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Solar Energy Storage Reactions. Determination of the Structure of the Complex Formed by Visible Irradiation of $Rh_2(bridge)_4^{2+}$ in Aqueous HCl Solutions

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Visible irradiation of $Rh_2(bridge)_4^{2+}$ in concentrated HCl solutions yields hydrogen gas and a yellow complex, $Rh_2(bridge)_4Cl_2^{2+}$. An X-ray crystal structure analysis of $[Rh_2(bridge)_4Cl_2]Cl_2\cdot 8H_2O$ (bridge = 1,3-diisocyanopropane) has been completed (final $R_F = 0.031$). The complex crystallizes in the space group $P2_1/m$ (No. 11); $a = 11.590$ (4), $b = 12.239$ (4), $c = 12.072$ (4) Å; $\beta = 92.90$ (2)°; $Z = 2$; d(calcd) = 1.686 (1), d(obsd) = 1.70 (2) g/cm^3. The structure is composed of $Rh_2(bridge)_4Cl_2^{2+}$ cations having approximate D_{4h} symmetry and a hydrogen-bonded network of Cl^- anions and water molecules. Each Rh atom is six-coordinate with Cl and Rh atoms in axial positions of a $Cl(RhC_4)Rh$ unit. The RhRh distance in the binuclear cation is 2.837 (1) Å, and RhCl is 2.447 (1) Å. The relative ease of reductive elimination of X from $Rh_2(bridge)_4X_2^{2+}$ (X = Cl, Br) complexes may be explained in part by the drive to reduce CC′ and NN′ nonbonded-atom repulsions that are caused by the close approach (~2.85 Å) of the $Rh(CN)_4$ planes.

Recently we reported[1] that visible irradiation (546 nm) of $Rh_2(bridge)_4^{2+}$ (bridge = 1,3-diisocyanopropane) in concentrated aqueous HCl solutions yields hydrogen gas and a yellow complex, $Rh_2(bridge)_4Cl_2^{2+}$. The latter complex has also been prepared by direct Cl_2 oxidation of $Rh_2(bridge)_4Cl_2^{2+}$, and we have suggested[1-3] that it contains a linear $ClRh^{II}Rh^{II}Cl^{2+}$ core unit.

We have also begun an investigation of the thermal reactions of $Rh_2(bridge)_4Cl_2^{2+}$ and $Rh_2(bridge)_4Br_2^{2+}$.[4,5] Understanding the thermodynamic and kinetic factors that control these reactions is a major goal of our current work, as the development of a cyclic system for uphill photoconversion ($2HX \xrightarrow{h\nu} H_2 + X_2$) depends on being able to return the photoproduct to its initial photoactive state. Clearly, examination of the details of the molecular structure of $Rh_2(bridge)_4Cl_2^{2+}$ is a necessary part of this study.

We have now obtained crystals of $[Rh_2(bridge)_4Cl_2]Cl_2\cdot 8H_2O$ from aqueous HCl solutions and have performed a complete X-ray structure analysis. The results are reported herein.

Experimental Section

A yellow solution of the cation $Rh_2(bridge)_4Cl_2^{2+}$ was obtained by room-light photolysis of an undegassed solution of 50 mg of $Rh_2(bridge)_4(BF_4)_2$[6] in 5 mL of 3 M HCl. The yellow complex is characterized[1] in solution by its intense UV absorption band at 338 nm (ϵ 56 200).

Collection and Data Reduction. X-ray quality single crystals were grown by the slow evaporation (~3 months) of the aqueous HCl solution described above. A crystal was mounted about its long dimension in a 0.3-mm glass capillary to limit loss of water. Initial oscillation photographs showed Laue symmetry $2/m$, indicating a monoclinic cell. Approximate unit-cell constants were determined from film data, and a restricted data set ($2\theta = 0$–$30°$) was collected in 12 h by diffractometer. The systematic absences $0k0$ ($k = 2N + 1$) were noted, indicating the space group $P2_1$ or $P2_1/m$, the latter of which was later indicated by intensity statistics. Unit-cell constants were obtained from a least-squares fit of 15 centered reflections. Crystal data are given in Table I. The density, 1.70 (2) g/cm^3 measured by the flotation method in a mixture of carbon tetrachloride and ethyl iodide, is in close agreement with the calculated value of 1.686 (1) g/cm^3 based on 2 formula units per unit cell.

