

the Ta-Ta distance is not short enough to make this inference unambiguous. The most direct comparisons we can make to related compounds are somewhat imperfect, but for what they are worth, they are as follows. In a series of  $\text{Nb}_2\text{Cl}_4\text{L}_4(\mu\text{-S})_2$  molecules,<sup>9,10</sup> the Nb-Nb distances are  $2.87 \pm 0.01 \text{ \AA}$ . This is about  $0.20 \text{ \AA}$  shorter than we find here. On the other hand in  $\text{Nb}_2\text{Cl}_{10}$ , where there cannot be a metal-metal bond, the distance is  $3.951(2) \text{ \AA}$ .<sup>11</sup> Although this is much longer, it must be noted that here the formal charge on the metal atoms is +5 rather than +4, and this should favor a longer distance.

To get some further insight into the likelihood that a metal-metal single bond might exist in  $[\text{TaCl}_3(\text{Me}_2\text{S})]_2(\mu\text{-SPh})_2$ , we have carried out a molecular orbital calculation on the idealized model system  $[\text{NbCl}_3(\text{H}_2\text{S})]_2(\mu\text{-SH})_2$  by the Fenske-Hall method.<sup>12</sup> In

Figure 3 we show a diagram dealing with only those MO's to which the metal atom d orbitals not primarily involved in metal-ligand  $\sigma$  bonding make their primary contributions. The center of gravity of this entire set of MO's is at ca.  $-5.5\text{eV}$ . The  $\pi$  and  $\delta$  interactions are so small that the  $\delta$ ,  $\delta^*$ ,  $\pi$ , and  $\pi^*$  orbitals are spread over only a narrow range, ca.  $1.1 \text{ eV}$ . The  $\sigma$  interaction, on the other hand, is much greater, and the electrons occupying the  $\sigma$ -bonding orbital are stabilized by several electron volts. The  $\sigma$ -bonding orbital, which is the HOMO of the molecule, has mainly metal character (77%) and thus we conclude that it is reasonable to regard this molecule as containing an authentic metal-metal bond. This conclusion is consistent with all of the experimental data.

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**Registry No.**  $[\text{TaCl}_3(\text{Me}_2\text{S})]_2(\mu\text{-SPh})_2$ , 99687-25-9;  $\text{Ta}_2\text{Cl}_6(\text{Me}_2\text{S})_3$ , 77827-59-9; diphenyl disulfide, 882-33-7; tantalum, 7440-25-7.

**Supplementary Material Available:** Tables of observed and calculated structure factors and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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## Synthesis and Reactivity of Hydroxo-Bridged Binuclear Ethylenediamine Complexes of Iridium(III) and the X-ray Crystal Structure of [Aquabis(ethylenediamine)iridium(III)]-( $\mu$ -hydroxo)hydroxobis(ethylenediamine)iridium(III) Dithionate Perchlorate Hydrate

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The preparations of salts of the binuclear cations  $\Delta, \Delta\text{-}[(\text{en})_2\text{Ir}(\text{OH})_2\text{Ir}(\text{en})_2]^{4+}$  (diol) and  $\Delta, \Delta\text{-}[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})]^{4+}$  (aqua hydroxo monool) are reported. One member of this series,  $\Delta, \Delta\text{-}[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{S}_2\text{O}_6)_{3/2}\text{ClO}_4 \cdot 2.75\text{H}_2\text{O}$ , has been structurally characterized at 105 K by X-ray crystallography. The compound crystallizes in the space group  $I2/a$  with  $a = 17.058(5) \text{ \AA}$ ,  $b = 18.140(2) \text{ \AA}$ ,  $c = 18.947(3) \text{ \AA}$ ,  $\beta = 93.68(2)^\circ$ , and  $Z = 8$ . On the basis of 4546 unique reflections, the structure has been refined to  $R = 0.034$  and  $R_w = 0.042$ . The terminally coordinated hydroxo and aqua groups in the complex cation interact by a very short symmetrical hydrogen bond,  $2.429(9) \text{ \AA}$ , the existence of which was predicted from thermodynamic and kinetic data. The four independent Ir-O distances are similar in magnitude,  $\langle \text{Ir-O} \rangle = 2.076 \text{ \AA}$ , and with the exception of one ethylenediamine ligand, the complex cation has almost mirror plane symmetry. The water of crystallization is distributed over six partially populated positions. The thermodynamics and kinetics for the equilibration reaction between diol and monool have been studied spectrophotometrically within the range  $[\text{H}^+] = 10^{-5}$  to  $1.0 \text{ M}$  ( $I = 1.0 \text{ M}$ ;  $(\text{Na,H})\text{ClO}_4$ ). The first-order rate constants,  $k_{\text{obsd}}$ , for the reaction show a  $[\text{H}^+]$  dependence, which was interpreted in terms of the equilibria shown in Scheme I. Rate constants and activation parameters (at  $25^\circ\text{C}$ ) are as follows:  $k_1 = 1.48(11) \times 10^{-6} \text{ s}^{-1}$  ( $\Delta H^\ddagger = 113(2) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 22(6) \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $k_{-1} = 2.58(35) \times 10^{-7} \text{ s}^{-1}$  ( $\Delta H^\ddagger = 114(4) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 13(4) \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $k_2 = 5.1(8) \times 10^{-7} \text{ s}^{-1}$  ( $\Delta H^\ddagger = 81(8) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -94(27) \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $k_2/K_{a3} = 2.40(5) \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$  ( $\Delta H^\ddagger - \Delta H^\circ = 68.8(17) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger - \Delta S^\circ = -84(6) \text{ J mol}^{-1} \text{ K}^{-1}$ ). Independently of the kinetic data a spectrophotometric determination of  $K_{a1}$  and  $K_1 = k_1/k_{-1}$  gave the following values (at  $25^\circ\text{C}$ ):  $K_{a1} = 0.0122(7)$  ( $\Delta H^\circ = 10.8(67) \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = -1(22) \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $K_1 = 5.7(8)$  ( $\Delta H^\circ = -1.5(47) \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = 10(15) \text{ J mol}^{-1} \text{ K}^{-1}$ ). The acid dissociation constant for the aqua hydroxo monool has been determined potentiometrically as  $\text{p}K_{a2} = 9.04(3)$  ( $\Delta H^\circ = 53.3(50) \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = 6(14) \text{ J mol}^{-1} \text{ K}^{-1}$ ) at  $25^\circ\text{C}$ .

### Introduction

The mechanism of the cleavage and formation of the hydroxo bridge in binuclear M(III) complexes in acidic solution has been the subject of several investigations.<sup>2-20</sup> Tri-, di- and mono-

hydroxo-bridged cobalt(III) complexes react essentially by an acid-catalyzed bridge cleavage (and formation), which presumably

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involves protonation of a hydroxo bridge to give aqua-bridged intermediates.<sup>2-8</sup> Recently studies of tri- and dihydroxo-bridged rhodium(III) species have been reported,<sup>9-12</sup> and by analogy with the cobalt(III) complexes, the second-order rate constants for the acid-catalyzed cleavage are generally much greater than the respective first-order constants for the uncatalyzed cleavage reaction.

The hydroxo-bridged binuclear chromium(III) complexes exhibit properties similar to those of the cobalt(III) and rhodium(III) analogues, but in the chromium(III) complexes studied until now the bridge cleavage proceeds predominantly by an uncatalyzed path.<sup>13-20</sup> The heterobinuclear dihydroxo-bridged complex  $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$  resembles the corresponding dichromium complex, and bridge cleavage probably occurs by chromium-oxygen bond breaking.<sup>18</sup>

Hydroxo-bridged complexes of iridium(III) have not been reported previously (however, see Note Added in Proof). The present work reports the preparation and the chemical properties of mono- and dibridged complexes, which we believe are the first examples of well-documented hydroxo-bridged iridium(III) complexes. A crystal structure determination of the monohydroxo-bridged cation  $[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})]^{4+}$  as a mixed dithionate perchlorate was undertaken to obtain structural data for hydroxo-bridged iridium(III) complexes and to investigate the nature of the intramolecular hydrogen bond, which has been postulated earlier by Springborg et al.<sup>11-12,15-17</sup>

## Experimental Section

**Materials.** *cis*- $[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})\text{S}_2\text{O}_6]$  was prepared as described previously.<sup>21</sup> All other reagents were of analytical grade.

**Instruments.** A Zeiss DMR 21 spectrophotometer was used for all spectrophotometric measurements. Data are given with the molar absorption coefficient  $\epsilon$  in  $\text{L mol}^{-1} \text{cm}^{-1}$  and the wavelength  $\lambda$  in nm. The pH measurements were made with a Radiometer GK 2301 combined glass and calomel electrode (modified to contain 1.0 M NaCl in the reference part) in conjunction with a Radiometer PHM 61 digital pH meter. Thermogravimetric measurements were performed on the thermobalance described by Pedersen.<sup>22</sup>

A CAD4 diffractometer equipped with an Enraf-Nonius gas-flow low-temperature device was used for the collection of intensity data. Molybdenum  $K\alpha$  radiation obtained from a highly mosaic graphite crystal was used.

