

- FAGGIANI, R., LOCK, C. J. L., EPPS, L. A., KRAMER, A. V. & BRUNE, D. (1988). *Acta Cryst.* **C44**, 777–779.
- LEVER, S. Z., BURNS, H. D., KERVITSKY, T. M., GOLDFARB, H. W., WOO, D. V., WONG, D. F., EPPS, L. A., KRAMER, A. V. & WAGNER, H. N. (1985). *J. Nucl. Med.* **26**, 1287–1294.
- LOCK, C. J. L. & PILON, P. (1981). *Acta Cryst.* **B37**, 45–47.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, J. M. & HALL, S. R. (1983). Editors. *The XTAL System of Crystallographic Programs*. Tech. Rep. TR-1364. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Acta Cryst. (1990). **C46**, 2327–2329

Structure of Aqua(ethylenediaminetetraacetato)ruthenium(III)

BY KEN-ICHI OKAMOTO* AND JINSAI HIDAKA

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

IKUO IIDA

Chemical Analysis Center, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

AND KATSUYUKI HIGASHINO AND KAN KANAMORI

Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930, Japan

(Received 5 February 1990; accepted 18 April 1990)

Abstract. [Ru(C₁₀H₁₃N₂O₈)(H₂O)], $M_r = 408.31$, monoclinic, $P2_1/c$, $a = 8.415$ (2), $b = 8.831$ (1), $c = 17.633$ (3) Å, $\beta = 99.66$ (1)°, $V = 1291.8$ (4) Å³, $Z = 4$, $D_x = 2.10$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu = 12.4$ cm⁻¹, $F(000) = 820$, room temperature, $R = 0.035$ for 3810 independent reflections [$I > 3\sigma(I)$]. The Ru is surrounded octahedrally by one O atom of water, and three O and two N atoms of the title ligand (Hedta).

Introduction. Recently the Ru^{III}-edta (edta: ethylenediaminetetraacetate) system has been discussed in relation to its catalytic activity (Taqi Khan, Shukla & Rao, 1989) and its reactivity in ligand substitution (Bajaj & van Eldik, 1988). In these circumstances, it is important to clarify the detailed structure of the Ru^{III}-edta complex. Based on the infrared spectrum, Mukaida, Okuno & Ishimori (1965) suggested that the Ru^{III}-(Hedta).5H₂O complex has a quinque-dentately coordinated edta ligand with a free carboxylic acid moiety. No X-ray studies of the Ru-edta complexes have been reported. Thus we report the crystal structure determination of [Ru(Hedta)(H₂O)].

Experimental. The title complex was prepared as follows: the crude powdery product of the Ru^{III}-edta complex was prepared according to the literature method (Mukaida, Okuno & Ishimori, 1965). The powder was dissolved in hot water (1 g in *ca* 60 cm³)

and the solution was kept at ambient temperature. Small yellow crystals appeared after 3–4 h. Crystals of a suitable size for X-ray analysis were obtained on growing for 2–3 days.

Yellow crystal 0.45 × 0.40 × 0.30 mm; Enraf-Nonius CAD-4 diffractometer, 50 kV and 26 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $22 < 2\theta < 26^\circ$; ω - 2θ scan, scan rate varied from 1 to 5° min⁻¹ (in ω), scan width (0.8 + 0.350 tan θ)°; three intensity standards were monitored every 2 h of X-ray exposure time and these intensities remained constant within experimental error throughout the data collection; orientation (for the same three reflections) was monitored after every 200th scan; 3995 unique reflections, $2\theta \leq 60^\circ$ ($0 \leq h \leq 11$, $0 \leq k \leq 12$, $-24 \leq l \leq 24$); 3810 reflections with $I > 3\sigma(I)$ were used for structure determination; intensities were corrected for Lorentz and polarization; an empirical absorption correction based on a series of ψ scans was applied (max. and min. transmission factors 0.92 and 1.00). The Ru-, three O-, and N-atom positions were determined from direct methods and the other non-H-atom positions were determined from successive difference Fourier maps. No H atoms were included in the calculation. The structure refined by full-matrix least squares using anisotropic thermal parameters for non-H atoms; $R = 0.035$ and $wR = 0.047$, $w = 4F_o^2/\sigma^2(F_o)^2$, $\Delta_{\max} = 0.03\sigma$; $|\Delta\rho|_{\max}$ in final difference Fourier map = 1.14 e Å⁻³ (these highest peaks correspond to the calculated hydrogen positions but their positions

