

Structural Comparison of Calcium and Magnesium Binding to 2,4-Dinitrophenoxide †

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Single-crystal *X*-ray studies of calcium bis-(2,4-dinitrophenoxide) heptahydrate (1) [$a = 10.627(5)$, $b = 25.536(11)$, $c = 7.922(2)$ Å, $\beta = 92.69(3)^\circ$, $D_{\text{calc.}} = 1.646$ g cm⁻³, $Z = 4$, monoclinic, space group $P2_1/a$, $R = 0.067$, $R_w = 0.097$] and magnesium bis-(2,4-dinitrophenoxide) octahydrate (2) [$a = 13.473(4)$, $b = 12.969(4)$, $c = 6.670(2)$ Å, $\beta = 104.98(2)^\circ$, $D_{\text{calc.}} = 1.577$ g cm⁻³, $Z = 2$, monoclinic, space group $P2_1/c$, $R = 0.086$, $R_w = 0.123$] allow a comparison of binding patterns. In structure (1) calcium is bonded to eight oxygen atoms: two from one of the 2,4-dinitrophenoxide anions (the phenoxy oxygen and one nitro oxygen atom) and six from water molecules, one of which bridges two adjacent calcium atoms. The remaining phenoxide is hydrogen-bonded to the co-ordinated water molecules. In structure (2) magnesium is octahedrally co-ordinated to six water oxygen atoms. The 2,4-dinitrophenoxide anions are not directly bound to magnesium, but are hydrogen-bonded to the water molecules.

Calcium has been shown to be a necessary participant in the mechanism of histamine release from mast cells.¹ Magnesium is unable to replace calcium in this sequence.² Thus it is of interest to investigate the differences in calcium and magnesium binding to molecules the effect of which on histamine release has been established *in vitro*, to provide a basis for understanding of calcium function at a molecular level.

Studies of Ca²⁺ and Mg²⁺ binding to small molecules have led to generalizations about their respective binding preferences. Calcium may co-ordinate to between five and nine atoms; it exhibits irregular geometries and prefers oxygen donor ligands. Calcium–oxygen binding distances show wide variation (2.20–2.80 Å). Magnesium is considerably more limited in binding pattern, routinely displaying octahedral co-ordination to six ligands, with a preference for nitrogen over oxygen donor atoms. Magnesium–ligand distances fall in a more restricted range.³

These expectations are borne out in a comparison of Ca²⁺ and Mg²⁺ binding to nicotinic acid.⁴ Calcium bis(nicotinate) pentahydrate crystallizes with a calcium atom bound to two nicotinate molecules *via* carboxylate groups, to two oxygen atoms of water molecules, and further to single carboxylate oxygen atoms of two different nicotinate anions which bridge neighbouring calcium atoms. The calcium cations are thus eight-co-ordinate and bridged in polymeric array. In the solid magnesium bis(nicotinate) decahydrate, Mg²⁺ adopts undistorted octahedral co-ordination to six water molecules, which are hydrogen bonded to four additional water molecules and to two nicotinate anions. The hexa-aquomagnesium is thus an isolated species, whereas calcium atoms are packed in layers in the unit cell bridged by a network of oxygen donor ligands. This layering of calcium atoms in a solid array has also been observed in dicalcium tetra-acetate dihydrate and tricalcium tetrasalicylate diacetate tetrahydrate–diacetic acid,⁵ and appears to be a recurring feature of calcium structural chemistry.

Previous structural generalizations about calcium binding stem from single-crystal *X*-ray observations of calcium with carboxylate ligands,⁶ with amino acids,⁷ with crown ethers,⁸ and with synthetic carriers such as ionomycin⁹ and A23187.¹⁰ These observations may not be relevant for ligands of other

types and they may not present a complete view of calcium behaviour in histamine release, where calcium appears to enter the cell, participate in some way in degranulation, and exit from the cell in some manner,¹¹ perhaps along with the histamine. It is unclear whether the role of calcium involves binding to histamine itself at some mechanistic stage.

Calcium has been shown to complex to histamine,¹² binding to the nitrogen atoms *ortho* to the side chain of the tautomeric form of 4-(2-aminoethyl)imidazole protonated at the side chain, and to two chloride atoms and two water oxygen atoms as well. It seems possible that, under other circumstances, calcium might display bidentate binding to the neutral histamine molecule, the amino group of the side chain displacing a halogen atom.

A study of the release of histamine from mast cells induced by Kö 1124¹³ indicated that the presence of 2,4-dinitrophenol decreased chemically mediated release. Although Kö 1124 has been shown to stimulate histamine release in the absence of calcium and to be inhibited by calcium concentrations of 10 mmol l⁻¹, its structure suggests that it should have considerable binding affinity for alkali or alkaline earth cations. We have prepared solid complexes of Ca²⁺ and Mg²⁺ with 2,4-dinitrophenoxide from aqueous media and determined their single-crystal *X*-ray structures as the basis for further structural investigation of this phenomenon.

Experimental

Syntheses.—*Calcium bis-(2,4-dinitrophenoxide) heptahydrate.* 2,4-Dinitrophenol (0.5523 g, 0.0030 mol) and NaOH (0.3200 g, 0.0080 mol) were added to water (50 ml). After stirring for 5 min, a clear yellow solution had formed. A heavy yellow precipitate resulted upon the addition of aqueous 0.5M-CaCl₂ (30 ml; 0.015 mol Ca²⁺). Recrystallization of a small portion from water yielded long yellow needles suitable for *X*-ray analysis.

