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Polynuclear coordination compounds of alkali metal ions with organic chromophores

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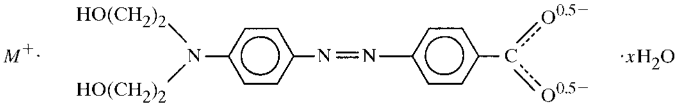
The crystal structures of sodium 4-({4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenyl}diazenyl)benzoate 3.5-hydrate, $Na^+\cdot C_{17}H_{18}N_3O_4^-\cdot 3.5H_2O$, (I), and potassium 4-({4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenyl}diazenyl)benzoate dihydrate, $K^+\cdot C_{17}H_{18}N_3O_4^-\cdot 2H_2O$, (II), are described. The results indicate an octahedral coordination around sodium in (I) and a trigonal prismatic coordination around potassium in (II). In both cases, coordination around the metal cation is achieved through O atoms of the water molecules and hydroxy groups of the chromophore. The organic conjugated part of the chromophore is approximately planar in (I), while a dihedral angle of 30.7 (2)° between the planes of the phenyl rings is observed in (II).

Comment

Organic π-electron conjugated systems containing electron donor–acceptor groups (chromophores) have received renewed interest recently. Owing to their large hyperpolarizabilities, they may be used to obtain materials able to display second-order non-linear optical (NLO) properties (Dalton *et al.*, 1999).

A large number of chemical variables may be considered in the synthesis of push–pull chromophores, such as the length of the conjugated system, its chemical nature (*i.e.* aromatic or polyenic), the presence of heteroatoms or heterocycles, and the strength of the donor–acceptor groups. All these variables affect to varying degrees the electronic properties of chromophores and, therefore, also their intrinsic NLO activity (*i.e.* β values) (Marder *et al.*, 1993; Kanis *et al.*, 1994; Morley, 1995).

Among chemical variables, the presence of metallic centres in the chromophores may also be considered (Whittall *et al.*, 1998). In this respect, a first possibility is to introduce covalently bonded metallic centres along the conjugated bridge, allowing conjugation through a possible $d\pi$–$p\pi$ contribution to the covalent bond between the metallic centre and the organic $p\pi$-conjugated system. Some interesting results have also been obtained with organometallic moieties covalently bonded to a conjugated organic system, acting generally as electron-donor (Houlton *et al.*, 1993; Coe *et al.*, 1999) or, more rarely, as acceptor groups (Bandy *et al.*, 1992; Lambert *et al.*, 1999). Another possibility not yet considered is to use metallic centres ionically bonded to a negatively charged organic conjugated system, thus working as electron-withdrawing groups through the ionic bond. The rather high polarizability of organic conjugated systems and the strength of the ionic bond could make this approach interesting, taking into account also the possibility of changing the metallic cation, thus modulating the strength of the ionic interaction and varying the coordination geometry. With these points in mind, we have undertaken a systematic study of a series of metal carboxylates containing the aminophenyldiazenyl chromophore group, whose good NLO activity is well known (Xie *et al.*, 1993). The structures of sodium 4-({4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenyl}diazenyl)benzoate 3.5-hydrate, (I), and potassium 4-({4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenyl}diazenyl)benzoate dihydrate, (II), are reported here.



(I) $M^+ = Na^+, x = 3.5$
(II) $M^+ = K^+, x = 2$

Both compounds crystallize in the hydrated form. The water content (thermogravimetry) indicates the presence of 3.5 water molecules for the unit formula in (I) and two in (II). The asymmetric unit of (II) contains two independent molecules. The coordination around each Na^+ cation is substantially octahedral and is achieved through O atoms of the water molecules and hydroxyl groups. A bridging water molecule is coordinated to the Na^+ cations of the two independent molecules, whose octahedra, therefore, share a vertex. The structure of the organic conjugated part is almost identical in the two independent molecules, showing in particular, a planar conformation. Coordination around the K^+ cations in (II) is trigonal prismatic, which is a rarer finding among six-coordinated atoms, and, as for (I), is achieved through O atoms of the water molecules and hydroxy groups. The conformation of the organic conjugated part is not planar in (II), a dihedral angle of 30.7 (2)° being observed between the planes of the phenyl rings, a result of a torsion around the N3—C11 bond. The geometry around the amino N atom is planar (sp^2 hybridization) in both structures, thus favouring electron donation toward the adjacent phenyl ring. Analysis of the bond distances in the phenyl rings shows some distorsions that in the case of the first phenyl ring (C5–C10), which is close to the amino donor group, point toward a quinoid pattern and are comparable with similar distortions found in the crystal structure of some NLO active compounds (Centore & Garzillo, 1997; Centore *et al.*, 1997).

