Acta Cryst. (1983). C**39**, 1640–1643

Structure of Nonactin–Calcium Perchlorate, $C_{40}H_{64}O_{12}.Ca(ClO_4)_2$, and a Comparative Study of Metal–Nonactin Complexes

BY C. K. VISHWANATH, N. SHAMALA, K. R. K. EASWARAN AND M. VIJAYAN

Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560 012, *India*

(*Received* 7 *March* 1983; *accepted* 1 *August* 1983)

Abstract. $M_r = 975{\cdot}9$, orthorhombic, *Pnna*, $a = 20{\cdot}262\,(3)$, $b = 15{\cdot}717\,(2)$, $c = 15{\cdot}038\,(1)$ Å, $V = 4788{\cdot}97$ Å^3, $Z = 4$, $D_x = 1{\cdot}35$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 2{\cdot}79$ mm^{-1}, $F(000) = 2072$, $T = 293$ K, $R = 0{\cdot}08$, 3335 observed reflections. The molecular structure and the crystal packing are similar to those observed in the nonactin complexes of sodium thiocyanate and potassium thiocyanate. The eight metal—O distances are nearly the same in the potassium complex whereas the four distances involving carbonyl O atoms are shorter than the remaining four involving the tetrahydrofuran-ring O atoms in the Na and the Ca complexes. This observation can be explained in terms of the small ionic radii of Na^+ and Ca^{2+}, and leads to a plausible structural rationale for the stronger affinity of nonactin for K^+ than for the other two metal ions.

Introduction. Nonactin (Fig. 1) is a well known macrotetrolide ionophore, first isolated from actinomycetes (Corbaz, Ettlinger, Gäumann, Keller-Schierlein, Kradolfer, Neipp, Prelog & Zähner, 1955), with a specificity for K (Mueller & Rudin, 1967). The crystal structures of the free molecule (Dobler, 1972) and of its K (Dobler, Dunitz & Kilbourn, 1969) and Na (Dobler & Phizackerley, 1974) complexes have already been reported. Despite the difference in ionic radii of K^+ and Na^+, the two metal complexes were found to have the same molecular structure. Here we report the crystal structure of the complex of nonactin with the divalent Ca^{2+} ion. The ionic radii of Ca^{2+} and Na^+ are nearly the same.

Experimental. Nonactin and $Ca(ClO_4)_2$ supplied by the Sigma Chemical Co. and Alpha Laboratories, respectively. Transparent, plate-like crystals obtained by slow evaporation of a solution of equimolar quantities of nonactin and calcium perchlorate in acetone. Unit-cell dimensions determined initially from X-ray diffraction photographs and subsequently refined using 25 reflections in the θ range 20 to 48°. Nonactin is soluble in almost all commonly used organic solvents and hence the density of the crystals could not be measured using the standard flotation technique; D_x was comparable to values for crystals of the Na and K complexes of nonactin. CAD-4 four-circle diffractometer, crystal $0{\cdot}6 \times 0{\cdot}5 \times 0{\cdot}3$ mm, graphite-monochromated Cu $K\alpha$ radiation, $\theta_{\max} = 60°$ ($\sin\theta/\lambda = 0{\cdot}5617$ Å^{-1}), ω–2θ scan, *h, k* and *l* values from 0 to 22, 0 to 17 and 0 to 16 respectively; two standard reflections, variations less than 10%. 3335 unique reflections measured, 2648 with $I > 2\sigma(I)$ used for structure refinement. Data not corrected for absorption. Structure solved by direct methods using *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Spherically averaged group scattering factors for tetrahydrofuran rings used in the calculation of *E* values. The *E* map computed with the most probable phase set yielded the structure of the calcium–nonactin complex cation located on a twofold axis. The *E* map contained two more peaks, each located on a twofold axis. These peaks, which also occurred in a subsequent difference Fourier map, were assigned to Cl atoms. The positional and thermal parameters of these atoms were refined, using the modified version of a block-diagonal *SFLS* program (which uses *F* magnitudes) originally written by Dr R. Shiono, to an *R* value of 0·20. A difference Fourier map was then calculated in an attempt to locate the perchlorate O atoms. The residual density around the Cl atoms was rather diffuse. Disordered models for perchlorate O atoms could, however, be constructed through a series of operations involving structure factor

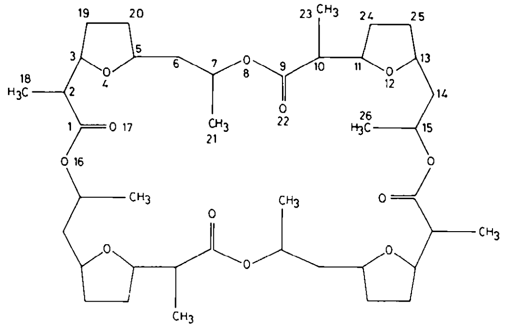

Fig. 1. Structural formula for nonactin along with the numbering scheme used.

