that implies re-formation of the adduct. In a solvent system such as tetrahydrofuran–ethanol, such bis(amine) species would be more labile toward displacement of the amine because of the good donor properties of the solvent molecules.

In spite of the limitations of the rate constant calculations, the proposed two-step mechanism for the reaction of NiMMK with 1,3-pn remains reasonable. In the first step, the bis(1,3-propanediamine) adduct that is proposed concurs with the prediction that six-coordinated nickel(II) complexes are generally more favorable than five-coordinate species. The reactant 1,3-pn is thus oriented for reaction to occur with the ligand system. However, since the reaction does not occur in solution in the absence of added base, we conclude that the coordinated 1,3-pn is not a sufficiently strong nucleophile to react with the coordinated CO group of the ligand. It was concluded earlier, from the kinetics data, that the hydroxide and ethoxide ions serve the same function in these reactions. The second step is suggested to involve deprotonation of the coordinated amine by the base (it is well-known that coordination of an amine results in increased acidity of the hydrogens) followed by attack of this much stronger nucleophilic species at the carbon atom of a coordinated CO group of the ligand and the regeneration of the base to give the product NiApSo. We conclude that the rate-determining step in the overall mechanism is the nucleophilic attack by the deprotonated amine; the solvent-dependence data is consistent with an ion–molecule reaction. Deprotonation of the amine cannot be the rate-determining step because both bases (hydroxide and ethoxide) give identical rates under similar experimental conditions, yet they are of different nucleophilicity. The proposed second step in the mechanism is similar to that reported by Sargeson in papers dealing with reactions of coordinated nucleophiles.[16] In these reactions, a base-catalyzed facile intramolecular condensation between a ligand containing a reactive carbonyl center and a coordinated ammonia was described.

The study of the reaction of NiMMK with 1,3-pn has provided clear evidence for the presence of a kinetic template effect and demonstrates the role of the metal ion in reactions of this type. In addition to serving as a template for the orientation of reactant molecules by using available coordination sites, the metal ion also serves as a center of positive charge, which results in polarization effects of the reactants, which in turn allows the reaction to proceed. This study has also enabled us to formulate a mechanism that describes the initial condensation reaction in the in situ formation of macrocyclic ligands derived from the MMK ligand. The reaction of NiMMK with ethylenediamine to produce Ni(Me_2Ph_4-[13]tetraenato$N_4(N_2)$) has been studied in THF–EtOH solution.[17] The kinetics data for the initial condensation reaction are similar to those reported here for the reaction of NiMMK with 1,3-pn, viz., rate $\propto$ [ethylenediamine]^2, [added base], and [NiMMK]. Under similar experimental conditions, the overall rate of the initial condensation reaction is similar to that observed for the reaction of NiMMK with 1,3-pn, indicating that the rate-determining step is similar in both systems. Small differences in the observed rates of reaction may be ascribed to differences in nucleophilic strengths of the deprotonated amines.

Subsequent papers in this series will report kinetics data and proposed mechanisms for several in situ macrocyclic ligand syntheses, probe the factors that are important in controlling the reactions, and, in particular, investigate the role of the metal ion.

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Kinetics and Mechanism of the Dioxygen Uptake of the Four-Coordinate (X = Cl) and Five-Coordinate (X = I, SCN, PPh_3) Complexes Ir(cod)(phen)X

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The reaction of [Ir(cod)(phen)]Cl (cod = cycloocta-1,5-diene, phen = phenanthroline) with dioxygen in methanol solution was studied kinetically in the absence and presence of SCN^- and I^-. The five-coordinate complexes IrX(cod)(phen) (X = I, SCN) are generated in solution on addition of NaI or NaSCN to an Ir(cod)(phen)$^+$ solution. The kinetic data obtained at normal and elevated pressures indicated that the five-coordinate complexes (X = I, SCN) are much more reactive toward dioxygen than the four-coordinate complex (X = Cl). An "end-on" oxidative addition of O_2 to IrX(cod)(phen) (X = I, SCN) is postulated.

