Inorganica Chimica Acta, *108* (1985) 159–164

Calcium and Magnesium Complexation with Nicotinic Acid Anion from Aqueous Media. [Ca(nicotinate)$_2$(H$_2$O)$_2$](H$_2$O)$_3$ and [Mg(H$_2$O)$_6$](nicotinate)$_2$(H$_2$O)$_4$; $C_{12}H_{18}CaN_2O_9$ and $C_{12}H_{28}MgN_2O_{14}$

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Received June 1, 1985

Abstract

$C_{12}H_{18}CaN_2O_9$: $M = 374.4$, monoclinic, $C2/c$, $a = 17.005(5)$, $b = 12.432(3)$, $c = 7.764(1)$ Å, $\beta = 92.60(2)°$, $V = 1639.6(6)$ Å^3, $Z = 4$, $D_x = 1.516$ g cm^{-3}, $F(000) = 784$, λ(Mo K$_\alpha$) = 0.71069 Å, μ(Mo K$_\alpha$) = 4.18 cm^{-1}, 295 K, final $R = 4.3\%$, $R_w = 6.6\%$ for 2132 observed reflections [$I > 3\sigma(I)$].

$C_{12}H_{28}MgN_2O_{14}$: $M = 448.7$, monoclinic, $P2_1/a$, $a = 13.797(5)$, $b = 23.228(10)$, $c = 6.904(3)$ Å, $\beta = 93.35(3)°$, $V = 2209(1)$ Å^3, $Z = 4$, $D_x = 1.349$ g cm^{-3}, $F(000) = 952$, λ(Mo K$_\alpha$) = 0.71069 Å, μ(Mo K$_\alpha$) = 1.39 cm^{-1}, 295 K, final $R = 6.8\%$, $R_w = 8.3\%$ for 1998 observed reflections [$I > 3\sigma(I)$].

In $C_{12}H_{18}CaN_2O_9$, calcium is bound to eight O atoms; six from carboxylate groups of four nicotinate anions and two from water molecules. In $C_{12}H_{28}MgN_2O_{14}$, Mg is octahedrally coordinated to six O atoms from six molecules of H_2O. The nicotinate anions present in the unit cell are hydrogen bonded to the water molecules and thus not bonded directly to Mg.

Introduction

Structural evaluation of Ca^{+2} and Mg^{+2} binding to small molecules has led to certain generalizations about their respective binding preferences: Calcium may coordinate to 5–9 atoms, showing irregular geometry, preferring oxygen donor ligands and showing bonded Ca–O distances of 2.20–2.80 Å. Magnesium prefers octahedral coordination to six ligands, nitrogen donor ligands being favored over oxygen species and Mg–ligand bond distances fall in a narrower range [1]. Thus the hydrated complexes of $CaCl_2$ and $MgCl_2$ with the cyclic polyether, 12-crown-4, show Ca^{+2} coordinated to eight O atoms, four from the ether and four from water molecules [2] in square antiprism geometry whereas Mg^{+2} displays octahedral geometry, bound to six O atoms from water molecules while the cyclic ether is hydrogen bonded to the water molecules [3].

In biological molecules, binding patterns may be different in subtle but significant ways because of the availability of multiple choices of complexation sites within the systems; because of steric constraints within these systems and because of the known flexibility of calcium binding to accommodate irregular geometries and a wide range of coordination numbers. The complexes formed by the addition of Ca(NCS)$_2$ or Mg(NCS)$_2$ to the synthetic ionophore, 1,5-bis(dicyclohexyl)-3-oxaglutaramide, demonstrate this difference, Ca^{+2} is coordinated to 9 oxygen atoms from three planar ionophore molecules, however Mg^{+2} is octahedrally coordinated to five oxygen atoms, the sixth site being filled by a nitrogen atom of NCS [4, 5].

We have undertaken an evaluation of the binding patterns of Ca^{+2} and Mg^{+2} to a series of low molecular weight species involved in alkali metal dependent biological processes.