0108-2701/83/121640-04$01.50

calculations and examination of various difference Fourier maps. According to this model, each perchlorate group has two disordered orientations. The successful refinement of the structure incorporating this model to a comparatively low R value indicated that the disordered model is essentially correct. The O atoms in the two disordered components were each assigned occupancy factors of 0·5. The fact that all the perchlorate O atoms had comparable temperature factors in the final refined structure indicated that the initial assignment of the occupancy factors was essentially correct. Positions of H atoms fixed from geometrical considerations. Non-hydrogen atoms refined anisotropically and H atoms isotropically in subsequent refinement cycles. Atomic parameters of perchlorate O atoms and of H atoms held constant in the last few cycles, to preserve the acceptability of bond lengths and angles involving them. Refinement converged at $R = 0\cdot078$ ($wR = 0\cdot090$, $S = 1\cdot336$, maximum LS shift/error $= 0\cdot59$). Weighting function used in the final cycles had the form $w = 1/(a + bF_o + cF_o^2)$ where $a = 1\cdot36$, $b = -0\cdot017$ and $c = 0\cdot0007$. Maximum and minimum heights in final difference Fourier synthesis 0·57 and $-0\cdot32\,\text{e}\,\text{Å}^{-3}$ respectively. All peaks with heights greater than $0\cdot3\,\text{e}\,\text{Å}^{-3}$, however, occurred close to the Ca^{2+} ion and the Cl atoms. Form factors for all atoms from *International Tables for X-ray Crystallography* (1974).

Discussion. The final positional parameters and the equivalent isotropic temperature factors (Hamilton, 1959) of the non-hydrogen atoms are given in Table 1.[*]

The crystal structures of the complexes of nonactin with potassium thiocyanate and sodium thiocyanate have already been reported (Dobler, Dunitz & Kilbourn, 1969; Dobler & Phizackerley, 1974). The space group of thc potassium thiocyanate complex (*Pnna*) is the same as that of the calcium perchlorate complex; the unit-cell dimensions of the sodium thiocyanate complex are very similar although the space group is different (*C*2/*c*). In all three complexes, the complexed cation is located on a twofold axis with only one half of the nonactin molecule in the asymmetric unit. The gross molecular structure and the crystal packing are nearly the same in the three complexes.

The main difference between the calcium perchlorate complex on the one hand and the sodium thiocyanate and potassium thiocyanate complexes on the other is that the latter contain only one anion (NCS^-) whereas the former contains two (ClO_4^-) per nonactin molecule. The changes arising from this difference can be understood by comparing the crystal structures of the calcium perchlorate (Fig. 2) and the potassium thiocyanate complexes. The disordered groups containing Cl(2) in the Ca complex correspond to the disordered thiocyanate group in the K complex. There are, however, no counterparts in the potassium thiocyanate complex for the perchlorate groups containing Cl(1) in the calcium perchlorate complex. As a consequence of the presence of these extra perchlorate anions in the Ca complex, the metal–nonactin complex as a whole is shifted by 0·36 Å (average shift) along the x axis with respect to its position in the K complex.

The bond lengths and the bond angles in the calcium perchlorate complex compare well with those found in free nonactin (Dobler, 1972) and its complexes with potassium thiocyanate (Dobler, Dunitz & Kilbourn, 1969) and sodium thiocyanate (Dobler & Phizackerley, 1974). A perspective view of the Ca complex is given in Fig. 3. The torsional angles which define the conformation of the cyclic backbone of the nonactin molecule in the Ca complex are listed in Table 2, along with those of free nonactin and the other two metal complexes. It

Table 1. *Final positional parameters* ($\times10^4$) *and equivalent isotropic temperature factors* ($\times10$) *for nonhydrogen atoms*

E.s.d.'s are given in parentheses. The numbering scheme shown in Fig. 1 is used in this and subsequent tables.