The crystal packing is of the layered type (Figs. 3 and 4), with the inorganic part of the structure lying on the (001) planes and the organic part placed between them. Carboxylate anions (COO^-) are located just outside the coordination spheres of the Na^+ and K^+ cations, giving an ionic bond; they

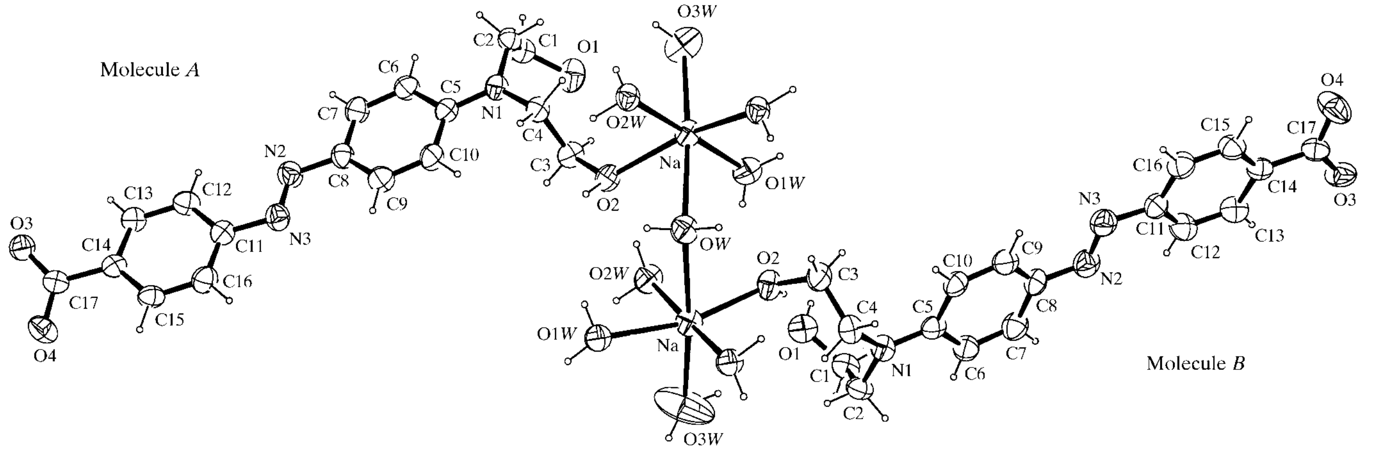


Figure 1

A molecular drawing of the crystallographically independent unit of (I) shown with 50% probability displacement ellipsoids.

are also involved, as acceptors, in hydrogen bonding with the water molecules coordinated to metal cations. The inorganic part is arranged in rows running along **b** (Fig. 5). In the case of (I), the rows are formed by NaO_6 octahedra sharing alternatively one vertex and one edge (sharing of edges being across inversion centres), and in (II) by screw related edge-sharing KO_6 trigonal prisms. The rows are held together along **a** by a complex hydrogen-bonding pattern between carboxylate and hydroxy groups of the molecules and water molecules coordinated to the metal ions.

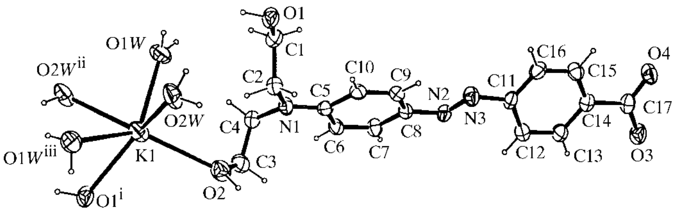


Figure 2

A molecular drawing of (II) shown with 50% probability displacement ellipsoids.

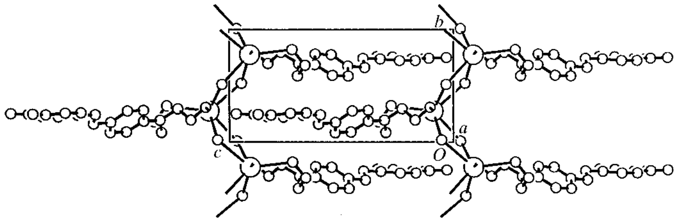


Figure 4

The crystal packing of (II) (H atoms have been omitted for clarity).

