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Kinetic Studies on Substitution Reactions of Delépine's Triangular Mixed-Valence Iridium(III,IV,IV) Complex $[Ir_3(\mu_3\text{-}N)(\mu\text{-}SO_4)_6(H_2O)_3]^{4-}$

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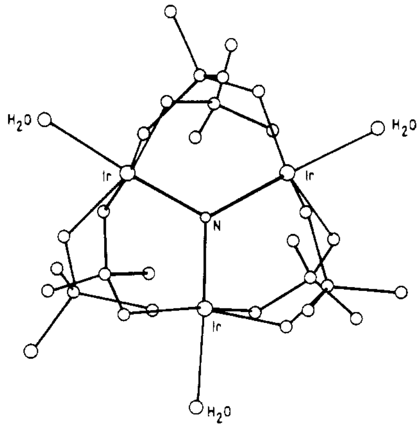
The visible range spectrum of the Ir(III,IV,IV) complex $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ($<10^{-3}$ M) remains unchanged at pHs 0–6 for >48 h, and the acid dissociation pK_a for the H_2O's is >7. Results from kinetic studies at 50 °C, $I = 1.0$ M ($LiClO_4$), are reported with azide, Cl^-, Br^-, and NCS^- as incoming ligands present in large excess. Ligand substitution occurs at the three H_2O sites, one on each metal. Uniphasic kinetics for azide, Cl^-, and Br^- are consistent with a mechanism in which the entering anion cannot distinguish one Ir from another. The three H_2O's are believed to be equivalent, and statistical kinetics hold. With azide at pHs in the range 0.2–4.4 the rate constant k_1 for reaction with N_3H (17.3×10^{-4} M^{-1} s^{-1}) is larger than that for N_3^- ($\sim 1.8 \times 10^{-4}$ M^{-1} s^{-1}) and electrostatics are important. At pH <2 H^+-assisted aquation of azide plays a prominent role, and the extent of complexing is drastically reduced. The rate constant for aquation of the protonated azido complex (acid dissociation p$K \leq -0.7$) is ≥ 0.033 s^{-1}, which is very much bigger than that obtained for the unprotonated azido complex ($\sim 3.5 \times 10^{-8}$ s^{-1}). Rate constants for the equilibration with Cl^- ($k_1 = 3.1 \times 10^{-4}$ M^{-1} s^{-1}; $k_{-1} = 1.6 \times 10^{-4}$ s^{-1}) and Br^- ($k_1 = 16.0 \times 10^{-4}$ M^{-1} s^{-1}; $k_{-1} = 2.4 \times 10^{-4}$ s^{-1}) have been determined under the same conditions. With thiocyanate more complex biphasic kinetics are observed, and N- and S-bonded thiocyanato complexes are believed to be involved. One of the two rate constants 4.3×10^{-4} M^{-1} s^{-1} and 1.67×10^{-4} M^{-1} s^{-1} is relevant in a comparison of k_1 values.

Introduction

Delépine has described the preparation of a series of unusual trinuclear iridium complexes in a series of papers dating from 1906.[1-6] The parent complex, which is the subject of the present study, is readily obtained by refluxing the NH_4^+ or Na^+ salt of $[IrCl_6]^{3-}$ with $(NH_4)_2SO_4$ in concentrated H_2SO_4. Delépine originally assigned the green product the formula $K_4H_2NIr_3(SO_4)_6 \cdot 3H_2O$, with Ir in oxidation state III. More recent analyses and physical measurements are consistent with a mixed-valence trimer Ir(III,IV,IV) of formula $K_4NIr_3(SO_4)_6 \cdot 3H_2O$.[7-9] The structure has been determined[10] and is as illustrated.



$[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$

Features to note are the octahedral coordination about each Ir, the coplanar triangular Ir_3N unit with the central μ_3-nitrido ligand on a threefold axis, six bridging μ-sulfato ligands, and one H_2O coordinated to each metal.

It has been shown that the complex has no unpaired electrons.[9] No electrochemical studies of the complex or redox interconversions have been reported, and the Ir(III,IV,IV) state appears remarkably stable. There are at 4 K two clearly resolved Mössbauer peaks, ratio 2:1, indicating nonequivalent Ir atoms,[9] but this tells little about the state of the Ir's at higher temperatures. No intervalence charge-transfer bands are observed in the 900–1500-nm region.[9]

So far no detailed studies on the solution chemistry of this mixed-valence ion have been carried out. Here we report the kinetics of substitution of the H_2O ligands, as well as some general properties relating to the complex in solution.