Intensity data were collected at room temperature (22 °C) on a Syntex $P2_1$ automated full-circle diffractometer with graphite-monochromatized Mo Kα radiation. A θ–2θ scan method was used to collect the quadrant $\pm h,+k,+l$ ($2\theta = 0$–$50°$). Each scan ranged from 1.2° below Kα_1 to 1.2° above Kα_2 for the calculated peak position at a rate of 2.02°/min. Stationary background counts, each of which equaled half of the scan time, were taken before and after each scan. Crystal decomposition was monitored by five check reflections which were measured every 95 reflections. No significant decay or fluctuation (±2% maximum) was observed in any of the check reflections during the 150 h of data collection. Multiple measurements were averaged and systematic absences were deleted giving a complete data set of 3289 independent reflections. All data were corrected for Lorentz and polarization effects. Observational variances, $\sigma^2(F_o)^2$, were calculated for each reflection based on counting statistics plus the term $(0.02P)^2$ where P is the scan count. No correction was made for absorption ($\mu = 13.02$ cm^{-1}) (crystal dimensions 0.08 × 0.035 × 0.031 cm). Data were placed on an absolute scale by Wilson's method, and the scale factor was subsequently refined.

Table I. Crystal Data for $[Rh_2(bridge)_4Cl_2]Cl_2\cdot 8H_2O$

formula wt 868.21
space group $P2_1/m$
$a = 11.590$ (4) Å
$b = 12.239$ (4) Å
$c = 12.072$ (4) Å
$\beta = 92.90$ (3)°
$Z = 2$
$V = 1710.2$ (94) Å^3
d(calcd) = 1.686 (1) g/cm^3
d(obsd) = 1.70 (2) g/cm^3
λ 0.710 69 Å
$T = 22$ (1) °C
$\mu = 13.02$ cm^{-1}

Structure Determination. The structure was solved by using the heavy-atom method. A Patterson synthesis indicated approximate coordinates for the Rh atom, and subsequent Fourier and difference Fourier maps yielded all nonhydrogen atoms. The initial agreement factor $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.39.

Scattering factors for Rh were from Cromer and Waber[7] and those for C, O, N, Cl from ref 8, and the hydrogen scattering factors were obtained from Stewart et al.[9] The quantity minimized in least-squares calculations was $\sum w(F_o^2 - (1/s^2)F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$ and s = scale factor. Anisotropic refinement of all nonhydrogen atoms converged at an R_F index of 0.08. Methylene hydrogens were placed in idealized positions (CH = 0.95 Å) and checked by difference mapping. Refinement decreased the R_F to 0.042. The water molecules and chloride ions are involved in a hydrogen-bonded network that is complicated by disorder. The structural model we adopted for this network is shown in Figure 1.

Initial treatment of the atom labeled as Cl^-1 as a fully occupied Cl^- ion gave at convergence very large temperature factors and a very short Cl^-1 to Cl^-1 distance of 2.97 Å, less than the sum of the van der Waals radii. Occupancy of this position by a full Cl^- would necessitate $[Rh_2(bridge)_4Cl_2]Cl_2\cdot HCl\cdot 7H_2O$ as the formula unit to satisfy the charge balance required by the dipositive cation. At this point, a model fitting "Cl^-1" as a disordered chloride–water pair was attempted. Refinement gave 0.51 (2) Cl^-1 and 0.49 (2) O3 at this position with a decrease in the thermal parameters. This model then gives $[Rh_2(bridge)_4Cl_2]Cl_2\cdot 8H_2O$ as the formula unit and a reasonable value for a chloride to oxygen (O3) hydrogen-bonding distance of 2.930 (1) Å. Examination of difference maps at the conclusion of refinement showed that the electron density is well represented by this model, although it appears that Cl^-1 and O3 may occupy slightly different positions. Further refinement based on two distinct sites for these atoms was not considered fruitful.