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
C(1)	6050 (6)	3493 (7)	3899 (7)	36 (5)
C(2)	6499 (6)	4046 (8)	3347 (8)	38 (6)
C(3)	6415 (5)	3805 (7)	2369 (8)	35 (5)
O(4)	5722 (3)	3865 (5)	2133 (5)	31 (3)
C(5)	5660 (6)	4229 (7)	1237 (7)	34 (5)
C(6)	5338 (7)	5100 (7)	1273 (8)	41 (6)
C(7)	4649 (7)	5150 (7)	1593 (7)	39 (6)
O(8)	4225 (4)	4582 (4)	1052 (5)	36 (3)
C(9)	4096 (5)	3811 (7)	1372 (7)	32 (5)
C(10)	3697 (6)	3271 (8)	729 (8)	38 (5)
C(11)	3743 (5)	2345 (7)	1021 (8)	35 (5)
O(12)	4437 (4)	2105 (4)	1037 (5)	35 (3)
C(13)	4515 (7)	1255 (7)	639 (8)	45 (6)
C(14)	4844 (8)	1311 (8)	−267 (8)	54 (7)
C(15)	5519 (8)	1697 (8)	−304 (8)	50 (7)
O(16)	5954 (5)	3794 (5)	4698 (5)	47 (4)
O(17)	5814 (4)	2822 (4)	3632 (5)	34 (3)
C(18)	7213 (7)	3893 (11)	3672 (11)	62 (8)
C(19)	6777 (6)	4371 (9)	1712 (9)	47 (6)
C(20)	6364 (6)	4234 (9)	872 (9)	47 (6)
C(21)	4352 (9)	6038 (8)	1485 (10)	58 (8)
O(22)	4301 (3)	3557 (4)	2086 (5)	30 (3)
C(23)	2982 (7)	3589 (10)	682 (12)	65 (8)
C(24)	3400 (7)	1706 (9)	407 (10)	53 (7)
C(25)	3810 (8)	911 (9)	588 (11)	60 (8)
C(26)	5849 (10)	1649 (11)	−1214 (9)	76 (10)
Ca	5045 (1)	2500	2500	23 (1)
Cl(1)	2500	0	2136 (6)	110 (5)
Cl(2)	3722 (3)	2500	7500	111 (6)
O1(Cl1)	2443	1000	2140	180
O2(Cl1)	2600	−266	1237	125
O3(Cl1)	3110	−167	2643	120
O4(Cl1)	1925	−249	2516	104
O1(Cl2)	3770	1577	7885	105
O2(Cl2)	3147	2916	7922	147
O3(Cl2)	4337	2780	7679	201
O4(Cl2)	3552	2311	6665	167

---

[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38792 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

can be readily seen that the conformation of the nonactin molecule is nearly the same in the three complexes. The conformation of free nonactin is very different (Dobler, 1972).

Four tetrahydrofuran-ring O atoms and four carbonyl O atoms coordinate to the metal ion in the three complexes. The coordination polyhedron can be described as a distorted cube. The eight *M*—O distances are all nearly the same in the K complex and the departures from ideal cubic symmetry result from distortions in O—*M*—O angles. The *M*—O distances are shorter in the Na and Ca complexes compared to those in the K complex; in addition, the *M*—O distances involving carbonyl O atoms are shorter compared to those involving tetrahydrofuran-ring O atoms in the Na and Ca complexes. The general shortening of the *M*—O distances in the Na and Ca complexes can be readily understood in terms of the smaller ionic radii of the Na$^+$ and Ca^{2+} ions compared to that of the K$^+$ ion. Further, *M*—O distances in the Ca complex are somewhat shorter than those in the Na complex, presumably because of the double charge on the Ca^{2+} ion since the ionic radii of the two ions are nearly the same.

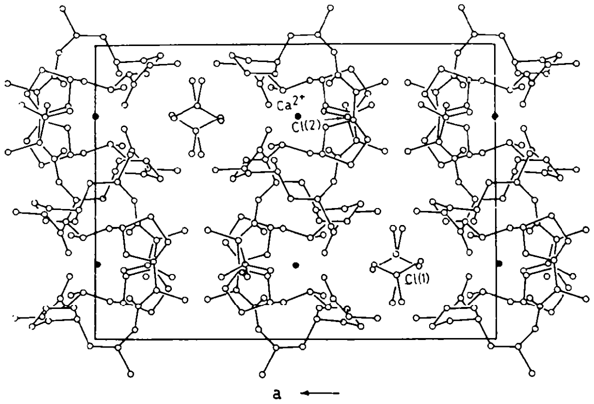

Fig. 2. Crystal structure, as viewed down the *b* axis, of the nonactin–calcium perchlorate complex.