Magnesium bis-(2,4-dinitrophenoxide) octahydrate. 2,4-Dinitrophenol (0.1841 g, 0.0010 mol) and NaOH (0.1067 g, 0.0027 mol) were added to water (50 ml), forming a clear yellow solution after stirring for 5 min. Addition of aqueous 0.5M-MgCl₂ (10 ml) resulted in a cloudy yellow solution. Gravity filtration effected no change, but addition of 95% EtOH (20 ml) resulted in a clear yellow solution. Partial evaporation produced long yellow needles which were used for the *X*-ray study.

† Supplementary data (see section 5.6.3 of Instructions for Authors, in the January issue). Thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 1. Crystal data for calcium bis-(2,4-dinitrophenoxide) heptahydrate (1) and magnesium bis-(2,4-dinitrophenoxide) octahydrate (2)

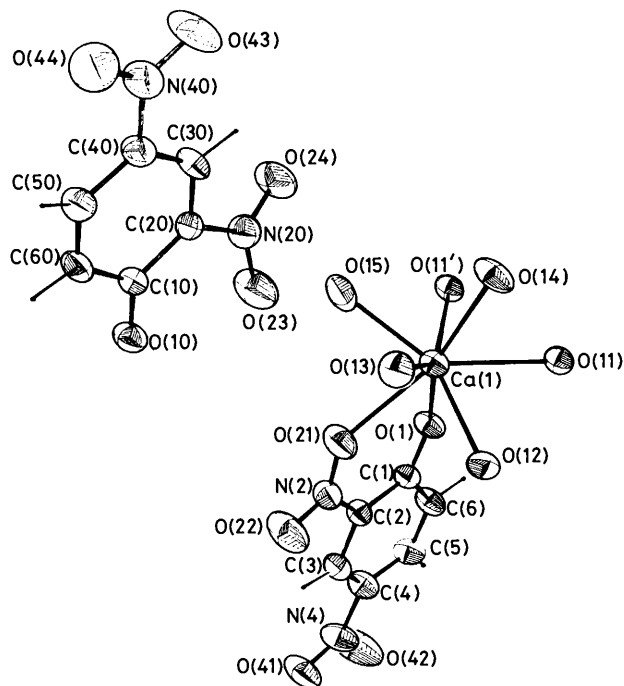
	(1)	(2)
Formula	C ₁₂ H ₂₀ CaN ₄ O ₁₇	C ₁₂ H ₂₂ MgN ₄ O ₁₈
Mol. wt	532.4	534.6
a/Å	10.627(5)	13.473(4)
b/Å	25.536(11)	12.969(4)
c/Å	7.922(2)	6.670(2)
α/°	90.00	90.00
β/°	92.69(3)	104.98(2)
γ/°	90.00	90.00
V/Å ³	2 147.4(15)	1 125.79(5)
F(000)	1 104	556
μ(Mo-K _α)/cm ⁻¹	3.718	1.642
λ(Mo-K _α)/Å	0.710 69	0.710 69
D _{calc./g cm⁻³}	1.646	1.577
Z	4	2
Obs. refl.	2 628	1 593
R/R _w	0.067/0.097	0.086/0.123
Space group	P2 ₁ /a	P2 ₁ /c

Table 2. Positional parameters for calcium bis-(2,4-dinitrophenoxide) heptahydrate (1)