Introduction

The reactions of dioxygen with transition-metal complexes can be divided into two groups: (a) The first consists of reactions of dioxygen with metal complexes in which a one-electron metal-to-ligand transfer occurs to form an "end-on" bonded superoxide complex.[1,2] The principal oxidation states of the metals involved in these reactions normally differ by one unit, e.g., Fe(II,III), Co(II,III), and Cu(I,II). The mechanism of these reactions is most probably an "end-on" attack of dioxygen on the metal center. (b) The second group consists of reactions of dioxygen with metal complexes in which a two-electron metal-to-ligand transfer occurs.[3-5] These

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complexes entail metals with principal oxidation states differing by two units, e.g., Ir(I,III), Rh(I,III) and Pt(0,II,IV). The mechanism of such reactions is believed to be a concerted three-centered oxidative addition reaction to form a "side-on" bonded peroxide complex in which the peroxide ligand occupies two coordination sites.[6] As a consequence of the three-center mechanism, dioxygen uptake by five-coordinate d^8 low-spin metal complexes is assumed to only occur subsequent to ligand dissociation, as is the case for hydrogen.[5]

In a previous communication[7] we reported a preliminary kinetic study on reaction 1 (X = Cl, I) in which it was shown

$$Ir(cod)(phen)X + O_2 \rightarrow [IrO_2(cod)(phen)]X \quad (1)$$

that the five-coordinate complex IrI(cod)(phen) is more susceptible to dioxygen attack than the corresponding four-coordinate complex (X = Cl). An "end-on" dioxygen attack on the metal center (X = I) was postulated to account for this. We have now extended this study to X = SCN and PPh_3, and the present paper gives a detailed account of the kinetics and mechanism of reaction 1 for X = Cl, I, SCN, and PPh_3. In addition the pressure dependence of such dioxygen uptake reactions has been measured.

Experimental Section

Materials. Analytical grade methanol (Merck), distilled from magnesium under a nitrogen atmosphere, was used for all of the kinetic experiments. Analytical grade sodium iodide, sodium thiocyanate, and lithium chloride (Merck) were dehydrated and stored under a nitrogen atmosphere.

Preparation of Complexes. IrX(cod)(phen) (X = Cl, I, SCN) were prepared according to literature methods.[8]

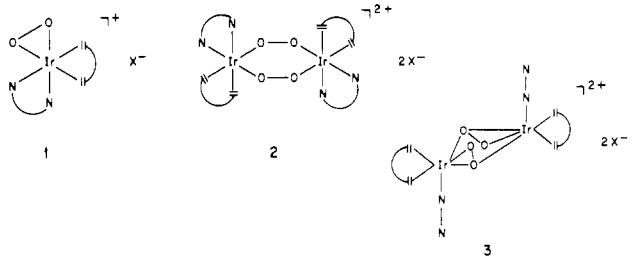
$[IrO_2(cod)(phen)]X$. [Ir(cod)(phen)]Cl was dissolved in methanol. For X = I or SCN, sodium iodide or sodium thiocyanate was added to the reaction solution. Dioxygen was bubbled through the solution for 2 h, and the solvent was removed under reduced pressure. For X = I or SCN the residue was dissolved in dichloromethane and filtered and the solvent removed from the filtrate under reduced pressure. Anal. Calcd for $[IrO_2(cod)(phen)]Cl$: C, 43.8; H, 3.8; N, 5.1; Cl, 6.5. Found: C, 44.0; H, 3.8; N, 5.1; Cl, 6.3. Calcd for $[IrO_2(cod)(phen)]I$: C, 37.6; H, 3.2; N, 4.4; I, 19.8. Found: C, 37.6; H, 3.3; N, 4.4; I, 20.2. Calcd for $[IrO_2(cod)(phen)]SCN$: C, 44.2; H, 3.5; N, 7.4; S, 5.6. Found: C, 44.1; H, 3.4; N, 7.6; S, 5.8.

