Table 2. *Main interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Se(1)—O(1)	1.674 (3)	Se(2)—O(5)	1.676 (3)
Se(1)—O(2)	1.629 (3)	Se(2)—O(6)	1.625 (3)
Se(1)—O(3)	1.622 (3)	Se(2)—O(7)	1.621 (3)
Se(1)—O(4)	1.626 (3)	Se(2)—O(8)	1.624 (3)
O(1)—O(2)	2.641 (4)	O(5)—O(6)	2.638 (4)
O(1)—O(3)	2.672 (4)	O(5)—O(7)	2.674 (4)
O(1)—O(4)	2.642 (5)	O(5)—O(8)	2.635 (4)
O(2)—O(3)	2.698 (4)	O(6)—O(7)	2.689 (4)
O(2)—O(4)	2.699 (4)	O(6)—O(8)	2.694 (4)
O(3)—O(4)	2.683 (3)	O(7)—O(8)	2.690 (4)
O(1)—Se(1)—O(2)	106.15 (16)	O(5)—Se(2)—O(6)	106.14 (17)
O(1)—Se(1)—O(3)	108.32 (16)	O(5)—Se(2)—O(7)	108.42 (16)
O(1)—Se(1)—O(4)	106.35 (15)	O(5)—Se(2)—O(8)	105.93 (15)
O(2)—Se(1)—O(3)	112.20 (14)	O(6)—Se(2)—O(7)	111.88 (14)
O(2)—Se(1)—O(4)	112.04 (14)	O(6)—Se(2)—O(8)	112.05 (14)
O(3)—Se(1)—O(4)	111.39 (16)	O(7)—Se(2)—O(8)	111.99 (16)
N(1)—H(1)	0.73 (4)	N(3)—H(9)	1.01 (4)
N(1)—H(1)	0.83 (4)	N(3)—H(10)	0.99 (2)
N(1)—H(3)	0.79 (4)	N(3)—H(11)	0.86 (4)
N(1)—H(4)	0.79 (3)	N(3)—H(12)	1.05 (3)
N(2)—H(5)	1.02 (4)		
N(2)—H(6)	1.10 (3)		
N(2)—H(7)	0.93 (4)		
N(2)—H(8)	1.00 (3)		

Table 3. *Hydrogen bonds* D—$H \cdots A$ *with distances* D—$A < 3$ Å *and* $H \cdots A < 2.5$ Å

D—$H \cdots A$	D—A (Å)	D—H (Å)	$H \cdots A$ (Å)	D—$H \cdots A$ (°)
O(1)—H(13)⋯O(1ⁱ)	2.529 (6)	0.83 (3)	1.72 (3)	166 (3)
O(5)—H(14)⋯O(5ⁱⁱ)	2.541 (6)	1.00 (3)	1.57 (3)	163 (3)
N(1)—H(1)⋯O(7ⁱ)	2.833 (4)	0.73 (4)	2.11 (4)	169 (4)
N(1)—H(3)⋯O(3ⁱ)	2.824 (4)	0.79 (4)	2.03 (4)	173 (3)
N(2)—H(5)⋯O(4)	2.921 (5)	1.02 (4)	1.96 (4)	157 (2)
N(2)—H(6)⋯O(8ⁱⁱ)	2.903 (4)	1.10 (3)	1.81 (3)	172 (2)
N(2)—H(7)⋯O(2ⁱⁱⁱ)	2.950 (4)	0.93 (4)	2.22 (4)	135 (3)
N(2)—H(7)⋯O(8ⁱⁱ)	2.911 (5)	0.93 (4)	2.41 (4)	113 (2)
N(2)—H(8)⋯O(6ᵛ)	2.893 (4)	1.00 (3)	2.07 (2)	139 (3)
N(3)—H(9)⋯O(7ᵛⁱ)	2.942 (5)	1.01 (4)	2.06 (4)	145 (3)
N(3)—H(10)⋯O(2ᵛⁱⁱ)	2.895 (4)	0.99 (2)	1.94 (2)	161 (3)
N(3)—H(11)⋯O(4ⁱⁱ)	2.893 (5)	0.86 (4)	2.40 (4)	117 (2)
N(3)—H(12)⋯O(3ᵛⁱⁱⁱ)	2.957 (4)	1.05 (3)	1.91 (3)	177 (3)