Atom	x[σ(x)]	y[σ(y)]	z[σ(z)]	U _{eq./ Å²_a}
Ca(1)	0.332 7(1)	-0.001 2(1)	0.344 4(2)	3.3(1)
O(11)	0.583 9(4)	0.000 6(2)	0.353 5(5)	3.3(2)
O(12)	0.392 5(5)	0.030 5(2)	0.073 7(6)	4.3(3)
O(13)	0.207 8(5)	-0.056 7(2)	0.133 3(6)	4.5(3)
O(14)	0.422 0(5)	-0.085 7(2)	0.374 4(8)	5.2(3)
O(15)	0.164 5(5)	-0.033 7(2)	0.507 7(7)	5.9(3)
O(16)	0.391 5(5)	0.493 4(2)	0.151 6(7)	5.2(3)
O(17)	0.124 5(5)	0.416 6(2)	0.136 2(8)	5.9(3)
O(1)	0.365 6(4)	0.088 1(2)	0.411 0(6)	3.6(3)
C(1)	0.326 2(6)	0.133 2(3)	0.358 7(8)	3.1(4)
C(2)	0.212 9(6)	0.142 2(3)	0.256 7(8)	3.2(3)
C(3)	0.174 4(6)	0.192 1(3)	0.207 0(9)	3.4(3)
C(4)	0.246 8(7)	0.234 5(3)	0.256 3(9)	3.8(4)
C(5)	0.358 8(7)	0.227 7(3)	0.353 7(9)	4.2(4)
C(6)	0.397 1(6)	0.179 4(3)	0.400 0(9)	3.7(4)
N(2)	0.129 6(5)	0.100 3(2)	0.200 4(8)	3.7(3)
O(21)	0.149 3(5)	0.055 1(2)	0.249 8(7)	5.2(3)
O(22)	0.040 6(6)	0.110 0(2)	0.102 0(9)	7.0(4)
N(4)	0.203 7(7)	0.285 5(3)	0.206 7(9)	5.2(4)
O(41)	0.113 9(5)	0.291 2(2)	0.108 0(8)	6.1(3)
O(42)	0.260 1(8)	0.323 0(2)	0.266 4(10)	9.9(5)
O(10)	0.269 3(4)	0.078 6(2)	-0.186 5(6)	3.8(3)
C(10)	0.267 4(6)	0.128 9(3)	-0.199 0(8)	3.2(4)
C(20)	0.166 5(6)	0.158 5(3)	-0.282 2(8)	3.2(4)
C(30)	0.167 0(6)	0.211 6(3)	-0.293 4(9)	3.6(4)
C(40)	0.267 0(7)	0.239 0(3)	-0.221 2(9)	3.6(4)
C(50)	0.367 7(6)	0.213 2(3)	-0.138 9(9)	3.6(4)
C(60)	0.368 2(6)	0.160 6(3)	-0.131 3(9)	3.7(4)
N(20)	0.058 6(6)	0.132 1(3)	-0.364 6(8)	4.1(4)
O(23)	0.034 2(6)	0.087 4(2)	-0.324 5(9)	7.3(4)
O(24)	-0.006 0(5)	0.155 6(2)	-0.470 4(8)	6.6(4)
N(40)	0.263 3(6)	0.294 8(3)	-0.230 3(9)	5.1(4)
O(43)	0.176 5(6)	0.315 6(2)	-0.314 8(10)	8.4(5)
O(44)	0.347 2(6)	0.319 9(2)	-0.154 2(9)	6.8(4)
H(3)	0.0950	0.1900	0.1357	
H(5)	0.4086	0.2614	0.3944	
H(6)	0.4786	0.1733	0.4687	
H(30)	0.0945	0.2322	-0.3278	
H(50)	0.4293	0.2306	-0.0615	
H(60)	0.4421	0.1468	-0.0731	

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

Single-crystal X-Ray Studies.—Crystals of the complexes (1) and (2) were sealed in capillary tubes and mounted on a Syntex

**Figure 1.** Projection view of calcium bis-(2,4-dinitrophenoxide) heptahydrate (1) with O(16) and O(17) omitted

P3 automated diffractometer. Unit-cell dimensions (Table 1) were determined by least-squares refinement of the best angular position for fifteen independent reflections ($2\theta > 15^\circ$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.710 69 \text{ \AA}$). Data points [5 137 for (1); 4 029 for (2)] were collected at room temperature using a variable scan rate, a θ - 2θ scan mode, and a scan width of 1.2° below $K_{\alpha 1}$ and 1.2° above $K_{\alpha 2}$ 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 measured after every 97 reflections and as the intensities of these reflections showed less than 6% variation, correction for decomposition was deemed unnecessary. The data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space-group-forbidden data, 2 628 [for (1)] and 1 593 [for (2)] reflections were considered observed [$I > 3\sigma(I)$]. The structures were solved using a Patterson synthesis to locate the heavy atoms. Successive least-squares/difference Fourier cycles allowed the location of the remainder of the non-hydrogen atoms. Refinement of the scale factor with positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.¹⁴ Hydrogen positional parameters were determined from a difference Fourier synthesis. These hydrogen positional parameters and the associated fixed isotropic thermal parameters ($U = 0.03$) were included in the final cycles of refinement but were held invariant. The final cycles of refinement [function minimized ($|F_o| - |F_c|$)²] led to a final agreement factor $R/R_w = 0.067/0.097$ [for (1)] or $0.086/0.123$ [for (2)] [$R = 100(\sum|F_o| - |F_c|)/\sum|F_o|$]. Anomalous dispersion corrections were made for Ca in (1) and for Mg in (2).¹⁵ Scattering factors were taken from Cromer and Mann.¹⁶ In the final cycles of refinement a weight = $1/\sigma|F|$ was applied.

Discussion

Calcium bis-(2,4-dinitrophenoxide) heptahydrate (1) crystallizes with Ca²⁺ displaying interactions with eight oxygen atoms, six