**Analyses.** C, H, N, Br, Cl, and S analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

**Preparative Procedures.**  $\Delta, \Delta-[(\text{en})_2\text{Ir}(\text{OH})_2\text{Ir}(\text{en})_2]\text{Br}_4 \cdot 2\text{H}_2\text{O}$ . Solid *cis*- $[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})\text{S}_2\text{O}_6]$  (3.00 g, 5.9 mmol)<sup>21</sup> was heated to 120 °C for 20 h (the loss of weight was 0.11 g). To the resulting crude  $\Delta, \Delta-[(\text{en})_2\text{Ir}(\text{OH})_2\text{Ir}(\text{en})_2](\text{S}_2\text{O}_6)_2$  was added 10 mL of a saturated solution of  $\text{NH}_4\text{Br}$ , and the suspension was stirred for 1 h at room temperature. The crude bromide salt was filtered off, washed with two 5-mL portions of 50% ethanol, and sucked as dry as possible. The product was dissolved by extraction on the filter with small portions of water at room temperature (total volume ca. 100 mL). A saturated solution of  $\text{NH}_4\text{Br}$  (ca. 50 mL) was then added to the filtrate with stirring, and the mixture was cooled in ice. Stirring and cooling was continued for 1 h, and the precipitate was isolated and washed as above and dried in air; yield 2.7 g (90%). Further reprecipitation did not change the UV spectrum. Anal. Calcd for  $\text{Ir}_2\text{C}_8\text{H}_{38}\text{N}_8\text{Br}_4\text{O}_4$ : C, 9.47; H, 3.78; N, 11.05; Br, 31.51. Found: C, 9.42; H, 3.85; N, 10.97; Br, 31.35. Thermogravimetry: loss of weight 37.4 mg/g of sample, corresponding to 2.11 mol of  $\text{H}_2\text{O}$ /mol of dimer.

$\Delta, \Delta-[(\text{en})_2\text{Ir}(\text{OH})_2\text{Ir}(\text{en})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ . A mixture of 10 mL of a saturated  $\text{NaClO}_4$  solution and 8 mL of water was added to the bromide (2.7 g, 2.66 mmol), and the suspension was stirred for 1 h at room temperature. The crude perchlorate salt was filtered off and sucked as

dry as possible before it was dissolved by extraction on the filter with ca. 40 mL of water at room temperature. The same volume of a saturated solution of  $\text{NaClO}_4$  was added to the filtrate with stirring, and the mixture was cooled in ice for 30 min. The precipitate was filtered off and washed, first with three 2-mL portions of 50% ethanol and then with two 3 mL-portions of 96% ethanol and finally diethyl ether, and dried in air; yield 2.6 g (91% based on the bromide). Further reprecipitation did not change the UV spectrum. The content of 1 mol of water of crystallization was estimated by comparing the UV spectrum with that of the bromide salt. The compound is explosive and was therefore not analyzed.

When the compound was recrystallized by dissolution in water at room temperature followed by cooling in ice, a dihydrate was obtained. This was confirmed by the UV spectrum and by thermogravimetry: loss of weight was 32.7 mg/g sample, corresponding to 1.98 mol of  $\text{H}_2\text{O}$ /mol of dimer.

$\Delta, \Delta-[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ . To  $\Delta, \Delta-[(\text{en})_2\text{Ir}(\text{OH})_2\text{Ir}(\text{en})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$  (1.00 g, 0.93 mmol) was added 2.000 mL of 1.00 M  $\text{HClO}_4$ . The suspension was stirred at 70 ( $\pm 1$ ) °C and a clear yellow solution formed within 5 min. After a further 11 min, 2 mL of a saturated solution of  $\text{NaClO}_4$  was added and the solution was cooled in ice. After 1 h, the solution was filtered and the filter was rinsed with two 0.25-mL portions of half-saturated  $\text{NaClO}_4$ . To the combined filtrate and washings was added 2.000 mL of 1.00 M  $\text{NaOH}$ , and the mixture was cooled in ice for 10 min. The crystals were filtered off, washed with 96% ethanol and then with diethyl ether, and dried in air. The product (0.9 g, 87%) was dissolved in 7.5 mL of ice-cold water; to the filtered solution was added 7.5 mL of a saturated solution of  $\text{NaClO}_4$ , and the mixture was cooled in ice. After 10 min, the crystals were filtered off, washed with 96% ethanol and then with diethyl ether, and dried in air; yield 0.75 g (83%). Reprecipitation did not change the UV spectrum. This product was not analyzed. The content of water of crystallization was determined by thermogravimetry and from the UV spectrum.

$\Delta, \Delta-[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{S}_2\text{O}_6)_2 \cdot \text{H}_2\text{O}$ . A solution of 1.0 g (0.92 mmol) of  $\Delta, \Delta-[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$  in 100 mL of water was applied on a column of Amberlite IRA-402 anion exchanger ( $\text{S}_2\text{O}_6^{2-}$ -form), ca. 15 cm long and ca. 2-cm diameter), and the column was washed with 100 mL of water. The eluates were evaporated to a volume of ca. 15 mL on a rotating vacuum evaporator (40 °C), and the mixture was allowed to stand overnight to complete the crystallization before the precipitate was filtered off, washed thoroughly with water, and dried in air; yield 0.74 g (80%). Anal. Calcd for  $\text{Ir}_2\text{C}_8\text{H}_{38}\text{N}_8\text{S}_8\text{O}_{16}$ : C, 9.47; H, 3.77; N, 11.04; S, 12.64. Found: C, 9.28; H, 3.70; N, 10.76; S, 12.41. Thermogravimetry: loss of weight 17.16 mg/g sample, corresponding to 0.95 mol of  $\text{H}_2\text{O}$ /mol of dimer.

$\Delta, \Delta-[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{S}_2\text{O}_6)_{3/2}(\text{ClO}_4) \cdot 2.75\text{H}_2\text{O}$ . To a filtered solution of 0.43 g (0.39 mmol) of  $\Delta, \Delta-[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$  in 1.2 mL of water was added 1.2 mL of a saturated solution of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  (0.84 mmol). After a couple of hours, the crystal cake was broken up and the mixture was left overnight before the precipitate was filtered off, washed with three 0.5-mL portions of water, and dried in air. The crystals were suitable for a single-crystal X-ray analysis; yield 0.39 g (92%). Anal. Calcd for  $\text{Ir}_2\text{C}_8\text{H}_{41.5}\text{N}_8\text{ClS}_3\text{O}_{18.75}$ : C, 9.01; H, 3.92; N, 10.51; Cl, 3.33; S, 9.02. Found: C, 8.92; H, 3.89; N, 10.44; Cl, 3.22; S, 8.81. Thermogravimetry indicated a content of water of crystallization of 2.5–3.5 mol/mol of dimer.

**Kinetic Experiments.** Pseudo-first-order rate constants,  $k_{\text{obsd}}$  and activation parameters were calculated as described previously.<sup>16</sup> The  $k_{\text{obsd}}$  values were calculated from absorbances measured at the wavelengths  $\lambda = 280, 270,$  and  $260$  nm. All kinetic runs were performed in duplicate.

In all kinetic runs the hydrogen ion concentration changed slightly. These changes were generally less than 1%, although in experiments with low initial  $[\text{H}^+]$ , changes of up to 8% were calculated (eq 1 and 3). However, the error introduced by this variation is very small, since at low  $[\text{H}^+]$  the dependence of  $k_{\text{obsd}}$  on  $[\text{H}^+]$  is small. For each experiment the hydrogen ion concentration at  $t_0$ ,  $[\text{H}^+]_0$ , and at equilibrium,  $[\text{H}^+]_{\infty}$ , were calculated, and the values  $[\text{H}^+] = 1/2([\text{H}^+]_0 + [\text{H}^+]_{\infty})$  were then used in the subsequent calculations.

**Determination of Equilibrium Constants.**  $K_1$  was determined spectrophotometrically from the molar absorption coefficients of 1 M  $\text{NaClO}_4$  solutions of pure diol,  $\epsilon_D$ , pure aqua hydroxo monool,  $\epsilon_M$ , and the equilibrium solution,  $\epsilon_{\infty}$ , measured at the wavelengths  $\lambda = 280, 270,$  and  $260$  nm and from the equation  $K_1 = (\epsilon_D - \epsilon_{\infty})/(\epsilon_{\infty} - \epsilon_M)$ . For each temperature  $\epsilon_{\infty}$  was determined as the average of four experiments with solutions initially containing pure diol,  $\epsilon_{\infty}(D)$ , and four experiments with solutions initially containing pure monool,  $\epsilon_{\infty}(M)$ . The deviations between the averaged  $\epsilon_{\infty}(D)$  and  $\epsilon_{\infty}(M)$  values were never greater than 0.4%. Values of  $\epsilon_D$  and  $\epsilon_M$  were each obtained as the average of four measurements. The parameters for  $K_1$  given in Table IX have been calculated from