Experimental Section

Materials. The title complex was prepared by the method of Brown et al.[9] on the basis of procedures originally used by Delépine. Either ammonium hexachloroiridate(III), $(NH_4)_3[IrCl_6]$ (1 g) or sodium hexachloroiridate(III) (1 g) and $(NH_4)_2SO_4$ (1 g) were added to concentrated H_2SO_4 (15 mL) in a 100-mL round-bottomed flask and refluxed (water condensor) for 8 h. The resulting green solution was cooled to room temperature, diluted with 20 mL of H_2O, filtered, and stored at −17 °C for 2 days. The solid obtained was filtered (glass sinter) and washed with methanol. To convert to the K^+ salt, a Dowex 50W-X2 (400 mesh) column (10 × 1.5 cm) was charged with K^+ by using a 2 M KNO_3 solution. After being washed with H_2O (500 mL), the acid salt (0.4 g) in H_2O (50 mL) was passed down the column. The solution obtained was concentrated to 15 mL and refrigerated at 4 °C for 24 h. The green nonhygroscopic powder obtained (0.2 g) was recrystallized from 2% H_2SO_4. Anal. Calcd for $K_4[Ir_3N(SO_4)_6(H_2O)_3]$: H, 0.44; N, 1.02; Ir, 41.9; SO_4, 41.8. Found: H, 0.41; N, 0.73; Ir, 40.93; SO_4, 42.51. The iridium was determined by the method of Zinser and Page[11] by fuming a sample with concentrated $HClO_4$ for 2 h, followed by treatment with NaCl and heating on a steam bath (7–10 h). Titration of the resulting Ir(IV) chloro complex (predominantly $[IrCl_6]^{2-}$) was carried out iodometrically with NaI and $Na_2S_2O_3$. The sulfate was determined gravimetrically as $BaSO_4$.

Solutions of NaN_3, NaCl, NaBr, and $HClO_4$ (all BDH, AnalaR) were prepared without further purification. A sample of NaNCS (BDH, reagent grade) was recrystallized twice from hot methanol. Solutions were standardized by titration against 0.10 M $AgNO_3$. Ionic strengths were adjusted to 1.0 M with $LiClO_4$ (BDH or Aldrich) which had been recrystallized three times. The stock solution was standardized by exchanging Li^+ for H^+ on an Amberlite IR120(H) ion-exchange resin and titrating the H^+.

Spectrum and Stability. The spectrum of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ in acid solutions (here 0.01 M $HClO_4$) gives absorption peaks (nm) at 440 (ϵ 3940 M^{-1} cm^{-1}/trimer) and 585 (1440) and a minimum at 515 (730). In addition shoulders are noted at around 310, 360, and 660 nm. No change in spectrum was observed over 48 h at 50 °C with pH in the range 1–3. Beer's Law is obeyed at pHs in the range 0–6 with the concentra-

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(1) Delépine, M. *C. R. Hebd. Seances Acad. Sci.* **1906**, *142*, 631, 1525; **1909**, *148*, 557.
(2) Delépine, M. *Bull. Soc. Chim. Fr.* **1909**, *5*, 359, 1084, 1126.
(3) Delépine, M. *C. R. Hebd. Seances Acad. Sci.* **1910**, *151*, 878.
(4) Delépine, M. *Ann. Chim. (Paris)* **1959**, *4*, 1115.
(5) Delépine, M. Lareze, F. *Ibid.* **1959**, *4*, 1131.
(6) Delépine, M. *C. R. Hebd. Seances Acad. Sci.* **1960**, *251*, 2633.
(7) Jørgensen, C. K. *Acta. Chem. Scand.* **1959**, *13*, 196.
(8) Cleare, M. J.; Griffiths, W. P. *J. Chem. Soc. A* **1970**, 1117.
(9) Brown, D. B.; Robin, M. B.; McIntyre, J. D. E.; Peck, W. F. *Inorg. Chem.* **1970**, *9*, 2315.
(10) Ciechanowicz, M.; Griffiths, W. P.; Pawson, D.; Skapski, A. C.; Cleare, M. J. *J. Chem. Soc. D* **1971**, 876.
(11) Zinser, E. J.; Page, J. A. *Anal. Chem.* **1970**, *42*, 787.

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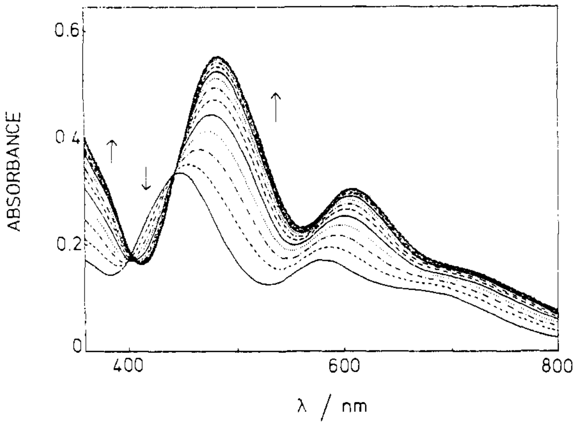

Figure 1. Scan spectra for the reaction (50 °C) of azide with Delépine's complex, $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$, at pH 2. Time interval between spectra 5 min; $[Ir_3] = 1 \times 10^{-4}$ M, $[N_3]_T = 0.5$ M, $I = 1.0$ M ($LiClO_4$).

tion of complex up to at least 1×10^{-3} M. No change in spectrum is observed at pHs 0–6. When the pH was increased to >6, rapidly established absorbance increases were noted at 440 and 585 nm. Over short time intervals these were reversible, but other processes are incident. A 1.0×10^{-4} M solution of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ in CO_2-free water gives a pH of 5.94. It is concluded that the acid dissociation pK_a for an H_2O ligand is >7.