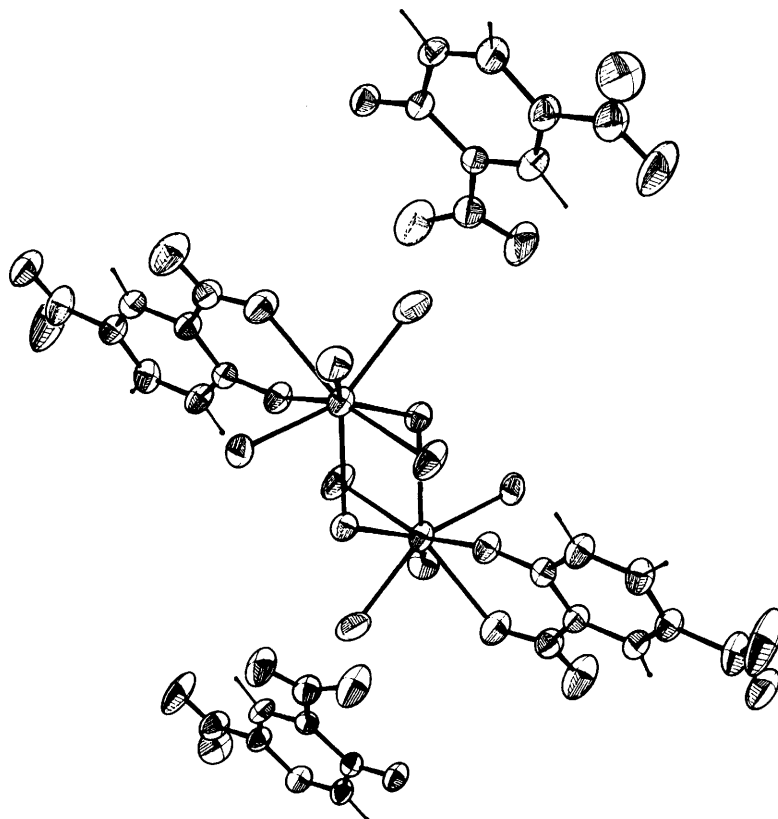


Figure 2. View of the dimeric unit of structure (1)

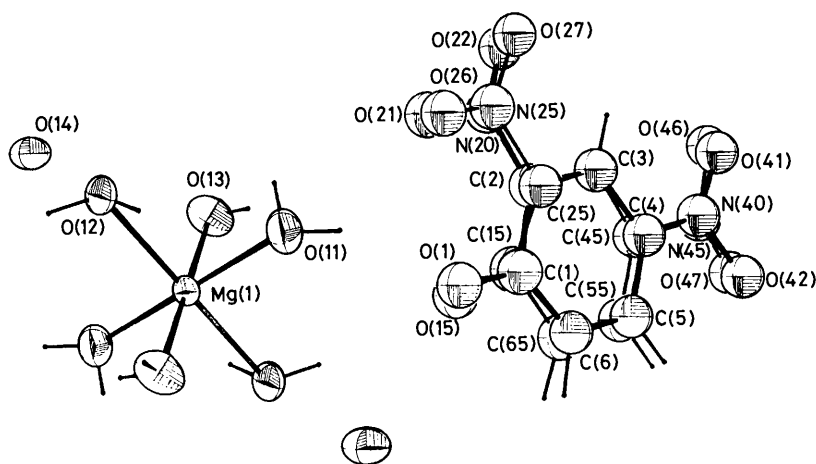


Figure 3. Projection view of magnesium bis-(2,4-dinitrophenoxide) octahydrate (2) showing the disordered 2,4-dinitrophenoxide group

from water molecules [Ca–O av. 2.478(5) Å] and two from a single 2,4-dinitrophenoxide anion which directs phenoxide oxygen [Ca–O 2.361(5) Å] and one oxygen of an *ortho*-nitro group [Ca–O 2.507(5) Å] towards Ca²⁺ (Figure 1). A centre of symmetry relates two calcium cations, which are bridged by symmetrically related O(11) atoms [Ca–Ca 4.231(2) Å]. The resulting +1 charge per calcium ion is balanced by a second 2,4-dinitrophenoxide group per asymmetric unit (Figure 2). Opportunities for hydrogen bonding are many (Table 6), with the non-bonded phenoxide oxygen atom displaying three distances to water oxygen atoms of less than 2.92 Å; one

intramolecular O–O distance of 2.805(7) Å between bound water molecules; one intermolecular distance of 2.762(7) Å between the bound oxide atom and a bound water oxygen atom of an adjacent calcium atom; three contact distances of less than 2.86 Å between nitro oxygen atoms and water oxygen atoms; and five close-contact distances between water molecules including those involving two additional water oxygen atoms, O(16) and O(17), crystallized in the unit cell.

Magnesium bis-(2,4-dinitrophenoxide) octahydrate (2) crystallizes with magnesium on a centre of symmetry and surrounded by six oxygen atoms of water molecules [Mg–O

Table 3. Positional parameters for magnesium bis-(2,4-dinitrophenoxide) octahydrate (2)