Kinetics. Oxygen-saturated methanol solutions were obtained by bubbling dioxygen through methanol distilled from magnesium, and the dioxygen concentration was determined by Winkler's method.[9] Diluted dioxygen solutions were prepared by mixing the saturated dioxygen solutions with nitrogen-saturated methanol. The concentrations of the dioxygen solutions varied from 1.88×10^{-2} to 5.65×10^{-3} mol dm^{-3} and the concentrations of the complex solutions from 1.35×10^{-4} to 4.15×10^{-5} mol dm^{-3}.

The reactions at normal pressure were followed on a Cary 15 spectrophotometer at temperatures of (40, 35, 30, 25) ± 0.1 °C. The spectrophotometer quartz cells were filled completely in order to prevent gas exchange during the reactions. Kinetic measurements at elevated pressures were performed on a Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell.[13] Quartz "pillbox" cells[14] were used in these measurements. Pseudo-first-order conditions were maintained by ensuring that the concentrations of dioxygen were at least a factor of 30 greater than those of the starting complexes. The reaction kinetics were followed independently at the wavelengths 266 and 550 nm, which corresponded to the rate of product formation and the rate of starting complex disappearance, respectively. Data were obtained at 5×10^{-4}, 8×10^{-4}, 10×10^{-4}, 12×10^{-4}, 15×10^{-4}, 100×10^{-4}, and 5000×10^{-4} mol dm^{-3} iodide and thiocyanate concentrations. The ionic strength was fixed at $\mu = 0.01$ mol dm^{-3} with lithium chloride.

The final UV–visible spectra of the reaction products generated in situ in the kinetic experiments were compared with those obtained from the prepared products and found to be identical.

Scheme I



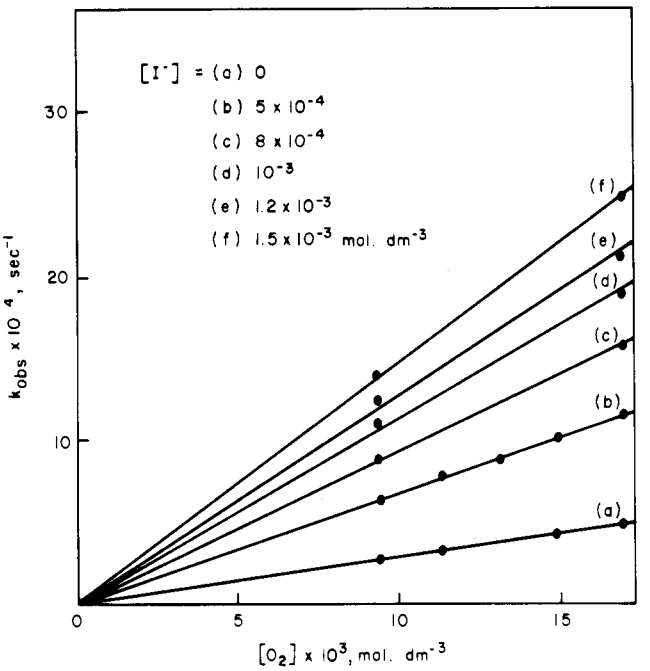


Figure 1. Plots of k_{obsd} vs. $[O_2]$ at different $[I^-]$ at 40 °C.

Results and Discussion

Compounds that analyzed for the stoichiometry $[IrO_2(cod)(phen)]X$ (X = Cl, I, SCN) were isolated as the products of reaction 1 and assigned as peroxo complexes[10] on the basis of the ν_{O-O} at 850 cm^{-1}. The complexes had identical UV–vis spectra, indicating the formation of salts, which was further confirmed by conductivity measurements. Since attempts to grow suitable crystals for an X-ray crystal structure determination of any of these dioxygen complexes were unsuccessful, three structures can be considered for this stoichiometry,[10] viz., **1**–**3** in Scheme I.