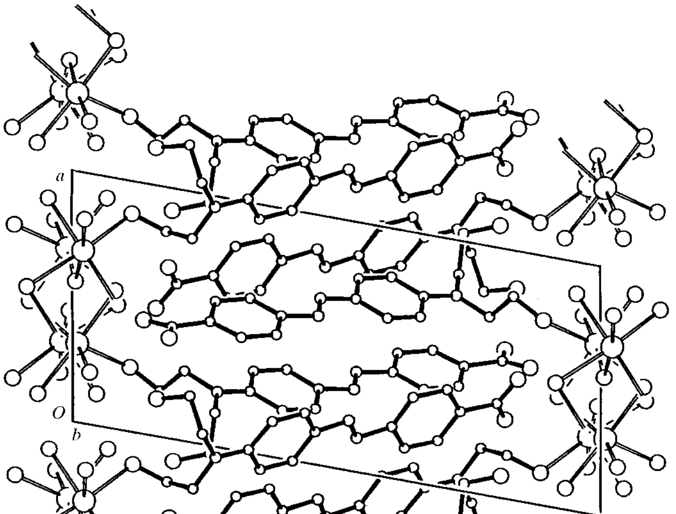


Figure 3

The crystal packing of (I) (H atoms have been omitted for clarity).

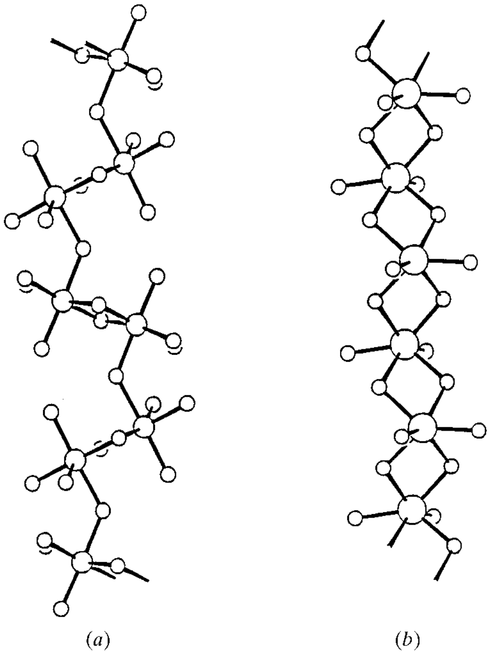

(a) (b)

Figure 5

Rows of coordination polyhedra for (a) (I) and (b) (II). Only metal and O atoms are shown.

The lateral packing of organic moieties is dominated, in both structures, by face-to-edge interactions between phenyl rings (*T* contacts), with molecular dipoles arranged in an antiparallel manner. For (I), this is simply a consequence of the centrosymmetric nature of the space group (actually the orientation of dipoles is antiparallel in the two molecules of the asymmetric unit), but for (II), it comes from the dipole of the independent molecule being perpendicular to the direction of the screw axes.

Experimental

The synthesis of 4-({4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenyl}diazenyl)benzoic acid was performed according to the well known diazotization-coupling procedure starting from *N*,*N*-bis(2-hydroxyethyl)aniline and 4-aminobenzoic acid. Carboxylate salts were prepared by reaction of the acid with the corresponding alkali metal hydroxides. As an example, for (II), 0.370 g (1.123 mmol) of the acid was heated in 20 ml of 95% ethanol. To the boiling suspension, a water solution of potassium hydroxide (0.5 g in 10 ml) was added, up to alkaline pH (13–14). The solution was boiled until the total volume reduced to about 10 ml. On cooling, orange crystals of the potassium salt were obtained. Yield: 0.383 g (0.949 mmol) (84.5% for the dihydrate salt). Analysis calculated for (I) ($C_{17}H_{18}N_3NaO_4 \cdot 3.5H_2O$): C 58.12, H 5.16, N 11.96, H_2O 15.2%; found: C 57.81, H 5.17, N 11.65, H_2O 15.7%. $\lambda_{\max}$/nm ($\varepsilon/10^4\ M^{-1}\ \mathrm{dm}^3$): 278 (1), 461 (3) in water; 271 (1), 418 (3) in ethanol. Analysis calculated for (II) ($C_{17}H_{18}KN_3O_4 \cdot 2H_2O$): C 55.57, H 4.94, N 11.44, H_2O 8.9%; found: C 55.42, H 4.86, N 11.57, H_2O 9.05%. $\lambda_{\max}$/nm ($\varepsilon/10^4\ M^{-1}\ \mathrm{dm}^3$): 278 (1), 458 (3) in water; 271 (1), 418 (3) in ethanol. Crystals of (I) and (II) suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation from methanol/water solutions.

