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Sodium Hydrogen Hexaacetatodirhodate(II)

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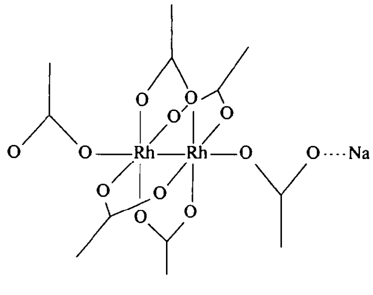
Abstract

The centrosymmetric title compound, Na(H)[$Rh_2(C_2H_3O_2)_6$], consists of dirhodium(II) tetraacetate with two additional axial acetate ligands. Charges are balanced by a sodium ion and a disordered proton. The sodium coordination sphere includes O atoms bound equatorially to the rhodium, as well as O atoms from the axial acetates. The Rh—Rh distance is 2.3827 (5) Å, Rh—O(axial) is 2.279 (2) Å, and the average Rh—O(equatorial) distance is 2.040 (4) Å.

Comment

Dirhodium tetraacetate complexes with a metal–metal bond and various axial ligands are well known (Cotton & Walton, 1993). The present compound, (I), was isolated during an attempt to extend the preparation of bis(acetato)dirhodium-11-tungstophosphate (Wei *et al.*, 1997) to the $[P_2W_{17}O_{61}]^{10-}$ system. X-ray structure analysis revealed a centrosymmetric dirhodium tetraacetate dimer with axial acetate ligands (Fig. 1). A similar arrangement of acetate ions has been observed in the compound $[Rh_2(O_2CCH_3)_4(O_2CCH_3)_2][Rh(tmtaa)(PhCCPh)]_2$ (Cotton & Czuchajowska-Wiesinger, 1992), where tmtaa is 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine. In that compound, the axial acetate ligands linked Rh atoms in the cation and anion. Here, the axial acetate connects to a sodium counterion. The sodium lies on a twofold axis and has a distorted octahedral coordination sphere containing O atoms from one of the acetates bound equatorially to a rhodium (O4), as well as from the axial acetate (O5 and O6). Asymmetric C—O distances for the axial acetate show a greater degree of single-bond character for the C5—O6 bond compared with the C5—O5 bond. A disordered proton is involved in an apparent hydrogen bond between O6 and O6^{iii}.



(I)

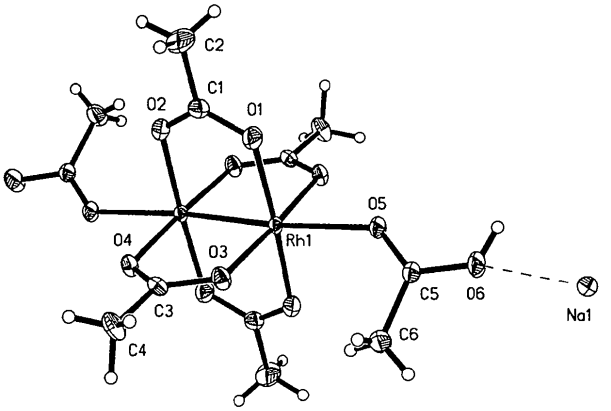


Fig. 1. View of the title compound. Anisotropic displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

Experimental

$K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ (Contant, 1990) was converted to the lithium salt by ion exchange. 10 ml of an aqueous solution which had been adjusted to pH 3.0 with 1.0 *M* HCl and containing 0.5 g of the lithium salt and 0.04 g $Rh_2(OAc)_4$ (Aldrich Chemical Company, Milwaukee, Wisconsin, USA) was heated in a Parr Acid Digestion bomb at 393 K for 17 h. The resulting mixture was loaded onto a Sephadex G-50 column and eluted with an aqueous solution of 0.1 *M* sodium acetate and 0.1 *M* acetic acid. The first dark-brown band was collected and 0.2 g solid CsCl was dissolved in it. After a dark-brown precipitate was removed by vacuum filtration, the blue filtrate was allowed to stand. After two days, blue plate-like crystals of the title compound formed. These displayed blue–green dichroism when observed under a polarizing microscope.

