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The Crystal Structure of 2,2′-Bipyridinium(1+) μ-Hydrogen-bis[(2,2′-bipyridine)oxodiperoxovanadate]-(1−)-x-hydrogen peroxide-(6−x)-water, (Hbipy)[H{$VO(O_2)_2$bipy}$_2$] · xH_2O_2 · $(6-x)H_2O$, $x \approx 0.5$, at −100 °C

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The crystal structure of the title compound has been determined at −100 °C by single-crystal X-ray methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with a=9.454(3) Å, b=9.103(4) Å, c=12.076(3) Å, α=111.32(3)°, β=100.68(2)°, γ=104.05(3)° and Z=1. The structure was solved by direct methods and least-squares refinement gave a final $R(F)$-value of 0.040 for 2583 observed, independent reflexions.

Two centrosymmetrically related $VO(O_2)_2$bipy entities are held together by a very strong, asymmetric hydrogen bond, the O−H···O distance being 2.456(4) Å. The complex can, therefore, be considered to be dinuclear. Apart from water of crystallization, where some water is replaced by hydrogen peroxide, the crystals are thus composed of $Hbipy^+$ and [H{$VO(O_2)_2$bipy}$_2$]$^-$ ions. The vanadium atoms have a pentagonal bipyramidal arrangement of ligands; the peroxo oxygen atoms and one nitrogen atom from 2,2′-bipyridine form the pentagonal plane while the vanadyl oxygen atom and the other nitrogen atom occupy the apical positions. In each bipyramid the vanadium atom is displaced 0.31 Å from the pentagonal plane towards the vanadyl oxygen atom. The $Hbipy^+$ ions are disordered in the crystals; they have two main positions with occupation number 0.5 about 0.6 Å from each other.

Interatomic distances within the complex are: V=O 1.612(2) Å, V−O_{peroxo} 1.869(2)−1.995(2) Å, V−$N_{equatorial}$ 2.154(3) Å, V−N_{apical} 2.290(2) Å and $(O-O)_{peroxo}$ 1.461(3)−1.471(3) Å.

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In connection with our synthesis of $NH_4[VO(O_2)_2bipy] \cdot 4H_2O$,[1] using the method of Beiles *et al.*,[2] a further crystalline phase was obtained. By powder photography we found this to be identical with a compound reported by Vuletić *et al.*,[3] which they formulated $(H_2bipy)[V_2O_2(O_2)_4(bipy)_2] \cdot 6H_2O$. They were, however, aware of the possibility of other formulations, compatible with the spectral and analytical data, for example $(H_2bipy)H_2$[O{$VO(O_2)_2$bipy}$_2$] · $5H_2O$. Their argument for proposing it to be dimeric seems, however, questionable. To definitely settle this question it was thought worthwhile to determine the crystal structure of the compound.

EXPERIMENTAL

Preparation. The orange crystals were prepared at 5 °C according to the method of Vuletić and Djordjević.[3] 0.45 g vanadium pentoxide and 1.5 g 2,2′-bipyridine were used; pH in the resulting solution was 3.5.

X-Ray methods. Intensity data were recorded at −100 °C with a SYNTEX $P2_1$ automatic four-circle single-crystal X-ray diffractometer using graphite-monochromatized Mo$K\alpha$ radiation and a single crystal with the dimensions 0.12×0.12×0.22 mm. The temperature was held at −100 °C with a SYNTEX LT1 low tempera-

ture device. The ω–2θ scan method was used and the 2θ scan speed was allowed to vary between 2 and 15° min^{-1} depending on the intensity of the measured reflexion. Data were collected for $2\theta \leq 50°$. A profile analysis based on the Lehmann-Larsen method[4] was applied to the 96-step profile collected for each reflexion. A reflexion measured after each twenty-fourth reflexion showed no significant difference in intensity during the collection of the data.

A total of 3164 independent reflexions were measured. Of these, 2583 having $I_o \geq 3\sigma(I_o)$ were regarded as being observed and were used in the subsequent calculations. Corrections were made for Lorentz and polarization effects but an absorption correction was not considered necessary.

The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 13 reflexions.