It is impossible to distinguish between the 1:1 monomeric electrolyte (structure **1**) and the two 2:1 dimeric electrolytes

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Table I. Kinetic Data for the Oxygenation of Ir(cod)(phen)$^+$ at Different Concentrations of Iodide, Thiocyanate, and Triphenylphosphine in Methanol at Different Temperatures (μ = 0.01)[a]

temp, °C	[Cl$^-$]	10^3[O$_2$]	10^4k_{obsd}	temp, °C	[Cl$^-$]	10^3[O$_2$]	10^4k_{obsd}
40	0.01	9.41	2.75	35	0.01	9.41	2.24
	0.01	11.29	3.25		0.01	16.94	3.98
	0.01	15.06	4.36	30	0.01	9.41	1.77
	0.01	16.94	4.90		0.01	16.94	3.27
	0.01	18.82	5.44	25	0.01	9.41	1.43
					0.01	16.94	2.69
temp, °C	10^4[I$^-$]	10^3[O$_2$]	10^4k_{obsd}	temp, °C	10^4[I$^-$]	10^3[O$_2$]	10^4k_{obsd}
40	5	9.41	6.47	40	5000	5.65	38.9
		11.29	7.76			7.53	51.3
		13.17	8.84			9.41	64.8
		15.06	10.30	35	5	16.94	10.37
		16.94	11.73			9.41	5.25
	8	9.41	8.84		8	9.41	7.81
		16.94	15.97			16.94	13.98
	10	9.41	10.66		5000	5.65	29.7
		16.94	19.08	30	5	16.94	9.12
	12	9.41	12.55			9.41	5.06
		16.94	21.39		8	9.41	6.88
	15	9.41	13.87			16.94	12.35
		16.94	25.02		5000	5.65	22.9
	100	9.41	42.00	25	5	16.94	7.68
		11.29	50.22			9.41	4.35
		13.17	57.75		8	9.41	5.53
		15.06	66.00			16.94	10.08
		16.94	75.00		5000	5.65	17.2
temp, °C	10^4[SCN]	10^3[O$_2$]	10^4k_{obsd}	temp, °C	10^4[SCN]	10^3[O$_2$]	10^4k_{obsd}
40	5	16.94	29.55	35	5	16.94	26.29
		15.06	26.10			9.41	14.60
		13.17	22.29		8	16.94	35.22
		11.29	19.57			9.41	19.96
		9.41	16.44		5000	3.77	34.08
	8	16.94	40.13	30	5	16.94	22.97
		9.41	22.62			9.41	12.90
	10	16.94	48.21		8	16.94	30.14
		9.41	27.02			9.41	17.46
	12	16.94	53.93		5000	3.77	25.59
		9.41	31.75	25	5	16.94	20.05
	15	5.65	20.49			9.41	11.10
		7.53	28.71			15.06	17.25
	5000	3.77	43.58		8	16.94	25.41
		5.65	66.00			9.41	13.79
					5000	3.77	19.96
temp, °C	10^6[PPh$_3$]	10^3[O$_2$]	10^4k_{obsd}	temp, °C	10^6[PPh$_3$]	10^3[O$_2$]	10^4k_{obsd}
40	5	15.06	3.55	40	10	13.17	1.65
		13.17	3.13			15.06	1.92
		9.41	2.22		50	15.06	≈0.00

[a] All concentrations in mol dm^{-3}; k_{obsd} is in s^{-1}.

(structure **2** or **3**) on the basis of conductivity measurements. To our knowledge complexes containing a double peroxide bridge (structure **2**) or a single nitrogen-bonded phenanthroline (structure **3**) have no precedent. On the other hand, a large number of complexes with structure **1** have been reported.[3,4] We will therefore only consider structure **1** in the discussion of the kinetic data reported in this paper.