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**Table I.** Ligand Field Spectral Data for ( $\mu$ -Hydroxo)- and Bis( $\mu$ -hydroxo)iridium(III) Complexes at 25 °C

cation	medium	( $\epsilon$ , $\lambda$ ) <sub>max</sub>	( $\epsilon$ , $\lambda$ ) <sub>min</sub>
$\Delta, \Delta$ -[(en) <sub>2</sub> Ir(OH) <sub>2</sub> Ir(en) <sub>2</sub> ] <sup>4+</sup> a,b	1 M NaClO <sub>4</sub>	(393, 271)	(359, 258)
$\Delta, \Delta$ -[(H <sub>2</sub> O)(en) <sub>2</sub> Ir(OH)Ir(en) <sub>2</sub> (OH) <sub>2</sub> ] <sup>5+</sup> c,d	1 M HClO <sub>4</sub>	(520, 271)	(436, 253)
$\Delta, \Delta$ -[(H <sub>2</sub> O)(en) <sub>2</sub> Ir(OH)Ir(en) <sub>2</sub> (OH)] <sup>4+</sup> c	1 M NaClO <sub>4</sub>	(445, 271)	(412, 257)
$\Delta, \Delta$ -[(HO)(en) <sub>2</sub> Ir(OH)Ir(en) <sub>2</sub> (OH)] <sup>3+</sup> c,e	1 M NaOH	(447, 280) <sub>sh</sub>	

<sup>a</sup>Perchlorate salt. Values identical with these were obtained in the following media: 1 M HClO<sub>4</sub>; 0.1 M NaOH, 0.9 M NaClO<sub>4</sub>. In 1 M NaOH the values ( $\epsilon$ ,  $\lambda$ )<sub>max</sub> = (411, 270) and ( $\epsilon$ ,  $\lambda$ )<sub>min</sub> = (406, 263) were found. <sup>b</sup>The bromide salt gave ( $\epsilon$ ,  $\lambda$ )<sub>max</sub> = (395, 271) and ( $\epsilon$ ,  $\lambda$ )<sub>min</sub> = (368, 258). <sup>c</sup>Perchlorate salt. <sup>d</sup>The dithionate salt gave ( $\epsilon$ ,  $\lambda$ )<sub>max</sub> = (521, 271) and ( $\epsilon$ ,  $\lambda$ )<sub>min</sub> = (431, 253). <sup>e</sup>Identical values were obtained in the following medium: 0.01 M NaOH, 0.99 M NaClO<sub>4</sub>.

measurements at 25, 40, 60, and 80 °C.

A potentiometric determination of  $K_1$  (at 60 °C) was made by titration of a  $5 \times 10^{-3}$  M solution of dimer in 1 M NaClO<sub>4</sub> equilibrated at 60 °C with 0.05 M NaOH, 0.95 M NaClO<sub>4</sub>. From the titration curve the amount of monool was calculated, and the value  $K_1 = 6.0$  (5) was obtained.

The acid dissociation constant,  $K_{a1}$ , was determined spectrophotometrically at 25 and 39.4 °C. The molar absorption coefficients,  $\epsilon$ , were measured at the wavelengths  $\lambda = 280, 270$  and 260 nm for solutions of  $\Delta, \Delta$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O in 1 M (Na,H)ClO<sub>4</sub> with [HClO<sub>4</sub>] = 10<sup>-3</sup> to 1.0 M and in pure 1 M NaClO<sub>4</sub> (8 different solutions at 25 °C and 10 at 39.4 °C). For each solution the  $\epsilon$  values were obtained as the average of four measurements. The variation of  $\epsilon$  with [H<sup>+</sup>] followed the expression  $\epsilon = (\epsilon_{HA}[H^+] + \epsilon_A K_{a1}) / ([H^+] + K_{a1})$ , where  $\epsilon_{HA}$  and  $\epsilon_A$  refer to the diaqua monool and aqua hydroxo monool, respectively. From this expression values of  $K_{a1}$  were calculated by nonlinear regression analysis, where the actual values for [H<sup>+</sup>] were obtained by iteration. The second acid dissociation constant,  $K_{a2}$ , for the monool was determined by glass-electrode measurements following procedures discussed previously<sup>16</sup> (Table IX).

**Crystallographic Study.** The  $\Delta, \Delta$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)]<sup>4+</sup> cation was crystallized with different anions to obtain suitable crystals for the X-ray crystallographic study. The dithionate tended to deteriorate and the perchlorate was not suited for a diffraction study. The only crystals of an acceptable quality were found in the mixed dithionate-perchlorate salt. The preparation of this compound is described above.

The white regularly shaped crystals were assigned to the monoclinic system from precession and Weissenberg photographs. The  $a$  and  $c$  axes were chosen to get an oblique angle close to 90°. The systematically absent reflections  $hkl$  for  $h + k + l = 2n + 1$  and  $h0l$  for  $h = 2n + 1$  are consistent with the space groups  $Ia$  and  $I2/a$ , which are nonstandard settings of the space groups  $Cc$  and  $C2/c$ . The structure was solved and refined in the space group  $I2/a$ , which has the following general equivalent positions:  $(x, y, z), (-x, -y, -z), (1/2 + x, -y, z), (1/2 - x, y, -z), (1/2 + x, 1/2 + y, 1/2 + z), (1/2 - x, 1/2 - y, 1/2 - z), (x, 1/2 - y, 1/2 + z), (-x, 1/2 + y, 1/2 - z)$ .

All the crystals examined changed color from white to violet when they were irradiated with X-rays (Cu K $\alpha$  and Mo K $\alpha$ ) but they all turned white again within 1 day after the radiation had ceased. No significant changes were observed in the diffraction pattern as the color of the crystals varied.

The temperature employed was 105 K, and during the data collection the variation of the temperature as measured with a thermocouple was less than 1 K. The cell parameters at 105 K were determined from a least-squares refinement of the setting angles of 18 reflections. The selection of scan type was based on the profile analysis of a number of reflections. Crystal data and some details for the data collection and structure determination are given in Table II. The intensities of the three standard reflections measured after every 10 800 s decreased 10% during the data collection. The data were corrected for background, Lorentz, polarization, and absorption ( $\mu(\text{Mo K}\alpha) = 94.39 \text{ cm}^{-1}$ ) effects. The latter correction was performed using a Gaussian integration procedure.<sup>23</sup> A rescale function linear in exposure time was applied to correct for the deterioration of the crystal. The symmetry related reflections were averaged, yielding 4546 independent reflections of which 3739 had  $I/\sigma(I) \geq 2.0$  and were classified as observed and used in the subsequent structure determination and refinement. The  $\sigma(I)$  values were calculated from counting statistics.

**Structure Determination and Refinement.** The structure was solved by the heavy-atom method, assuming the space group to be  $I2/a$ , which was subsequently confirmed by the structure solution and refinement. The positions of the two independent iridium atoms in the monool complex were deduced from the Patterson function. The remaining non-hydrogen atoms were located after subsequent least-squares refinements, mini-

**Table II.** Crystallographic Data for  $\Delta, \Delta$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)](S<sub>2</sub>O<sub>6</sub>)<sub>3/2</sub>ClO<sub>4</sub>·2.75H<sub>2</sub>O

formula	Ir <sub>2</sub> ClS <sub>3</sub> C <sub>8</sub> N <sub>8</sub> O <sub>18.75</sub> H <sub>41.5</sub>
fw	1066.03
space group	monoclinic, $I2/a$
cell params (105 K)	
$a/\text{Å}$	17.058 (5)
$b/\text{Å}$	18.140 (2)
$c/\text{Å}$	18.947 (3)
$\beta/\text{deg}$	93.68 (2)
$V/\text{Å}^3$	5851 (3)
$Z$	8
$\rho(\text{calcd})/\text{g cm}^{-3}$	2.420
developed faces	{100}, {001}, {110}
	Data collection
cryst dimens/mm <sup>3</sup>	0.18 × 0.11 × 0.29
scan type	$\omega$ - $\theta$
scan width/deg	$\Delta\omega = 1.00 + 0.35(\tan \theta)$
bkgd	25% of full scan width on both sides
max scan time/s	120
$\theta$ limits/deg	$1.5 \leq \theta \leq 24$
octants colld	$h, k, \pm l$
no. of unique data	4546
internal $R$ values	$R = 0.025$
from averaging	$R_w = 0.026$
no. of data with $I/\sigma(I) \geq 2.0$	3739
no. of variables	365
$R$	0.034
$R_w$	0.042

mizing  $\sum w||F_o| - |F_c||^2$ , and difference Fourier calculations. Atomic scattering factors were taken from Cromer and Waber's tabulation,<sup>24</sup> using the values for the uncharged atoms, except for hydrogen for which the values of Stewart et al.<sup>25</sup> were employed. The atomic scattering factors for Ir, Cl, and S were corrected for the effect of anomalous dispersion by using the values given by Cromer and Liberman.<sup>26</sup>

The X-ray System<sup>27</sup> was used for the crystallographic computations and ORTEP<sup>28</sup> for the illustrations. After anisotropic thermal parameters were refined for the heavier atoms, Ir, Cl, and S, an inspection of the thermal parameters and the difference Fourier synthesis showed the water of crystallization to be disordered. Although the chemical analysis indicated ca. three H<sub>2</sub>O's per formula unit, the structure determination indicated a water content corresponding to two and three-fourths H<sub>2</sub>O's per formula unit distributed over six partially populated positions. Several different models were used to describe the disordered water structure. Starting values for the different population parameters were estimated from the peak heights, and they were included in the refinements. Anisotropic thermal parameters were gradually introduced for all the non-hydrogen atoms. The hydrogen atoms of the complex cation could all be located in a difference Fourier synthesis calculated at this stage. The positions of the hydrogen atoms bonded to the oxygen atoms of the cation were taken from the difference map. The other hydrogen atoms were introduced in their idealized positions. A common isotropic