Experimental

[Ca(nicotinate)$_2$(H$_2$O)$_2$](H$_2$O)$_3$ (I) was crystallized from an aqueous solution of Na(nicotinate) (0.5 m) added to aqueous $CaCl_2$ (0.25 m). The clear colorless prisms formed over a 36 h period at room temperature. [Mg(H$_2$O)$_6$](nicotinate)$_2$(H$_2$O)$_4$ (II) crystals were prepared by crystallizing a commercial sample of Mg nicotinate (Pfaltz and Bauer) from water. The crystals formed as clear needles. Both crystalline materials showed a tendency to become powder on standing in air and thus crystals of (I) and (II) were sealed in capillaries before mounting on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). Data (5559 (I); 6729 (II)) points were collected at room temperature using a

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TABLE I. Crystal Data for $[Ca(nicotinate)_2(H_2O)_2](H_2O)_3$ (I) and $[Mg(H_2O)_6](nicotinate)_2(H_2O)_4$ (II).

	(I)	(II)
Formula	$C_{12}H_{18}CaN_2O_9$ [a]	$C_{12}H_{28}MgN_2O_{14}$
M	374.4	448.7
a (Å)	17.005(5)	13.797(5)
b (Å)	12.432(3)	23.228(10)
c (Å)	7.764(1)	6.904(3)
β (°)	92.60(2)	93.35(3)
V (Å^3)	1639.6(6)	2209.1(14)
$F(000)$	784	952
μMo Kα (cm^{-1})	4.18	1.39
λMo Kα (Å)	0.71069	0.71069
D_c (g cm^{-1})	1.516	1.349
Z	4	4
Observed relfections	2132	1998
R/R_w (%)	4.3/6.6	6.8/8.3
Space group	$C2/c$	$P2_1/a$

[a] Asymmetry unit = 1/2 of stoichiometric unit.

variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. After removal of redundent and space group forbidden data, 2132(I); 1998(II), reflections were considered observed $[I > 3.0\sigma(I)]$. The structures were solved by direct methods using MULTAN 80 [6]. Refinement of scale factor, positional and anisotropic thermal parameters for all nonhydrogen atoms was carried out to convergence [7]. For (I) hydrogens associated with the nicotinate, the coordinated water molecule and one of the noncoordinated water molecules were located from a difference Fourier synthesis and their positional parameters and a fixed isotropic thermal parameter (U = 3.8) were included but not varied in the final cycles of refinement. The hydrogen atoms of O30, a noncoordinated water molecule, were not located. For (II), hydrogen atoms associated with three of the six water molecules coordinated to magnesium were located from a difference Fourier synthesis and their positional parameters were included in the final cycles of refinement but were held invariant. The hydrogen atoms of the nicotinate were similarly located and their positional and isotropic thermal parameters were refined in a final least-squares cycle (H24 proved unstable to refinement and its associated parameters were fixed). Other hydrogen atoms were not located. The final cycle of refinement [function minimized $\Sigma(|F_o| - |F_c|)^2$] led to a final agreement factor, R = 4.3% (I); 6.8% (II), $[R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100]$. Anomalous dispersion corrections were made for Ca(I) and Mg(II). Scattering factors were taken from Cromer and Mann [8]. Weight schemes were applied to down weight the high intensity reflections based on the ratio of a threshold value to F_o. The validity of this weighting scheme was confirmed by analysis of the ΔF values in equally populated groups of similar F_o for which the variance in average weighted delta F^2 differed by less than a factor of 3.5.

Discussion

A projection view of the $[Ca(nicotinate)_2(H_2O)_2]$-$(H_2O)_3$ (I) asymmetric unit is presented in Fig. 1, based on the positional parameters of Table II, (derived bond angles and distances, Table IV) shows the binding of calcium to be quite different from that of $[Mg(H_2O)_6](nicotinate)_2(H_2O)_4$ (II) (Fig. 2) (derived bond angles and distances for (II) given in Table V, based on the positional parameters of Table III). Figure 1 shows the calcium to exist on a two fold symmetry axis and to be eight coordinate with a distorted square antiprism geometry. Six of the oxygen atoms bound to calcium are from carboxylate groups of nicotinate anions, the other two coordinated oxygen atoms being from water molecules (Ca–OH$_2$, 2.402(2) Å). Each carboxylate group serves as a bidentate ligand to one calcium atom