CRYSTAL DATA

$C_{30}H_{38}N_6O_{16+x}V_2$, $x \approx 0.5$ F.W.=848.55

Space group $P\bar{1}$ (No. 2)
a=9.454(3) Å, b=9.103(4) Å, c=12.076(3) Å

α=111.32(3)°, β=100.68(2)°, γ=104.05(3)°,

Z=1, D_c=1.56 g cm^{-3}, μ(Mo$K\alpha$)=0.64 mm^{-1}

STRUCTURE DETERMINATION

The positions of the non-hydrogen atoms of the complex were obtained from a Fourier-map based on phases determined by the multi-solution programme MULTAN.[5] The remaining non-hydrogen atoms in the 2,2′-bipyridinium cation and the water molecules were located from an electron density difference map.

Least-squares refinement of an overall scale factor and positional and isotropic thermal parameters yielded an R-value of 0.103 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). Introduction of anisotropic thermal parameters reduced R to 0.062. The hydrogen atoms of the bipyridine ligand were clearly observed in a subsequent difference map, but those of the cation were not. Inclusion of positional and isotropic thermal parameters for the hydrogen atoms of the bipyridine ligand resulted in a further reduction of the R-value to 0.055.

The electron density difference map at this stage was not, however, featureless, having a maximum peak height of 1.1 e $Å^{-3}$, and the obtained bond distances within the cation deviated substantially from their "normal" values. Despite the rather low R-value the model had to be improved on some crucial points.

During the structure determination it was observed that the atoms in the cation had considerably higher thermal parameters (B=6.0–8.6 $Å^2$) than those in the bipyridine ligand (B=1.9–3.1 $Å^2$). Moreover, the difference synthesis excluding the cation contribution to the F_c's showed elontaged cation atom peaks and that with the cation contribution included in the F_c's revealed another ring system displaced about 0.6 Å from the original one. This indicates a disordered cation. According to Leipoldt *et al.*[6] the magnitude of unresolved disorder can be estimated, if one assumes equal occupation numbers of two gaussian distributions, with $\Delta U = (\frac{1}{2} \times \Delta X)^2$, where ΔX is the distance between the two unresolved positions. The average discrepancy between the U-values for the atoms in the cation and the corresponding ones in the ligand was found to be 0.062 $Å^2$, leading to an X-value of 0.5 Å; this is the order of magnitude also derived from the difference maps. Insertion of two different ring systems with occupation numbers 0.5 and refinement of positional and isotropic thermal parameters reduced the R-value from 0.103 to 0.081 and most of the B-values (B=2.0–6.6 $Å^2$) for the cation atoms.

All difference maps also exhibited two peaks, approximately on the line joining the atoms O1 and O1′ and 1 Å from them, with peak heights half that of a hydrogen atom peak, where O1 and O1′ are symmetry-related peroxo oxygen atoms in different complexes. This indicates the presence of a hydrogen atom between O1 and O1′, statistically occupying two positions with occupation number 0.5, thus explaining the very short contact distance 2.456 Å between these oxygen atoms. In view of the very strong hydrogen bond the complex can be considered to be dinuclear and we prefer to formulate it $[H\{VO(O_2)_2 bipy\}_2]^-$. In order to maintain electroneutrality the cation then has to be the unusual $Hbipy^+$. Owing to the disordered cation this could not be settled from the Fourier maps. It is, however, strongly supported by our recent structure determination of $(Hbipy)[VO(O_2)_2bipy]\cdot$

$(3+x)H_2O_2 \cdot (2-x)H_2O$,[7] which crystallizes, on prolonged standing, from the same solution as the title compound at the same temperature and pH. For this compound we clearly demonstrated crystallographically that only one of the two cation nitrogen atoms is protonated, and it is also obvious from considerations of electroneutrality.

It was observed that the water oxygen atom Ow2 had large thermal parameters and that there were two peaks 1.4 Å apart about Ow2 in the difference map based on anisotropic thermal parameters. In view of the observations made for $(Hbipy)[VO(O_2)_2bipy] \cdot (3+x)H_2O_2 \cdot (2-x)H_2O$,[7] this indicates that some hydrogen peroxide has replaced water of crystallization. This is further supported by the fact that the amount of electrons in the Ow2 peak is somewhat larger than in Ow1 and Ow3. Using varying occupation numbers for the hydrogen peroxide oxygen atoms Op1 and Op2 as well as for Ow2, least-squares refinement of positional and isotropic thermal parameters was undertaken. The *R*-value was reduced from 0.081 to a minimum value of 0.070 with occupation number 0.25 for Op1 and Op2 and 0.75 for Ow2; the atoms then had reasonable *B*-values.

