Structure and Reactivity of the $H_3O_2^-$ Bridging Ligand in *trans*-Hydroxoaquabis(ethylenediamine)-rhodium(III)

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Bino *et al.* have published a series of papers [1–4] on the occurrence of $H_3O_2^-$ as a bridging ligand in a variety of complexes. For instance they found this to be the case in a series of trinuclear complexes [1–3] of the type $\{[M_3O_2(pr)_6(H_2O)_2]_2-(H_3O_2)\}(NCS)_3 \cdot H_2O$ (M = W and Mo) and $[W_3O_2-(pr)_6(H_2O)(H_3O_2)] \cdot NCS$, where pr = $O_2CC_2H_5$. In addition, they also found [4] this to occur in two classical hydroxo aqua complexes of chromium(III) and cobalt(III), *viz. cis*-$[Cr(bpy)_2(H_3O_2)]_2I_4 \cdot 2H_2O$ and *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$, which turned out to have binuclear and polynuclear structures, respectively. In the former case the hydroxo aqua ions are dimers bridged by two H_3O_2 bridges, whereas in the latter case the hydroxo aqua ions are polynuclear chains of metal atoms bridged by single H_3O_2 ligands. These results have important consequences for the solution chemistry of such bridged species, especially in terms of the olation reactions [4–6] of such species to produce hydroxo bridged complexes.

We have a general interest in the behaviour of hydroxoaquametal ions from another point of view. Earlier studies have demonstrated the general tendency of hydroxometal species to take up $CO_2(aq)$ and $SO_2(aq)$ to produce monodentate carbonate and O-bonded sulfito complexes, respectively [7, 8]. In the case of *cis*-hydroxo-aqua species [9] the CO_2 uptake process is followed by a ring-closure reaction to produce a bidentate carbonato complex. Such a subsequent ring-closure step is not possible in the case of the *trans*-species [10, 11], and stable *trans*-carbonato-aqua complexes were identified. The analogous sulfito complexes do not undergo ring closure, but rather tend to exhibit O- to S-bonded isomerization followed by subsequent substitution to produce disulfito complexes [12–16]. The *trans*-hydroxoaquabis(ethylenediamine)rhodium(III) complex, $Rh(en)_2(H_2O)OH^{2+}$, is extremely stable and

shows no meaningful isomerization to the *cis* form. The present study was undertaken to determine the possible role the $H_3O_2^-$ bridging ligand could play in the solid state and solution chemistry of this complex with respect to the type of reactions referred to above. In addition, no hydrogen oxide ($H_3O_2^-$) bridging has been reported for any rhodium(III) complex to date.

Experimental

The complex *trans*-$[Rh(en)_2(H_2O)OH](ClO_4)_2$ was prepared according to the procedure reported before [10], and UV–Vis spectral data and chemical analysis were in excellent agreement with those found before [10]. Crystals suitable for X-ray analysis were obtained by recrystallizing the material at pH 6.

The light yellow compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.757(2)$, $b = 8.171(1)$, $c = 15.100(2)$ Å, $\beta = 98.93(1)^\circ$, $Z = 2$, $D_{exp} = 2.16$ g cm^{-3}, $D_{calc} = 2.163$ g cm^{-3} and $\mu = 16.2$ cm^{-1}. The three dimensional intensity data were collected on a Philips PW 1100 diffractometer. Mo Kα ($\lambda = 0.7107$ Å) radiation with a graphite monochromator in the incident beam was used. Three reflections were used as standards and remeasured after every 60 reflections. No systematic variations in the intensities were observed. A transparent prismatic shaped crystal with dimensions $0.20 \times 0.19 \times 0.25$ mm was used for the data collection at 25 °C. A total of 2163 reflections were measured for θ values between 3° and 30° of which 1813 were considered as observed ($I > 3\sigma(I)$). There were a few (nine in total) $h0l$ reflections with an intensity slightly larger than $3\sigma(I)$ but these were not considered as observed. Lorentz and polarization corrections were applied.