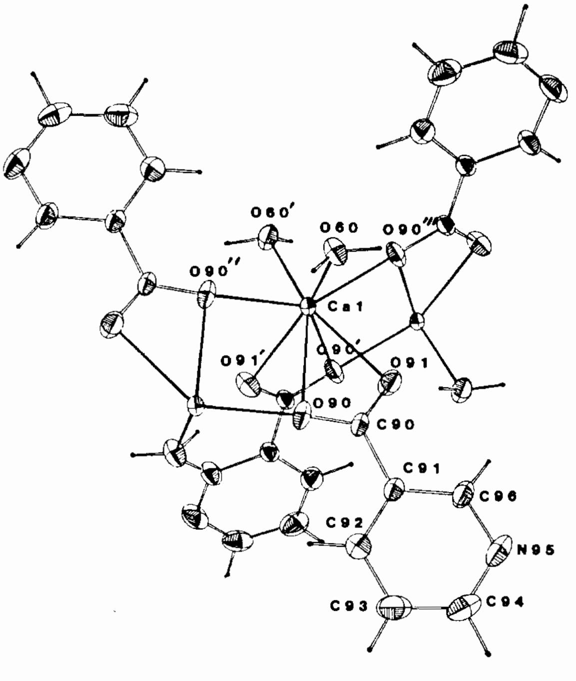

Fig. 1. Projection view of $[Ca(nicotinate)_2(H_2O)_2](H_2O)_3$ with noncoordinated water molecules omitted. Symmetry as in Table IV.

TABLE II. Positional Parameters for [Ca(nicotinate)$_2$(H$_2$O)$_2$](H$_2$O)$_3$ (**I**).

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U_{eq} (Å^2)^a
Ca1	0.0000(0)	−0.04718(4)	0.2500(0)	1.70(2)
O10	0.5000(0)	0.0265(3)	0.7500(0)	6.66(13)
O30	0.4245(2)	−0.1228(2)	−0.0402(4)	7.20(10)
O60	0.1000(1)	−0.1529(1)	0.1214(2)	2.82(4)
O90	0.0563(1)	0.1025(1)	0.0167(2)	2.88(4)
O91	0.1011(1)	0.0881(1)	0.2860(2)	3.00(4)
C90	0.0972(1)	0.1368(1)	0.1437(2)	1.99(5)
C91	0.1429(1)	0.2390(1)	0.1271(2)	2.13(5)
C92	0.1263(1)	0.3108(2)	−0.0062(3)	3.11(6)
C93	0.1708(2)	0.4039(2)	−0.0141(4)	4.04(8)
C94	0.2307(2)	0.4208(2)	0.1062(4)	3.91(8)
N95	0.2486(1)	0.3513(2)	0.2347(3)	3.83(7)
C96	0.2041(1)	0.2630(2)	0.2442(3)	2.97(6)
H10	0.4801	−0.0305	−0.1795	
H60	0.1463	−0.1500	0.1785	
H61	0.1002	−0.1340	0.0201	
H92	0.0840	0.2948	−0.0890	
H93	0.1593	0.4551	−0.1031	
H94	0.2588	0.4907	0.1027	
H96	0.2182	0.2224	0.3335	

$^a U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$; $\sigma(U_{eq}) = \frac{1}{3}\{|\sigma(U_{11})|^2 + |\sigma(U_{22})|^2 + |\sigma(U_{33})|^2\}^{1/2}$.

TABLE III. Positional Parameters for [Mg(H$_2$O)$_6$](nicotinate)$_2$(H$_2$O)$_4$ (**II**).