Disorder was found in the position of ClC, the bridgehead carbon of one bridging ligand. This atom was represented with a 60:40 twofold disorder model, which yielded reasonable CC distances upon convergence of the refinement. The final R_F is 0.031 with a "goodness of fit", $[\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, of 2.76 (water hydrogen atoms are not included). A list of final positional and thermal parameters

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Table II. Final Atom Parameters[a-c,e]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	5191 (2)	−13407 (2)	28418 (2)	245 (1)	184 (1)	219 (1)	−5 (1)	7 (1)	3 (1)
Cl	4798 (7)	6574 (7)	29053 (7)	429 (5)	172 (4)	355 (5)	−20 (3)	31 (4)	13 (3)
Cl$^-$1	55379 (15)	−13028 (16)	−20871 (17)	590 (12)	748 (14)	874 (16)	48 (9)	134 (12)	−16 (10)
Cl$^-$2	−33563 (12)	−25000 (0)	20508 (13)	372 (8)	483 (8)	490 (9)	0 (0)	40 (7)	0 (0)
C1A	14722 (30)	−13400 (23)	42398 (29)	315 (18)	185 (15)	313 (19)	−23 (13)	18 (16)	23 (13)
N1	20032 (30)	−13276 (21)	50553 (26)	518 (20)	247 (15)	333 (17)	−46 (13)	−128 (16)	3 (13)
C1CA	24734 (84)	−25000 (0)	66372 (68)	531 (59)	371 (48)	230 (44)	0 (0)	−83 (43)	0 (0)
C1CB	32626 (127)	−25000 (0)	61584 (110)	467 (92)	450 (74)	337 (74)	0 (0)	−234 (70)	0 (0)
C2A	−8781 (30)	−13357 (23)	37355 (28)	313 (18)	190 (15)	268 (17)	−4 (13)	−13 (15)	−1 (13)
N2	−16433 (25)	−13136 (20)	42690 (25)	298 (16)	212 (14)	332 (16)	8 (12)	67 (14)	−29 (12)
C1B	26897 (47)	−14469 (33)	60860 (36)	824 (35)	496 (26)	375 (24)	−118 (23)	−329 (25)	65 (18)
C4C	38540 (43)	−25000 (0)	3160 (42)	297 (26)	499 (31)	296 (26)	0 (0)	83 (22)	0 (0)
C3C	−15685 (44)	−25000 (0)	−9305 (39)	376 (29)	378 (27)	228 (24)	0 (0)	0 (22)	0 (0)
C2C	−25491 (45)	−25000 (0)	56137 (42)	388 (29)	339 (26)	335 (27)	0 (0)	167 (24)	0 (0)
C2B	−26375 (31)	−14570 (26)	49363 (34)	297 (19)	281 (18)	503 (23)	4 (14)	165 (17)	−47 (15)
C3A	−4631 (28)	−13340 (22)	14425 (28)	276 (17)	167 (14)	277 (18)	11 (12)	35 (15)	−6 (13)
N3	−10435 (25)	−13198 (20)	6625 (23)	333 (16)	224 (14)	258 (15)	32 (12)	−2 (14)	−12 (11)
C3B	−18078 (34)	−14470 (27)	−3212 (30)	389 (21)	390 (21)	261 (18)	78 (16)	−78 (16)	−25 (15)
C4A	19475 (30)	−13284 (23)	19870 (28)	291 (18)	217 (16)	260 (17)	3 (13)	3 (15)	24 (13)
N4	27732 (25)	−13127 (21)	15370 (24)	302 (16)	268 (15)	296 (15)	1 (12)	13 (13)	43 (12)
C4B	38474 (30)	−14491 (27)	9784 (31)	261 (18)	386 (20)	358 (20)	−16 (14)	80 (16)	60 (15)
O1	14492 (27)	−13282 (22)	89668 (27)	525 (18)	484 (18)	659 (21)	33 (14)	−104 (16)	58 (14)
O2	−54058 (36)	−25000 (0)	36127 (34)	558 (27)	457 (23)	531 (25)	0 (0)	128 (22)	0 (0)
O4	−56036 (32)	−3046 (28)	40208 (30)	906 (28)	699 (24)	780 (25)	166 (21)	229 (22)	−92 (19)
O5	−33754 (27)	789 (26)	15281 (27)	625 (21)	545 (18)	705 (22)	−2 (16)	138 (18)	−20 (17)