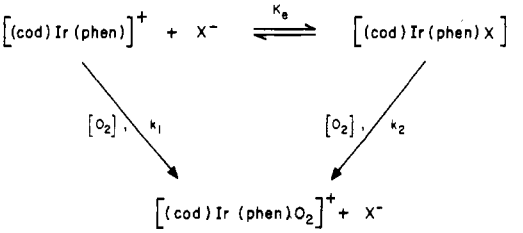
Addition of NaX (X = I, SCN) to [Ir(cod)(phen)]Cl in methanol solution establishes equilibrium 2.[11] The equilibrium

$$\mathrm{Ir(cod)(phen)^+ + X^- \overset{K_e}{\rightleftharpoons} IrX(cod)(phen)} \qquad (2)$$

constants K_e were determined spectrophotometrically. As expected, the K_e value was found to be larger for X = SCN than for X = I (see Table II). In contrast, no five-coordinate species were detected spectrophotometrically for X = Cl.

The rate of reaction 1 was found to be first order in both [complex] and [dioxygen], increased with increasing [NaX] (X = I, SCN), decreased with increasing [PPh$_3$], and was independent of [Cl$^-$]. Plots of k_{obsd} vs. [O$_2$] at different [I$^-$] are shown in Figure 1. A similar family of linear plots was

Scheme II



obtained for the thiocyanate system. These data are collected in Table I and conform to the rate law

$$k_{obsd} = \{(k_1 + k_2K_e[X^-])/(1 + K_e[X^-])\}[O_2] \qquad (3)$$

which can be derived from Scheme II.

Rate law 3 simplified to $k_{obsd} = k_1[O_2]$ and $k_{obsd} = k_2[O_2]$ when X = Cl (and no NaI or NaSCN was added to the reaction solution) and when 0.5 mol dm^{-3} NaI or NaSCN was added, respectively. The k_1 and k_2 values obtained under these conditions are given in Table II. The k_1 and k_2 values, as

Table II. Rate and Equilibrium Constants and Activation Parameters[a] for the Reaction

$$Ir(cod)(phen)X + O_2 \xrightarrow[\mu = 0.01]{X^-} IrO_2(cod)(phen)^+X^-$$

X^-	temp, °C	k_1[b]	k_1[c] (I^-)	k_1[c] (SCN)
Cl^-	25	0.0156 ± 0.0003	0.0159 ± 0.0006	0.0172 ± 0.0048
	30	0.0190 ± 0.0002	0.0190 ± 0.0007	0.0202 ± 0.0037
	35	0.0237 ± 0.0001	0.0231 ± 0.0021	0.0246 ± 0.0030
	40	0.0290 ± 0.0002	0.0236 ± 0.0024	0.0289 ± 0.0021

X^-	temp, °C	k_2[b]	k_2[c]	K_e[d]	K_e[c]
I^-	25	0.2044	0.3069 ± 0.0024	227 ± 5	222 ± 5
	30	0.4044	0.4081 ± 0.0026	201 ± 8	200 ± 4
	35	0.5250	0.5311 ± 0.0077	171 ± 8	163 ± 10
	40	0.6862 ± 0.0024	0.7053 ± 0.0098	155 ± 16	152 ± 6
SCN^-	25	0.5294	0.5297 ± 0.0255	500 ± 24	455 ± 40
	30	0.6788	0.6819 ± 0.0196	439 ± 8	406 ± 22
	35	0.9040	0.9102 ± 0.0162	350 ± 14	335 ± 11
	40	1.162 ± 0.006	1.172 ± 0.012	281 ± 19	287 ± 6

X^-	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[c]
Cl^- (k_1)	26.8 ± 2.1	−192 ± 8
I^- (k_2)	40.6 ± 0.8	−121 ± 4
SCN^- (k_2)	43.9 ± 0.8	−105 ± 4

[a] Rate constants are in $dm^3\ mol^{-1}\ s^{-1}$; equilibrium constants are in $dm^3\ mol^{-1}$; activation enthalpy is in kJ mol^{-1}; activation entropy is in J $mol^{-1}\ K^{-1}$. [b] Experimentally obtained when $[X^-] = 0$ (k_1) and $[X^-] = 0.50$ mol dm^{-3} (k_2). [c] All the data in the SPSS program were used, with rate law 3 as model equation. [d] K_e values were determined spectrophotometrically.

well as the K_e value, can also be calculated on the basis of all the data available in Table I, by using rate law 3 as model equation in the SPSS nonlinear least-squares-fit program[12] (Table II). From Table II it can be seen that the k_1, k_2, and K_e values obtained in the latter fashion correspond well with those obtained previously. Figure 1 shows the correlation between these calculated k values and the experimental k values.