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

Lattice parameters and other data of the conventional primitive triclinic lattice cell are given in square brackets. The reflections were measured in 100 scan steps [$\Delta\omega = (1.75 + 0.35\tan\theta')°$; $\sin\theta' = 1.002\sin\theta$]; the 12 steps at each side of the reflection profile were taken as the background. All H atoms were observed in difference Fourier maps and refined with isotropic temperature factors.

The authors are indebted to Professor Z. Gałdecki for performing the refinement in his laboratory. This work was supported by a grant from the Committee for Scientific Research.

References

Augustyniak, A. M. (1992). In preparation.

Davis, B. L. & Johnson, L. R. (1984). *J. Appl. Cryst.* **17**, 331–333.

Furukava, K., Akahoshi, S., Fukami, T. & Hukuda, K. (1990). *J. Phys. Soc. Jpn*, **59**, 4560–4561.

Kamoun, M., Halouani, M. & Daoud, A. (1987). *Phase Transit.* **9**, 327–335.

Leclaire, A., Ledésert, M., Monier, J. C., Daoud, A. & Damak, M. (1985). *Acta Cryst.* B41, 209–213.

Makarova, I. P., Verin, I. A. & Shchagina, I. M. (1986). *Kristallografiya*, **31**, 178–180.

Noda, Y., Kasatani, H., Watanbe, Y., Terauchi, H. & Gesi, K. (1990). *J. Phys. Soc. Jpn*, **59**, 3249–3253.

Noda, Y., Uchiyama, S., Kafuku, K., Kasatani, H. & Terauchi, H. (1990). *J. Phys. Soc. Jpn*, **59**, 2804–2810.

Sheldrick, G. M. (1986). *SHELXTL-Plus*. PC version. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.

Tanaka, M. & Shiozaki, Y. (1981). *Acta Cryst.* B37, 1171–1174.

Metallointercalators: Structure of *rac*-Bis(ethylenediamine)(9,10-phenanthrenequinone diimine)rhodium(III) Tribromide Trihydrate

William P. Schaefer, Achim H. Krotz, Louis Y. Kuo, Thomas P. Shields and Jacqueline K. Barton

Division of Chemistry and Chemical Engineering† and The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA

Abstract

Bis(ethylenediamine)(phenanthrenequinone diimine)-rhodium(III) tribromide trihydrate has a nearly planar phenanthrenequinone diimine ligand and two ordered ethylenediamine ligands, giving a distorted octahedral coordination to the compound. The N—Rh—N angles range from 77.1 (6) to 96.5°, with the largest deviations from 90° associated with the N atoms of the phenanthrenequinone diimine ligand. The two Rh—N distances involving these N atoms are 0.05 Å shorter than Rh—N distances to ethylenediamine ligands; other distances and angles are within normal ranges.

† Contribution No. 8584.

Comment

9,10-Phenanthrenequinone diimine (phi) complexes of rhodium(III) are of increasing interest owing to their ability to bind DNA strongly *via* interacalation (Pyle & Barton, 1990; Pyle, Long & Barton, 1989). Upon photoactivation, the complexes promote efficient strand cleavage (Sitlani, Long, Pyle & Barton, 1992). The intercalated complex provides an anchor on the DNA helix from which specific interactions with DNA can be introduced. During the course of our investigations of site-specific metallointercalators, we designed the title compound to explore the contributions of hydrogen bonding and van der Waals interactions to the site-recognition characteristics of these intercalating complexes.

The complex cation was synthesized by reacting [RhCl$_2$(en)$_2$]Cl (Kuo, Shields, Krotz & Barton, 1992) with 9,10-diaminophenanthrene followed by oxidation with air (Pyle, Chiang & Barton, 1990). A small orange–red lath with dimensions 0.04 × 0.02 × 0.20 mm was obtained from an aqueous solution of *rac*-[Rh(en)$_2$(phi)]Cl$_3$ and several potential counterions (NaBr, NaClO$_4$, KPF$_6$, KH$_2$PO$_4$) by slow evaporation at room temperature.