Block-diagonal least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms and positional parameters for the hydrogen atoms of the bipyridine ligand reduced *R* to 0.040. The B_{iso}'s of the carbon atoms were used as the B_{iso}'s for the corresponding hydrogen atoms and were not refined. The weighting scheme used was that of Cruickshank:[8] $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$ with $a=15.0$, $c=0.015$ and $d=0.0$. The scattering factors for V, O, N, C and H were taken from the *International Tables for X-Ray Crystallography, Vol. 4,* (1974).

An electron density difference synthesis calculated after the final cycle of refinement showed no peak higher than 0.42 e $Å^{-3}$.

The Fourier syntheses and the least-squares refinements were performed according to space group $P\bar{1}$. As a consequence of this some atoms had to be considered statistically distributed in the model arrived at. Therefore, space group *P*1 was tested, but the positional parameters did not differ significantly from those obtained by refinement in space group $P\bar{1}$. Therefore, since there was no improvement in the disorder resolution, space group $P\bar{1}$ was finally adopted.

Calculations were carried out on an IBM 3033 computer using the crystallographic programmes described in Ref. 9.

Lists of the structure factors and thermal parameters are available from R.S. on request.

RESULTS AND DISCUSSION

The positional parameters, obtained in the last cycle of refinement, as well as U_{eq} are given in Table 1. The content of the unit cell is shown in Fig. 1 and the anion in Fig. 2. Bond distances and angles are given in Table 2 and hydrogen bond distances in Table 3.

The structure investigation has shown that the compound initially crystallizing from a solution of vanadium(V) oxide and 2,2′-bipyridine in 25 %

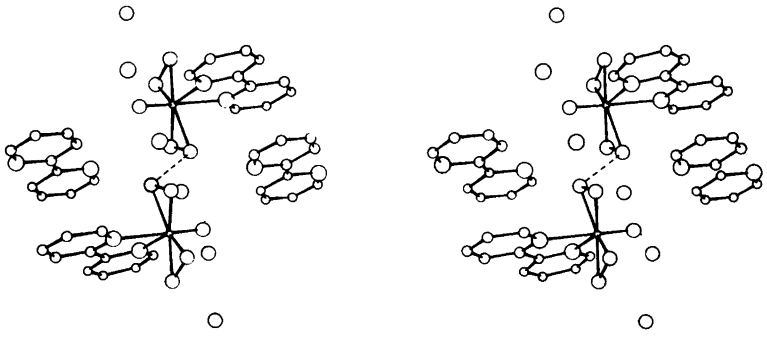

Fig. 1. Stereoscopic drawing of the cell content (the hydrogen atoms are omitted). The origin is in the center of $Hbipy^+$. The *a* axis runs out of, the *b* axis across and the *c* axis up the page. The average cation position is shown. Due to the disorder of the cation it has not been possible to settle whether it adopts the *trans* or the *cis* configuration.

Table 1. Atomic fractional coordinates for (Hbipy)[H{$VO(O_2)_2$bipy}$_2$] · $xH_2O_2 \cdot (6-x)H_2O$, $x \approx 0.5$. Space group $P\bar{1}$. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$. The occupation numbers are 0.5 for N3, N4 and C11–C20, 0.75 for Ow2, 0.25 for Op1 and Op2, and 1.0 for all other atoms.