All the calculations were done on a Univac 1100 computer using the X-ray 72 system of programs. The atomic coordinates of the atom in the isomorphous cobalt compound [4] were used as initial parameters. Anisotropic thermal parameters were used for all the non-hydrogen atoms and isotropic ones for the hydrogen atoms. The final R value was 0.029 using unit weights.

Results and Discussion

The final atomic positional parameters along with their ·estimated standard deviations are listed in Table I. See also 'Supplementary Material'. The most important bond lengths and angles are given in Table II. Figure 1 shows the numbering system of the atoms in the $[Rh(en)_2H_3O_2]^{2+}$ ion.

The $Rh(en)_2^{3+}$ units are linked by $H_3O_2^-$ bridges to form infinite chains of *trans*-$[Rh(en)_2(H_3O_2)]^{2+}$.

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TABLE I. Atomic Coordinates ($\times 10^4$, 10^3 for Hydrogen Atoms) (with e.s.d.s in parentheses)
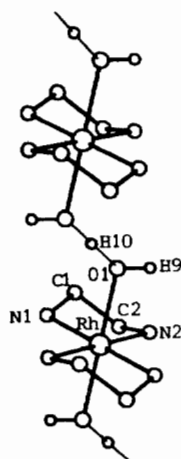
Atom	x	y	z
Rh	5000	0000	0000
Cl	315(1)	4645.6(9)	1386.5(5)
O(1)	1507(3)	9634(3)	−442(1)
O(2)	2218(5)	3600(4)	1220(2)
O(3)	262(5)	6069(3)	819(2)
O(4)	658(5)	5153(4)	2305(2)
O(5)	−1872(5)	3770(4)	1175(2)
N(1)	5359(5)	7603(3)	434(2)
N(2)	4513(5)	418(3)	1309(2)
C(1)	5583(6)	7581(4)	1424(2)
C(2)	3944(6)	8837(4)	1710(2)
H(1)	727(6)	783(5)	168(2)
H(2)	534(6)	674(5)	160(2)
H(3)	234(7)	849(5)	148(2)
H(4)	401(6)	875(5)	231(3)
H(5)	648(7)	711(5)	30(2)
H(6)	424(7)	698(5)	22(2)
H(7)	343(7)	113(5)	134(3)
H(8)	590(8)	88(5)	163(3)
H(9)	140(9)	867(7)	−66(3)
H(10)	000	000	000

TABLE II. Bond Lengths (Å) and Bond Angles (°) (with e.s.d.s in parentheses)

Rh−O(1)	2.040(2)	O(1)−H(10)	1.211(2)
Rh−N(1)	2.065(2)	O(1)−O(1)'	2.422(3)
Rh−N(2)	2.068(3)	Cl−O(2)	1.442(3)
N(1)−C(1)	1.481(4)	Cl−O(3)	1.442(3)
N(2)−C(2)	1.485(4)	Cl−O(4)	1.431(3)
C(1)−C(2)	1.502(5)	Cl−O(5)	1.440(3)
O(1)−H(9)	0.85(5)		
O(1)−Rh−N(1)	90.6(1)	N(1)−C(1)−C(2)	108.7(2)
O(1)−Rh−N(2)	93.7(1)	N(2)−C(2)−C(1)	106.8(3)
N(1)−Rh−N(2)	82.8(1)	O(2)−Cl−O(3)	108.7(2)
N(1)−Rh−N(2)'	97.2(1)	O(2)−Cl−O(4)	110.2(2)
Rh−O(1)−H(9)	106(3)	O(2)−Cl−O(5)	109.2(2)
Rh−O(1)−H(10)	122.5(1)	O(3)−Cl−O(4)	109.2(2)
H(9)−O(1)−H(10)	115(4)	O(3)−Cl−O(5)	109.4(2)
Rh−N(1)−C(1)	108.7(2)	O(4)−Cl−O(5)	110.1(2)
Rh−N(2)−C(2)	108.5(2)		

Fig. 1. Numbering scheme of atoms in *trans*-[Rh(en)$_2$-(H$_3$O$_2$)]$_n^{2n+}$.