Products and Stoichiometry. We were unable to carry out a satisfactory separation of the highly charged products of substitution by column chromatography. The following observations have helped establish that nature of the reactions. With azide and NCS^- large changes in absorbance are observed. Scan spectra for a typical azide run are shown in Figure 1. The product spectrum is sufficiently like that of the starting complex to suggest that the $Ir_3N(SO_4)_6$ core is retained intact. No sulfate is released and no precipitate of $BaSO_4$ was observed after 6 h of standing with $BaCl_2$ (~0.05 M). Complexes of the kind $K_4[Ir_3N(SO_4)_6L_3]$, where L = pyridine, NH_3, or β-picoline, have been isolated and characterized.[3,6]

A large excess of reactant was used in the present studies with the complex $(0.5–1.0) \times 10^{-4}$ M. Extensive (equilibration) complexation is observed, and substitution of all three H_2O ligands is believed relevant.

Kinetic Studies. The pH of run solutions in the range 1.0–4.4 was measured with a Radiometer (PHM 62) pH meter and Russell combination glass electrode (WR/322), with saturated KCl replaced by NaCl to enable the pH of ClO_4^- solutions to be determined. No buffers were used. The pH meter was calibrated with solutions at $I = 1.0$ M ($LiClO_4$). All kinetic measurements were at 50 °C on a Perkin-Elmer Lambda 5 UV–vis spectrophotometer complete with digital temperature controller. Runs with azide and NCS^- were monitored at 475 nm, and those with Cl^- and Br^-, at 290 nm. Optical cells were carefully stoppered in the case of azide runs to avoid loss of HN_3. Complexing of Cl^- and Br^- for H_2O do not give a big change in absorbance, and the range of halide concentrations was restricted to the higher values. Plots of absorbance changes ln ΔA against time were linear to 3–4 half-lives and gave first-order rate constants k_{eq}, except in the case of NCS^- runs, where a consecutive treatment was required. For those cases in which the final absorbance was uncertain the Guggenheim method was used.[12]

It has been demonstrated that at 22 °C $[Ir(NH_3)_5N_3]^{2+}$ undergoes acid decomposition in 2 M $HClO_4$ to give a coordinated nitrene product and N_2 ($t_{1/2} \sim 3$ h).[13] In the present study, the azido complex aquates much more rapidly and no contribution from such a decomposition was detected. Aquation of the azido complex regenerates the spectrum of the aqua complex. The behavior observed is thus consistent with that of many other azido complexes where only acid-catalyzed aquation occurs.[14,15]

NMR Studies. It has previously been shown that it is sometimes possible to distinguish between N- and S-bonded thiocyanate by ^{14}N NMR,[16] N-bonded complexes having a diagnostic resonance shift δ of between −10 and −100, while S-bonded forms give a positive shift of +0–40, both relative to free thiocyanate. A solution of complex (0.01 M) in 1 M NCS^- at pH 2 was left at 40 °C for 3 h, during which time the color changed from green to green-brown. The resulting NMR spectrum in a 10-mm-diameter tube, run overnight at 20 °C, showed only free thiocyanate and gave no information regarding the nature of bound thiocyanate.

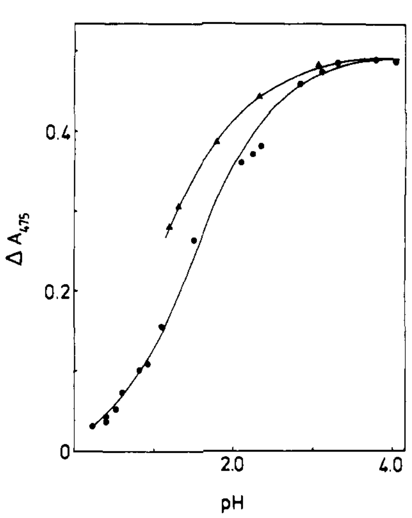

Figure 2. Variation of absorbance change with pH for studies on the reaction of azide 0.40 M (●) and 1.0 M (▲) with $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ (~1×10^{-4} M) at 50 °C, $I = 1.0$ M ($LiClO_4$).

Table I. First-Order Equilibration Rate Constants (50 °C) for the Azide Substitution of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ($(0.5–1.0) \times 10^{-4}$ M), $I = 1.0$ M ($LiClO_4$)

$[N_3]_T = 0.40$ M							
pH	0.22	0.30	0.40	0.50	0.52	0.60	0.60
$10^4k_{eq}/s^{-1}$	47[a]	40[a]	34[a]	27.5[a]	26.1	23.9	23.3[a]
pH	0.82	0.90	1.10	1.50	2.20	2.26	2.33
$10^4k_{eq}/s^{-1}$	15.5	13.5	10.4	8.3	7.4	7.2	7.2
pH	2.85	3.11	3.33	3.80	4.06	4.40	
$10^4k_{eq}/s^{-1}$	6.7	6.1	6.2	5.6	4.8	3.4	
$[N_3]_T = 1.0$ M							
pH	1.18	1.31	1.74	1.78	2.31		
$10^4k_{eq}/s^{-1}$	18.9	20.3	18.9	17.4	14.7		

[a] Obtained by equilibrating with azide at pH ~3, adjusting the pH, and monitoring the subsequent (largely aquation) process.