The data in Table II indicate that the five-coordinate IrX(cod)(phen) complexes are more susceptible to dioxygen attack than the four-coordinate $[Ir(cod)(phen)]^+Cl^-$ complex, with the rate of dioxygen uptake increasing in the order SCN > I ≫ Cl.

We have also studied reaction 1 kinetically for X = PPh_3. From the data in Table I it can be seen that direct attack of dioxygen on the five-coordinate complex $Ir(cod)(phen)(PPh_3)^+$ does not occur as manifested by rate law 4 but proceeds solely via the four-coordinate complex $Ir(cod)(phen)^+$.

$$k_{obsd} = k_1[O_2]/(1 + K_e[PPh_3]) \qquad (4)$$

The intimate mechanisms of pathways k_1 and k_2 need to be clarified. Pathway k_1 most probably proceeds via a concerted three-centered mechanism, as is generally accepted for the oxidative addition of dioxygen to the platinum group d^8 metal complexes.[6] The interesting question is posed as to which mechanism is operative for pathway k_2. Three basically different modes of dioxygen activation can be distinguished, as shown in Scheme III.

Side-on attack of dioxygen to form a seven-coordinate low-spin peroxo Ir(III) intermediate, as shown for pathway i in Scheme III, is unlikely because to our knowledge no evidence in favor of the existence of seven-coordinate d^6 platinum group metal complexes with 20 valence electrons has appeared in the literature to date.[5b] Alternatively, the formation of side-on superoxo complexes (in this case an Ir(II) superoxide complex) is also unknown. According to the 16–18-electron rule,[5b] an end-on oxidative addition of dioxygen to the five-coordinate complex IrX(cod)(phen) is a plausible mechanism (pathway iii, Scheme III), viz., formation of a six-coordinate monodentate peroxo Ir(III) intermediate and subsequent dissociation of X prior to ring closure of the peroxo ligand.

Scheme III. Possible Pathways for Dioxygen Activation by a Coordinatively Saturated Ir(I) Complex

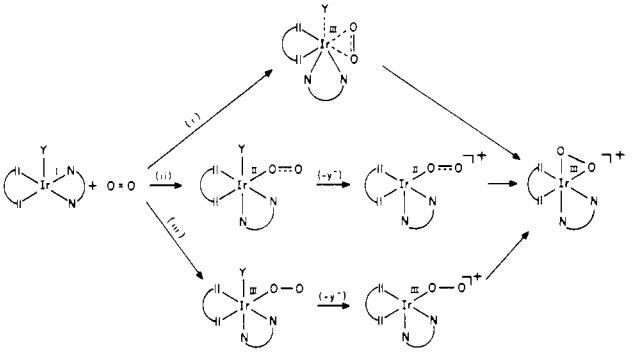


Table III. High-Pressure Kinetic Data for the Oxygenation of $Ir(cod)(phen)^+$ in the Absence and Presence of Iodide

pressure, bar	$10^3 k_{obsd}$,[a] s^{-1}	$(10^3 k_{obsd})_{cor}$,[b] s^{-1}
	$Ir(cod)(phen)^+Cl^-$[c]	
10	0.615 ± 0.026	0.615 ± 0.026
500	1.255 ± 0.100	1.184 ± 0.094
1000	2.018 ± 0.134	1.802 ± 0.119
1500	3.91 ± 0.39	3.313 ± 0.330
$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	−31.1 ± 1.7	−28.3 ± 1.7
	Ir(cod)(phen)I[d]	
10	2.78 ± 0.25	2.78 ± 0.25
250	4.29 ± 0.19	4.16 ± 0.18
500	6.42 ± 0.70	6.06 ± 0.66
750	10.85 ± 0.84	9.95 ± 0.77
$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	−44.4 ± 1.6	−41.6 ± 1.6