Atom	$x[\sigma(x)]$	$y[\sigma(y)]$	$z[\sigma(z)]$	$U_{eq}/\text{\AA}^2$ ^a
Mg(1)	1.000 0	0.000 0	1.000 0	2.4(1)
O(11)	1.049 8(4)	0.070 3(4)	1.283 7(8)	4.4(2)
O(12)	0.885 2(3)	0.111 9(4)	0.919 8(8)	4.0(2)
O(13)	1.092 3(4)	0.094 8(4)	0.877 9(8)	5.0(6)
O(14)	0.915 7(4)	0.175 4(4)	0.474 5(8)	4.5(3)
O(1)	1.200 0(7)	0.009 7(7)	1.629 0(14)	3.2(5)
C(1)	1.300 0(10)	0.024 1(9)	1.669 4(20)	3.0(6)
C(2)	1.339 4(9)	0.130 8(9)	1.634 6(16)	2.1(5)
C(3)	1.442 8(5)	0.152 2(5)	1.697 1(11)	3.3(3)
C(4)	1.511 3(8)	0.074 6(9)	1.762 0(18)	2.2(5)
C(5)	1.481 1(9)	-0.028 9(9)	1.765 3(19)	2.7(6)
C(6)	1.377 8(10)	-0.047 8(9)	1.719 0(18)	2.3(6)
N(20)	1.274 8(7)	0.216 0(8)	1.592 7(15)	1.8(5)
O(21)	1.178 4(7)	0.207 8(7)	1.545 6(15)	2.9(5)
O(22)	1.310 6(8)	0.296 9(7)	1.555 9(19)	4.6(6)
N(40)	1.613 9(8)	0.099 2(8)	1.799 4(21)	4.1(6)
O(41)	1.644 9(8)	0.182 1(10)	1.808 6(26)	7.3(9)
O(42)	1.680 7(8)	0.023 7(10)	1.859 4(22)	6.9(7)
O(15)	0.208 7(6)	0.501 9(6)	0.102 1(15)	3.0(4)
C(15)	0.300 3(8)	0.472 4(9)	0.142 5(16)	2.1(5)
C(25)	0.338 0(9)	0.371 0(10)	0.175 4(19)	2.8(6)
C(45)	0.514 9(10)	0.428 0(11)	0.223 9(19)	3.3(6)
C(55)	0.479 5(10)	0.533 9(10)	0.228 3(21)	3.2(7)
C(65)	0.378 0(10)	0.555 8(10)	0.183 2(22)	3.5(7)
N(25)	0.264 4(10)	0.281 9(9)	0.124 6(18)	3.9(7)
O(26)	0.177 3(7)	0.292 9(7)	0.105 3(15)	3.2(5)
O(27)	0.305 8(7)	0.190 8(7)	0.131 2(17)	5.8(5)
N(45)	0.629 3(8)	0.407 0(10)	0.283 6(19)	4.6(5)
O(46)	0.650 7(9)	0.309 3(9)	0.271 3(26)	7.1(9)
O(47)	0.683 7(7)	0.470 8(7)	0.312 3(15)	3.5(5)
H(11)	1.1036	0.0722	1.3816	
H(12)	1.0512	0.1287	1.2391	
H(21)	0.8985	0.0927	1.0513	
H(22)	0.8247	0.0900	0.8454	
H(31)	1.1446	0.0815	0.8084	
H(32)	1.1131	0.1032	0.9925	
H(3)	1.4679	0.2228	1.6949	
H(5)	1.5311	-0.0834	1.8047	
H(6)	1.3575	-0.1216	1.7291	
H(55)	0.5319	0.5889	0.2632	
H(65)	0.3535	0.6262	0.1679	

^a As Table 2.

2.066(5) Å] arranged in octahedral array (O–Mg–O 88.1–91.9 or 180°) (Figure 3). The asymmetric unit contains one 2,4-dinitrophenoxide anion which displays hydrogen-bonded interactions with two of the water molecules of the octahedral array and to O(14), the additional water molecule in the asymmetric unit (Table 7). This 2,4-dinitrophenoxide molecule is disordered by a 9.1° rotation relative to C(3), which is common to both rings of the disordered solution. Both 50% occupancy rings were clearly discernible and refinement proceeded in satisfactory fashion. The disorder of the 2,4-dinitrophenoxide molecule does not provide alternative hydrogen bonding opportunities. Other hydrogen-bonded interactions involve the bonded and non-bonded water molecules and oxygen atoms of the *ortho*- and *para*-nitro groups. Thus the patterns observed for Ca/Mg binding to nicotinic acid are also observed with 2,4-dinitrophenoxide. One might suspect that Mg²⁺ is unable to accommodate the O–Mg–O angle subtended by bonds to the oxide and an *ortho*-nitro oxygen atom of 2,4-dinitrophenoxide as a bidentate ligand [67.6(2)° angle subtended at Ca²⁺ in (1) by bonds to O(21) and O(1)], as it was unable to accommodate the bite angle of a carboxylate group of nicotinic acid [49.3(1)°

Table 4. Bond angles (°) and distances (Å) for calcium bis-(2,4-dinitrophenoxide) heptahydrate (1)

