-ferrocenoylglycine benzyl ester, an effective dihydrogen phosphate anion sensing agent

John F. Gallagher, Peter T. M. Kenny and Michael J. Sheehy

School of Chemical Sciences, Dublin City University, Dublin 9, Ireland. E-mail: gallagherjfg@dcu.ie

(*Received 11 March 1999; accepted 12 April 1999*)

Abstract

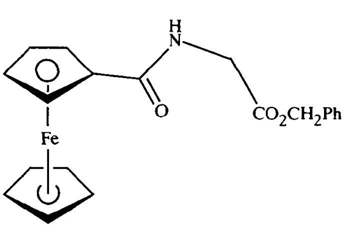
The title compound, benzyl *N*-(ferrocenecarbonyl)glycinate, $[\mathrm{Fe}(\mathrm{C_5H_5})(\mathrm{C_{15}H_{14}NO_3})]$, a glycine benzyl ester derivative, is an effective anion sensor for electrochemically sensing the dihydrogen phosphate anion ($\mathrm{H_2PO_4^-}$). Intermolecular N—H···O hydrogen bonds form one-dimensional chains with graph set $C(4)$ [N···O 2.811 (3) Å]. A two-dimensional network is formed by linking the chains through $\mathrm{C_{ar}}$—H···O═$\mathrm{C_{ester}}$ interactions about inversion centres [graph set $R_2^2(14)$; C···O 3.406 (4) Å]. An intramolecular $\mathrm{C_{Cp}}$—H···O═$\mathrm{C_{ester}}$ interaction [C···O 3.540 (3) Å] with graph set $S(9)$ completes the hydrogen bonding.

Comment

The design of new redox-active ligands for application in diverse research areas such as medicinal chemistry and materials science has engrossed scientists in recent years. Ferrocene derivatives, which are efficient redox systems, have been studied extensively in charge-transfer chemistry, hydrogen-bonding and molecular-recognition science, peptide chemistry and non-linear optical materials (Moore *et al.*, 1993; Chesney *et al.*, 1998; Glidewell *et al.*, 1997; Degani & Heller, 1986; Kraatz *et al.*, 1997; Long, 1995). Anion recognition is

© 1999 International Union of Crystallography
Printed in Great Britain – all rights reserved

of current interest, especially with regard to the design of molecular sensing and switching devices (Beer, 1998; Kingston *et al.*, 1999). An understanding of the interactions present in the crystal structure of a potential anion receptor can provide valuable information on the hydrogen-bonding modes and binding sites in solution studies. The structure of *N*-ferrocenoylglycine benzyl ester, (I), is reported herein.



(I)

Compound (I), which crystallizes in space group $P2_1/c$, is depicted with the atomic numbering scheme in Fig. 1, with selected geometric dimensions in Table 1. Bond lengths and angles are in accord with the anticipated values (Orpen *et al.*, 1994). There is no disorder in the structure and examination of the structure with *PLATON* (Spek, 1998) shows that there are no solvent-accessible voids in the crystal lattice.

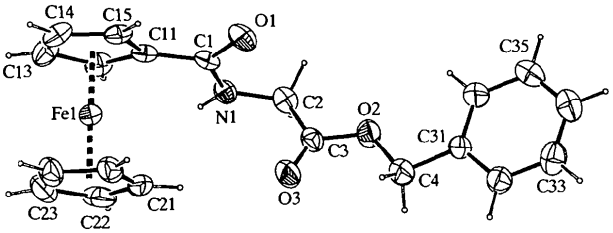


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The dihedral angle between the C_5 planes is 2.8 (2)° with the rings deviating from the fully eclipsed conformation by 5.1 (3)° [range 4.6 (2)–5.5 (3)°]. The Fe to cyclopentadienyl ring centroid distance is 1.6427 (14) Å for the substituted ring and 1.6461 (16) Å for the unsubstituted ring (Spek, 1998), which are comparable with values of 1.6449 (4) and 1.6464 (4) Å in the related methyl ester derivative, (II) (Gallagher *et al.*, 1999). The range of C_{Cp}—C_{Cp} distances in (I) is 1.400 (4)–1.428 (4) Å [mean 1.412 (4) Å] and 1.398 (5)–1.407 (5) Å [mean 1.401 (5) Å] for the substituted and unsubstituted rings, respectively. The Csp^3 atom, C1, is displaced by 0.030 (5) Å from the substituted C_5 ring plane towards the Fe atom due to the intramolecular interaction C21—H21···O2, and the amide C1/O1/N1/C2 plane is at an angle of 16.6 (2)° to the C11–C15 plane [these values are 0.032 (5) Å and 16.67 (17)° in (II), respectively]. The Fe1—C11—C1 angle of 124.74 (17)° is similar to the value of 124.87 (17)° in (II).