Atom	x	y	z	U_{eq}/Å^2
V	0.1626(1)	0.4498(1)	0.8377(1)	0.0194(1)
O1	0.0832(2)	0.4168(2)	0.9720(2)	0.0290(6)
O2	0.2346(2)	0.5453(3)	1.0140(2)	0.0328(6)
O3	0.3585(2)	0.5532(3)	0.8364(2)	0.0350(6)
O4	0.2643(2)	0.4217(2)	0.7134(2)	0.0313(6)
O5	0.0666(2)	0.5649(2)	0.8129(2)	0.0294(6)
N1	−0.0177(3)	0.2256(3)	0.6992(2)	0.0238(6)
N2	0.2272(3)	0.2244(3)	0.8410(2)	0.0241(6)
C1	−0.1403(3)	0.2360(4)	0.6298(3)	0.0319(8)
C2	−0.2562(4)	0.0959(4)	0.5350(3)	0.0385(10)
C3	−0.2430(4)	0.0598(4)	0.5106(3)	0.0369(9)
C4	−0.1183(4)	−0.0725(4)	0.5813(3)	0.0334(9)
C5	−0.0064(3)	0.0726(3)	0.6759(3)	0.0242(7)
C6	0.1309(3)	0.0711(3)	0.7568(3)	0.0241(7)
C7	0.1609(4)	−0.0746(4)	0.7488(3)	0.0335(8)
C8	0.2930(4)	−0.0605(4)	0.8299(4)	0.0368(9)
C9	0.3915(4)	0.0970(4)	0.9168(4)	0.0374(9)
C10	0.3538(3)	0.2355(4)	0.9190(3)	0.0291(8)
N3[a]	−0.098(1)	0.104(1)	0.969(1)	0.045(2)
C11	−0.042(1)	−0.017(1)	0.975(1)	0.026(2)
C12[a]	−0.125(1)	−0.182(1)	0.886(1)	0.038(2)
C13	−0.270(1)	−0.218(1)	0.792(1)	0.084(4)
C14	−0.316(1)	−0.076(1)	0.796(1)	0.083(4)
C15	−0.240(1)	0.065(1)	0.871(1)	0.080(4)
N4[a]	−0.165(1)	0.097(1)	0.921(1)	0.036(2)
C16	−0.103(1)	−0.028(1)	0.930(1)	0.026(1)
C17[a]	−0.180(1)	−0.197(1)	0.849(1)	0.037(2)
C18	−0.308(1)	−0.222(1)	0.767(1)	0.063(3)
C19	−0.378(1)	−0.120(1)	0.751(1)	0.049(2)
C20	−0.299(1)	0.047(1)	0.832(7)	0.048(2)
Ow1	0.5644(3)	0.3661(3)	0.7450(2)	0.0462(7)
Ow2	0.1496(5)	0.5034(5)	0.5280(4)	0.0618(13)
Ow3	0.5734(4)	0.3894(4)	0.5207(3)	0.0743(11)
Op1	0.2027(16)	0.5869(10)	0.5755(9)	0.044(3)
Op2	0.1168(13)	0.4523(12)	0.4760(11)	0.054(3)
H(O1)	0.024(10)	0.484(15)	0.996(13)	
H(C1)	−0.140(5)	0.353(5)	0.656(4)	
H(C2)	−0.344(5)	0.102(6)	0.486(5)	
H(C3)	−0.318(5)	−0.151(5)	0.448(4)	
H(C4)	−0.106(5)	−0.174(5)	0.568(4)	
H(C7)	0.094(5)	−0.179(5)	0.688(4)	
H(C8)	0.308(5)	−0.162(5)	0.825(4)	
H(C9)	0.481(5)	0.115(5)	0.968(4)	
H(C10)	0.410(5)	0.341(5)	0.977(4)	

[a] Due to the disorder it has not been possible to determine whether the positions of N3 and C12 and/or N4 and C17, respectively, are interchanged or not.

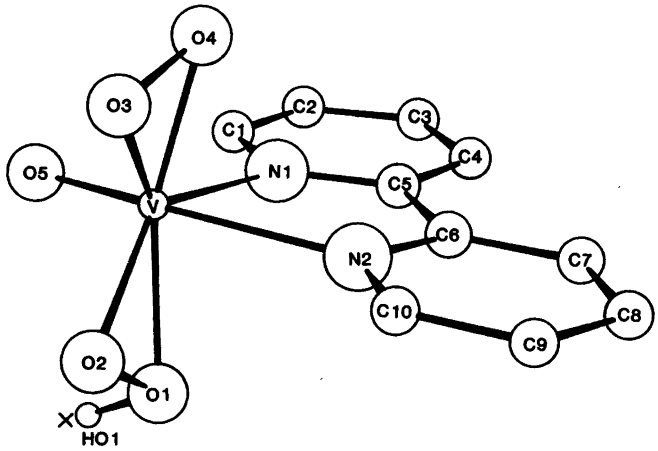

Fig. 2. The asymmetric part of the anion $[H\{VO(O_2)_2bipy\}_2]^-$. H(O1) has occupancy 0.5. × indicates the center of symmetry.