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**Table III.** Positional Parameters and Equivalent Isotropic Thermal Parameters<sup>a</sup>

atom	x	y	z	$U_{iso}^b/\text{\AA}^2$
Cation				
Ir1	0.49054 (2)	0.20309 (2)	0.07891 (2)	0.0143
Ir2	0.49205 (2)	0.06711 (2)	0.23143 (2)	0.0142
O1	0.4070 (4)	0.1218 (4)	0.0584 (4)	0.027
O2	0.4135 (4)	0.0293 (3)	0.1514 (3)	0.024
O12	0.5398 (4)	0.1436 (3)	0.1643 (3)	0.021
N11	0.5703 (5)	0.1488 (4)	0.0209 (4)	0.022
N12	0.5817 (5)	0.2775 (4)	0.0932 (4)	0.021
N13	0.4379 (5)	0.2609 (4)	-0.0061 (4)	0.018
N14	0.4109 (5)	0.2632 (4)	0.1351 (4)	0.022
N21	0.5822 (5)	-0.0032 (4)	0.2052 (5)	0.028
N22	0.5737 (5)	0.0993 (4)	0.3102 (4)	0.020
N23	0.4394 (5)	-0.0082 (4)	0.2958 (4)	0.024
N24	0.4032 (5)	0.1353 (4)	0.2638 (4)	0.018
C11	0.6484 (6)	0.1807 (6)	0.0327 (6)	0.030
C12	0.6394 (6)	0.2625 (5)	0.0388 (6)	0.029
C13	0.3661 (6)	0.2976 (5)	0.0166 (5)	0.024
C14	0.3809 (6)	0.3262 (5)	0.0909 (5)	0.020
C21	0.6383 (7)	-0.0073 (7)	0.2690 (8)	0.050
C22	0.6502 (7)	0.0631 (7)	0.3008 (6)	0.039
C23	0.3575 (6)	0.0174 (5)	0.3051 (5)	0.023
C24	0.3613 (6)	0.0984 (6)	0.3208 (5)	0.027
Anions				
O13	0.3010 (2)	0.31858 (13)	0.3401 (2)	0.031
O31	0.2295 (5)	0.3592 (5)	0.3427 (5)	0.049
O32	0.3610 (5)	0.3544 (4)	0.3841 (4)	0.039
O33	0.2904 (6)	0.2464 (4)	0.3665 (5)	0.062
O34	0.3220 (6)	0.3163 (6)	0.2683 (4)	0.059
S4	0.53695 (14)	0.31919 (12)	0.31573 (12)	0.0176
S5	0.6557 (2)	0.29409 (13)	0.29852 (13)	0.0233
S6	0.5445 (2)	0.45982 (12)	0.99305 (12)	0.0216
O41	0.5042 (4)	0.3446 (4)	0.2470 (3)	0.025
O42	0.5401 (4)	0.3779 (3)	0.3681 (3)	0.022
O43	0.5045 (4)	0.2506 (3)	0.3392 (4)	0.026
O51	0.6873 (5)	0.2633 (5)	0.3651 (4)	0.039
O52	0.6876 (5)	0.3641 (4)	0.2797 (5)	0.042
O53	0.6482 (4)	0.2413 (4)	0.2410 (3)	0.026
O61	0.5065 (5)	0.4031 (3)	0.9501 (3)	0.031
O62	0.5670 (5)	0.4355 (4)	1.0639 (4)	0.034
O63	0.6043 (5)	0.4985 (4)	0.9569 (4)	0.037
Water Molecules				
O5 (0.4)	0.728 (2)	0.4683 (12)	0.4015 (13)	0.058 (6)
O6 (0.6)	0.1104 (9)	0.0016 (7)	0.0463 (8)	0.039 (3)
O7 (0.4)	0.1415 (14)	-0.0014 (11)	0.0223 (11)	0.041 (5)
O8 (0.6)	0.7421 (9)	0.0278 (7)	0.1355 (7)	0.040 (3)
O9 (0.5)	0.25000	0.1331 (13)	0.0	0.055 (7)
O10 (0.5)	0.2439 (12)	0.4466 (10)	0.0395 (10)	0.062 (5)

<sup>a</sup>Numbers in parentheses after atoms denote population parameters of those atoms. <sup>b</sup> $U_{iso} = 1/3 \sum_{ij} U_{ij} \bar{a}_i \bar{a}_j a_i^* a_j^*$  for atoms refined with anisotropic thermal parameters.

thermal parameter  $U = 0.05 \text{\AA}^2$ , was used for all the hydrogen atoms. It was only attempted to refine the positional parameters of the hydrogen atom, H3, which is involved in the intramolecular hydrogen bond. The remaining hydrogen atoms were included as fixed contributions to  $F$ . The intramolecular hydrogen bond distances calculated after these refinements were O1-H3 = 1.34 (15) Å and O2-H3 = 1.13 (15) Å, showing that within the experimental accuracy H3 is placed symmetrically between the two oxygen atoms. The weights were changed from unit weights to weights of the form  $w^{-1} = \sigma^2(F) + 0.0013|F|^2$  in the final refinement cycles ( $\sigma(F)$  calculated as  $\sigma(|F|^2)/2F$ ). This weighting scheme was chosen as it gave a uniform distribution of  $\langle w\Delta^2 \rangle$  vs.  $F_o$  and  $(\sin \theta)/\lambda$ . For the oxygen atoms corresponding to the disordered water molecules, refinements with fixed population parameters were alternating with refinements where the population parameters were varied and the thermal parameters fixed. These types of refinements were considered to be convergent when all the shifts relative to the previous refinement of the same type were less than 1 standard deviation. The refined population parameters were pp(O5) = 0.40 (4), pp(O6) = 0.66 (3), pp(O7) = 0.41 (3), pp(O8) = 0.68 (4), pp(O9) = 0.52 (4), and pp(O10) = 0.55 (3). The correlation coefficients were less than 0.5. The possible hydrogen bonds involving the partially populated water molecule sites were analyzed. The knowledge that in hydrogen-bonded O-O systems the

**Table IV.** Possible Hydrogen Bonds A-H...B Involving the Protons of the Cation,  $\Delta, \Lambda - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)]^{4+}$ 

A	H	B	A...B/Å	H...B/Å	A-H...B/deg
O12	H12	O53	2.886 (9)	2.081	170
O1	H1	O9	2.840 (7)	2.18	135
O2	H2	O42 <sup>a</sup>	2.888 (9)	1.81	163
O2	H3	O1	2.429 (9)	1.34	159
N11	H9111	O6 <sup>b</sup>	2.846 (15)	1.98	161
N11	H9112	O42 <sup>c</sup>	2.949 (10)	2.08	159
N12	H9121	O62 <sup>d</sup>	2.929 (10)	2.07	156
N12	H9122	O53	3.026 (10)	2.13	168
N13	H9141	O61 <sup>d</sup>	2.974 (10)	2.12	155
N13	H9142	O32 <sup>c</sup>	3.174 (10)	2.30	161
N14	H9132	O41	2.963 (10)	2.09	160
N21	H9221	O42 <sup>a</sup>	3.249 (11)	2.44	150
N21	H9222	O6 <sup>b</sup>	3.080 (17)	2.34	139
N21	H9222	O8	3.157 (17)	2.43	137
N22	H9211	O43	3.052 (10)	2.33	135
N22	H9211	O53	3.192 (10)	2.44	139
N22	H9212	O61 <sup>c</sup>	2.954 (11)	2.09	161
N23	H9231	O41 <sup>a</sup>	2.967 (10)	2.16	150
N23	H9232	O62 <sup>e</sup>	2.858 (11)	2.20	129
N24	H9241	O43	3.015 (10)	2.16	159
N24	H9242	O31 <sup>f</sup>	2.935 (11)	2.07	161

<sup>a</sup>1 - x, y - 1/2, 1/2 - z. <sup>b</sup>1/2 + x, -y, z. <sup>c</sup>x, 1/2 - y, z - 1/2. <sup>d</sup>x, y, z - 1. <sup>e</sup>1 - x, y - 1/2, 1/2 - z. <sup>f</sup>1/2 - x, 1/2 - y, 1/2 - z.