In the asymmetric unit, molecules of (I) associate through intermolecular N—H···O hydrogen bonds [N1···O1^{i} 2.811 (3) Å; symmetry code: (i) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$], forming a one-dimensional chain with graph set $C(4)$ as depicted in Fig. 2 (details in Table 2). The chains are linked through C_{ar}—H···O═C_{ester} hydrogen bonds [C32···O3^{ii} 3.406 (4) Å; symmetry code: (ii) $-x$, $-y$, $1-z$] about inversion centres with graph set $R_2^2(14)$, forming a two-dimensional network. An intramolecular C_{Cp}—H···O═C_{ester} interaction [C21···O3 3.540 (3) Å] with graph set $S(9)$ completes the hydrogen bonding with an H21···O3···H32^{ii} angle of 82°. The N—H···O═C hydrogen-bonding arrangement with graph set $C(4)$ is present in (II) [N···O 2.804 (3) Å], with a C_{Cp}—H···O interaction [C···O 3.309 (4) Å] completing the intermolecular hydrogen bonding; an analogous C_{Cp}—H···O═C_{ester} intramolecular interaction [C···O 3.364 (4) Å] is also observed. The hydrogen-bonding patterns in the crystal structures of a diverse range of ferrocene alcohol derivatives have been reported (Ferguson *et al.*, 1993; Gallagher *et al.*, 1994; Glidewell *et al.*, 1997). For example, benzoylferrocenyldiphenylmethanol forms a

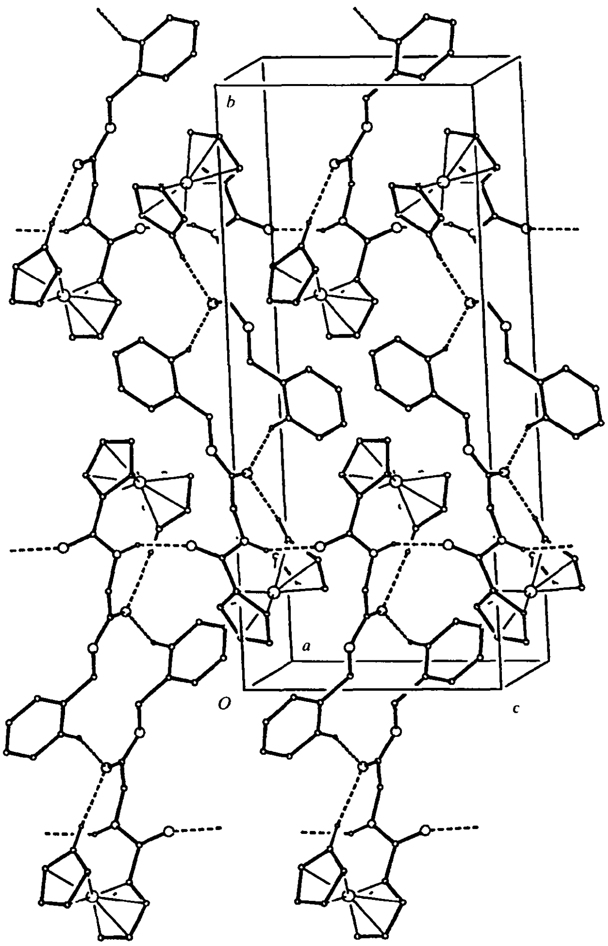


Fig. 2. A view of the interactions in the crystal structure.

dimer with graph set $R_4^4(16)$ through C—H···O hydrogen bonds (Glidewell *et al.*, 1997). We have recently described cyclic (pyrrole)N—H···π(pyrrole) hydrogen bonding involving four pyrrole groups in bis(2-pyrrolyl)methylferrocene, an organometallic porphyrin precursor (Gallagher & Moriarty, 1999).

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for molecules containing the *N*-ferrocenoyl moiety indicates that many of these structures contain a macrocyclic component (Beer, 1998). Several heterobimetallic macrocyclic receptors (Kingston *et al.*, 1999) exhibit electrochemical shifts of a similar magnitude to that observed in (I) with $H_2PO_4^-$. However mono- and disubstituted ferrocene complexes with flexible acyclic podand ligands are attracting greater interest as anion-sensor systems (Beer *et al.*, 1999).