Table 2. Bond distances and angles in $(Hbipy)[H\{VO(O_2)_2bipy\}_2] \cdot xH_2O_2 \cdot (6-x)H_2O$, $x \approx 0.5$.

	Distance/Å		Angle/°
V–O1	1.995(2)	O1–V–O2	44.4(1)
V–O2	1.892(2)	O2–V–O3	89.2(1)
V–O3	1.869(2)	O3–V–O4	132.7(1)
V–O4	1.903(2)	O4–V–N1	85.5(1)
V–O5	1.612(2)	N1–V–O1	90.2(1)
V–N1	2.154(3)	O5–V–N2	162.5(1)
V–N2	2.290(3)	N1–V–N2	72.1(1)
O1–O2	1.471(3)	V–O1–O2	64.1(1)
O1–H(O1)	0.93(11)	V–O2–O1	71.5(1)
O3–O4	1.461(3)	V–O3–O4	68.4(1)
N1–C5	1.353(4)	V–O4–O3	66.0(1)
N1–C1	1.344(4)	C5–N1–C1	118.7(2)
C1–C2	1.390(5)	N1–C1–C2	122.7(3)
C2–C3	1.381(5)	C1–C2–C3	118.3(3)
C3–C4	1.377(5)	C2–C3–C4	119.6(3)
C4–C5	1.395(4)	C3–C4–C5	119.4(3)
C5–C6	1.479(4)	C4–C5–N1	121.2(3)
C6–C7	1.396(4)	C4–C5–C6	123.2(2)
C7–C8	1.383(5)	N1–C5–C6	115.6(2)
C8–C9	1.386(5)	C5–C6–N2	114.3(2)
C9–C10	1.384(4)	C5–C6–C7	123.9(3)
C10–N2	1.336(4)	N2–C6–C7	121.8(3)
N2–C6	1.349(4)	C6–C7–C8	118.8(3)
C1–H(C1)	0.99(4)	C7–C8–C9	119.4(3)
C2–H(C2)	0.96(5)	C8–C9–C10	118.4(3)
C3–H(C3)	0.90(4)	C9–C10–N2	123.0(3)
C4–H(C4)	0.92(4)	C10–N2–C6	118.6(2)
C7–H(C7)	0.93(4)	O1–H(O1)···O1′	176(11)
C8–H(C8)	0.95(4)		
C9–H(C9)	0.89(5)		
C10–H(C10)	0.90(4)		
Op1–Op2	1.300(14)		

Table 3. Hydrogen bond distances (Å). Ow1–Ow3 are water oxygen atoms and Op1 and Op2 are hydrogen peroxide oxygen atoms. N3 and N4 are bipyridinium(1+) nitrogen atoms.

N3···O1 (*x*,*y*,*z*)	2.928(6)
N4···O1 (*x*,*y*,*z*)	3.034(6)
O1···O1′ ($\bar{x}$,1−*y*,2−*z*)	2.456(4)
Ow1···Ow3 (*x*,*y*,*z*)	2.807(5)
Ow1···O2 (1−*x*,1−*y*,2−*z*)	2.869(4)
Ow1···O4 (*x*,*y*,*z*)	2.981(3)
Ow1···O3 (*x*,*y*,*z*)	2.991(3)
Ow2···Op2 ($\bar{x}$,1−*y*,1−*z*)	2.640(12)
Ow2···O4 (*x*,*y*,*z*)	2.728(5)
Ow2···Ow2 ($\bar{x}$,1−*y*,1−*z*)	2.764(8)
Ow2···Ow3 (1−*x*,1−*y*,1−*z*)	2.811(6)
Ow3···Op1 (1−*x*,1−*y*,1−*z*)	2.598(11)
Ow3···Ow3 (1−*x*,1−*y*,1−*z*)	2.839(7)
Ow3···Op2 (1−*x*,1−*y*,1−*z*)	2.920(12)
Op1···O4 (*x*,*y*,*z*)	2.694(9)
Op1···Op2 ($\bar{x}$,1−*y*,1−*z*)	2.873(16)
Op2···Op2 ($\bar{x}$,1−*y*,1−*z*)	2.646(23)