Compound (I)

Crystal data

$Na^+ \cdot C_{17}H_{18}N_3O_4^- \cdot 3.5H_2O$
$M_r = 414.39$
Triclinic, $P\bar{1}$
$a = 9.023$ (3) Å
$b = 11.818$ (3) Å
$c = 19.400$ (5) Å
$\alpha = 99.31$ (4)°
$\beta = 99.41$ (4)°
$\gamma = 93.36$ (2)°
$V = 2006.3$ (10) Å^3

$Z = 4$
$D_x = 1.372$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 7.1$–9.9°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Plate, orange
0.6 × 0.4 × 0.1 mm

Data collection

Nonius MACH3 diffractometer
ω/θ scans
7259 measured reflections
7030 independent reflections
4387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 24.9°$

$h = -10 \rightarrow 10$
$k = -14 \rightarrow 13$
$l = 0 \rightarrow 23$
2 standard reflections
frequency: 120 min
intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.209$
$S = 1.00$
7030 reflections
514 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1333P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.008$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Na1—O2WA$^{\rm i}$	2.394 (3)	Na2—O3WB	2.354 (4)
Na1—O1WA	2.402 (3)	Na2—O1WB$^{\rm ii}$	2.402 (3)
Na1—O2WA	2.425 (3)	Na2—O2WB	2.431 (3)
Na1—O3WA	2.429 (3)	Na2—O2B	2.452 (3)
Na1—O2A	2.445 (3)	Na2—O1WB	2.486 (3)
Na1—OW	2.608 (3)	Na2—OW	2.498 (3)
O3A—C17A	1.259 (4)	O3B—C17B	1.260 (5)
O4A—C17A	1.252 (4)	O4B—C17B	1.252 (5)
N1A—C5A	1.373 (4)	N1B—C5B	1.369 (5)
N2A—N3A	1.245 (4)	N2B—N3B	1.249 (5)
N2A—C8A	1.402 (5)	N2B—C8B	1.407 (5)
N3A—C11A	1.424 (5)	N3B—C11B	1.434 (5)
C5A—C10A	1.402 (5)	C5B—C6B	1.405 (5)
C5A—C6A	1.410 (5)	C5B—C10B	1.408 (5)
C6A—C7A	1.369 (5)	C6B—C7B	1.363 (6)
C7A—C8A	1.382 (5)	C7B—C8B	1.386 (6)
C8A—C9A	1.396 (5)	C8B—C9B	1.397 (6)
C9A—C10A	1.364 (5)	C9B—C10B	1.362 (5)
O2WA—Na1—O2A	88.82 (10)	O3WB—Na2—O2B	97.04 (14)
O3WA—Na1—O2A	100.78 (11)	O2WB—Na2—O2B	77.37 (10)
O3WA—Na1—OW	175.50 (12)	O3WB—Na2—OW	174.15 (17)
C8A—N2A—N3A—C11A	177.2 (3)	C8B—N2B—N3B—C11B	177.5 (3)
C2A—N1A—C5A—C6A	−0.6 (5)	C2B—N1B—C5B—C6B	−6.2 (5)
N3A—N2A—C8A—C7A	178.1 (3)	N3B—N2B—C8B—C7B	179.2 (3)
N2A—N3A—C11A—C16A	−179.4 (3)	N2B—N3B—C11B—C16B	−171.9 (3)

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $1 - x, 1 - y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
OW—H1WW···O3B$^{\rm i}$	0.94	2.27	3.121 (4)	150
OW—H2WW···O3A$^{\rm ii}$	0.90	1.97	2.858 (4)	168
O1WA—HA11···O1A$^{\rm iii}$	0.90	1.89	2.787 (4)	176
O1WA—HA21···O2B	0.84	2.12	2.910 (4)	157
O2WA—HA12···O4B$^{\rm i}$	0.97	1.77	2.717 (4)	165
O2WA—HA22···O3A$^{\rm iv}$	0.82	1.98	2.785 (4)	167
O3WA—HA13···O3A$^{\rm iv}$	0.90	1.97	2.835 (4)	160
O3WA—HA23···O1WA$^{\rm iii}$	0.80	2.12	2.890 (4)	160
O2WB—HB12···O1B$^{\rm v}$	0.97	1.84	2.801 (4)	178
O2WB—HB22···O2A	0.94	1.88	2.809 (4)	172
O1WB—HB11···O4A$^{\rm vi}$	0.99	1.80	2.775 (4)	168
O1WB—HB21···O3B$^{\rm i}$	0.89	1.94	2.808 (4)	166
O1A—HO1A···O4B$^{\rm vii}$	0.82	1.94	2.682 (4)	150
O2A—HO2A···O3B$^{\rm i}$	0.96	1.73	2.689 (4)	171
O1B—HO1B···O4A$^{\rm viii}$	0.96	1.70	2.642 (4)	165
O2B—HO2B···O1B	0.89	1.85	2.720 (4)	164