Experimental

The title compound was synthesized according to the literature method of Gallagher *et al.* (1999). Dark-yellow crystals were recrystallized from ethyl acetate/petroleum ether (b.p. 313–333 K) in 80% yield.

Crystal data

$[Fe(C_5H_5)(C_{15}H_{14}NO_3)]$
$M_r = 377.21$
Monoclinic
$P2_1/c$
$a = 7.9167\ (7)$ Å
$b = 22.1936\ (16)$ Å
$c = 9.9382\ (11)$ Å
$\beta = 96.612\ (11)^\circ$
$V = 1734.5\ (3)$ Å^3
$Z = 4$
$D_x = 1.444$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 18.92$–24.20°
$\mu = 0.888$ mm^{-1}
$T = 294\ (1)$ K
Block
0.43 × 0.42 × 0.26 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (3 ψ scans; North *et al.*, 1968)
$T_{min} = 0.732$, $T_{max} = 0.818$
3405 measured reflections
3222 independent reflections

2238 reflections with $I > 2\sigma(I)$
$R_{int} = 0.010$
$\theta_{max} = 25.4^\circ$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 240 min
intensity variation: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.085$
$S = 1.020$
3222 reflections
227 parameters
H-atom parameters constrained

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.175$ e Å^{-3}
$\Delta\rho_{min} = -0.207$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0013 (5)

$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.3662P]$ where $P = (F_o^2 + 2F_c^2)/3$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.231 (3)	N1—C1	1.333 (3)
O2—C3	1.330 (3)	N1—C2	1.432 (3)
O2—C4	1.436 (3)	C1—C11	1.476 (4)
O3—C3	1.193 (3)	C2—C3	1.501 (4)
Fe1—C11—C1	124.74 (17)	O2—C3—O3	123.5 (3)
C1—C11—C12	128.5 (3)	O3—C3—C2	126.4 (3)
C1—C11—C15	124.2 (3)	C4—C31—C32	118.8 (3)
O1—C1—N1	120.8 (3)	C4—C31—C36	122.9 (3)
C2—N1—C1—O1	0.8 (4)	N1—C1—C11—Fe1	74.9 (3)
C4—O2—C3—O3	3.9 (4)	O2—C4—C31—C36	5.0 (4)
N1—C2—C3—O3	17.6 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86	2.01	2.811 (3)	154
C32—H32···O3^{ii}	0.93	2.54	3.406 (4)	156
C21—H21···O3	0.93	2.63	3.540 (3)	165

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, -y, 1 - z$.

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ from the systematic absences. H atoms were allowed for as riding atoms, with N—H 0.86 Å and C—H 0.93 to 0.98 Å.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

JFG thanks Dublin City University and Forbairt for funding a research visit to the University of Guelph (July–August, 1998) and especially Professor George Ferguson for use of his diffractometer and computer system. PTMK and MJS thank Forbairt and the Irish American Partnership for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1028). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Beer, P. D. (1998). *Acc. Chem. Res.* **31**, 71–80.

Beer, P. D., Cadman, J., Lloris, J. M., Martínez-Máñez, R., Padilla, M. E., Pardo, T., Smith, D. K. & Soto, J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 127–133.

Chesney, A., Bryce, M. R., Batsanov, A. S., Howard, J. A. K. & Goldenberg, L. M. (1998). *J. Chem. Soc. Chem. Commun.* pp. 677–679.

Degani, Y. & Heller, A. (1986). *J. Phys. Chem.* **91**, 1289–1292.

Enraf–Nonius (1992). *CAD-4-PC*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1998). *PREP8. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL97 Programs.* University of Guelph, Canada.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993). *Acta Cryst.* C**49**, 967–971.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gallagher, J. F., Ferguson, G., Glidewell, C. & Zakaria, C. M. (1994). *Acta Cryst.* C**50**, 18–23.
Gallagher, J. F., Kenny, P. T. M. & Sheehy, M. J. (1999). *Inorg. Chem. Commun.* **2**, 200–202.
Gallagher, J. F. & Moriarty, E. M. (1999). *Acta Cryst.* C**55**, 1079–1082.
Glidewell, C., Ahmed, S. Z., Gallagher, J. F. & Ferguson, G. (1997). *Acta Cryst.* C**53**, 1775–1778.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kingston, J. E., Ashford, L., Beer, P. D. & Drew, M. G. B. (1999). *J. Chem. Soc. Dalton Trans.* pp. 251–257.
Kraatz, H.-B., Lusztyk, J. & Enright, G. D. (1997). *Inorg. Chem.* **36**, 2400–2405.
Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 21–38.
Moore, A. J., Skabara, P. J., Brycc, M. R., Batsanov, A. S., Howard, J. A. K. & Daley, S. T. A. K. (1993). *J. Chem. Soc. Chem. Commun.* pp. 417–419.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G., & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, Appendix A. Weinheim: VCH Publishers.
Sheldrick, G. M. (1997*a*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1998). *PLATON. Molecular Geometry Program.* Version of November 1998. University of Utrecht, The Netherlands.

