

Stoichiometry, products and kinetics of oxidation of neutral 2,6-diacetylpyridine-bis(*N*⁴-azacyclic thiosemicarbazone)cobalt(II) complexes by dioxygen in aprotic solvents

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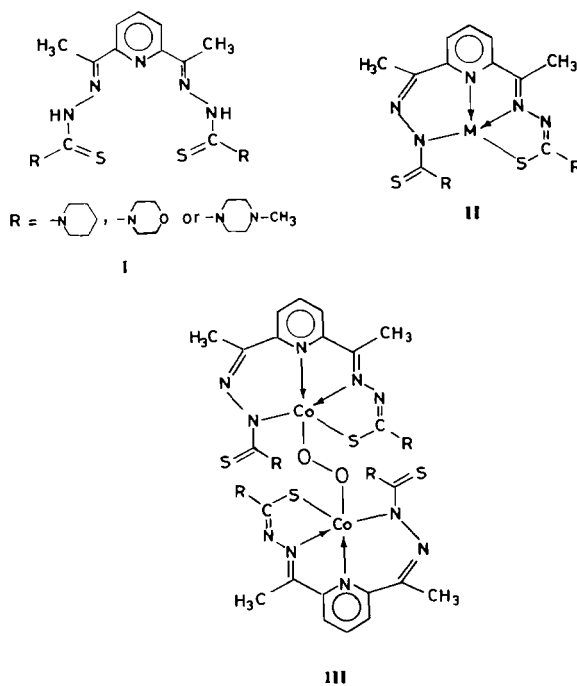
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Abstract

Low-spin, square planar cobalt(II) complexes are obtained by reaction of equimolar cobalt(II) acetate with potentially five-coordinate 2,6-diacetylpyridine-bis(*N*⁴-azacyclic thiosemicarbazone) ligands. When the *N*⁴-azacyclic moiety is piperidyl, morpholyl and *N*-methylpiperazyl, the cobalt(II) complexes are abbreviated as [Co(DAPP)], [Co(DAPM)] and [Co(DAPN)], respectively. The complexes are freely soluble in methylene chloride and nitrobenzene. They rapidly react with dioxygen in these solvents to form the corresponding diamagnetic μ -peroxodicobalt(III) complexes with stoichiometry $2\text{Co(II)} + \text{O}_2 \rightarrow (\text{Co(III)})_2\text{O}_2$, as indicated by manometric oxygen uptake, cryoscopic measurements in nitrobenzene and the appearance of a $\nu(\text{O}-\text{O})$ band at 860 cm^{-1} . Comparison of the infrared spectra of the cobalt(II) and cobalt(III) complexes and the ¹H NMR spectra of cobalt(III) complexes with corresponding data for the structurally known nickel(II) complex [Ni(DAPM)] indicates that the bis-thiosemicarbazone ligands act as dibasic tetradentate molecules. However, cobalt is unsymmetrically bonded to the thiohydrazone portions of the ligand. Reduction of dioxygen to bound peroxide by large excesses of these cobalt(II) complexes in nitrobenzene and methylene chloride is governed by the third-order rate law $d[(\text{Co(III)})_2\text{O}_2]/dt = k_2[\text{Co(II)}]^2[\text{O}_2]$. Very negative ΔS_2^\ddagger , small ΔH_2^\ddagger and minimal solvent effects suggest that assembly of the activated complex is rate-determining. Rate constants k_2 at 25 °C decrease in order [Co(DAPN)] > [Co(DAPM)] > [Co(DAPP)].

Introduction

Thiosemicarbazones and their metal complexes are of current interest with respect to their biological activity in general and antineoplastic activity in particular [1–11]. Their antimicrobial and antiviral action has been reviewed by Levinson [12]. Mohan *et al.* [13, 14] reported the synthesis, characterization and antitumor activity of a series of 2,6-diacetylpyridine bis(thiosemicarbazones) (I) and their metal complexes. They assigned a distorted six-coordinate structure for Fe(III) complexes. A distorted five-coordinate structure was suggested for Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pt(II) complexes. Here, the ligands I would act as dibasic pentadentate molecules and coordinate the central metal ions through the two thiol sulfur, the two azomethine nitrogen and the pyridyl nitrogen atoms. However, spectroscopic and X-ray structural evidence [15] indicates that potentially five-coordinate ligands I behave as dibasic four-coordinate molecules towards Ni(II), Cu(II) and Pd(II) and form monomeric square planar complexes II. Here, the metal ion is unsym-



metrically situated with respect to the thiohydrazone portions of the ligand; coordination by one of the side-chains is normal, while coordination to the other is very unusual since the thioamide nitrogen is coordinated instead of the azomethine and the sulfur of this side of **I** is not coordinated at all.