[a] Average of at least three values. [b] Corrected for the compressibility of methanol. [c] Temperature = 40 °C; [LiCl] = 0.01 mol dm^{-3}; $[Ir(cod)(phen)^+] = 10^{-4}$ mol dm^{-3}; λ = 315 nm; $[O_2] = 0.018\,82$ mol dm^{-3}. [d] Temperature = 25 °C; [LiI] = 0.5 mol dm^{-3}; $[Ir(cod)(phen)^+] = 10^{-4}$ mol dm^{-3}; λ = 300–305 nm; $[O_2] = 0.009\,41$ mol dm^{-3}.

The inertness of $Ir(PPh_3)(cod)(phen)^+$ toward dioxygen attack can be explained in terms of this mechanism (pathway iii) if the assumption is made that the dissociation of PPh_3 from the six-coordinate intermediate is too slow to allow chelation of the end-on bonded dioxygen molecule.

Pathway ii of Scheme III, which describes the formation of a six-coordinate superoxide Ir(II) intermediate, must also be considered a possibility. An unequivocal differentiation between pathways ii and iii on the basis of the kinetic data is unfortunately not possible.

Considering the thermodynamic parameters calculated for the reaction paths designated by k_1 and k_2, it can be seen from Table II that the $\Delta H^{\ddagger}$ values are low and decrease in the order $SCN^- > I^- > Cl^-$. Thus, although the stability of the transition states depicted by k_1 and k_2 decreases in the order $Cl^- > I^- > SCN$, the $\Delta S^{\ddagger}$ values (Table II) compensate so as to increase the rate of reaction 1 in the series $Cl^- < I^- < SCN^-$.

The difference in $\Delta S^{\ddagger}$ values may be due to the overlap between the dioxygen and metal orbitals in the transition state being much less for X = I or SCN than for X = Cl. This would be expected if the k_1 reaction path is a concerted three-centered process and the k_2 reaction path involves an "end-one" attack of dioxygen. It was therefore decided to test this hypothesis by means of a high-pressure kinetic study on reaction 1. These data are presented in Table III.

Some preliminary stopped-flow measurements under pressure[15] clearly demonstrated the rapid formation of Ir(cod)(phen)I in 0.5 mol dm^{-3} NaI. The subsequent decreases in absorbance at ca. 300 nm, ascribed to the dioxygen-uptake reaction, results in good first-order plots at low pressures. However, at higher pressures a further reaction interferes at longer reaction times so that no usable infinity absorbances measurements are obtained. The Guggenheim method was applied in such cases to determine k_{obsd}. The interference increases markedly with pressure so that reaction 1 could not be studied at pressures higher than 750 bar in the presence of excess I^-. It is clear, therefore, that the mechanism of dioxygen uptake by the five-coordinate species Ir(cod)(phen)X is indeed a multistep process. No such effects were observed in the absence of excess I^-. The plots of ln k vs. pressure obtained by using the data in Table III are linear, and the volumes of activation were calculated from their slopes.