The slightly distorted octahedral coordination about the Rh atom is caused by the small 'bite' of the three bidentate ligands; the three N—Rh—N angles subtended by the ligands average only 81°. The Rh—N distances are normal, as are distances and angles in the rest of the molecule. All the coordinated N atoms form hydrogen bonds to either water molecules [N2···O2, 2.92 (2); N3···O1, 2.91 (2) Å] or bromide ions [N1···Br2, 3.44 (2); N3···Br1, 3.36 (2); N4···Br1, 3.40 (2); N5···Br1, 3.46 (2); N6···Br1, 3.36 (2); N6···Br3, 3.39 (2) Å]. This hydrogen-bonding network extends further with hydrogen bonds between bromide ions and water molecules [Br1···O2, 3.56 (2); Br2···O2, 3.56 (2); Br2···O3, 3.43 (2); Br3···O1, 3.30 (2); Br3···O2, 3.29 (2); Br3···O3, 3.31 (2) Å]. Such an intricate network of interactions helps to explain the small displacement parameters for the atoms of the cation.
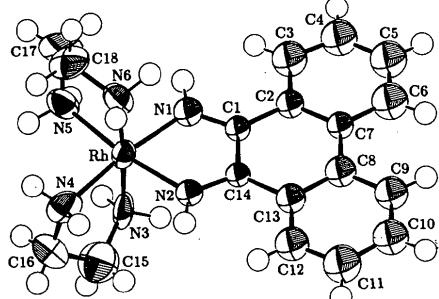

Fig. 1. An *ORTEP* drawing of the cation with 70% probability ellipsoids. H atoms are shown as circles of small arbitrary size.
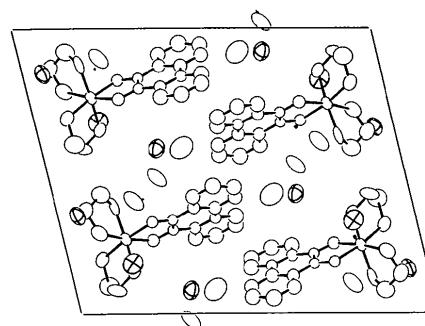

Fig. 2. An *ORTEP* drawing of the contents of one unit cell (unit cell outlined) projected down the *b* axis. Atoms are shown as 70% probability ellipsoids, with H atoms omitted.

Experimental

Crystal data
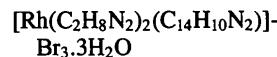
[Rh(C$_2$H$_8$N$_2$)$_2$(C$_{14}$H$_{10}$N$_2$)]-Br$_3$.3H$_2$O
M_r = 723.11
Monoclinic
$P2_1/c$
a = 19.975 (7) Å
b = 8.377 (3) Å
c = 16.234 (6) Å
β = 103.59 (4)°
V = 2640 (2) Å^3
Z = 4

D_x = 1.82 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 3.1–8.4°
μ = 5.16 mm^{-1}
T = 294 K
Lath
0.20 × 0.08 × 0.04 mm
Orange-red

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical
T_{min} = 0.861 , T_{max} = 1.00
5284 measured reflections
2451 independent reflections
2451 observed reflections

R_{int} = 0.080 for 1511 duplicates
θ_{max} = 20°
h = 0 → 19
k = −8 → 8
l = −15 → 15
3 standard reflections frequency: 150 min intensity variation: within counting statistics

Refinement

Refinement on F^2
Final R = 0.116 for 2059 reflections with $F_o^2 > 0$, 0.052 for 1077 reflections with $F_o^2 > 3\sigma(F_o)^2$
wR = 0.015
S = 1.16
2451 reflections
200 parameters

H-atom parameters not refined
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −1.64 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/B
Rh	0.1728 (1)	−0.0080 (2)	0.2614 (1)	0.0284 (4)
N1	0.2483 (8)	−0.1607 (16)	0.2560 (9)	2.5 (3)†
C1	0.3108 (9)	−0.1192 (20)	0.2921 (10)	1.9 (4)†