* To whom correspondence should be addressed.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for non-H atoms
$$B_{\text{eq}} = 8\pi^2/3(\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	B_{eq}
Ru	0.80292 (3)	0.32482 (3)	0.35681 (2)	1.133 (4)
O(1)	0.6407 (3)	0.3427 (3)	0.2613 (2)	1.93 (5)
O(2)	0.5203 (4)	0.2091 (4)	0.1603 (2)	2.83 (6)
O(3)	1.0007 (3)	0.3534 (3)	0.3086 (2)	1.91 (5)
O(4)	1.2033 (4)	0.2215 (4)	0.2740 (2)	2.89 (6)
O(5)	0.3308 (4)	0.1641 (4)	0.4743 (2)	2.79 (6)
O(6)	0.2494 (3)	0.4036 (4)	0.4500 (2)	2.40 (6)
O(7)	0.9492 (3)	0.3089 (3)	0.4626 (1)	1.59 (4)
O(8)	0.9539 (4)	0.2732 (4)	0.5882 (2)	2.38 (6)
O(W)	0.7766 (3)	0.5584 (3)	0.3823 (2)	2.00 (5)
N(1)	0.8272 (4)	0.1069 (4)	0.3225 (2)	1.44 (5)
N(2)	0.6325 (3)	0.2376 (3)	0.4222 (2)	1.28 (5)
C(1)	0.6235 (5)	0.2211 (5)	0.2179 (2)	1.86 (6)
C(2)	0.7434 (5)	0.0942 (5)	0.2407 (2)	2.16 (7)
C(3)	1.0776 (5)	0.2255 (5)	0.2997 (2)	1.90 (6)
C(4)	1.0046 (4)	0.0821 (5)	0.3282 (2)	1.84 (6)
C(5)	0.3510 (4)	0.2892 (5)	0.4498 (2)	1.71 (6)
C(6)	0.4895 (4)	0.3390 (4)	0.4105 (2)	1.72 (6)
C(7)	0.8827 (4)	0.2732 (4)	0.5213 (2)	1.50 (6)
C(8)	0.7059 (4)	0.2288 (5)	0.5055 (2)	1.77 (6)
C(9)	0.7498 (5)	0.0062 (4)	0.3749 (2)	1.91 (6)
C(10)	0.5941 (4)	0.0805 (4)	0.3880 (2)	1.74 (6)

Table 2. Bond distances (\AA) and angles ($^\circ$)