Treatment of Data. Statistical kinetics are assumed to apply to the replacement of the three H_2O ligands with measured formation rate constants corresponding to the final stage of reaction.[17] Unweighted linear least-squares fits were used in estimating errors.

Results

Reaction with Azide. Absorbance changes are dependent on pH (Figure 3) and on total azide, $[N_3]_T$, the latter consistent with an equilibration process. At pH >3 complexation can be assumed complete with absorbance changes the same for $[N_3]_T = 0.4$ and 1.0 M. The acid dissociation constant for HN_3 is 5.0×10^{-5} M ($pK_a = 4.3$) at 50 °C, $I = 1.0$ M ($NaClO_4$).[18] At the lower pHs the extent of reaction decreases sharply (Figure 2) as protonation and aquation of coordinated azide become increasingly important. First-order rate constants, k_{eq}, are listed in Table I. More precise k_{eq} values at the lower pHs were obtained by equilibrating with azide at pH ~3, adjusting the pH to the required lower value at $[N_3]_T = 0.40$ M, and monitoring the reequilibration process.

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(12) (a) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; p 49. (b) *Ibid.*, p 166.

(13) (a) Lane, B. C.; McDonald, J. W.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 3786. (b) Gafney, H. D.; Reed, J. L.; Basolo, F. *J. Am. Chem. Soc.* **1973**, *95*, 7998.

(14) Davis, C. S.; Lalor, G. C. *J. Chem. Soc. A* **1970**, 445.

(15) Staples, P. J. *J. Chem. Soc. A* **1968**, 2731.

(16) Howarth, O. W.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc.* **1964**, 3335.

(17) Instances in which a sequence of two (pseudo-) first-order reactions conform to a monophasic rather than a biphasic equation, and the conditions that need to be satisfied have been considered previously: (a) Buckingham, D. A.; Frances, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630. (b) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235. (c) Armstrong, F. A.; Henderson, R. A.; Sykes, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 6545.

(18) Castillo-Blum, S.; Sykes, A. G. *Inorg. Chem.* **1984**, *23*, 1049.

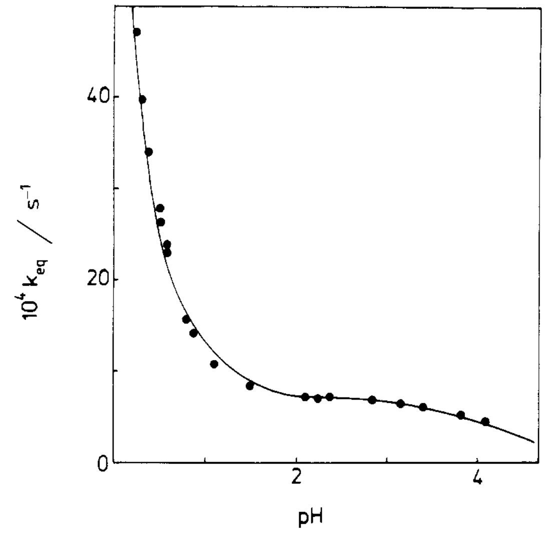


Figure 3. Variation of first-order equilibration rate constants (k_{eq}) with pH for the reaction of azide (0.40 M) with $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ (~1 × 10^{-4} M) at 50 °C, I = 1.0 M ($LiClO_4$). The line drawn is that generated by inserting constants obtained into eq 2.

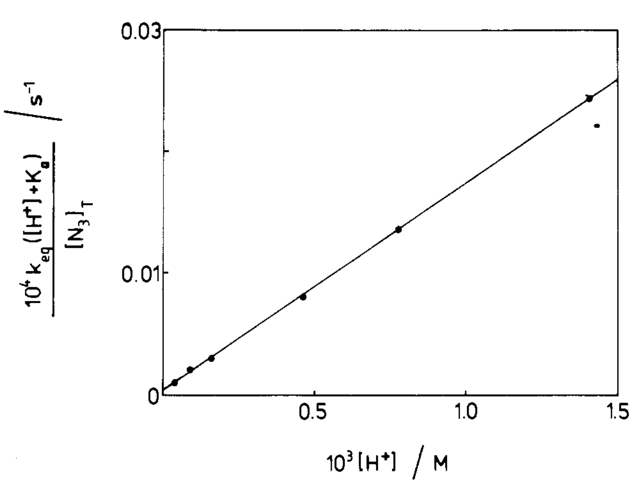
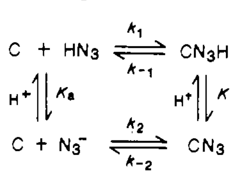


Figure 4. Determination of second-order rate constants (50 °C) for the reaction of azide, k_1 (for HN_3) and k_2 (for N_3^-), with $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$, I = 1.0 M ($LiClO_4$) (eq 3), from equilibration rate constants obtained at pH 3-4.