C2	0.3724 (10)	−0.2172 (21)	0.2982 (12)	2.4 (4)†
C3	0.3672 (11)	−0.3706 (24)	0.2633 (13)	3.8 (5)†
C4	0.4257 (11)	−0.4625 (24)	0.2717 (12)	4.0 (5)†
C5	0.4887 (11)	−0.3948 (24)	0.3096 (13)	4.1 (5)†
C6	0.4948 (11)	−0.2470 (25)	0.3407 (13)	4.1 (5)†
C7	0.4367 (10)	−0.1464 (20)	0.3350 (11)	2.1 (4)†
C8	0.4418 (9)	0.0137 (25)	0.3700 (10)	2.9 (4)†
C9	0.5061 (10)	0.0827 (23)	0.4081 (12)	3.3 (5)†
C10	0.5094 (11)	0.2332 (25)	0.4430 (13)	3.9 (5)†
C11	0.4513 (12)	0.3158 (24)	0.4473 (13)	4.3 (5)†
C12	0.3877 (1)	0.2544 (23)	0.4097 (13)	3.5 (5)†
C13	0.3827 (10)	0.1080 (22)	0.3708 (11)	2.7 (4)†
C14	0.3157 (9)	0.0406 (18)	0.3278 (10)	1.8 (4)†
N2	0.2577 (8)	0.1106 (15)	0.3209 (9)	2.2 (3)†
N3	0.1624 (8)	−0.0998 (18)	0.3759 (10)	0.0395 (64)
C15	0.1335 (12)	0.0259 (31)	0.4193 (13)	0.0664 (76)
C16	0.0792 (12)	0.1100 (30)	0.3621 (16)	0.0688 (83)
N4	0.1033 (9)	0.1587 (17)	0.2833 (10)	0.0452 (56)
N5	0.0936 (8)	−0.1423 (17)	0.1895 (10)	0.0408 (48)
C17	0.0958 (12)	−0.1354 (22)	0.0970 (14)	0.0551 (96)
C18	0.1145 (12)	0.0368 (24)	0.0819 (12)	0.0536 (79)
N6	0.1759 (8)	0.0854 (18)	0.1470 (10)	0.0395 (45)
Br1	0.9452 (1)	0.0854 (3)	0.1552 (2)	0.0592 (7)
Br2	0.1764 (1)	0.0171 (3)	0.6748 (2)	0.0657 (8)
Br3	0.3205 (1)	−0.0022 (3)	0.0807 (1)	0.0625 (7)
O1	0.6990 (8)	0.1547 (16)	0.5224 (9)	0.0733 (53)
O2	0.2205 (8)	0.0961 (17)	0.8964 (9)	0.0740 (50)
O3	0.3095 (9)	0.1075 (18)	0.5829 (10)	0.0963 (57)

† Isotropic displacement parameter, B.

Table 2. *Bond distances* (Å) *and angles* (°)