Ru—O(1)	1.988 (3)	O(8)—C(7)	1.230 (4)
Ru—O(3)	2.007 (3)	N(1)—C(2)	1.499 (5)
Ru—O(7)	2.060 (2)	N(1)—C(4)	1.495 (5)
Ru—O(W)	2.131 (3)	N(1)—C(9)	1.507 (5)
Ru—N(1)	2.038 (3)	N(2)—C(6)	1.487 (5)
Ru—N(2)	2.130 (3)	N(2)—C(8)	1.496 (4)
O(1)—C(1)	1.312 (5)	N(2)—C(10)	1.526 (5)
O(2)—C(1)	1.225 (5)	C(1)—C(2)	1.516 (6)
O(3)—C(3)	1.325 (5)	C(3)—C(4)	1.529 (6)
O(4)—C(3)	1.218 (5)	C(5)—C(6)	1.518 (5)
O(5)—C(5)	1.208 (5)	C(7)—C(8)	1.519 (5)
O(6)—C(5)	1.324 (5)	C(9)—C(10)	1.517 (6)
O(7)—C(7)	1.295 (5)		
O(1)—Ru—O(3)	97.6 (1)	Ru—N(2)—C(6)	108.0 (2)
O(1)—Ru—O(7)	173.4 (1)	Ru—N(2)—C(8)	110.2 (2)
O(1)—Ru—O(W)	91.2 (1)	Ru—N(2)—C(10)	103.4 (2)
O(1)—Ru—N(1)	85.0 (1)	C(6)—N(2)—C(8)	111.0 (3)
O(1)—Ru—N(2)	93.4 (1)	C(6)—N(2)—C(10)	112.3 (3)
O(3)—Ru—O(7)	88.8 (1)	C(8)—N(2)—C(10)	111.5 (3)
O(3)—Ru—O(W)	95.2 (1)	O(1)—C(1)—O(2)	123.2 (4)
O(3)—Ru—N(1)	82.0 (1)	O(1)—C(1)—C(2)	116.6 (3)
O(3)—Ru—N(2)	163.0 (1)	O(2)—C(1)—C(2)	120.2 (4)
O(7)—Ru—O(W)	86.7 (1)	N(1)—C(2)—C(1)	112.6 (3)
O(7)—Ru—N(1)	97.5 (1)	O(3)—C(3)—O(4)	122.7 (4)
O(7)—Ru—N(2)	80.7 (1)	O(3)—C(3)—C(4)	115.8 (3)
O(W)—Ru—N(1)	174.9 (1)	O(4)—C(3)—C(4)	121.4 (4)
O(W)—Ru—N(2)	97.6 (1)	N(1)—C(4)—C(3)	107.9 (3)
N(1)—Ru—N(2)	86.0 (1)	O(5)—C(5)—O(6)	124.6 (4)
Ru—O(1)—C(1)	114.9 (2)	O(5)—C(5)—C(6)	126.4 (4)
Ru—O(3)—C(3)	113.5 (3)	O(6)—C(5)—C(6)	109.0 (3)
Ru—O(7)—C(7)	117.9 (2)	N(2)—C(6)—C(5)	115.3 (3)
Ru—N(1)—C(2)	107.6 (2)	O(7)—C(7)—O(8)	124.1 (3)
Ru—N(1)—C(4)	105.5 (2)	O(7)—C(7)—C(8)	117.2 (3)
Ru—N(1)—C(9)	107.4 (2)	O(8)—C(7)—C(8)	118.7 (3)
C(2)—N(1)—C(4)	110.9 (3)	N(2)—C(8)—C(7)	113.4 (3)
C(2)—N(1)—C(9)	111.4 (3)	N(1)—C(9)—C(10)	108.1 (3)
C(4)—N(1)—C(9)	113.6 (3)	N(2)—C(10)—C(9)	108.8 (3)

could not be refined). All calculations were performed on a VAX computer using *SDP* (Frenz, 1978). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The final atomic parameters are listed in Table 1.* The molecular structure and numbering scheme are illustrated in the *ORTEP* (Johnson, 1976) plot given in Fig. 1. Bond distances and angles are listed in Table 2.

Fig. 1 clearly indicates that the neutral complex is a six-coordinate structure and the coordination geometry around the Ru^{III} ion is approximately octahedral. The Ru atom is bonded to the O atom of the water molecule, and three O and two N atoms of the edta ligand, which acts as a quinquedentate ligand. A similar structure was also observed for the corresponding Fe^{III} complex, $[\text{Fe}(\text{Hedta})(\text{H}_2\text{O})]$ (Kennard, 1967), with a similar d^5 configuration, although many Fe^{III} complexes with the edta ligand adopt a seven-coordinate structure with the seventh coordination site occupied by H_2O (Lind, Hoard, Hamor & Hamor, 1964; Solans, Altaba & Garcia-Oricain, 1984; Lopez-Alcala, Puerta-Vizcaino, Gonzalez-Vilchez, Duesler & Tapscott, 1984) or a six-coordinate structure with the sexidentate edta ligand (Kushi, Morimasa, Yoshitsugu & Yoneda, 1985). The Ru—N distances in the complex are significantly