Ca(1)–O(11)	2.667(5)	N(4)–O(42)	1.214(10)
Ca(1)–O(11')	2.512(4)	C(4)–C(5)	1.399(10)
Ca(1)–O(12)	2.405(5)	C(5)–C(6)	1.345(10)
Ca(1)–O(13)	2.521(5)	C(6)–C(1)	1.430(9)
Ca(1)–O(14 ⁺)	2.365(5)	O(10)–C(10)	1.288(8)
Ca(1)–O(15 ⁺)	2.403(6)	C(10)–C(20)	1.445(9)
Ca(1)–O(1)	2.361(5)	C(20)–N(20)	1.458(9)
Ca(1)–O(21)	2.507(5)	N(20)–O(23)	1.217(9)
O(1)–C(1)	1.287(8)	N(20)–O(24)	1.216(8)
C(1)–C(2)	1.437(9)	C(20)–C(30)	1.361(10)
C(2)–N(2)	1.445(9)	C(30)–C(40)	1.373(10)
N(2)–O(21)	1.234(8)	C(40)–N(40)	1.429(9)
N(2)–O(22)	1.222(8)	N(40)–O(43)	1.233(10)
C(2)–C(3)	1.390(10)	N(40)–O(44)	1.232(9)
C(3)–C(4)	1.374(10)	C(40)–C(50)	1.392(10)
C(4)–N(4)	1.429(9)	C(50)–C(60)	1.345(10)
N(4)–O(41)	1.214(9)	C(60)–C(10)	1.427(9)
O(11)–Ca(1)–O(11')	70.5(1)	N(2)–C(2)–C(3)	115.0(6)
O(11)–Ca(1)–O(12)	73.3(1)	C(2)–N(2)–O(21)	120.1(5)
O(11)–Ca(1)–O(13)	121.5(2)	C(2)–N(2)–O(22)	119.5(6)
O(11)–Ca(1)–O(14 ⁺)	67.4(2)	O(21)–N(2)–O(22)	120.4(6)
O(11)–Ca(1)–O(15 ⁺)	139.5(2)	C(1)–C(2)–C(3)	122.3(6)
O(11)–Ca(1)–O(1)	80.8(2)	C(2)–C(3)–C(4)	119.2(6)
O(11)–Ca(1)–O(21)	139.5(2)	C(3)–C(4)–N(4)	118.1(6)
O(12)–Ca(1)–O(11')	138.7(2)	N(4)–C(4)–C(5)	121.2(7)
O(12)–Ca(1)–O(13)	75.5(2)	C(4)–N(4)–O(41)	121.3(6)
O(12)–Ca(1)–O(14 ⁺)	105.9(2)	C(4)–N(4)–O(42)	117.8(7)
O(12)–Ca(1)–O(15 ⁺)	146.1(2)	O(41)–N(4)–O(42)	121.0(7)
O(12)–Ca(1)–O(1)	80.3(2)	C(3)–C(4)–C(5)	120.7(6)
O(12)–Ca(1)–O(21)	77.0(2)	C(4)–C(5)–C(6)	120.2(7)
O(13)–Ca(1)–O(11')	141.8(2)	C(5)–C(6)–C(1)	123.1(6)
O(13)–Ca(1)–O(14 ⁺)	75.5(2)	O(10)–C(10)–C(20)	124.3(6)
O(13)–Ca(1)–O(15 ⁺)	77.4(2)	O(10)–C(10)–C(60)	121.9(6)
O(13)–Ca(1)–O(1)	139.3(2)	C(20)–C(10)–C(60)	113.8(6)
O(13)–Ca(1)–O(21)	75.3(2)	C(10)–C(20)–N(20)	121.0(6)
O(14 ⁺)–Ca(1)–O(11')	77.7(2)	N(20)–C(20)–C(30)	115.9(6)
O(14 ⁺)–Ca(1)–O(15 ⁺)	86.3(2)	C(20)–N(20)–O(23)	119.3(6)
O(14 ⁺)–Ca(1)–O(1)	143.5(2)	C(20)–N(20)–O(24)	119.2(6)
O(14 ⁺)–Ca(1)–O(21)	148.8(2)	O(23)–N(20)–O(24)	121.5(6)
O(15 ⁺)–Ca(1)–O(11')	74.2(2)	C(10)–C(20)–C(30)	123.0(6)
O(15 ⁺)–Ca(1)–O(1)	108.6(2)	C(20)–C(30)–C(40)	119.1(6)
O(15 ⁺)–Ca(1)–O(21)	76.8(2)	C(30)–C(40)–N(40)	117.9(6)
O(1)–Ca(1)–O(11')	75.0(2)	N(40)–C(40)–C(50)	120.9(6)
O(1)–Ca(1)–O(21)	67.6(2)	C(40)–N(40)–O(43)	118.3(6)
O(21)–Ca(1)–O(11')	121.1(2)	C(40)–N(40)–O(44)	118.4(6)
O(1)–C(1)–C(2)	125.1(6)	O(43)–N(40)–O(44)	123.2(7)
O(1)–C(1)–C(6)	120.3(6)	C(30)–C(40)–C(50)	121.2(6)
C(2)–C(1)–C(6)	114.5(6)	C(40)–C(50)–C(60)	119.6(6)
C(1)–C(2)–N(2)	122.7(6)	C(50)–C(60)–C(10)	123.3(6)

^a N', 1 – x, –y, 1 – z; N'', ½ – x, –½ + y, 1 – z.

observed⁴ for O–Ca–O] and thus surrounds itself with water atoms in both cases. This view is counterbalanced by the realization that magnesium is a smaller ion than calcium and displays shorter bonding distances to oxygen; thus bite angles subtended at magnesium will be larger than those observed at calcium for the same ligand.

In fact, Mg²⁺ co-ordination to 2,4-dinitrophenoxide has been previously observed in the crystal structures of bis-(*N*-methylimidazole)magnesium bis-(2,4-dinitrophenoxide) and dipyrindinemagnesium bis-(2,4-dinitrophenoxide),¹⁷ complexes in which magnesium displays binding to two 2,4-dinitrophenoxide groups (intraligand O–Mg–O angles 80.8–81.2°) and two sp²-hybridized nitrogen atoms of aromatic ring systems. Thus complexation patterns of magnesium may be altered in mixed ligand binding.