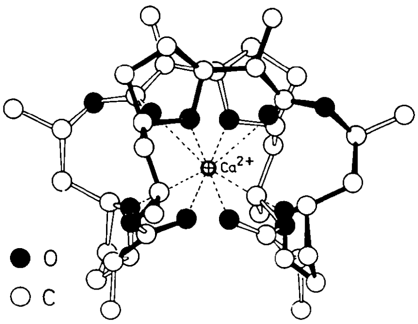

Fig. 3. Perspective view of the nonactin–calcium perchlorate complex. Broken lines show *M*—O interactions.

Table 2. *Torsion angles* (°) *which define the conformation of the cyclic backbone of the molecule in the structures of free nonactin and of its metal complexes*

The primed atoms are related to the unprimed ones by twofold symmetry. *M*—O distances in the complexes are also given.

	Nonactin (free)	Nonactin-calcium perchlorate	Nonactin-potassium thiocyanate	Nonactin-sodium thiocyanate
O(16)–C(1)–C(2)–C(3)	−66	−163 (1)	−146	−152
C(1)–C(2)–C(3)–O(4)	175	55 (1)	62	58
C(2)–C(3)–O(4)–C(5)	138	140 (1)	151	148
C(3)–O(4)–C(5)–C(6)	−154	−113 (1)	−123	−121
O(4)–C(5)–C(6)–C(7)	−72	−64 (1)	−64	−55
C(5)–C(6)–C(7)–O(8)	−67	−56 (1)	−62	−61
C(6)–C(7)–O(8)–C(9)	153	97 (1)	117	103
C(7)–O(8)–C(9)–C(10)	−177	−176 (1)	178	174
O(8)–C(9)–C(10)–C(11)	78	164 (1)	151	156
C(9)–C(10)–C(11)–O(12)	−179	−58 (1)	−66	−56
C(10)–C(11)–O(12)–C(13)	−143	−137 (1)	−144	−146
C(11)–O(12)–C(13)–C(14)	150	108 (1)	119	120
O(12)–C(13)–C(14)–C(15)	73	60 (1)	54	58
C(13)–C(14)–C(15)–O(16′)	64	57 (1)	66	58
C(14)–C(15)–O(16′)–C(1′)	−161	−97 (1)	−115	−107
C(15)–O(16′)–C(1′)–C(2′)	178	180 (1)	−177	−177
M—O distances (Å)				
M—O(17)	–	2·363 (8)	2·44	2·73
M—O(22)	–	2·328 (6)	2·39	2·81
M—O(4)	–	2·606 (7)	2·79	2·89
M—O(12)	–	2·597 (8)	2·74	2·81

A uniform reduction in all the *M*—O distances in the case of the Na and Ca complexes to the minimum permissible value would have resulted in unacceptable contact distances between adjacent O atoms in the coordination polyhedron. The ion–dipole interaction being larger for the carbonyl O atoms than that for the ethereal O atoms (tetrahydrofuran-ring O atoms), the former come closer to the metal ion than the latter in the Ca and Na complexes. While the carbonyl O atoms come as close to the metal ion as is permitted by the ionic radii of the Ca^{2+} and Na$^+$ ions, a closer approach of the tetrahydrofuran-ring O atoms is prevented by the repulsive O···O interactions – hence the asymmetry in the *M*—O distances in the Na and Ca complexes. Thus, while all eight *M*—O interactions are strong in the complex of nonactin with a large metal ion like K$^+$, four interactions are strong and the remaining four weak in the complexes of nonactin with the smaller Na$^+$ and Ca^{2+} ions. This appears to be the reason for the stronger affinity of nonactin for K than for Na or Ca.

The authors thank the University Grants Commission, India, and the Department of Science and Technology, India, for support.

References

Corbaz, R., Ettlinger, L., Gäumann, E., Keller-Schierlein, W., Kradolfer, F., Neipp, L., Prelog, V. & Zähner, H. (1955). *Helv. Chim. Acta*, **38**, 1445–1448.
Dobler, M. (1972). *Helv. Chim. Acta*, **55**, 1371–1384.

DOBLER, M., DUNITZ, J. D. & KILBOURN, B. T. (1969). *Helv. Chim. Acta*, **52**, 2573–2583.

DOBLER, M. & PHIZACKERLEY, R. P. (1974). *Helv. Chim. Acta*, **57**, 664–674.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MUELLER, P. & RUDIN, D. O. (1967). *Biochem. Biophys. Res. Commun.* **26**, 398–404.