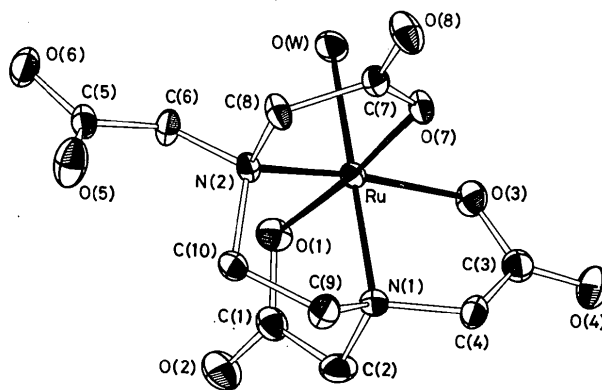


Fig. 1. *ORTEP* drawing of $[\text{Ru}(\text{Hedta})(\text{H}_2\text{O})]$ (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

different [2.038 (3) and 2.130 (3) \AA], although the difference between them is somewhat larger than that of the corresponding $[\text{Fe}(\text{Hedta})(\text{H}_2\text{O})]$ [2.19 (3) and 2.25 (3) \AA] (Kennard, 1967). The M —N (M : Ru and Fe) distances seem to depend on the species occupying the position *trans* to the N atom, that is, the M —N bond *trans* to the O atom in the carboxylate group is longer than that *trans* to the O

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates (calculated) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53206 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atom in the water molecule. The average Ru—O(edta) distance is 2.018 (3) Å and Ru—O(water) is 2.131 (3) Å. Although the Ru—O distances are somewhat longer than those of the corresponding Fe^{III} complex [1.98 (3) and 2.07 (3) Å, respectively], the bond angles for each chelate ring of the Ru complex, N(1)—Ru—O(1) [85.0 (1)°], N(1)—Ru—O(3) [82.0 (1)°], N(2)—Ru—O(7) [80.7 (1)°] and N(1)—Ru—N(2) [86.0 (1)°], are larger than those of the corresponding Fe^{III} complex [83 (1), 77 (1), 78 (1) and 83 (1)°, respectively (Kennard, 1967)]. The bond angles between the *trans* positions for the Ru complex, O(1)—Ru—O(7) [173.4 (1)°], N(2)—Ru—O(3) [163.0 (1)°] and N(1)—Ru—O(W) [174.9 (1)°] are also closer to 180° than those of the corresponding Fe^{III} complex [167 (1), 155 (1) and 168 (1)°, respectively]. These indicate that [Ru(Hedta)(H₂O)] assumes a more regular octahedral structure than [Fe(Hedta)(H₂O)].

Intermolecular hydrogen bonds are recognized between the non-coordinated O atoms in edta and the O atom in water, O(2)⋯O(W) ($1-x, -\frac{1}{2}+y, \frac{1}{2}-z$) [2.819 (4) Å], O(4)⋯O(W) ($1-x, -\frac{1}{2}+y, \frac{1}{2}-z$)

[3.139 (5) Å] and O(6)⋯O(W) ($1-x, 1-y, 1-z$) [3.020 (5) Å].