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U_{eq} (Å^2)^a
Mg1	0.2250(2)	0.4887(1)	0.1839(4)	3.4(1)
O10	0.0521(4)	0.3543(2)	0.3982(8)	4.0(2)
O11	−0.0532(4)	0.4266(2)	0.3509(8)	4.6(3)
O20	0.4160(4)	0.3586(2)	−0.0042(8)	4.3(3)
O21	0.2660(4)	0.3265(2)	−0.0707(8)	4.4(3)
O30	0.1808(4)	0.4043(2)	0.6707(8)	5.1(3)
O31	0.0332(4)	0.1342(3)	0.3392(9)	6.1(3)
O32	0.0666(4)	0.0160(3)	0.2830(9)	5.7(3)
O33	0.0418(5)	0.0954(3)	0.7245(10)	6.8(4)
O40	0.1509(5)	0.4990(3)	−0.0876(9)	6.2(3)
O50	0.2965(5)	0.4721(3)	0.4510(9)	6.3(3)
O60	0.0979(4)	0.5050(2)	0.3226(9)	4.9(3)
O70	0.3494(4)	0.4678(2)	0.0479(9)	5.0(3)
O80	0.1859(4)	0.4032(2)	0.1746(9)	4.9(3)
O90	0.2654(4)	0.5717(2)	0.1933(11)	6.1(4)
C10	−0.0324(5)	0.3737(3)	0.3766(10)	3.4(4)
C11	−0.1155(5)	0.3310(3)	0.3786(11)	3.4(4)
C12	−0.0969(5)	0.2722(3)	0.4090(11)	3.8(4)
C13	−0.1759(7)	0.2350(3)	0.4090(13)	5.0(5)
C14	−0.2676(7)	0.2564(4)	0.3819(15)	6.0(5)
N15	−0.2863(5)	0.3123(4)	0.3527(12)	5.9(4)
C16	−0.2108(5)	0.3485(3)	0.3544(12)	4.2(4)
C20	0.3554(5)	0.3197(3)	−0.0504(11)	3.5(4)
C21	0.3956(5)	0.2601(3)	−0.0773(10)	3.3(3)
C22	0.4941(6)	0.2488(4)	−0.0718(12)	4.1(4)
C23	0.5249(6)	0.1935(4)	−0.0952(13)	5.0(5)
C24	0.4596(6)	0.1503(3)	−0.1227(13)	5.0(5)
N25	0.3639(5)	0.1600(3)	−0.1298(10)	4.2(3)
C26	0.3335(5)	0.2145(3)	−0.1085(11)	3.7(4)

(Continued)

TABLE III. *(Continued)*

H12	−0.0212(74)	0.2577(44)	0.4229(153)
H13	−0.1597(49)	0.1909(29)	0.4119(98)
H14	−0.3336(65)	0.2263(40)	0.3867(132)
H16	−0.2219(69)	0.3906(42)	0.3132(140)
H22	0.5312(59)	0.2786(37)	−0.0456(113)
H23	0.5981(75)	0.1874(40)	−0.0768(132)
H24	0.4830	0.1110	−0.1369
H26	0.2664(50)	0.2256(30)	−0.1035(104)
H61	0.1041	0.5322	0.4570
H62	0.0476	0.4812	0.3110
H71	0.3792	0.4326	0.0300
H72	0.3644	0.4871	−0.0448
H81	0.1162	0.3735	0.2371
H82	0.2186	0.3759	0.0969

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}); \sigma(U_{eq}) = \frac{1}{3}\{|\sigma(U_{11})|^2 + \sigma|(U_{22})|^2 + |\sigma(U_{33})|^2\}^{1/2}$.

TABLE IV. Selected Bond Angles (°) and Distances (Å) for [Ca(nicotinate)$_2$(H$_2$O)$_2$](H$_2$O)$_3$ (**I**).[a]

Ca1−O60	2.402(2)	O60−Ca1−O60′	113.6(1)
Ca1−O90	2.797(2)	O60−Ca1−O90	79.9(1)
Ca1−O90‴	2.345(2)	O60−Ca1−O90‴	75.0(1)
Ca1−O91	2.412(2)	O60−Ca1−O91	85.1(1)
C90−O90	1.255(2)	O90−Ca1−O90‴	76.2(1)
C90−O91	1.260(2)	O90−Ca1−O90″	129.0(1)
C90−C91	1.498(3)	O90−Ca1−O91	49.3(1)
C91−C92	1.386(3)	O91−Ca1−O91′	91.6(1)
C92−C93	1.386(3)	O90−C90−O91	122.1(2)
C93−C94	1.367(4)	O90−C90−C91	119.5(1)
C94−N95	1.344(3)	O91−C90−C91	118.4(2)
N95−C96	1.337(3)	C90−C91−C92	121.4(2)
C96−C91	1.382(3)	C91−C92−C93	118.5(2)
		C92−C93−C94	119.3(2)
		C93−C94−N95	123.0(2)
		C94−N95−C96	117.3(2)
		N95−C96−C91	123.5(2)

[a] ′ = symmetry operation −*x*, *y*, 1/2 − *z*
″ = symmetry operation *x*, −*y*, 1/2 + *z*
‴ = symmetry opeartion −*x*, −*y*, −*z*