The variation of k_{eq} with pH at $[N_3]_T$ = 0.40 M is shown in Figure 3. Consistent with the above observations, a reaction scheme as in (1) is proposed, where C represents $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$. This



(1)

gives expression 2. At pH >3, the back-reactions involving k_{-1}

$$k_{eq} = \frac{(k_1[H^+] + k_2K_a)[N_3]_T}{[H^+] + K_a} + \frac{k_{-1}[H^+] + k_{-2}K}{[H^+] + K} \qquad (2)$$

and k_{-2} can be neglected (Figure 2), and (2) simplifies to (3). The

$$\frac{k_{eq}([H^+] + K_a)}{[N_3]_T} = k_1[H^+] + k_2K_a \qquad (3)$$

applicability of (3) is illustrated in Figure 4, which gives k_1 = (17.3 ± 0.1) × 10^{-4} M^{-1} s^{-1} and k_2 = ~1.8 × 10^{-4} M^{-1} s^{-1}. At pH <0.7, K_a is $\ll [H^+]$ and k_2 and k_{-2} can be ignored, and assuming $K \gg [H^+]$, (2) simplifies to (4). It can be seen from Figure 5 that

$$k_{eq} = k_1[N_3]_T + k_{-1}[H^+]/K \qquad (4)$$

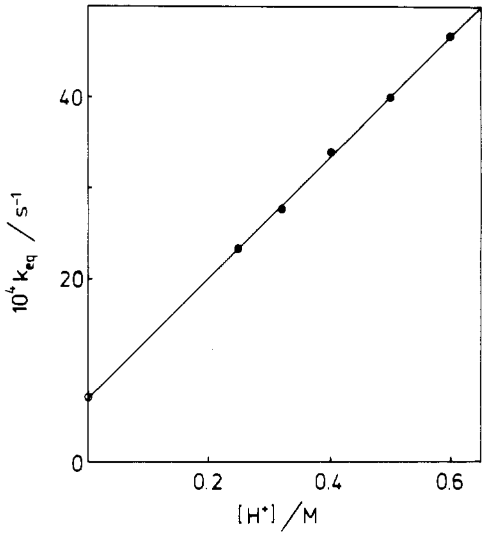


Figure 5. Determination of the rate constant k_{-1} for the aquation of protonated azido complex and the corresponding acid dissociation constant K (eq 4) from equilibration rate constants for the reaction of azide (0.40 M) with $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ (~1 × 10^{-4} M) at pH <0.7, I = 1.0 M ($LiClO_4$).

Table II. First-Order Equilibration Rate Constants (50 °C) for the Reaction of Chloride and Bromide with $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ (~1 × 10^{-4} M), with pH in the Range 2.5–3.0 Except As Stated and I = 1.0 M ($LiClO_4$)

$[Cl^-]$/M	0.5	0.7	0.8	0.9	1.0	
$10^4k_{eq}/s^{-1}$	3.7	3.9	4.2	4.8[a]	4.7	
$[Br^-]$/M	0.5	0.7	0.8	0.9	1.0	1.0
$10^3k_{eq}/s^{-1}$	1.07	1.39	1.46	1.60	1.92[a]	1.86

[a] pH 1.0.

this relationship holds with the intercept (6.7 × 10^{-4} s^{-1}), agreeing with that calculated from the known value of $k_1[N_3]_T$ (6.9 × 10^{-4} s^{-1}). With the inclusion of the latter k_{-1}/K = (67 ± 2) × 10^{-4} M^{-1} s^{-1}. Since it can be concluded that $K \geq 5$ M^{-1} (corresponding to a pK of <−0.7) it follows that k_{-1} is ≥ 0.033 s^{-1}. The ratio Kk_1/k_{-1} can be obtained, and since K_a is known, k_2/k_{-2} is 5.2 × 10^3 M^{-1}. Hence, since an approximate value of k_2 has been determined, k_{-2} is ~3.5 × 10^{-8} s^{-1}. The fit of k_1 (17.3 × 10^{-4} M^{-1} s^{-1}), k_{-1}/K (67 × 10^{-4} M^{-1} s^{-1}), k_2 (1.8 × 10^{-4} M^{-1} s^{-1}), and k_{-2} (3.5 × 10^{-8} s^{-1}) to eq 2 generates the line in Figure 3, which is in good agreement with experimental points.

Reactions with Cl^- and Br^-. Both reactions were monitored at 290 nm. Absorbance changes were small (ΔA = 0.063 for 1 M Cl^- and 0.016 for 1 M Br^-). First-order equilibration rate constants, k_{eq}, are listed in Table II. The dependences on halide ion concentrations are illustrated in Figure 6. The equilibration kinetics conform to (5). For Cl^-, k_1 = (3.1 ± 0.3) × 10^{-4} M^{-1}

$$k_{obsd} = k_1[X^-] + k_{-1} \qquad (5)$$

s^{-1} and k_{-1} = (1.6 ± 0.3) × 10^{-4} s^{-1}, and for Br^-, k_1 = (16.0 ± 1.6) × 10^{-4} M^{-1} s^{-1} and k_{-1} = (2.4 ± 1.3) × 10^{-4} s^{-1}. Equilibrium constants from these values are 1.95 ± 0.3 M^{-1} for Cl^- and 6.5 ± 3.5 M^{-1} for Br^-.