Acta Cryst. (1999). C**55**, 1260–1262

Sodium (nitrilotriacetato)magnesate pentahydrate

Masami Kaneyoshi,† Andrew Bond and William Jones

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England. E-mail: adb29@cam.ac.uk

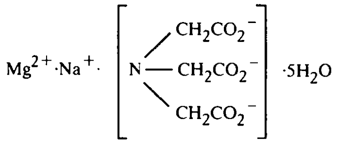
(*Received 8 February 1999; accepted 1 April 1999*)

Abstract

In the title compound, triaqua-μ-nitrilotriacetato-magnesiumsodium dihydrate, $[MgNa(C_6H_6NO_6)(H_2O)_3]\cdot 2H_2O$, a nitrilotriacetate ligand chelates one Mg atom *via* three Mg—O bonds and one Mg—N bond. Each ligand also binds to two Na atoms and another Mg atom such that an infinite layer of stoichiometry $MgNa(C_6H_6NO_6)(H_2O)_3$ is formed. Adjacent layers are bound *via* hydrogen bonds with two interlayer water molecules.

Comment

Nitrilotriacetic acid (NTA) is found as a multidentate ligand in many metal–chelate compounds (Skrzypczak-Jankun & Smith, 1994; Martell, 1975). A magnesium-chelated NTA complex has been proposed recently as a guest species within a layered double hydroxide (Kaneyoshi & Jones, 1999). The crystal structure of the title compound, (I), contains Mg atoms chelated by NTA molecules *via* three Mg—O bonds [2.042 (2)–2.096 (2) Å] and one Mg—N bond [Mg1—N1 2.232 (2) Å]. In addition, each Mg atom is bound to one O atom of a neighbouring NTA molecule [Mg1—O5^{i} 2.029 (2) Å; symmetry code: (i) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$] and one O atom of a water molecule [Mg1—O7 2.066 (2) Å], resulting in a distorted octahedral coordination geometry. The Na atoms are also octahedrally coordinated by four O atoms of different NTA molecules [2.385 (2)–2.453 (2) Å] and two O atoms of water molecules [Na1—O8 2.402 (2) and Na1—O9 2.331 (2) Å].



(I)

The three carboxylate groups of each NTA molecule adopt different bonding patterns. The first (C2, O1 and O2) binds to the chelated Mg atom and one Na atom *via* O2, and is involved in interlayer hydrogen bonding through O1 [O1^{ii}···O8 2.762 (3) Å and O1^{ii}···H8*A*—O8 167 (3)°; symmetry code: (ii) $2-x, \frac{1}{2}+y, \frac{3}{2}+z$]. The second (C4, O3 and O4) binds to one Mg atom and one Na atom *via* O3 and O4, respectively. In the third carboxylate group (C6, O5 and O6), O5 and O6 each bind to both an Mg atom and an Na atom, acting as bridges between adjacent $MgNa(C_6H_6NO_6)(H_2O)_3$ units.

The interactions between the metal atoms and the NTA ligands, together with hydrogen-bonding interactions, give rise to infinite $MgNa(C_6H_6NO_6)(H_2O)_3$ lay-

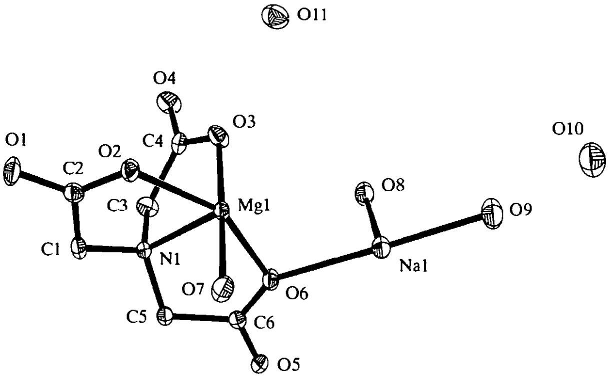


Fig. 1. The asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

---

† Present address: Magnetic Materials Research Center, Shin-Etsu Chemical Co. Ltd, 2-1-5 Kitago, Takefu-shi, 915-0802, Japan.

© 1999 International Union of Crystallography
Printed in Great Britain – all rights reserved