Structures (1) and (2) provide an opportunity to observe effects

Table 5. Bond angles (°) and distances (Å) for magnesium bis-(2,4-dinitrophenoxide) octahydrate (2)^a

Mg(1)–O(11)	2.050(5)	C(6)–C(1)	1.377(17)
Mg(1)–O(12)	2.087(4)	O(15)–C(15)	1.253(14)
Mg(1)–O(13)	2.060(6)	C(15)–C(25)	1.406(17)
O(1)–C(1)	1.317(16)	C(25)–N(25)	1.503(17)
C(1)–C(2)	1.520(17)	N(25)–O(26)	1.155(16)
C(2)–N(20)	1.389(15)	N(25)–O(27)	1.303(15)
N(20)–O(21)	1.260(13)	C(25)–C(3)	1.414(14)
N(20)–O(22)	1.207(15)	C(3)–C(45)	1.402(15)
C(2)–C(3)	1.376(13)	C(45)–N(45)	1.513(16)
C(3)–C(4)	1.358(13)	N(45)–O(46)	1.308(17)
C(4)–N(40)	1.378(16)	N(45)–O(47)	1.181(15)
N(40)–O(41)	1.149(16)	C(45)–C(55)	1.456(19)
N(40)–O(42)	1.320(16)	C(55)–C(65)	1.352(18)
C(4)–C(5)	1.404(17)	C(65)–C(15)	1.481(17)
C(5)–C(6)	1.368(18)		
O(11)–Mg(1)–O(12)	88.3(2)	C(4)–C(5)–C(6)	117(1)
O(11)–Mg(1)–O(13)	90.7(2)	C(5)–C(6)–C(1)	127(1)
O(11)–Mg(1)–O(12')	91.7(2)	O(15)–C(15)–C(25)	128(1)
O(11)–Mg(1)–O(13')	89.3(2)	O(15)–C(15)–C(65)	115(1)
O(12)–Mg(1)–O(13')	88.1(2)	C(25)–C(15)–C(65)	116(1)
O(1)–C(1)–C(2)	118(1)	C(15)–C(25)–N(25)	120(1)
O(1)–C(1)–C(6)	128(1)	N(25)–C(25)–C(3)	116(1)
C(2)–C(1)–C(6)	112(1)	C(25)–N(25)–O(26)	121(1)
C(1)–C(2)–N(20)	122(1)	C(25)–N(25)–O(27)	116(1)
N(20)–C(2)–C(3)	116(1)	O(26)–N(25)–O(27)	122(1)
C(2)–N(20)–O(21)	122(1)	C(15)–C(25)–C(3)	122(1)
C(2)–N(20)–O(22)	118(1)	C(25)–C(3)–C(45)	120(1)
O(21)–N(20)–O(22)	118(1)	C(3)–C(45)–N(45)	122(1)
C(1)–C(2)–C(3)	120(1)	N(45)–C(45)–C(55)	119(1)
C(2)–C(3)–C(4)	120(1)	C(45)–N(45)–O(46)	113(1)
C(3)–C(4)–N(40)	117(1)	C(45)–N(45)–O(47)	120(1)
N(40)–C(4)–C(5)	120(1)	O(46)–N(45)–O(47)	127(1)
C(4)–N(40)–O(41)	124(1)	C(3)–C(45)–C(55)	119(1)
C(4)–N(40)–O(42)	117(1)	C(45)–C(55)–C(65)	121(1)
O(41)–N(40)–O(42)	118(1)	C(55)–C(65)–C(15)	121(1)
C(3)–C(4)–C(5)	122(1)		

^a $N', 2 - x, -y, 2 - z$.**Table 6.** Possible hydrogen-bonded contact distances in calcium bis-(2,4-dinitrophenoxide) heptahydrate (1)^a

O(11)–O(10 ¹)	2.911(7)
O(11)–O(17 ²)	2.772(7)
O(11)–O(14)	2.805(7)
O(12)–O(10)	2.687(7)
O(12)–O(17 ²)	2.834(8)
O(13)–O(16 ³)	2.760(7)
O(13)–O(17 ⁴)	2.925(8)
O(14)–O(43 ⁷)	2.762(8)
O(14)–O(1 ⁸)	2.762(7)
O(15)–O(16)	2.876(8)
O(15)–O(21 ⁵)	2.856(8)
O(16)–O(10 ⁶)	2.790(7)
O(16)–O(23 ⁶)	2.856(8)

^a Symmetry operations: (1) $1 - x, -y, -z$; (2) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (3) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (4) $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (5) $\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$; (6) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (7) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$; (8) $1 - x, -y, 1 - z$.

of complexation and hydrogen bonding upon planarity of the dinitrophenoxide ring system. In two studies of the solid-state structure of 2,4-dinitrophenol,^{18,19} in which an intramolecular hydrogen atom links phenol oxygen and an oxygen atom of the *ortho*-nitro group, torsion angles of 2.6 (2.2)° and 4.8 (4.9)° were observed between the panes of the aromatic ring and the *ortho*-

Table 7. Possible hydrogen-bonded contact distances in magnesium bis-(2,4-dinitrophenoxide) octahydrate (2)^a

O(1)–O(11)	2.758(9)	O(1)–H(11)	1.99
O(1)–O(13 ¹)	2.706(12)	O(1)–H(31 ¹)	1.82
O(1)–O(14 ²)	2.848(10)		
O(15)–O(11 ³)	2.759(9)	O(15)–H(11 ³)	2.00
O(15)–O(13 ⁴)	2.984(12)	O(15)–H(31 ⁴)	2.10
O(15)–O(14 ⁵)	2.773(10)		
O(11)–O(21)	2.768(10)		
O(11)–O(12)	2.883(6)	O(11)–H(21)	2.23
O(11)–O(13)	2.924(8)	O(11)–H(32)	2.35
O(11)–O(12 ²)	2.968(8)		
O(11)–O(13 ²)	2.889(7)		
O(11)–O(14 ³)	2.815(8)		
O(11)–O(26 ⁶)	2.964(10)	H(11)–O(26 ⁶)	2.34
O(12)–O(13)	2.884(8)		
O(12)–O(42 ⁷)	2.913(12)	H(22)–O(42 ⁷)	2.15
O(12)–O(14 ⁸)	2.799(7)		
O(12)–O(47 ⁸)	2.833(10)	H(22)–O(47 ⁸)	2.02
O(13)–O(26 ⁹)	2.794(12)	H(31)–O(26 ⁹)	2.23
O(13)–O(21 ¹⁰)	2.911(10)		