Reaction with NCS^-. Scan spectra, Figure 7, indicate an increase in absorbance and shift in peak positions to higher wavelengths, e.g. 440–475 nm. Absorbance-time changes at a fixed wavelength (generally 475 nm) indicate two principal stages for reaction. The subsequent decrease in absorbance in a less well-defined process corresponds to a further reaction. Although we have tended to ignore this stage (which is slow), its existence makes it more difficult to determine accurately absorbance values corresponding to completion of the second stage (Figure 8). Interpretation of this system is therefore complex. A consecutive reaction treatment of the kind applying to a sequence A → B → C[12b] gives two rate constants (k_a and k_b, Table III). This

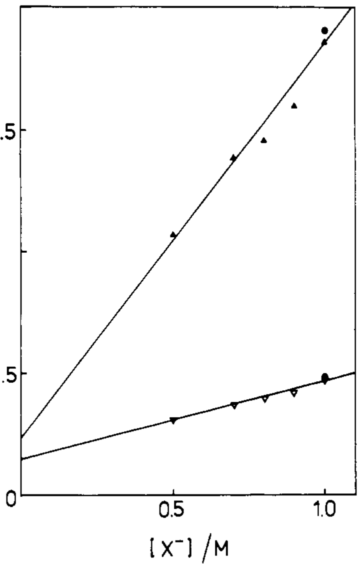


Figure 6. Dependence of k_{eq} (50 °C) for the reactions of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ with $X^- = Cl^-$ (▽) and Br^- (▲) at pH 2.5 and pH 1.0 (●), $I = 1.0$ M ($LiClO_4$).

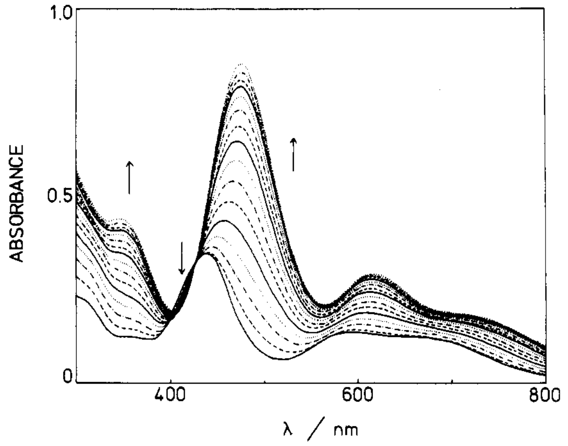


Figure 7. Scan spectra of the reaction (50 °C) of thiocyanate (0.3 M) with $[IrN(SO_4)_6(H_2O)_3]^{4-}$ (1×10^{-4} M) at pH 2. Time interval between spectra 1 h, $I = 1.0$ M ($LiClO_4$).

Table III. First-Order Equilibrium Rate Constants (50 °C) for the Two Stages in the Reaction of Thiocyanate with $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ($(0.5\text{-}1.0) \times 10^{-4}$ M) with pH in the Range 1-3 and $I = 1.0$ M ($LiClO_4$)

$[SCN^-]$, M	10^4k_a(av), s^{-1}	10^4k_b(av), s^{-1}	$[SCN^-]$, M	10^4k_a(av), s^{-1}	10^4k_b(av), s^{-1}
0.1	0.60	0.22	0.6	2.55	1.02
0.2	0.97	0.37	0.7	2.70	1.25
0.3	1.30	0.53	0.8	3.65	1.37
0.4	1.65	0.70	0.9	3.75	1.61
0.5	2.05	0.84	1.0	4.70	1.66

treatment must be regarded as nonrigorous and approximate only, since when $[NCS^-]$ is varied over the range 0.1-1.0 M, it is clear that equilibration processes are involved (Figure 8). In fact, both k_a and k_b appear to give linear $[NCS^-]$ dependences, summarized by (6). The first stage (k_a) gives $k_1 = (4.3 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1} and $k_{-1} = (0.036 \pm 0.15) \times 10^{-4}$ s^{-1}; the second stage (k_b) gives $k_2 = (1.67 \pm 0.04) \times 10^{-4}$ M^{-1} s^{-1} and $k_{-2} = (0.035 \pm 0.025) \times 10^{-4}$ s^{-1}. One but not both thiocyanate dependences is probably valid from such a simplistic treatment.