**Table V.** O-O Distances (Å) and Possible Hydrogen Bonds Less Than 3 Å for the Partially Populated Water Positions<sup>g</sup>

O5 (0.4)-O8 <sup>d</sup> (0.6)	0.90 (3)	O6 (0.6)-O7 (0.4)	0.72 (3)
O5 (0.4)-O2 <sup>f</sup>	2.78 (3)	O6 (0.6)-O32 <sup>e</sup>	2.95 (2)
O5 (0.4)-O7 <sup>f</sup> (0.4)	2.64 (3)	O6 (0.6)-O1 <sup>a</sup>	2.95 (2)
O5 (0.4)-O7 <sup>c</sup> (0.4)	2.85 (4)	O7 (0.4)-O8 <sup>h</sup> (0.6)	2.70 (3)
O5 (0.4)-O6 <sup>f</sup> (0.4)	2.94 (3)	O7 (0.4)-O1 <sup>a</sup>	2.80 (2)
O8 (0.6)-O52 <sup>d</sup>	2.76 (2)	O9 (0.5)-O31 <sup>e</sup>	2.982 (9)
O8 (0.6)-O6 <sup>g</sup> (0.6)	2.78 (2)	O9 (0.5)-O32 <sup>e</sup>	2.998 (8)
		O9 (0.5)-O1 <sup>a</sup>	2.840 (7)
		O10 (0.5)-O10 <sup>a</sup> (0.5)	1.53 (3)
		O10 (0.5)-O63 <sup>b</sup>	2.77 (2)
		O10 (0.5)-O63 <sup>i</sup>	2.94 (2)

<sup>a</sup>1/2 - x, y, -z. <sup>b</sup>1 - x, 1 - y, 1 - z. <sup>c</sup>1/2 + x, 1/2 + y, 1/2 + z. <sup>d</sup>1/2 - x, 1/2 - y, 1/2 - z. <sup>e</sup>1/2 - x, 1/2 - y, 1/2 - z. <sup>f</sup>1 - x, 1/2 + y, 1/2 - z. <sup>g</sup>1/2 + x, -y, z. <sup>h</sup>x - 1/2, -y, z. <sup>i</sup>x - 1/2, 1 - y, z - 1. <sup>j</sup>The population parameter is given in parentheses following the atom to which it belongs.

O-O distances are normally in the range 2.4-3.0 Å leads to restrictions on the population parameters, which are within 1 estimated standard deviation of the refined population parameters (see Table V) pp(O5) = pp(O7) = 0.40 (4), pp(O6) = pp(O8) = 0.60 (4), and pp(O9) = pp(O10) = 0.50 (3). In the final refinement cycles the population parameters for oxygen were fixed at these restricted values. No attempts were made to localize the hydrogen atoms bonded to the water molecules.

The population parameters of 0.4 and 0.6 indicate that the structure cannot be described as an ordered monoclinic structure at lower symmetry. The final model included refinement of the scale factor, positional and anisotropic thermal parameters for all the 38 non-hydrogen atoms of the cation and anions, and positional and isotropic thermal parameters for the six partially populated water positions. The refinement of these 365 parameters converged at the  $R$  values  $R = 0.034$  and  $R_w = 0.042$ . The maximum shift was 0.0156σ. A final difference Fourier map showed no residual density in the region of the water molecules. The largest peak (2.0 e Å<sup>-3</sup>) was found close to the perchlorate group, indicating disorder of this group that could not be resolved. The values of  $|F_o|$  and  $|F_c|$  were examined. This analysis indicated that no correction for secondary extinction was necessary. The final positional parameters of the individual non-hydrogen atoms are given in Table III. The anisotropic thermal parameters, positional parameters for the hydrogen atoms, and a listing of observed and calculated structure factor amplitudes are available as supplementary material.

## Results and Discussion

Heating (120 °C, 20 h) of solid *cis*-[Ir(en)<sub>2</sub>(H<sub>2</sub>O)(OH)]S<sub>2</sub>O<sub>6</sub> yields  $\Delta, \Lambda - [(en)_2Ir(OH)_2Ir(en)_2](S_2O_6)_2$  quantitatively. From this crude dithionate salt pure salts of the diol cation have been obtained as the tetrabromide dihydrate and the tetraperchlorate

monohydrate. The perchlorate salt of the diol dissolves in strong perchloric acid, giving quantitatively the acid form of the corresponding monohydroxo-bridged complex,  $\Delta, \Lambda$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(H<sub>2</sub>O)]<sup>5+</sup> (diaqua monool), and by subsequent addition of the appropriate amount of base the perchlorate of the aquahydroxo monool cation,  $\Delta, \Lambda$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O, can be precipitated. A dithionate monohydrate and a mixed dithionate perchlorate of this cation have also been characterized, and the crystal structure of the latter salt is described below. Solid aqua hydroxo monool (dithionate or perchlorate) is stable for months at room temperature.

**Crystal Structure of the Aqua Hydroxo Monool Salt  $\Delta, \Lambda$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)](S<sub>2</sub>O<sub>6</sub>)<sub>3/2</sub>(ClO<sub>4</sub>)·2.75H<sub>2</sub>O.** The interactions between the ions in the crystal are strongly dominated by hydrogen bonds between the dinuclear cations, anions, and water of crystallization. The fact that the water in the structure is distributed over six partially populated positions leads to different possible geometrical patterns for the hydrogen-bonding system.

The hydrogen atoms of the cation, which all were localized in the difference density map, are involved in the hydrogen bonds listed in Table IV. These hydrogen bonds are mainly to the oxygen atoms of the anions. The bifurcated hydrogen bonds from N21 to O6 and O8 as well as from N22 to O43 and O53 exhibit the same geometric features as the similar bifurcated hydrogen bonds observed in the neutron diffraction study of  $\alpha$ -glycine.<sup>30</sup> The remaining hydrogen bonds are of the more common almost linear geometry. It is considerably more difficult to describe the hydrogen bonds in which the water molecules occupying the partially populated sites are involved. In Table V are listed interatomic distances less than 3 Å from the water oxygen atoms to other atoms in the structure. An inspection of this table reveals why certain constraints were imposed on the population parameters. The distances can be rationalized in terms of different but energetically similar hydrogen-bonding systems with O(H<sub>2</sub>O)-O-(H<sub>2</sub>O) distances in the range 2.6–2.8 Å similar to the O-O distances observed in other hydrates.<sup>31</sup> A stereopair showing these complex intermolecular interactions is provided as supplementary material.

The shortest hydrogen bond is the intramolecular bond between the terminally coordinated aqua and hydroxo groups, O(H<sub>2</sub>O)-O(OH) = 2.429 (9) Å. The hydrogen atom is, within the experimental uncertainty, placed symmetrically between the two oxygen atoms with an O-H-O angle of ca. 160°. However, on the basis of the X-ray diffraction data alone, we cannot rule out completely that this hydrogen bond is asymmetric. The interactions in this system are so strong that, according to Bino et al.,<sup>32-34</sup> it should be classified as an independent ion, hydrogen oxide H<sub>3</sub>O<sub>2</sub><sup>-</sup>. In *cis*-aquahydroxobis(2-pyridylmethylamine)-chromium(III) dithionate there are similar interactions between cations related by a 2-fold screw axis, although the O(H<sub>2</sub>O)-O(OH) distance is longer (2.586 (6) Å) and in this structure the Cr-O(H<sub>2</sub>O) and Cr-O(OH) distances are significantly different.<sup>35</sup> The two chromium complex cations related by the

**Table VI.** Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in the Cation

Ir1-O12	2.077 (6)	Ir2-O12	2.082 (6)
Ir1-O1	2.070 (7)	Ir2-O2	2.074 (6)
Ir1-N11	2.054 (8)	Ir2-N21	2.083 (9)
Ir1-N12	2.063 (8)	Ir2-N22	2.058 (8)
Ir1-N13	2.075 (7)	Ir2-N23	2.073 (8)
Ir1-N14	2.087 (8)	Ir2-N24	2.079 (8)
N11-C11	1.456 (14)	N21-C21	1.494 (16)
N12-C12	1.495 (14)	N22-C22	1.481 (15)
N13-C13	1.483 (13)	N23-C23	1.493 (13)
N14-C14	1.488 (12)	N24-C24	1.490 (13)
C11-C12	1.497 (14)	C21-C22	1.42 (2)
C13-C14	1.505 (13)	C23-C24	1.500 (14)
O1-Ir1-O12	90.8 (3)	O2-Ir2-O12	91.9 (2)
N11-Ir1-O12	85.4 (3)	N21-Ir2-O12	86.5 (3)
N12-Ir1-O12	88.5 (3)	N22-Ir2-O12	89.0 (3)
N13-Ir1-O12	178.1 (8)	N23-Ir2-O12	177.3 (3)
N14-Ir1-O12	96.8 (3)	N24-Ir2-O12	96.0 (3)
N11-Ir1-O1	91.7 (3)	N21-Ir2-O2	94.3 (3)
N12-Ir1-O1	173.9 (4)	N22-Ir2-O2	176.8 (3)
N13-Ir1-O1	87.5 (3)	N23-Ir2-O2	85.8 (3)
N14-Ir1-O1	90.3 (3)	N24-Ir2-O2	87.9 (3)
N11-Ir1-N12	82.2 (3)	N21-Ir2-N22	82.6 (3)
N13-Ir1-N14	82.5 (3)	N23-Ir2-N24	82.3 (3)
Ir1-O12-Ir2	131.9 (3)	Ir2-O2-O1	107.4 (3)
Ir1-O1-O2	111.0 (3)	Ir2-N21-C21	106.3 (7)
Ir1-N11-C11	111.1 (6)	Ir2-N22-C22	110.3 (6)
Ir1-N12-C12	108.4 (6)	Ir2-N23-C23	108.0 (6)
Ir1-N13-C13	109.0 (6)	Ir2-N24-C24	109.8 (6)
Ir1-N14-C14	109.0 (6)	N21-C21-C22	111.5 (10)
N11-C11-C12	107.9 (8)	N22-C22-C21	110.3 (9)
N12-C12-C11	108.0 (8)	N23-C23-C24	107.4 (8)
N13-C13-C14	109.5 (8)	N24-C24-C23	108.2 (8)
N14-C14-C13	107.0 (7)		
N11-C11-C12-N12	52.2 (10)	N21-C21-C22-N22	48.9 (13)
N13-C13-C14-N14	-53.2 (10)	N23-C23-C24-N24	53.9 (10)