atom[d]	x	y	z	atom[d]	x	y	z
H1BA	2521	−863	6579	H2CA	−3143	−2500	6128
H1BB	3499	−1407	5942	H2CB	−1816	−2500	6018
H1BC	2215	−1365	6699	H3BA	−1678	−850	−806
H1BD	3274	−885	6132	H3BB	−2574	−1452	−114
H1CA	1672	−2500	6786	H3CA	−768	−2500	−1103
H1CB	2916	−2500	7324	H3CB	−2028	−2500	−1602
H1CC	3682	−2500	6873	H4BA	4475	−1449	1524
H1CD	3803	−2500	5599	H4BB	3942	−834	498
H2BA	−3316	−1489	4450	H4CA	4517	−2500	−110
H2BB	−2696	−843	5413	H4CB	3177	−2500	−172

[a] Final value of the scale factor is 0.847 22 (90). [b] The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23})]$. [c] Hydrogen atom parameters were not refined. [d] Thermal parameters are of the form $\exp[-B((\sin^2\theta)/\lambda^2)]$. All values for B are 5.00 Å^2. [e] Coordinates are ×10^5 and U_{ij} values are ×10^4.

Table III. Selected Bond Distances (Å)

	A. $Rh_2(bridge)_4Cl_2^{2+}$		
Rh–Rh	2.837 (1)	Rh–Cl	2.447 (1)
Rh–C1A	1.970 (3)	C1A–N1	1.134 (4)
Rh–C2A	1.991 (3)	C2A–N2	1.122 (4)
Rh–C3A	1.989 (3)	C3A–N3	1.129 (4)
Rh–C4A	1.995 (3)	C4A–N4	1.124 (4)
N1–C1B	1.450 (5)	C1B–C1CA	1.478 (7)
N2–C2B	1.450 (4)	C1B–C1CB	1.450 (10)
N3–C3B	1.454 (4)	C2B–C2C	1.517 (4)
N4–C4B	1.455 (4)	C3B–C3C	1.516 (4)
		C4B–C4C	1.515 (4)
	B. Hydrogen-Bonded Network		
Cl–O1	3.205 (3)	Cl$^-$1–Cl$^-$1	2.930 (3)
Cl$^-$1–O4	3.057 (3)	O1–O1	2.868 (4)
Cl$^-$1–O5	3.025 (3)	O1–O5	2.780 (4)
Cl$^-$2–O2	3.107 (2)	O2–O4	2.743 (4)
Cl$^-$2–O5	3.219 (3)	O4–O4	2.787 (4)