hydrogen peroxide at 5 °C and pH 3.5 can, quite unexpectedly, be formulated (Hbipy)[H{VO$(O_2)_2$bipy}$_2$]·xH$_2$O$_2$·(6−x)H$_2$O, $x\approx0.5$. On prolonged standing of the reaction mixture at 5 °C, we obtained another crystalline phase at the same pH. This has recently been shown by us to be an entirely new compound, (Hbipy)[VO$(O_2)_2$ bipy]·(3+x)H$_2$O$_2$·(2−x)H$_2$O, containing the unusual monoprotonated 2,2′-bipyridinium(1+) cation.[7] The title compound might therefore be considered to be a reaction intermediate with a half-life long enough to make it isolable.

The crystals of the title compound consist of Hbipy$^+$ and [H{VO$(O_2)_2$bipy}$_2$]$^-$ ions and water of crystallization, where some water is replaced by hydrogen peroxide, and are held together by ionic and hydrogen bond forces.

In the dinuclear complex the two VO$(O_2)_2$bipy entities, related by an inversion center, are held together by a very strong hydrogen bond. The complex thus differs from the dinuclear [O{VO$(O_2)_2$}$_2$]$^{4-}$ in which the two vanadium atoms are joined by an oxygen bridge.[10] The configuration of ligands about the vanadium atoms is pentagonal bipyramidal as shown in Fig. 2. The V=O, V−N$_{equatorial}$ and V−N$_{apical}$ bond distances are normal (see Table 3 in Ref. 11) as are the bond lengths and angles in the bipyridine ligand.[1,11,12] The vanadium atom is displaced 0.308 Å from the pentagonal plane towards the vanadyl oxygen atom. Such a displacement is usually observed for transition metal complexes (see Ref. 11 and references therein).

Three of the V−O$_{peroxo}$ bond lengths lie in the range 1.869–1.903 Å and are thus normal vanadium–oxygen single bonds (see Table 3 in Ref. 11), while the fourth, V–O1, is about 0.1 Å longer. This lengthening is readily explained by the presence of a very strong hydrogen bond between O1 and O1′, the O1···O1′ distance being 2.456 Å, which weakens the V–O1 bond substantially. A similar kind of elongation of the metal–peroxo bond has previously been observed in (pyH)$_2$[MoO$(O_2)_2$OOH]$_2$,[13] and in (NH$_4$)$_8$[Mo$_{10}$O$_{22+x}$(O$_2$)$_{12-x}$]·12H$_2$O.[14] In these cases the peroxo oxygen atom attached to one molybdenum atom is also involved in a weak Mo···O bond to a second molybdenum atom. There seems to be a correlation between the Mo–O and Mo···O bond lengths; the stronger the long range Mo···O bond the weaker the Mo–O one. This type of correlation has been observed between the O–H and O···O distances in asymmetric hydrogen bonds.[15,16] Therefore, the O1–H(O1) distance should also be expected to be significantly longer. This, however, has not been possible to verify with certainty in this investigation because of the statistical disorder of the hydrogen atom.

Each pyridine ring in the bipyridine ligand is planar within 1.7 σ and the planes intersect each other at 1.6°. The bipyridinium ion is disordered in the structure and occupies mainly two positions 0.6 Å from each other with occupation numbers 0.5. The ion is planar within 1.3 σ and almost parallel to the bipyridine ligand; their planes make an angle of 2°. Average bond distances in the cation are: C–N 1.41(5)* and C–C 1.37(8)* Å. The distance between the carbon atoms joining the pyridine rings is 1.47(1) Å. Due to the disorder the observed bond distances and angles in the cation are not reliable and have therefore been omitted from Table 2.

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* The r.m.s. deviation from the mean is given in parenthesis.

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