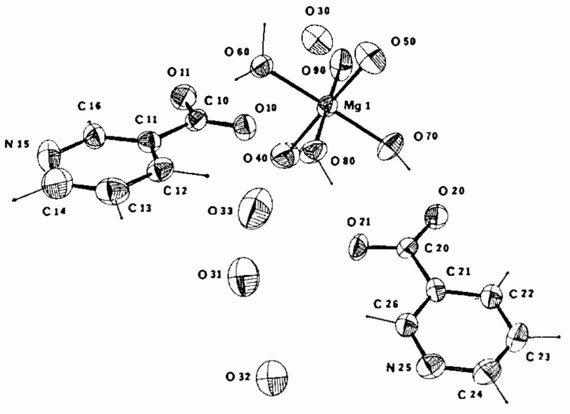

Fig. 2. Projection view of atoms of the asymmetric unit of [Mg(H$_2$O)$_6$](nicotinate)$_2$(H$_2$O)$_4$.

TABLE V. Selected Bond Angles (°) and Distances (Å) for [Mg(H$_2$O)$_6$](nicotinate)$_2$(H$_2$O)$_4$ (**II**).

Mg1−O40	2.096(7)	O40−Mg1−O50	175.9(4)
Mg1−O50	2.076(7)	O40−Mg1−O60	90.6(3)
Mg1−O60	2.081(6)	O40−Mg1−O70	89.7(3)
Mg1−O70	2.062(6)	O40−Mg1−O80	88.3(3)
Mg1−O80	2.058(6)	O40−Mg1−O90	92.3(3)
Mg1−O90	2.009(6)	O50−Mg1−O60	89.7(3)
C10−O10	1.25(1)	O50−Mg1−O70	89.7(3)
C10−O11	1.27(1)	O50−Mg1−O80	87.7(3)
C10−C11	1.51(1)	O50−Mg1−O90	91.9(3)
C11−C12	1.41(1)	O60−Mg1−O70	176.8(3)
C12−C13	1.39(1)	O60−Mg1−O80	87.9(2)
C13−C14	1.36(1)	O60−Mg1−O90	92.9(2)
C14−N15	1.34(1)	O70−Mg1−O80	88.9(2)
N15−C16	1.34(1)	O70−Mg1−O90	90.2(2)
C16−C11	1.38(1)	O80−Mg1−O90	179.1(6)
C20−O20	1.26(1)	O10−C10−O11	124.5(7)
C20−O21	1.24(1)	C10−C11−C12	120.3(6)
C20−C21	1.51(1)	C16−C11−C12	118.0(7)
C21−C22	1.38(1)	C11−C12−C13	117.9(7)
C22−C23	1.37(1)	C12−C13−C14	119.7(7)
C23−C24	1.35(1)	C13−C14−N15	123.0(9)
C24−N25	1.34(1)	C14−N15−C16	117.7(7)
N25−C26	1.34(1)	N15−C16−C11	123.6(7)
C26−C21	1.37(1)	O20−C20−O21	125.1(6)
		C20−C21−C22	122.6(7)
		C26−C21−C22	117.5(7)
		C21−C22−C23	119.1(8)
		C22−C23−C24	120.3(8)
		C23−C24−N25	122.0(8)
		C24−N25−C26	117.9(6)
		N25−C26−C21	123.3(7)

(Ca1−O90, 2.797(2) Å, Ca1−O91, 2.412(2) Å) while one of the carboxylate oxygens ligates as well to a calcium atom in a symmetry related position (Ca1−O90‴, 2.345(2) Å, ‴ = −*x*, −*y*, −*z*).

Carboxylates commonly show monodentate, bidentate or quadridentate ligation when complexed to calcium [9]. In the structure of calcium 1–glutamate chloride monohydrate [10], octahedral calcium is found coordinated to five unidentate carboxylate groups and to one water molecule (Ca–O, 2.335 Å). The carboxylate groups of calcium malonate dihydrate [11, 12], however, display two different modes of binding, one carboxylate serves as a bidentate ligand to a single calcium atom, whereas a second carboxylate group is bidentate to one calcium atom but each oxygen atom is also bridging to an adjacent calcium atom. Thus a single carboxylate group bridges a series of three calcium atoms, giving an overall quadridentate donicity (Ca–O, 2.471 Å). The title structure displays another type of carboxylate binding. Each carboxylate is tridentate in binding character. It is evident that calcium displays longer bonding distances with increasing coordination number. The Ca–O distances displayed in (I) are consistent with observations for eight coordinate calcium bound to oxygen [11, 12, 13].