**Table VII.** Bond Lengths (Å) and Bond Angles (deg) in the Anions

Perchlorate			
C13-O31	1.428 (9)	O31-C13-O32	109.0 (5)
C13-O32	1.433 (8)	O31-C13-O33	109.6 (6)
C13-O33	1.418 (8)	O31-C13-O34	108.3 (5)
C13-O34	1.429 (9)	O32-C13-O33	108.4 (5)
		O32-C13-O34	110.7 (5)
		O33-C13-O34	110.8 (6)
Dithionate			
S6-S6'	2.132 (4)	S6'-S6-O61	105.1 (3)
S6-O61	1.439 (7)	S6'-S6-O62	104.1 (3)
S6-O62	1.440 (7)	S6'-S6-O63	104.8 (3)
S6-O63	1.446 (8)	O61-S6-O62	113.1 (4)
		O61-S6-O63	112.6 (4)
		O62-S6-O63	115.8 (5)
S4-S5	2.121 (4)		
S4-O41	1.458 (7)	S5-O51	1.450 (8)
S4-O42	1.454 (7)	S5-O52	1.434 (8)
S4-O43	1.442 (7)	S5-O53	1.450 (7)
S5-S4-O41	104.2 (3)	S4-S5-O51	104.7 (3)
S5-S4-O42	105.5 (3)	S4-S5-O52	103.3 (3)
S5-S4-O43	104.5 (3)	S4-S5-O53	102.6 (3)
O41-S4-O42	111.8 (4)	O51-S5-O52	115.5 (5)
O41-S4-O43	114.6 (4)	O51-S5-O53	114.1 (4)
O42-S4-O43	114.8 (4)	O52-S5-O53	114.5 (5)

crystallographic 2-fold symmetry in the bipyridine complex *cis*-[(bpy)<sub>2</sub>Cr(H<sub>2</sub>O)(OH)]I<sub>2</sub>·H<sub>2</sub>O interact by a very short H<sub>2</sub>O-OH hydrogen bond with an O-O separation of 2.444 (8) Å. The Cr-O-O-Cr fragment assumes a gauche conformation with a torsion angle of 64°. Although the O-O distance is similar in the present structure, the dihedral angle of the Ir1-O1-O2-Ir2

(29)  $\Delta$  and  $\Lambda$  refer to the absolute configurations around the two iridium(III) centers of the binuclear complexes, and it is noted that the present hydroxo-bridged complexes are all *meso* compounds. Strictly speaking, however, the unsymmetrical cation [(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)]<sup>4+</sup> may exist in the two diastereoisomers  $\Delta, \Lambda$  and  $\Lambda, \Delta$ . These diastereoisomers, however, will interconvert rapidly since only acid-base processes are involved. From this dynamical point of view it seems reasonable to consider the terminally coordinated hydroxo and water groups as indistinguishable, and in the text we have therefore chosen to consider the aqua hydroxo complex as a *meso* isomer,  $\Delta, \Lambda$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)]<sup>4+</sup>. Furthermore, it is noted that a symmetrical intramolecular hydrogen bond between the terminally coordinated OH and OH<sub>2</sub> groups leads to a true identity of these groups, as shown in the crystal structure of  $\Delta, \Lambda$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)](S<sub>2</sub>O<sub>6</sub>)<sub>3/2</sub>ClO<sub>4</sub>·2.75H<sub>2</sub>O.

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Table VIII

complex	M-O-M/deg	M-M/Å	(M-O)/Å	ref
$\Delta, \Delta$ -[(en) <sub>2</sub> Cr(OH) <sub>2</sub> Cr(en) <sub>2</sub> ] <sup>4+</sup>	100.0 (2)	3.032 (3)	1.979 (5)	a
$\Delta, \Delta$ -[(OH)(en) <sub>2</sub> Cr(OH)Cr(en) <sub>2</sub> (OH)] <sup>3+</sup>	135.4 (2)	3.677 (2)	1.988 (6)	37
<i>cis</i> -[(NH <sub>3</sub> ) <sub>5</sub> Cr(OH)Cr(NH <sub>3</sub> ) <sub>4</sub> (OH)] <sup>4+</sup>	142.8 (5)	3.744 (3)	1.975 (15)	b
<i>trans</i> -[(H <sub>2</sub> O)(NH <sub>3</sub> ) <sub>4</sub> Cr(OH)Cr(NH <sub>3</sub> ) <sub>5</sub> ] <sup>5+</sup>	155.1 (3)	3.873 (2)	1.983 (1)	c
[(NH <sub>3</sub> ) <sub>5</sub> Cr(OH)Cr(NH <sub>3</sub> ) <sub>5</sub> ] <sup>5+</sup>	166 (1)	3.852 (9)	1.94 (2)	d
[(NH <sub>3</sub> ) <sub>5</sub> CrOCr(NH <sub>3</sub> ) <sub>5</sub> ] <sup>4+</sup>	180.0	3.642 (1)	1.821 (3)	e
$\Delta, \Delta$ -[(H <sub>2</sub> O)(en) <sub>2</sub> Ir(OH)Ir(en) <sub>2</sub> (OH)] <sup>4+</sup>	131.9 (3)	3.7965 (8)	2.076 (6)	this work

<sup>a</sup>Cline, S. J.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1662. <sup>b</sup>Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1980**, *19*, 3116. <sup>c</sup>Cline, S. J.; Glerup, J.; Hodgson, D. J.; Jensen, G. S.; Pedersen, E. *Inorg. Chem.* **1981**, *20*, 2229. <sup>d</sup>Veal, J. T.; Jeter, D. Y.; Hempel, J. C.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1973**, *12*, 2928. <sup>e</sup>Yevitz, M.; Stanko, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1512.

Table IX. Kinetic and Thermodynamic Data at 25 °C and Unit Ionic Strength, (Na,H)ClO<sub>4</sub><sup>a</sup>

reacn	10 <sup>6</sup> k/ s <sup>-1</sup>	ΔH <sup>‡</sup> / kJ mol <sup>-1</sup>	ΔS <sup>‡</sup> / J mol <sup>-1</sup> K <sup>-1</sup>
k <sub>1</sub>	1.48 (11)	113 (2)	22 (6)
k <sub>-1</sub>	0.258 (35)	114 (4)	13 (14)
k <sub>-2</sub>	0.51 (8)	81 (8)	-94 (27)
reacn	10 <sup>4</sup> k/ s <sup>-1</sup> M <sup>-1</sup>	(ΔH <sup>‡</sup> - ΔH <sup>‡0</sup> )/ kJ mol <sup>-1</sup>	(ΔS <sup>‡</sup> - ΔS <sup>‡0</sup> )/ J mol <sup>-1</sup> K <sup>-1</sup>
k = k <sub>2</sub> /K <sub>a3</sub>	2.40 (5)	68.8 (17)	-84 (6)
reacn	K	ΔH <sup>‡0</sup> / kJ mol <sup>-1</sup>	ΔS <sup>‡0</sup> / J mol <sup>-1</sup> K <sup>-1</sup>
K <sub>a1</sub>	10 <sup>-1.91</sup> (2) M	10.8 (67)	-1 (22)
K <sub>a2</sub>	10 <sup>-9.04</sup> (3) M	53.3 (50)	6 (14)
K <sub>1</sub>	5.7 (8)	-1.5 (47)	10 (15)

<sup>a</sup>See eq 1-3 and Scheme I.

system is 7.4° and corresponds to a *cis* conformation. The strong hydrogen bonds that are formed between a carboxylate group and a carboxylic acid have very similar O-O separations.<sup>36</sup>

In Table VIII are listed some structural details for other dinuclear complexes in which oxygen acts as a bridging ligand. The Ir1-Ir2 distance in the present structure as well as the Ir1-O12-Ir2 angle show that this complex is structurally closely related to the monool complex ( $\mu$ -hydroxo)bis[bis(ethylenediamine)hydroxochromium(III)] triperchlorate monohydrate.<sup>37</sup> The two non-bridging hydroxo groups in this complex interact through an intramolecular hydrogen bond with an O-O distance of 2.729 (6) Å. This indicates that the geometry of the M-OH-M system in monohydroxo-bridged binuclear complexes is not significantly affected by the strength of intramolecular hydrogen bonds. The Ir1-O1 and Ir2-O2 bond lengths are virtually identical (within the experimental error), 2.070 (7) and 2.074 (6) Å, respectively, which supports the evidence for a symmetrical H<sub>2</sub>O-OH<sup>-</sup> bridge. The two Ir-O distances to the bridging hydroxo group are of similar magnitude, Ir1-O12 = 2.077 (6) Å and Ir2-O12 = 2.082 (6) Å. An inspection of the bond angles and bond lengths listed in Table VI reveals that if only the arrangement of the ligating atoms is considered, the dinuclear cation has mirror plane symmetry. The absolute configuration around the two Ir atoms is  $\Delta$  and  $\Lambda$ , respectively. The Ir-N(en) distances are identical, (Ir-N) = 2.072 Å, and similar to the Ir-N(en) bond lengths found in *mer*-[Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O and *mer*-[Ir(en)(en\*)Cl<sub>3</sub>].<sup>38,39</sup> From the drawing of the cation in Figure 1 and the torsion angles listed in Table VI, it is apparent that with regard to the conformations of the ethylenediamine ligands the cation does not possess mirror plane symmetry. Although the four en groups can be assigned *gauche* conformations, the two groups N11-C11-C12-N12 and N21-C21-C22-N22 are related by the symmetry of a 2-fold axis. However, both the short C21-C22 bond of 1.42 (2) Å and the thermal parameters of C21 might indicate that the crystal also contains a small proportion of the N21-C21-C22-