$$k = k_1[NCS^-] + k_{-1} \qquad (6)$$

Discussion

Mössbauer studies have indicated the presence of two different Ir states per $[Ir_3N(SO_4)_6(H_2O)_3]^{3-}$ trimer (ratio 2:1) at 4 K.[10] The crystallographic equivalence of the metals is not necessarily inconsistent with this finding since the complex may adopt three orientations with equal probability or alternatively there may be time-averaging within a given complex ion. However, at 50 °C, the temperature of the present study, it would be surprising if Ir(III) (t_{2g}^6) and Ir(IV) (t_{2g}^5) states bridged by sulfate (and nitride) did not rapidly electron exchange, leading to equivalence of the Ir atoms. We would not expect the difference in Ir-O bond lengths for the two states to be large, a comparable situation being with $[Ru(H_2O)_6]^{2+}$ (t_{2g}^6) and $[Ru(H_2O)_6]^{3+}$ (t_{2g}^5), where it has been shown that the Ru-O bonds differ by 0.09 Å.[19] This is not to say that once the symmetry has been destroyed by replacement of one of the H_2O ligands, some nonequivalence of the Ir's might not result. With azide, which was studied most extensively, the kinetics are emphatically uniphasic, and this does not appear to be the case. A biphasic process in which the entering group binds preferentially at either an Ir(III) or an Ir(IV) site is ruled out therefore, and the behavior observed is consistent with a mechanism in which the entering group cannot distinguish one Ir from another because internal electron exchange is relatively rapid. We note that one of the crossover points in scan spectra (Figure 1) is not retained, indicating that the three sites do not remain identical and/or entirely independent of one another. This effect is low key and may be no more than the result of changes in overall charge affecting the reactivity (and absorbance) of the complex as the H_2O's are successively replaced.

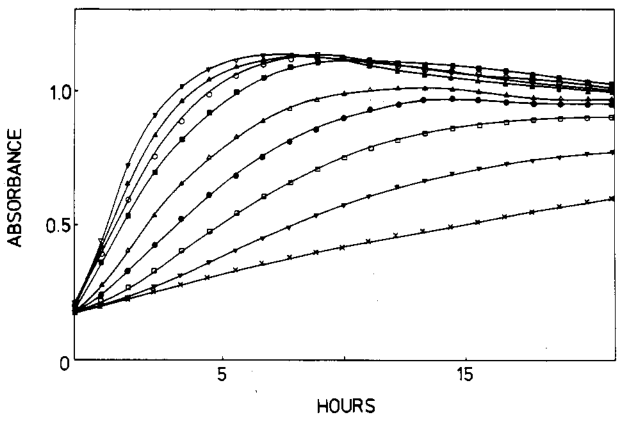


Figure 8. Change in absorbance with time for the reaction (50 °C) of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ($\sim 1 \times 10^{-4}$ M) with thiocyanate, at pH 1-3, $I = 1.0$ M ($LiClO_4$): (×) $[NCS^-] = 0.1$ M; (▼) $[NCS^-] = 0.2$ M; (□) $[NCS^-] = 0.3$ M; (●) $[NCS^-] = 0.4$ M; (△) $[NCS^-] = 0.5$ M; (■) $[NCS^-] = 0.6$ M; (○) $[NCS^-] = 0.8$ M; (▲) $[NCS^-] = 0.9$ M; (▽) $[NCS^-] = 1.0$ M.

Protonation of free azide ($pK_a = 4.3$) is $>10^5$ times more extensive than for coordinated azide ($pK < -0.7$). The latter thus compares with pK_a's obtained for $[Ir(NH_3)_5(N_3H)]^{3+}$ (−2.1)[13a] and $[Rh(NH_3)_5(N_3H)]^{3+}$ (−2.2).[14] It has been found that the rate constant for the reaction of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ with HN_3 is about 10 times that for N_3^-, an effect that stems from the influence of the overall negative charge on the complex. It is possible also that HN_3 forms H bonds to the μ-sulfato ligands. Aquation of the protonated azido complex is $>10^6$ times more favorable than aquation of unprotonated azide. These features explain the behavior observed in Figures 2 and 3, a notable trend being the tendency to much less extensive complex formation at pHs <1 as the H^+-assisted aquation step becomes more influential. In comparison the reactions of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ with Cl^- and Br^- are relatively straightforward, although the precision of individual k_{eq} values suffers from the smallness of absorbance changes. With NCS^- on the other hand, the reaction is biphasic, and a third stage (not yet assigned) is also observed. The most likely explanation of the biphasic behavior is that N- and S-bonded thiocyanato complexes are involved.[18] Iridium(III) is regarded as borderline in the hard and soft acid-base classification.[19] In

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(19) Bernard, P.; Burgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.

Table IV. Summary of Rate Constants (50 °C) for Substitution of H_2O on $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$, I = 1.0 M ($LiClO_4$)

reactant	10^4k_1, M^{-1} s^{-1}	reactant	10^4k_1, M^{-1} s^{-1}
HN_3	17.3	Br^-	16.0
N_3^-	1.8	NCS^-	4.3[a]
Cl^-	3.1		

[a] It is possible that the rate constant 1.67 × 10^{-4} M^{-1} s^{-1} for what appears to be the second process applies.

the present studies the formation constant for the bromo complex is 3 times more favorable than the chloro complex, consistent with the $Ir_3N(SO_4)_6$ core having a preference for the softer reactants. Azide and S-bonded thiocyanate are about equally effective in the spectrochemical series[20] and are expected to shift electronic UV–vis bands to higher wavelengths. An N-bonded thiocyanate is expected to give behavior similar to that of H_2O, if anything giving a small shift to lower wavelengths. On this basis Figures 1 and 5 suggest that the S-bonded thiocyanato complex is the dominant product.