Crystal data

Na(H)[$Rh_2(C_2H_3O_2)_6$]
$M_r = 584.08$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$C2/c$
$a = 14.6450(9)$ Å
$b = 17.9176(12)$ Å
$c = 8.1520(5)$ Å
$\beta = 114.1880(10)°$
$V = 1951.3(2)$ Å^3
$Z = 4$
$D_x = 1.988$ Mg m^{-3}
D_m not measured

Cell parameters from 4358 reflections
$\theta = 1.90–28.28°$
$\mu = 1.77$ mm^{-1}
$T = 173(2)$ K
Rectangular
0.16 × 0.07 × 0.06 mm
Blue

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (Blessing, 1995)
$T_{min} = 0.796$, $T_{max} = 0.928$
6017 measured reflections
2344 independent reflections

2095 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 28.28°$
$h = -13 \rightarrow 19$
$k = -23 \rightarrow 20$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.069$
$S = 1.160$
2344 reflections
162 parameters
All H-atom parameters refined, except H6O for which only coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0084P)^2 + 12.89P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -1.08$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Rh1—O1	2.037 (3)	O5—C5	1.244 (4)
Rh1—O2^{i}	2.038 (3)	O5—Na1^{iii}	2.401 (2)
Rh1—O4^{i}	2.039 (2)	O6—C5	1.287 (4)
Rh1—O3	2.046 (2)	O6—Na1	2.391 (3)
Rh1—O5	2.279 (2)	O6—H6O	0.83 (3)
Rh1—Rh1^{i}	2.3827 (5)	C5—C6	1.491 (5)
O4—Na1^{ii}	2.363 (3)		
C3—O4—Na1^{ii}	136.3 (2)	Rh1—O5—Na1^{iii}	94.59 (9)
Rh1^{i}—O4—Na1^{ii}	102.57 (10)	C5—O6—Na1	152.4 (3)
C5—O5—Na1^{iii}	127.8 (2)	C5—O6—H6O	117 (10)
C5—O6—O6^{iii}	111.6 (3)	Na1—O6—O6^{iii}	93.4 (2)
O1—Rh1—Rh1^{i}	87.99 (7)	O2^{i}—Rh1—Rh1^{i}	88.42 (7)
O4^{i}—Rh1—Rh1^{i}	88.46 (7)	O3—Rh1—Rh1^{i}	87.92 (7)
O5—Rh1—Rh1^{i}	172.54 (6)		

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

The data were corrected for absorption and other systematic errors by comparison of equivalent reflections measured at different φ and ω values (Blessing, 1995). The compound was ESR-silent and its ^{1}H NMR spectrum showed two resonances with a 2:1 ratio at 1.8 and 1.9 p.p.m., corresponding to the bridging and axial ligands, respectively. No line broadening was observed. The UV–vis spectrum revealed an absorption band at 580 nm, analogous to that of $Rh_2(OAc)_4$. These spectroscopic measurements were consistent with the observed Rh—Rh distance, which indicated a rhodium(II) dimer as opposed to a mixed-valence compound. Charge-balancing considerations therefore required a second positive ion in addition to the sodium. A close O6···O6^{iii} distance of 2.456 (6) Å suggested hydrogen bonding. A weak peak was found near O6 in the Fourier difference synthesis at a location reasonable for a H atom. A proton at this position must be disordered due to the proximity of the inversion centre relating O6 and O6^{iii}. In the final model, this peak was included as a H atom (H6O) at 50% occupancy. The positional parameters were refined, subject to a restraint of 0.85 (3) Å for the O—H distance, and the isotropic displacement parameter was constrained to approximately 1.5 times the U_{eq} of O6. The additional three parameters lowered wR^2(all data) from 0.0698 to 0.0692 which is an improvement at a confidence level greater than 95% according to the usual statistical tests (Prince & Spiegelman, 1992). The final O6—H6O distance was 0.83 (3) Å, the H6O—O6^{iii} distance was 1.63 (7) Å and the O6—H6O—O6^{iii} angle 172 (8)°. Methyl H atoms were refined isotropically without restraint in observed positions. Final C—H distances ranged from 0.75 (7) to 1.02 (7) Å, with a mean of 0.90 [9] Å. The C—C—H angles ranged from 109 (4) to 115 (4)°, with a mean of 112 [2]°, and the H—C—H angles ranged from 96 (7) to 118 (7)°, with a mean of 106 [8]°. Methyl H-atom U values ranged from 0.032 (13) to 0.15 (4) Å^2, with a mean of 0.08 [4] Å^2. The largest residual density peaks ($|\Delta\rho| > 1.0$ e Å^{-3}) were -1.08 and -1.06 e Å^{-3}, at distances of 0.84 and 0.83 Å from Rh1, respectively.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1090). Services for accessing these data are described at the back of the journal.

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