Rh—N1	1.996 (15)	C7—C8	1.45 (3)
Rh—N2	2.007 (14)	C8—C9	1.41 (3)
Rh—N3	2.066 (15)	C8—C13	1.42 (3)
Rh—N4	2.058 (16)	C9—C10	1.38 (3)
Rh—N5	2.065 (16)	C10—C11	1.37 (3)
Rh—N6	2.029 (16)	C11—C12	1.37 (3)
N1—C1	1.29 (2)	C12—C13	1.37 (3)
C1—C2	1.46 (3)	C13—C14	1.47 (3)
C1—C14	1.45 (2)	C14—N2	1.28 (2)
C2—C3	1.40 (3)	N3—C15	1.46 (3)
C2—C7	1.41 (3)	C15—C16	1.44 (3)
C3—C4	1.38 (3)	C16—N4	1.52 (3)
C4—C5	1.39 (3)	N5—C17	1.51 (3)
C5—C6	1.33 (3)	C17—C18	1.52 (3)
C6—C7	1.42 (3)	C18—N6	1.48 (3)
N1—Rh—N2	77.1 (6)	C7—C2—C3	122.0 (17)
N1—Rh—N3	92.2 (6)	C4—C3—C2	119.5 (19)
N1—Rh—N4	172.0 (6)	C5—C4—C3	118.4 (19)
N1—Rh—N5	96.5 (6)	C6—C5—C4	122.7 (20)
N1—Rh—N6	91.2 (6)	C7—C6—C5	121.8 (20)
N2—Rh—N3	90.2 (6)	C6—C7—C2	115.3 (17)
N2—Rh—N4	96.3 (6)	C8—C7—C2	121.8 (17)
N2—Rh—N5	172.1 (6)	C8—C7—C6	122.8 (17)
N2—Rh—N6	92.6 (6)	C9—C8—C7	121.6 (17)
N3—Rh—N4	83.3 (6)	C13—C8—C7	122.3 (17)
N3—Rh—N5	94.6 (6)	C13—C8—C9	116.1 (17)
N3—Rh—N6	176.0 (6)	C10—C9—C8	120.4 (18)
N4—Rh—N5	90.5 (6)	C11—C10—C9	121.7 (20)
N4—Rh—N6	93.6 (6)	C12—C11—C10	119.7 (20)
N5—Rh—N6	82.9 (6)	C13—C12—C11	119.9 (19)
Rh—N1—C1	117.8 (12)	C12—C13—C8	122.0 (18)
Rh—N2—C14	117.4 (12)	C14—C13—C8	116.6 (16)
Rh—N3—C15	107.5 (13)	C14—C13—C12	121.4 (17)
Rh—N4—C16	108.8 (13)	C13—C14—C1	120.8 (15)
Rh—N5—C17	110.0 (12)	N2—C14—C1	114.4 (15)
Rh—N6—C18	110.5 (12)	N2—C14—C13	124.8 (15)
C2—C1—N1	125.8 (16)	C16—C15—N3	111.4 (19)
C14—C1—N1	113.3 (15)	N4—C16—C15	109.5 (19)
C14—C1—C2	120.9 (15)	C18—C17—N5	105.1 (16)
C3—C2—C1	120.5 (17)	N6—C18—C17	109.8 (17)
C7—C2—C1	117.3 (16)		

R values quoted are on F; the high value for all data with $F_o^2 > 0$ is due to the small size of the crystal and the consequently weak data. There were essentially no reflections beyond 20° in θ. H atoms were positioned by calculation (C—H or N—H, 0.95 Å) and were repositioned once near the end of refinement. $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2)$ for a single datum is derived from counting statistics plus an additional term, $(0.014I)^2$. Variances of the merged data were obtained by propagation of error plus another additional term, $(0.014I)^2$. Values for f' were taken from Cromer (1974). Programs from the *CRYM* crystallographic computing system (Duchamp, 1964) were used together with *OR-TEP* (Johnson, 1976).

References

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Duchamp, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, paper B-14, p. 29.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-3794, 3rd revision. Oak Ridge National Laboratory, Tennessee, USA.

Kuo, L. Y., Shields, T. P., Krotz, A. H. & Barton, J. K. (1992). In preparation.

Pyle, A. M. & Barton, J. K. (1990). *Prog. Inorg. Chem.* 38, 413–475.

Pyle, A. M., Chiang, M. Y. & Barton, J. K. (1990). *Inorg. Chem.* 29, 4487–4495.

Pyle, A. M., Long, E. C. & Barton, J. K. (1989). *J. Am. Chem. Soc.* 111, 4520–4522.

Sitlani, A., Long, E. C., Pyle, A. M. & Barton, J. K. (1992). *J. Am. Chem. Soc.* 114, 2303–2312.

Structure of *trans*-Dichloro(dimethyl sulfoxide)(piperidine)platinum(II)

Karin Lövqvist and Åke Oskarsson*

Inorganic Chemistry 1, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

Abstract

In the title compound the Pt atom coordinates one S atom, one N atom and two chloride ions in the *trans* position. The coordination geometry is square planar with distances Pt—S 2.212 (6), Pt—N 2.083 (18), and Pt—Cl 2.292 (6) and 2.296 (5) Å.