A possible interpretation of the kinetics is that N- and S-bonded thiocyanato complexes are formed concurrently and that the second stage involves isomerization to an equilibrium mixture in which the S-bonded form is predominant. Jackson et al.[23] have commented on the difficulties implicit in kinetic studies of such reactions even for a relatively simple case such as NCS^- with $[Co(NH_3)_5H_2O]^{3+}$. If such a scheme applies in the present study, then the thiocyanate dependences for both k_a and k_b (Table III) and the consecutive treatment applied will not be completely valid. A further point to note is that for consecutive reactions the mathematics do not specify the order of the two exponential terms,[24] and what might appear to be the first stage may in fact be the second. Our experience with other similar systems leads us to believe that the thiocyanate dependence and rate constants obtained are probably meaningful for either k_a or k_b, but not both. Incidence of the third stage excludes a more detailed treatment.

Formation rate constants are compared in Table IV, where for a statistical situation k_1 is for the third stage and should be multiplied by 3 to obtain the rate constant for the reaction in which the first H_2O is replaced.[17] Two possible entries are included for NCS^- (see above). Rate constants obtained are relatively high for substitution at Ir(III) or Ir(IV).[23] According to Ciechanowicz et al.[10] the Ir–N distance of 1.918 Å obtained in the crystal structure determination is somewhat shorter than would be expected for a single bond, suggesting that there is some π-bonding between the $2p_z$ orbital of the N atom (perpendicular to the plane of the complex) and the Ir atoms. It seems likely therefore that the μ_3-nitrido ligand introduces a labilizing effect, although the Ir–O distances (2.005–2.056 Å) and Ir–H_2O distance of 2.059 Å are described as unexceptional.[10] The stability (and retention) of Ir–N bonds in the Ir_3N core throughout a number of reactions, including those in which the bridging sulfates are replaced by terminal chlorides in $[Ir_3NCl_{12}(H_2O)_3]^{4-}$, is noted.[1-6] The comparison in Table IV is also of interest because of the high negative charge on $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$. Substitution studies on cyano complexes are quite extensive, in particular those for Co(III),[26] where the evidence is strongly in favor of a dissociative process. Certainly the high negative charge on $[Ir_3(N(SO_4)_6(H_2O)_3]^{4-}$ is not expected to be conducive to an associative process with negatively charged ligating groups. A further important point with regard to the structure is that the μ-sulfato and μ_3-nitrido ligands are fairly rigidly held and cannot move as the H_2O ligands are replaced. The rate constants obtained differ by a factor of 5–6 for the 1– reactants and give a spread of about 1 order of magnitude overall, with HN_3 benefiting from its neutral charge and possibly also the ability of HN_3 to hydrogen bond to the μ-sulfato ligands. On present information, the most likely mechanism is I_d, with ion-pair formation at a relatively low level due to the similarity of reactant charges.

Herrmann in a recent review[27] has considered the different structure types in which nitride functions as a ligand to transition metals. Examples include $[OsNCl_5]^{2-}$,[28] the μ-bridged complex $[(Br)_5TaNTa(Br)_5]^{3-}$,[29] and the recently prepared complex $[Ru_4(\mu_4\text{-}N)(CO)_{12}(\mu\text{-}NO)]$.[30] The complex $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ is the only example of a trigonal-planar μ_3-N complex. A T-shaped Mo_3N moiety has been reported in $[Mo_3(\mu_3\text{-}N)O(CO)_4(\eta^5\text{-}C_5H_5)_3]$.[31] Together these various examples suggest a varied chemistry that has so far been little studied.

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Registry No. $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$, 103004-19-9; $K_4[Ir_3N(SO_4)_6(H_2O)_3]$, 103004-20-2; N_3^-, 14343-69-2; Cl^-, 16887-00-6; Br^-, 24959-67-9; NCS^-, 302-04-5.

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(20) Schmidtke, H.-H.; *Inorg. Chem.* **1966**, *5*, 1682.

(21) Pearson, R. G. *Chem. Br.* **1969**, 103.

(22) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; p 67.

(23) Jackson, W. G.; Jurisson, S. S.; McGregor, B. C. *Inorg. Chem.* **1985**, *24*, 1788.

(24) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 69–71.

(25) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357.

(26) E.G.: Burnett, M. G.; Gilfillan, W. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1578. Haim, A. *Inorg. Chem.* **1982**, *21*, 2887 and references therein.

(27) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 64.

(28) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 709.

(29) Frank, K.-P.; Strahle, J.; Weidlein, J. *Z. Naturforsch., B: Anofg. Chem., Org. Chem.* **1980**, *B35*, 300.

(30) Hard, J. P.; Johnson, B. F. G.; Lewis, J.; Mace, J. M.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1526.

(31) Feasey, N. D.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 75.