The large negative values of $\Delta V^{\ddagger}$ for k_1 (at $[I^-] = 0$) and k_2 (at $[I^-] = 0.5$ mol dm^{-3}) emphasize the associative nature of the dioxygen-uptake reactions, which is in agreement with the negative $\Delta S^{\ddagger}$ values reported in Table II. However, the trend in $\Delta V^{\ddagger}$ is opposite to that seen in $\Delta S^{\ddagger}$ for k_1 and k_2. Such tendencies have been reported for various systems in recent years.[16] In order to interpret the magnitude of $\Delta V^{\ddagger}$ it is important to keep in mind that $\Delta V^{\ddagger}$ in general consists of two major contributions: $\Delta V^{\ddagger}_{intr}$, which arises from the changes in bond lengths and bond angles, and $\Delta V^{\ddagger}_{solv}$, which is ascribed to the changes in solvation on going from the ground state to the transition state. For the dioxygen uptake by $Ir(cod)(phen)^+$ no significant contribution from $\Delta V^{\ddagger}_{solv}$ is expected since no changes in charge, i.e., in electrostriction, occur during this process. The measured $\Delta V^{\ddagger}$, therefore, mainly represents $\Delta V^{\ddagger}_{intr}$ and reflects the significant decrease in volume during the associative bond-formation step. However, for the dioxygen uptake by Ir(cod)(phen)I, the process must include release of I^- to produce the final product, viz., $IrO_2(cod)(phen)^+$. This is expected to cause significant changes in solvation due to the creation of charges and results in a negative contribution from $\Delta V^{\ddagger}_{solv}$ toward the overall $\Delta V^{\ddagger}$ values. The more negative value of $\Delta V^{\ddagger}$ for k_2 illustrates that at least some charge separation has occurred during this dioxygen uptake process. This is in line with the suggested reaction paths ii and iii in Scheme III. The complete release of I^-, which is probably a fast step at normal pressure, may slow down at higher pressures due to its dissociative nature and so interfere with the dioxygen-uptake reaction. In addition, electron transfer is expected to result in a negative contribution[17,18] toward $\Delta V^{\ddagger}$. It follows that although the magnitude of $\Delta V^{\ddagger}$ unequivocally depicts the nature of the dioxygen-uptake process, the various contributing effects do not allow a differentiation between routes i, ii, and iii in Scheme III at this stage.

Registry No. $[IrO_2(cod)(phen)]Cl$, 80584-38-9; $[IrO_2(cod)(phen)]I$, 80584-39-0; $[IrO_2(cod)phen)]SCN$, 80584-41-4; $[Ir(cod)(phen)]Cl$, 53522-11-5; Ir(cod)(phen)I, 41392-85-2; Ir(cod)(phen)SCN, 66779-01-9; O_2, 7782-44-7.

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Complexes of Platinum(II) with Chiral Diamines and Guanosine. Stereochemical Investigation Related to the Mechanism of the Antitumor Activity of *cis*-Bis(amine)platinum(II) Type Complexes

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Platinum(II) complexes of 2 mol of guanosine and a series of chiral and *meso*-1,2-diamines have been synthesized. Comparison of the circular dichroism spectra of these complexes with those of guanosine and of the complexes with only one guanosine show that in bis complexes the two guanosine molecules are arranged to form, stereospecifically, a guanosine–Pt–guanosine chirrole irrespective of the absolute configuration of the diamine. The geometry of the chirrole has been established by an analysis of the chiroptical properties of the derivatives of chiral cyclohexanediamines and 9-methylguanine to be that of a right-hand propeller with the two guanosine molecules arranged "head-to-tail". It is proposed that this arrangement arises from the formation of hydrogen bonds between O(6) of guanosine and the NH_2 groups of the diamines. In the case of chiral diamines the spatial orientation of the hydrogen bonds controls the thread of the propeller, the resulting structure being rather rigid. Variable-temperature ^1H NMR spectra help to support this picture.

Introduction

The antitumor activity of bis(amine)platinum(II) complexes with two cis anionic leaving groups is by far one of the most outstanding results in the field of the bioactivity of metal complexes.[1,2] Although the clinical application of *cis*-$[(NH_3)_2PtCl_2]$ is already widespread corresponding to the commercial production of the drug,[3] its mechanism of action is still a subject of intense research. Up to now a satisfactory and definitive answer has not been reached; the only well-established evidence is the direct interaction of platinum with DNA[4] and in particular with the guanine base.[5,6]

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