Symmetry codes: (i) $1 + x, y, 1 + z$; (ii) $x, y, z - 1$; (iii) $-x, 2 - y, -z$; (iv) $1 - x, 2 - y, 1 - z$; (v) $-x, 1 - y, -z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $x, y, 1 + z$; (viii) $x - 1, y, z - 1$.

Compound (II)

Crystal data

$K^+ \cdot C_{17}H_{18}N_3O_4^- \cdot 2H_2O$
$M_r = 403.48$
Monoclinic, $P2_1$
$a = 8.238$ (8) Å
$b = 7.498$ (6) Å
$c = 15.016$ (8) Å
$\beta = 92.81$ (5)°
$V = 926.4$ (13) Å^3
$Z = 2$

$D_x = 1.446$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 7.3$–8.6°
$\mu = 0.33$ mm^{-1}
$T = 293$ (2) K
Plate, orange
0.3 × 0.3 × 0.1 mm

Data collection

Nonius MACH3 diffractometer
ω/θ scans
1927 measured reflections
1757 independent reflections
1427 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\rm max} = 24.9°$

$h = -9 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 17$
2 standard reflections
frequency: 120 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.104$
$S = 1.03$
1757 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.3483P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.03 (9)

Table 3
Selected geometric parameters (Å, °) for (II).

K1—O1$^{\rm i}$	2.687 (4)	N3—C11	1.428 (5)
K1—O2*W*	2.759 (4)	O3—C17	1.262 (5)
K1—O1*W*	2.796 (4)	O4—C17	1.256 (5)
K1—O2*W*$^{\rm ii}$	2.946 (5)	C5—C6	1.407 (6)
K1—O2	2.974 (4)	C5—C10	1.421 (6)
K1—O1*W*$^{\rm iii}$	3.060 (4)	C6—C7	1.372 (6)
N1—C5	1.361 (5)	C7—C8	1.384 (6)
N2—N3	1.254 (5)	C8—C9	1.395 (6)
N2—C8	1.416 (5)	C9—C10	1.350 (5)
O1$^{\rm i}$—K1—O2	101.42 (10)	O1*W*—K1—O2	93.88 (11)
O2*W*—K1—O2	91.27 (12)		
C8—N2—N3—C11	176.9 (4)	N3—N2—C8—C7	178.5 (4)
C2—N1—C5—C6	179.6 (4)	N2—N3—C11—C16	155.2 (5)

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

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—HO1···O3$^{\rm i}$	0.90	1.84	2.724 (4)	169
O1*W*—H2O1···O3$^{\rm i}$	0.90	2.02	2.831 (6)	148
O1*W*—H1O1···O4$^{\rm ii}$	0.95	1.88	2.824 (6)	177
O2*W*—H2O2···O3$^{\rm i}$	0.94	1.99	2.855 (6)	152
O2*W*—H1O2···O4$^{\rm iii}$	0.94	1.85	2.785 (5)	171
O2—HO2···N2$^{\rm iv}$	1.08	2.09	3.108 (6)	156

Symmetry codes: (i) $x-1, y, z-1$; (ii) $4-x, y-\frac{1}{2}, 1-z$; (iii) $4-x, \frac{1}{2}+y, 1-z$; (iv) $3-x, \frac{1}{2}+y, 1-z$.

All H atoms were stereochemically positioned, but those of the water molecules and the hydroxy groups were located in difference Fourier maps. For all H atoms, refinement was by the riding model, with $U_{\rm iso}$ equal to $U_{\rm eq}$ of the carrier atom.

For both compounds, data collection: *MACH3 Software* (Nonius, 1996); cell refinement: *CELLDIM* (Nonius, 1996); data reduction: *XCAD4-PC* (Harms, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1999) and *PLATON92* (Spek, 1992).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1508). Services for accessing these data are described at the back of the journal.

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