Acta Cryst. (1983). C**39**, 1643–1646

The Structure of (Formato)bis(1,10-phenanthroline)copper(II) Perchlorate, $[Cu(C_{12}H_8N_2)_2(CHO_2)]ClO_4$

BY C. ESCOBAR AND O. WITTKE

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 5487, *Santiago, Chile*

(*Received* 7 *January* 1983; *accepted* 9 *August* 1983)

Abstract. $M_r = 568{\cdot}43$, monoclinic, space group $C2/c$, $a = 16{\cdot}7721\,(6)$, $b = 11{\cdot}5806\,(3)$, $c = 12{\cdot}5735\,(3)$ Å, $\beta = 111{\cdot}370\,(2)^\circ$, $V = 2274{\cdot}25\,(8)$ Å^3, $Z = 4$, $D_m = 1{\cdot}658$, $D_x = 1{\cdot}660$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}17$ mm^{-1}, $F(000) = 1156$, $T = 298$ K, $R = 0{\cdot}048$ for 2139 independent reflections with $I > 3\sigma(I)$. The metal ion is hexacoordinated to the four N atoms of the phenanthrolines, and to the oxygen atoms of the formate ion forming a distorted octahedral configuration with bond lengths Cu—N 1·985 (3) and 2·111 (3) Å and Cu—O 2·353 (6) Å. The bidentate formate ion has a twofold symmetry axis with a particularly short C—O distance of 1·189 (6) Å.

Introduction. This structural study is one of a series on compounds obtained at the Department of Chemistry as part of a programme of studies in oxidation of inorganic complexes. It is directed towards the change in copper coordination produced by the replacement of a coordinated chloride ion by a formate ion in an otherwise identical-composition complex (Boys, Escobar & Martínez-Carrera, 1981).

Experimental. Prismatic transparent deep turquoise crystals, D_m by flotation; crystal $0{\cdot}14 \times 0{\cdot}32 \times 0{\cdot}24$ mm, Philips PW 1100 diffractometer, graphite monochromatized Mo $K\alpha$, $\omega/2\theta$ scan; 4553 reflections with $2\theta < 66^\circ$ in the range −25 to 23, 0 to 17, 0 to 19 for h,k,l, respectively, 4219 unique reflections, two standards monitored every 80 reflections constant within ±2%, 34 strong reflections $2\theta < 38^\circ$ for cell determination; Lp correction, absorption ignored, anomalous-dispersion correction for Cu and Cl atoms; systematic absences hkl, $h + k$ odd and $h0l$, l odd; direct methods (*MULTAN*, Main, Lessinger, Woolfson, Germain & Declercq, 1976) and anisotropic full-matrix refinement in both Cc and $C2/c$ indicated centrosymmetric one; H-atom parameters not refined, but included in model with calculated positions [bond distance 0·89 Å, average of C—H distances in phenanthroline given by Simmons, Lundeen & Seff (1978)], isotropic U values ($U = U_{eq}$ of the corresponding C atom); $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$) minimized with $w = 1$ at the beginning and $w = w_1 w_2$ at the final stages of refinement ($w_1 = 1$ if $\sin\theta > 0{\cdot}25$, otherwise $w_1 = \sin\theta/0{\cdot}25$ and $w_2 = 1$ if $|F_o| < 45$, otherwise $w_2 = 45/|F_o|$); $R = 0{\cdot}048$, $R_w = 0{\cdot}057$, $S = 1{\cdot}44$ for the 2139 (m) reflections with $I > 3\sigma(I)$ used in the refinement of 169 (n) parameters; overdetermination ratio (m/n) is 12·7 and $R = 0{\cdot}071$ for the 4219 unique reflections; mean Δ/σ 0·01, largest 0·15; max. $\Delta\rho$ excursions in final difference Fourier +0·91 e Å^{-3} at 0·95 Å from Cu atom and three peaks less than +0·60 e Å^{-3} near formate O(3) atom, min. −0·34 e Å^{-3};* scattering factors for non-hydrogen neutral atoms and for Cu^{2+} from Cromer & Mann (1968); for H atoms from Stewart, Davidson & Simpson (1965); dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations carried out on an IBM 370/145 computer using XRAY76 (Stewart, 1976), mean planes and torsion angles with *NRC*22 (Ahmed, Hall, Pippy & Huber, 1973).

---

* Lists of structure factors, anisotropic thermal parameters, calculated positional parameters for hydrogen atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38806 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/121643-04$01.50