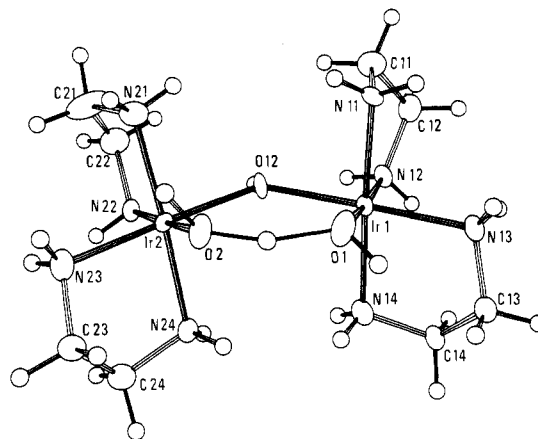
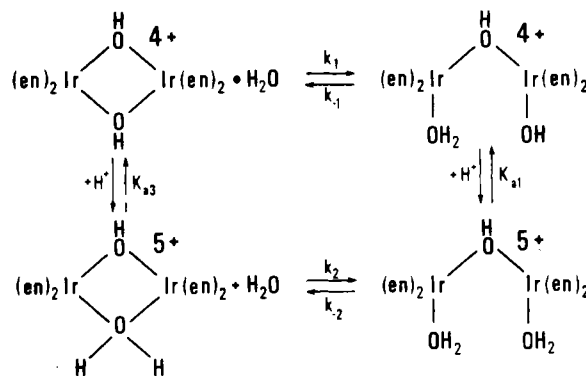


Figure 1. Perspective view of the cation in  $\Delta, \Delta$ -[(H<sub>2</sub>O)(en)<sub>2</sub>Ir(OH)Ir(en)<sub>2</sub>(OH)](S<sub>2</sub>O<sub>6</sub>)<sub>3/2</sub>ClO<sub>4</sub>·2.75H<sub>2</sub>O. The thermal ellipsoids are scaled to include 50% probability. The hydrogen atoms are drawn as spheres with radii of 0.1 Å.

Scheme I



N22(en) group in another conformation. Table VII gives the molecular dimensions of the anions in the structure. The conformation of the dithionate ion placed on a general position is almost staggered, the dihedral angle O51-S5-S4-O41 being 175.7 (4)°, making it similar to the dithionate ion, which is placed on a crystallographic center of inversion. The geometries of both ions are similar to those found for dithionate ions in other crystal structures.<sup>40-42</sup> Similarly the bond lengths and bond angles within the perchlorate ion agree well with those found in other salts of this ion.<sup>37</sup>

**Spectral Data and Acid-Base Properties of the Dimers.** Spectral data for the diol,  $\Delta, \Delta$ -[(en)<sub>2</sub>Ir(OH)<sub>2</sub>Ir(en)<sub>2</sub>]<sup>4+</sup>, extrapolated back to the time of dissolution are given in Table I. It is noteworthy that the same spectrum has been obtained for [H<sup>+</sup>] varying from 1.0 to 10<sup>-13</sup> M. This implies that protonation of the diol to give an aqua-bridged species must be negligible for [H<sup>+</sup>] ≤ 1.0 M and

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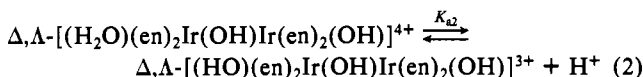
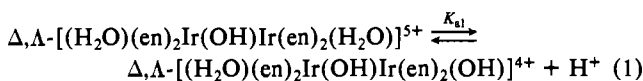
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therefore that  $K_{a3} \gg 1$  (see Scheme I). The significant difference (see footnote a in Table I) between the spectrum in 1 M NaOH and the spectra at  $[\text{OH}^-] \leq 0.1$  M indicates that deprotonation to form an oxo-bridged cation  $\Delta, \Delta\text{-}[(\text{en})_2\text{Ir}(\text{O})(\text{OH})\text{Ir}(\text{en})_2]^{3+}$  takes place in the strong basic solution and that the acid dissociation constant for this process is  $K_a \leq 10^{-14}$  M. The corresponding chromium(III) complex<sup>15</sup> has  $K_a \sim 10^{-12}$  M.

The absorption spectra of solutions of  $\Delta, \Delta\text{-}[(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})\text{Ir}(\text{en})_2(\text{OH})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$  were measured in the  $[\text{H}^+]$  region  $1.0 \geq [\text{H}^+] \geq 10^{-14}$  M. The spectra could be interpreted in terms of the acid-base equilibria 1 and 2.

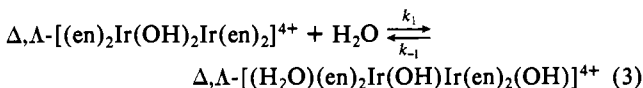


The spectral data in the acidic region allowed a determination of  $\text{p}K_{a1}$ , which was confirmed within experimental uncertainty by glass-electrode measurements. The second acid dissociation constant,  $K_{a2}$ , was determined by glass-electrode measurements alone. The results are shown in Table IX. Spectral data for the three monool cations are presented in Table I.

The difference between the two  $\text{p}K_a$  values is 7.1, which is much greater than the difference of 1.85 units between the two  $\text{p}K_a$  values<sup>21</sup> for the monomeric complex  $\text{cis-}[\text{Ir}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ . A similar large separation between the  $\text{p}K_a$  values has also been observed for monools of rhodium(III)<sup>11,12</sup> and chromium(III),<sup>15-17</sup> and has been explained on the basis of intramolecular hydrogen bond formation. In the case of the aqua hydroxo monools, where terminally bound  $\text{H}_2\text{O}$  donates hydrogen to terminally bound  $\text{OH}^-$ , the hydrogen bond should be stronger than in the diaqua or dihydroxo monools, since coordinated water is a better hydrogen donor than coordinated hydroxide, which in turn is a better hydrogen acceptor than water. The present crystal structure substantiates this proposal, and it seems likely that the very strong intramolecular hydrogen bond interaction observed in the crystal also exists in solution.

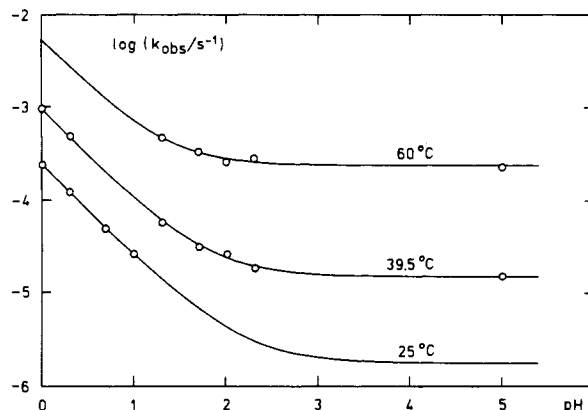
**Thermodynamics and Kinetics of the Equilibrium between Monool and Diol.** The thermodynamics and kinetics of the equilibration between monool and diol were studied spectrophotometrically in the  $[\text{H}^+]$  region  $1.0 \geq [\text{H}^+] \geq 10^{-5}$  M.

The absorption spectra of aqueous solutions of salts of monool or diol changed with time and became constant and identical within hours ( $[\text{H}^+] = 1.0$  M) or weeks ( $[\text{H}^+] = 10^{-5}$  M) at 25 °C. These final spectra are therefore those of equilibrium mixtures as defined by eq 1 and eq 3.



The equilibrium constant  $K_1 = k_1/k_{-1}$  was determined spectrophotometrically (1 M  $\text{NaClO}_4$  solutions equilibrated at pH  $\sim 6$ ). At this pH the diol cation will have its highest relative concentration, and the stoichiometry can be expressed by eq 3 only. Solutions equilibrated in the acidic or basic regions contain negligible amounts of diol due to the equilibria given in eq 1 and 2. It is therefore difficult to measure  $K_1$  in these pH regions. The determination was complicated by the fact that the molar absorption coefficients of the two species differ at most by  $\sim 13\%$ . In cases where  $K_1$  is either considerably smaller than 1 or, as in the present case, considerably larger than 1, this means that small errors in the experimental absorbances will give rise to very large errors in  $K_1$ . The results obtained from measurements at 25, 40, 60, and 80 °C are given in Table IX.