Table IV. Selected Bond Angles (deg) in $Rh_2(bridge)_4Cl_2^{2+}$

Cl–Rh–C1A	89.04 (9)	C2B–C2C–C2B	114.63 (29)
Cl–Rh–C2A	87.88 (9)	C3B–C3C–C3B	116.39 (28)
Cl–Rh–C3A	90.67 (9)	C4B–C4C–C4B	116.23 (28)
Cl–Rh–C4A	91.48 (9)	Rh–Rh–C1A	90.03 (9)
C1A–Rh–C2A	88.40 (13)	Rh–Rh–C2A	90.18 (9)
C1A–Rh–C3A	179.15 (13)	Rh–Rh–C3A	90.24 (8)
C1A–Rh–C4A	89.95 (13)	Rh–Rh–C4A	90.43 (9)
C2A–Rh–C3A	90.79 (12)	Rh–Rh–Cl	177.86 (2)
C2A–Rh–C4A	178.24 (13)	Rh–C1A–N1	178.55 (30)
C3A–Rh–C4A	90.86 (12)	Rh–C2A–N3	177.48 (29)
C1A–N1–C1B	173.43 (36)	Rh–C3A–N3	178.25 (28)
C2A–N2–C2B	171.61 (33)	Rh–C4A–N4	177.69 (29)
C3A–N3–C3B	172.86 (32)	N1–C1B–C1CA	112.08 (39)
C4A–N4–C4B	172.35 (33)	N1–C1B–C1CB	111.77 (49)
C1B–C1CA–C1B	121.43 (43)	N2–C2B–C2C	111.57 (28)
C1B–C1CB–C1B	125.40 (70)	N3–C3B–C3C	111.62 (28)
		N4–C4B–C4C	111.68 (27)

is given in Table II. Selected bond distances and angles are given in Tables III and IV, respectively. A list of final calculated and observed structure factors is available.[10]

Results and Discussion

The $Rh_2(bridge)_4Cl_2^{2+}$ cation contains two approximately square pyramidal RhC_4Cl^+ units connected by a direct RhRh bond (Figure 2). The binuclear complex is bisected by a crystallographic mirror plane that requires the bridging ligands to be rigorously eclipsed (the idealized symmetry of the cation is D_{4h} if the central methylene groups are not included).

The RhRh distance (2.837 (1) Å) is significantly shorter than that (3.263 (1) Å) in the unoxidized complex $Rh_2(bridge)_4^{2+}$.[2,3,11] This 0.4-Å decrease in bond length reflects a considerable strengthening of the RhRh bond, which is consistent with the formal increase in bond order from 0 to 1 on oxidative addition of Cl_2 to $Rh_2(bridge)_4^{2+}$ (the change in the metal–metal electronic configuration presumably is $\sigma^2\sigma^{*2}$ to σ^2).[1-4,12] The RhRh distance in $Rh_2(bridge)_4Cl_2^{2+}$ very likely would be even shorter if ligand–ligand repulsive interactions were not so severe (vide infra). In this connection we note that a nonbridged Rh(II) isocyanide dimer, $Rh_2(p\text{-}CNC_6H_4CH_3)_8I_2(PF_6)_2$, exhibits a RhRh distance of 2.785 Å.[13] The RhCl bond length in $Rh_2(bridge)_4Cl_2^{2+}$ is 2.447 (1) Å, comparable to the terminal Rh^{III}Cl bond distance of 2.393