^a Symmetry operations: (1) $x, y, 1 + z$; (2) $2 - x, -y, 2 - z$; (3) $-1 + x, \frac{1}{2} - y, -1.5 + z$; (4) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (5) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (6) $1 + x, \frac{1}{2} - y, 1.5 + z$; (7) $-1 + x, y, -1 + z$; (8) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (9) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (10) $x, \frac{1}{2} - y, -\frac{1}{2} + z$.**Table 8.** Equations of planes in structures (1) and (2)

(1)

Plane 1	O(1), C(1)–C(6), std. devn. 0.013; bound molecule	$PX + QY + RZ = S, P = -5.8185, Q = 2.4313, R = 6.7822, S = 0.8590$
Plane 2	N(20), O(23), O(24) (<i>ortho</i>)	$PX + QY + RZ = S, P = -6.6528, Q = 9.0411, R = 5.7307, S = -1.2849$
Plane 3	N(40), O(43), O(44) (<i>para</i>)	$PX + QY + RZ = S, P = -6.2423, Q = 0.8014, R = 6.6176, S = -2.9314$
Plane 4	O(10), C(10)–C(60), std. devn. 0.000 02; unbound molecule	$PX + QY + RZ = S, P = -5.3316, Q = 1.5428, R = 7.0150, S = -2.6228$
Plane 5	N(20), O(23), O(24) (<i>ortho</i>)	$PX + QY + RZ = S, P = -6.652, Q = 9.0411, R = 5.7307, S = -1.2849$
Plane 6	N(40), O(43), O(44) (<i>para</i>)	$PX + QY + RZ = S, P = -6.2423, Q = 0.8014, R = 6.6176, S = -2.9314$

Angles between planes:

bound 2,4-dinitrophenoxide	
Plane 2/Plane 1	<i>ortho</i> -nitro group 6.42
Plane 3/Plane 1	<i>para</i> -nitro group 8.36
unbound 2,4-dinitrophenoxide	
Plane 4/Plane 1	<i>ortho</i> -nitro group 20.77
Plane 5/Plane 1	<i>para</i> -nitro group 6.05

(2)

Plane 1	O(1), C(1)–C(6), std. devn. 0.061	$PX + QY + RZ = S, P = -3.1974, Q = 2.1154, R = 6.5795, S = 8492$
Plane 2	N(20), O(21), O(22) (<i>ortho</i>)	$PX + QY + RZ = S, P = -3.4399, Q = 4.3772, R = 6.2781, S = 6.5593$
Plane 3	N(40), O(41), O(42) (<i>para</i>)	$PX + QY + RZ = S, P = -4.7483, Q = 1.0483, R = 6.6150, S = 4.3441$
Plane 4	O(15), C(15)–C(65), std. devn. 0.060	$PX + QY + RZ = S, P = -2.7285, Q = -0.1329, R = 6.6586, S = 0.0928$

Table 8 (continued)

(2)

Plane 5	N(25), O(26), O(27) (<i>ortho</i>)	
	$PX + QY + RZ = S$, $P = -1.4862$, $Q = -0.01979$,	
	$R = 6.5934$, $S = 0.3728$	
Plane 6	N(45), O(46), O(47) (<i>para</i>)	
	$PX + QY + RZ = S$, $P = -1.9913$, $Q = -1.2675$,	
	$R = 6.5962$, $S = 0.1018$	

Angles between planes:

Plane 1/Plane 2	<i>ortho</i> -nitro group	10.49
Plane 3/Plane 1	<i>para</i> -nitro group	8.24
Plane 5/Plane 4	<i>ortho</i> -nitro group	5.36
Plane 6/Plane 4	<i>para</i> -nitro group	5.92

and *para*-nitro groups, respectively. The hydrogen atom of the phenol appears to be involved in a bifurcated hydrogen bond with an intra- and an inter-molecular component. Structures (1) and (2), with the hydrogen atoms of water molecules available for hydrogen bonding, present additional possibilities, as previously discussed. The torsion angles between planes of aromatic rings and nitro groups in (2) are 10.49 (5.36)° and 8.24 (5.92)° for *ortho*- and *para*-substituted groups, respectively, for each of the two overlapping rings of the disordered solution. These values may be the subject of less interpretation in view of the partial occupancy of these ring positions. In structure (1), the differences in torsion angles between planes of aromatic rings and nitro groups for bonded and non-bonded phenoxide rings are notable: 6.42° (*ortho*) and 8.36° (*para*) for bonded 2,4-dinitrophenoxide and 20.77° (*ortho*) and 6.05° (*para*) for the non-bonded molecule. The hydrogen-bonding network is thus of sufficient strength to cause rotation about C–N bonds and significant nonplanarity of the 2,4-dinitrophenoxide system.

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