The equilibrium constant  $K_1$  was also determined by glass-electrode measurements; i.e., the content of aqua hydroxo monool in equilibrated mixtures was determined by a normal titration with base. Two necessary prerequisites for such a titration are that the diol does not exhibit acid-base properties in the buffer region for the monool (pH  $\sim 9$ ) and that other reactions between the



**Figure 2.** Plot of observed pseudo-first-order rate constants,  $k_{\text{obs}}$ , obtained for solutions initially containing diol (O) as a function of  $\text{pH} = -\log [\text{H}^+]$ . The solid lines represent values of  $k$  calculated by eq 4 with the parameters given in Table IX.

bridged species during the titrations can be ignored. Both requirements are fulfilled in the present case. One experiment at 60 °C gave the value  $K_1 = 6.0$  (5), which is in agreement with the value  $K_1 = 5.4$  at 60 °C obtained from the spectrophotometric data (Table IX). The value  $K_1 = 5.7$  at 25 °C in the present system is of the same order of magnitude as in the corresponding rhodium(III) ammine and ethylenediamine systems ( $K_1 = 3.0$  and 11.2, respectively)<sup>11,12</sup> and the corresponding chromium(III) ammine and ethylenediamine systems ( $K_1 = 0.32$  and 0.75, respectively).<sup>15,16</sup>

Kinetic data were obtained from spectrophotometric measurements, and pseudo-first-order constants,  $k_{\text{obs}}$ , for solutions initially containing pure diol were calculated using nonlinear regression analysis. Kinetic measurements were made for  $[\text{H}^+]$  varying from 1.0 to  $\sim 10^{-5}$  M and at 25.0, 39.5, and 60 °C. As mentioned, the change in absorbance for solutions initially containing monool is negligible (low pH) or very small (neutral pH), and kinetic measurements starting with this species were therefore not made.

The stoichiometry of the equilibrium mixture is defined by eq 1 and 3, but the kinetic data require an additional, acid-catalyzed reaction path as shown in Scheme I. Since  $K_{a3} \gg [\text{H}^+]$ , as shown above, this scheme yields rate expression<sup>11,16</sup> 4. Two of the

$$k_{\text{calcd}} = k_1 + \frac{[\text{H}^+]K_1k_{-2}}{K_{a1}} + \frac{K_{a1}K_1^{-1}k_1 + [\text{H}^+]k_{-2}}{K_{a1} + [\text{H}^+]} \quad (4)$$

parameters,  $K_1$  and  $K_{a1}$ , have been determined in separate experiments as described above. From these values, the two rate constants,  $k_1$  and  $k_{-2}$ , were determined by the method of nonlinear regression analysis (Figure 2) and gave the parameter values shown in Table IX. A listing of the observed and calculated rate constants, from eq 4, is given in the supplementary material.

The kinetic data for the ethylenediamine-iridium(III) system may be compared with those for the rhodium(III)<sup>11,12</sup> and chromium(III)<sup>15-17</sup> systems with ammonia or ethylenediamine as nonbridging ligands. For iridium(III), rhodium(III), and chromium(III), the bridge-cleavage reactions proceed by both an uncatalyzed and an acid-catalyzed path, although the presumed acid-catalyzed path in the chromium ethylenediamine systems (meso and racemic) does not contribute significantly to the rate for  $[\text{H}^+] \leq 1.0$  M. The activation parameter  $\Delta H^\ddagger(k_1) = 113$  (2)  $\text{kJ mol}^{-1}$  for the uncatalyzed bridge-cleavage reactions in the present system may be compared with those for the ethylenediamine systems of rhodium(III)<sup>11</sup> ( $\Delta H^\ddagger(k_1) = 86$  (3)  $\text{kJ mol}^{-1}$ ) and chromium(III)<sup>15</sup> ( $\Delta H^\ddagger(k_1) = 79.9$  (19)  $\text{kJ mol}^{-1}$ ), and it should be noted that the order  $\text{Ir} > \text{Rh} > \text{Cr}$  is consistent with the kinetic data for corresponding monomeric species, e.g. the data for water exchange of  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ .<sup>43</sup> The acid-catalyzed

(43) Gamsjäger, H.; Murmann, R. K. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 317.

path is proposed to involve protonation of one hydroxo bridge to give a labile aqua-bridged intermediate, which, however, was not identified. Spectroscopic results indicate that this species is a very strong acid with  $K_{a3} \gg 1.0$ , and similar strongly acidic properties have been estimated for the corresponding rhodium(III) and chromium(III) intermediates.<sup>11,15</sup>

The quantity  $(k_2/K_{a3})/k_1$  gives the ratio between the rate of acid-catalyzed bridge cleavage at  $[H^+] = 1 \text{ M}$  and the rate of uncatalyzed bridge cleavage. This ratio is approximately 160 in the present iridium(III) system, while it was found to be 300 in the rhodium(III) system.<sup>11</sup> In the chromium(III) system, for which the acid-catalyzed path could not be determined, an upper limit value of 0.05 has been estimated.<sup>15,16</sup> The considerably enhanced relative efficiency of the acid-catalyzed path in iridium(III) and rhodium(III) compared with chromium(III) could be due to the differences in  $K_{a3}$ , which would correspond qualitatively to the greater acidity of monomeric chromium(III) complexes than complexes of iridium(III) and rhodium(III).<sup>11,21,44,45</sup>

Both  $k_{-1}$  and  $k_{-2}$  refer to reactions in which the leaving group is a water ligand, and since coordinated hydroxide is a much better nucleophile than coordinated water, an associative mechanism would predict  $\Delta H^*(k_{-1}) < \Delta H^*(k_{-2})$ , whereas a dissociative mechanism would predict  $\Delta H^*(k_{-1}) \sim \Delta H^*(k_{-2})$ . The  $\Delta H^*$  values in the present iridium(III) system therefore suggest a large degree of dissociative behavior. The observation that  $\Delta H^*(k_{-2})$  seems to be significantly smaller than  $\Delta H^*(k_{-1})$  might be explained by the possible influence on  $\Delta H^*$  by intramolecular hydrogen-bond formation in the aqua hydroxo monool. The effect of such interactions on the activation parameters would be an increase in  $\Delta H^*(k_{-1})$  relative to  $\Delta H^*(k_{-2})$ , since in the  $k_{-1}$  path the hydrogen bond has to be broken prior to bridge formation. The observation that in the rhodium(III) system  $\Delta H^*(k_{-1}) < \Delta H^*(k_{-2})$  for ammonia<sup>12</sup> but  $\Delta H^*(k_{-1}) \sim \Delta H^*(k_{-2})$  for ethylenediamine<sup>11</sup> may in part be rationalized in terms of the observed differences in the degree of intramolecular hydrogen-bond stabilization of the aqua hydroxo monools in the two systems.

### Conclusions

The observation that the equilibration between mono- and dihydroxo-bridged iridium(III) complexes proceeds by an uncatalyzed and an acid-catalyzed path is in keeping with the results obtained for the analogous ammine and amine complexes of

rhodium(III) and chromium(III). It is concluded that the observed trends in the thermodynamic and kinetic properties of the binuclear systems essentially parallel those observed for corresponding mononuclear systems, but in addition it is found that intramolecular hydrogen bonding in the binuclear species plays a very important role.

The thermodynamic and kinetic data for the iridium(III) system support previous proposals that the aqua hydroxo mono-hydroxo-bridged species are strongly stabilized by an intramolecular hydrogen bond between terminally coordinated hydroxide and water. This proposal is further substantiated by the fact that a strong hydrogen bond interaction of this kind has been found in the crystal structure of  $\Delta, \Delta - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)](S_2O_6)_{3/2}ClO_4 \cdot 2.75H_2O$ .

The impact of such interactions on the thermodynamic properties (e.g. acid strength of terminally coordinated water) and the kinetic properties (e.g. activation parameters of the bridge-formation reaction  $k_{-1}$ ) have been rationalized in a quantitative way.

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**Note Added in Proof.** After submission of our manuscript, we noted that the preparation and X-ray structure determination of another  $\mu$ -hydroxo iridium(III) complex, viz. tris( $\mu$ -hydroxo)bis[( $\eta^5$ -pentamethylcyclopentadienyl)iridium(III)] acetate tetradecahydrate, had been published.<sup>46</sup>

**Registry No.**  $\Delta, \Delta - [(en)_2Ir(OH)_2Ir(en)_2]Br_4$ , 99664-01-4;  $\Delta, \Delta - [(en)_2Ir(OH)_2Ir(en)_2](ClO_4)_4$ , 95179-47-8;  $\Delta, \Delta - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)](ClO_4)_4$ , 99665-01-7;  $\Delta, \Delta - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)](S_2O_6)_2$ , 99618-17-4;  $\Delta, \Delta - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)](S_2O_6)_{3/2}(ClO_4) \cdot 2.75H_2O$ , 99664-03-6;  $[Ir(en)_2(H_2O)(OH)]S_2O_6$ , 91947-50-1;  $\Delta, \Delta - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH_2)](ClO_4)_5$ , 99665-02-8;  $\Delta, \Delta - [(H_2O)(en)_2Ir(OH)Ir(en)_2(OH_2)](S_2O_6)_{5/2}$ , 99618-19-6;  $\Delta, \Delta - [(en)_2Ir(OH)_2Ir(en)_2]^{4+}$ , 95179-46-7;  $\Delta, \Delta - [(HO)(en)_2Ir(OH)Ir(en)_2(OH)]^{3+}$ , 99618-20-9.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, positional parameters for the hydrogen atoms, observed and calculated structure amplitudes, and observed and calculated rate constants for the equilibration reaction between diol and monools and a stereoscopic view of the packing in the unit cell viewed along the  $b$  axis, with the possible hydrogen bonds shown (25 pages). Ordering information is given on any current masthead page.

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