The three water molecules per calcium atom which are not coordinated, appear to be in full occupancy positions. Their high temperature parameters indicate large thermal motion or disorder. O30 is hydrogen bonded to H10 of O10 (O30....H10, 1.86 Å).

The [Ca(nicotinate)$_2$(H$_2$O)$_2$](H$_2$O)$_3$ (I) cell thus contains strings of calcium atoms (Ca–Ca distance 4.055 Å) surrounded by oxygen atoms of tridentate carboxylate groups and water molecules (Fig. 3).

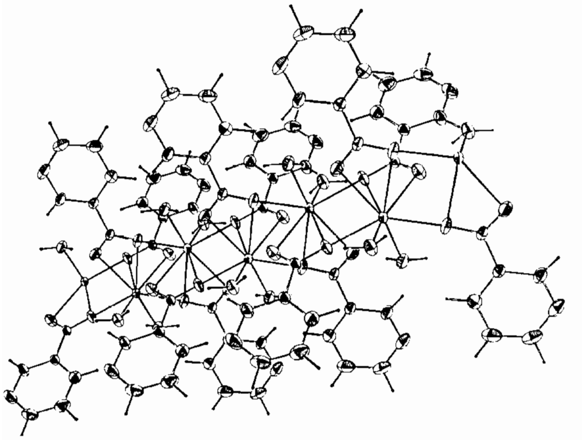

Fig. 3. Expanded projection view of [Ca(nicotinate)$_2$(H$_2$O)$_2$](H$_2$O)$_3$.

In (**II**) magnesium is octahedrally coordinated to six oxygen atoms from water molecules at an average Mg–O distance of 2.064(7) Å. The nicotinate anions are hydrogen bonded to the water molecules and not coordinated directly to magnesium. Four additional water molecules, not bonded to magnesium, crystallize in the unit cell. Magnesium is thought to prefer nitrogen donor ligands to those that coordinate via oxygen. For example, magnesium complexes to two picolinate anions (picolinate = orthocarboxypyridine) in [Mg(picolinate)$_2$(H$_2$O)$_2$] via monodentate carboxylate coordination and also coordination to the nitrogen of each picolinate. Two water molecules complete the octahedral coordination sphere [13, 14]. In a related structure, [Mg(isonicotinate)$_2$(H$_2$O)$_4$] [isonicotinate = paracarboxypyridine], magnesium binds to the oxygen of one carboxylate group and to the nitrogen of a second nicotinate as well as to four water molecules. Thus the nicotinate anions bridge pairs of magnesium ions [15]. In the title structure (**II**), nicotinic acid (*meta*-carboxypyridine) is not coordinated to the magnesium, perhaps because monodentate carboxylate binding would place the *meta* nitrogen atom in a position to interfere with other coordinated ligands. Coordination both to carboxylate oxygen and to nitrogen would force distortion of magnesium's preferred octahedral coordination geometry. Magnesium avoids bidentate binding to carboxylate groups perhaps because the 'bite' of a carboxylate group (O. . .O, 2.22 Å av.) is smaller than the average distance between two oxygen atoms coordinated to magnesium (2.9 Å) in octahedral geometry. Thus considerable distortion would be required to accommodate bidentate carboxylate binding. Alkaline earth metals are known to form complexes of more than one stoichiometry with simple anions and thus title structure (**II**) may be only one of several structural modifications of magnesium and aqueous nicotinic acid.

The title structures reinforce the basic ideas of calcium versus magnesium binding; calcium is extremely flexible in binding geometry and will accommodate bidentate and bridging carboxylate groups, and will further fit in water molecules to fill the coordination sphere whereas magnesium displays more selectivity in binding as well as rigid geometrical and quantitative preferences.

Supplementary Material

Anisotropic thermal parameters for (I) and (II) and listings of observed and calculated structure factors for (I) and (II) are available from the authors on request.

Acknowledgement

The Etta Louise Gerry Foundation for financial support.

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