References

- BAJAJ, H. C. & VAN ELDIK, R. (1988). *Inorg. Chem.* **27**, 4052–4055.
 FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTROF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KENNARD, C. H. L. (1967). *Inorg. Chim. Acta*, **1**, 347–354.
 KUSHI, Y., MORIMASA, K., YOSHITSUGU, K. & YONEDA, H. (1985). *35th Symp. Coord. Chem.*, Hiroshima, Japan. Abstract 2B01.
 LIND, M. D., HOARD J. L., HAMOR, M. J. & HAMOR, T. A. (1964). *Inorg. Chem.* **3**, 34–43.
 LOPEZ-ALCALA, J. M., PUERTA-VIZCAINO, M. C., GONZALEZ-VILCHEZ, F., DUESLER, E. N. & TAPSCOTT, R. E. (1984). *Acta Cryst.* **C40**, 939–941.
 MUKAIDA, M., OKUNO, H. & ISHIMORI, T. (1965). *Nippon Kagaku Zasshi*, **86**, 598–600.
 SOLANS, X., ALTABA, M. F. & GARCIA-ORICAIN, J. (1984). *Acta Cryst.* **C40**, 635–638.
 TAQUI KHAN, M. M., SHUKLA, R. S. & RAO, A. P. (1989). *Inorg. Chem.* **28**, 452–458.

Acta Cryst. (1990). **C46**, 2329–2331

The Structure of 1,1,1,2,2,2,3,3-Octacarbonyl- μ -(1-3- η -cyclododeca-1,6,9-trien-1-yl-3-ylidene)-2,3- μ -hydrido-3-[(*As, As, As', As'*-tetraphenyl)methylenebis(arsine)-*As*]-triangulo-triruthenium(0)(3 Ru–Ru)

BY HOONG-KUN FUN,* OMAR BIN SHAWKATALY† AND SIANG-GUAN TEOH‡§

School of Physics, Chemical Sciences Programme, Centre for Off-Campus Studies, School of Chemistry, Universiti Sains Malaysia, Minden, 11800 Penang, Malaysia

(Received 27 November 1989; accepted 6 April 1990)

Abstract. [Ru₃(C₁₂H₁₅)(H)(C₂₅H₂₂As₂)(CO)₈], *M_r* = 1159.85, orthorhombic, *Pca*2₁, *a* = 30.385 (2), *b* = 10.047 (2), *c* = 14.402 (3) Å, *V* = 4396 (1) Å³, *Z* = 4, *D_x* = 1.752, *D_m* = 1.740 Mg m⁻³ (flotation in chloroform and iodomethane), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.14$ cm⁻¹, *F*(000) = 2280, *T* = 295 K, *R* = 0.0429 for 3712 observed reflections. The structure contains a triangle of Ru atoms; Ru(1) and Ru(2) are bonded to three CO groups, and Ru(3) to two. The hydride bridges Ru(2) and Ru(3). The C₁₂H₁₅ ligand is bound in the $\mu_3\text{-}2\eta^1, \eta^3$ mode to the Ru₃ face. Ru–Ru distances: 2.981 (1) Å (H– bridged), 2.775 (1) and

2.777 (1) Å; The dpam [bis(diphenylarsino)methane] ligand is monodentate with an Ru(3)—As distance of 2.431 (2) Å.

Introduction. The reaction between Ru₃(CO)₁₂ and 1,5,9-cyclododecatriene [CDT] results in the complex Ru₃(μ -H)($\mu_3\text{-}2\eta^1, \eta^3\text{-C}_{12}\text{H}_{15}$) (1) in high yield (Bruce, Cairns & Green, 1972). These authors have also examined the substitution reaction of complex (1) with PMe₂Ph, P(OMe)₃ and P(OCH₃)₂OEt. However, it was not possible for them to determine the precise stereochemistry of the products formed. As part of our study on the coordination of Group 15 bidentate ligands to transition metal clusters, we have determined the structure of the title compound Ru₃(μ -H)($\mu_3\text{-}2\eta^1, \eta^3\text{-C}_{12}\text{H}_{15}$)($\mu_1\text{-Ph}_2\text{AsCH}_2\text{AsPh}_2$)-(CO)₈.

* School of Physics.

† Chemical Sciences Programme, Centre for Off-Campus Studies.

‡ School of Chemistry.

§ To whom correspondence should be addressed.