Both the rhodium atom and the central hydrogen atom of the H$_3$O$_2^-$ bridge are on an inversion centre at $\frac{1}{2}$00 and 000, respectively. The structure is as can be expected, basically the same as the isomorphous cobalt complex [4]. Although the possibility exists that the central hydrogen atom of the H$_3$O$_2^-$ bridge is disordered across the inversion centre, since this hydrogen atom has a much larger thermal parameter than the other hydrogen atoms, the two oxygen atoms bonded to the rhodium atom are crystallographically equivalent. This clearly indicates that the deprotonation of Rh(en)$_2$(H$_2$O)$_2^{3+}$ does not produce an aquahydroxo species in the solid state as formulated in the usual way: [Rh(en)$_2$(H$_2$O)(OH)]$^{2+}$.

The O--O distance in the H$_3$O$_2^-$ bridging group for a number of different complexes is listed in Table III. In all these cases the protonation of the dihydroxo species (or the deprotonation of the diaqua species) produces the H$_3$O$_2^-$ bridged species rather than aquahydroxo species in the solid state. The two oxygen atoms bonded to the metal ions are absolutely equivalent in all these cases. This is however not always the case. The structures of *trans*-[MoO$_2$(CN$_4$)]$^{4-}$, -[MoO(OH)(CN)$_4$]$^{3-}$ and -[MoO-(OH$_2$)(CN)$_4$]$^{2-}$ clearly show that protonation only occurs at one oxygen atom to produce the oxohydroxo and oxoaqua species [17, 18]. The bond

TABLE III. Structural Data for Compounds Containing H$_3$O$_2^-$ Bridges

Compound	O--O (Å)	M−O (Å)	Reference
trans-[Rh(en)$_2$(H$_3$O$_2$)](ClO$_4$)$_2$	2.422(3)	2.040(2)	this work
trans-[Co(en)$_2$(H$_3$O$_2$)](ClO$_4$)$_2$	2.441(2)	1.916(1)	4
trans-[Ru(bpy)$_2$(H$_3$O$_2$)](ClO$_4$)$_2$	2.538(6)	2.007(3)	19
cis-[Cr(bpy)$_2$(H$_3$O$_2$)]$_2$I$_4$·2H$_2$O	2.446(5)	1.928(3), 1.925(3)	4
{[Mo$_3$O$_2$(Pr)$_6$(H$_2$O)$_2$]$_2$(H$_3$O$_2$)}·6H$_2$O	2.52(1)	2.009(7)	1

distances and angles within the ethylenediamine ligands and perchlorate ions are normal and within experimental error limits similar to those in $[Co(en)_2(H_3O_2)](ClO_4)_2$ [4].

In solution, however, there is good evidence that the $H_3O_2^-$ bridged species does exist as the *trans*-aquahydroxo complex. The relatively high concentration of solvent water molecules in dilute aqueous solution would favour dissociation of such dimers into monomeric aquahydroxo species. It is, therefore, to be expected that $H_3O_2^-$ bridged species will only exist in concentrated solution, *i.e.* during crystallization. It is also possible that the bridging $H_3O_2^-$ groups only exist in the solid state as the result of a (crystal) packing effect. The *trans*-Rh(en)$_2$(H$_2$O)-OH^{2+} ion in solution exhibits similar kinetic behaviour with respect to CO_2 uptake as the *trans*-Rh(en)$_2$(X)OH$^+$ species, where X = Cl$^-$, Br$^-$ and I$^-$ [11], to produce *trans*-Rh(en)$_2$(H$_2$O)OCO$_2^+$ [10]. It is quite possible that the latter species also produces a bridged complex in the solid state; this aspect is presently under investigation.

Supplementary Material

Listings of thermal parameters and observed and calculated structure factor amplitudes (13 pages) are available from the authors on request.

Acknowledgements

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