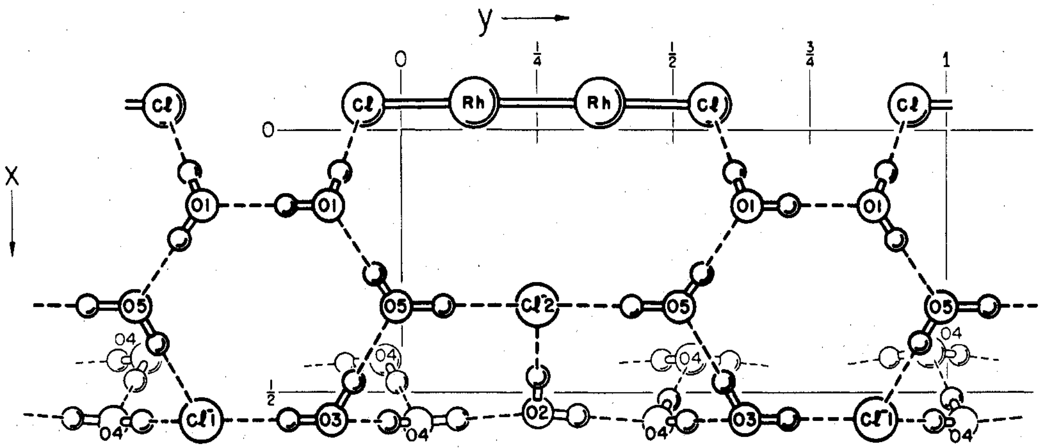

Figure 1. Projection of the hydrogen-bonded network of $[Rh_2(bridge)_4Cl_2]Cl_2\cdot 8H_2O$ on the *ab* plane as viewed down the axis. There are crystallographic mirror planes at $y = {}^1/_4$ and $y = {}^3/_4$. Thus, atoms O3 and Cl^-1 equally share a single site (see text), and the hydrogen atoms of the water molecules O1, O2, O4, and O5 are disordered in a complicated fashion.

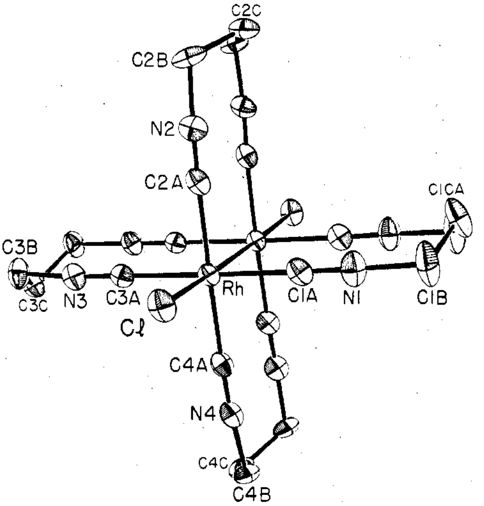

Figure 2. View of the structure of $Rh_2(bridge)_4Cl_2^{2+}$.

(2) Å found[14] in μ-chloro-μ-hydrido-bis[chloro(pentamethylcyclopentadienyl)rhodium(III)].

There is little distortion about the Rh atom. Deviations from planarity in the $Rh-(C\equiv N)_4$ group are no larger than ±0.02 Å; these distortions, which are somewhat smaller than those found[11] in $Rh_2(bridge)_4^{2+}$ and $Rh_2(TM4\text{-}bridge)_4^{2+}$ (TM4-bridge = 2,4-dimethyl-2,5-diisocyanohexane), increase the distances between the CC′ and NN′ mirror-related atoms relative to the RhRh distance.

Possibly the most interesting aspect of the structure of $Rh_2(bridge)_2Cl_2^{2+}$ is the presence of very short nonbonded contacts involving the eclipsed $C\equiv N$ groups. The average mirror-related CC′ and NN′ distances are only 2.85 (1) and 2.89 (2) Å, respectively. We note, for example, that the interplanar spacings in graphite and in a variety of so-called one-dimensional (1-D) organic compounds are much larger (3.35 Å for graphite[15] and 3.17 and 3.47 Å for TCNQ and TTF in (TTF)(TCNQ)[16]). In several transition-metal 1-D complexes (e.g., $Mg_{0.86}Pt(ox)_2\cdot 5.3H_2O$[17]) the interplanar spacing is comparable to that found here (2.85 Å), but in those cases the two ligand planes are staggered such that the actual closest atom–atom contact distance is substantially greater (2.97 Å).

The short nonbonded CC′ and NN′ distances in $Rh_2(bridge)_4Cl_2^{2+}$ are due in part to the strong RhRh bonding interaction that forces the planes close together. Counteracting this favorable interaction are the repulsions of the interacting $C\equiv N$ groups. One consequence of the latter effect most likely is the relative ease with which X groups may be reductively eliminated from $Rh_2(bridge)_4X_2^{2+}$ complexes,[4,5] as considerable driving force for such reactions may be derived from the decrease in steric crowding achieved by increasing the interplanar spacing.

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Registry No. $[Rh_2(bridge)_4Cl_2]Cl_2\cdot 8H_2O$, 70982-68-2; $Rh_2(bridge)_4(BF_4)_2$, 61156-15-8.

Supplementary Material Available: Table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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