In seeking to explore the special coordinative properties of these biologically active ligands **I** (R = piperidyl, morpholyl and *N*-methylpiperazyl), the present work reports the synthesis and characterization of the air-sensitive cobalt(II) complexes **II**. The stoichiometry and kinetics of their oxidation to diamagnetic μ -peroxodicobalt(III) complexes **III** by dioxygen has been determined in aprotic solvents. The molecularities of the reactants and products were established by cryoscopy in nitrobenzene.

Experimental

Materials

Anhydrous cobalt(II) acetate was obtained from the hydrate (BDH) by heating overnight at 120 °C under vacuum. Piperidine, morpholine and *N*-methylpiperazine (Aldrich) were distilled from potassium hydroxide under reduced pressure before use. 2,6-Diacetylpyridine (Aldrich) was used as received. Methylene chloride and nitrobenzene were distilled from phosphorous(V) oxide and stored over 4 Å molecular sieves. Ligands **I** (R = piperidyl, morpholyl and *N*-methylpiperazyl) were prepared by the reported method [14]. All other chemicals and solvents were of reagent grade.

Preparation of cobalt complexes

Preparation of cobalt(II) complexes **II** (*M* = Co(II); *R* = piperidyl, morpholyl and *N*-methylpiperazyl)

The cobalt(II) complexes were prepared by the following general method. A solution of the respective ligand **I** (5 mmol) in anhydrous methylene chloride (30 ml) was flushed with dry dinitrogen for 15 min. Anhydrous cobalt(II) acetate (5 mmol) was then added under dinitrogen and the mixture was stirred until all of the solid had dissolved, yielding a reddish brown solution. The methylene chloride was removed in a vacuum rotary evaporator, leaving a reddish brown solid which was stored under vacuum. The product yield was quantitative in all reactions. Cobalt(II) complexes **II** (*M* = Co(II)) were stable to air in the solid state for at least two weeks but were oxidized in solution in a few minutes.

Preparation of μ -peroxocobalt(III) complexes **III**

Method 1. These complexes were obtained by flushing reddish brown methylene chloride solutions of **II** (*M* = Co(II)) with dioxygen. An immediate colour change to brown was observed. The gas stream was stopped after 30 min and the methylene chloride was removed in a vacuum rotary evaporator, leaving a brown solid.

Method 2. A clear solution of cobalt(II) acetate tetrahydrate (5 mmol) in methanol (30 ml) was added dropwise to the respective ligand **I** (5 mmol) in methanol (30 ml) with stirring. The resulting solution was refluxed for 3 h in air and then allowed to stand overnight. The brown precipitate was filtered, washed with methanol and ether and dried *in vacuo*.

Physical measurements

Elemental cobalt analyses were performed by Dr T. R. Gilbert with an inductively coupled plasma spectrometer at Northeastern University, Boston, MA, U.S.A. Nitrogen and sulfur analyses were performed by Micanal, Tucson, AZ, U.S.A. The molecular weights of complexes **II** and **III** were determined by measuring the freezing point depression of dinitrogen-saturated dry nitrobenzene solutions containing a known amount of solute. The freezing point depression constant ($K_f = 7.0 \text{ }^\circ\text{C m}^{-1}$) for nitrobenzene was determined using benzil as a standard.

Electronic spectra were recorded with a Perkin-Elmer 552 spectrophotometer in matched quartz cells at room temperature. Deoxygenated methylene chloride was used as the reference. IR spectra (KBr disks) were obtained with a Pye Unicam SP2000 spectrophotometer calibrated with the 906.5 or 3026.3 cm^{-1} absorptions of polystyrene. ^1H NMR spectra were recorded with a Varian type EM-390 (90 MHz) spectrometer at 38 °C. Tetramethylsilane (TMS) was employed as an internal standard. Magnetic susceptibilities were measured by the Gouy method calibrated with $\text{HgCo}(\text{SCN})_4$. Pascal constants were used to correct all data for diamagnetism [16].

The rates of oxidation of excesses of cobalt(II) complexes **II** by dioxygen in methylene chloride and nitrobenzene were measured in the thermostatted cell compartment of a Pye Unicam SP 1801 spectrophotometer with an expanded absorption scale and zero suppression to maximize the absorption change during reaction. The reactant concentrations were $[\text{Co}(\text{II})] = (2.0\text{--}25.0) \times 10^{-3} \text{ M}$ and $[\text{O}_2] = 3.5 \times 10^{-4} \text{ M}$ over the temperature range 16.3–46.6 °C. The reactions were monitored at wavelengths between 400 and 650 nm. In all cases the cobalt(II) reactant was in sufficient stoichiometric excess to ensure pseudo-first-order conditions [17].

Results and discussion

Reddish brown cobalt(II) complexes **II** ($M = \text{Co(II)}$; $R = \text{piperidyl, morpholyl and } N\text{-methylpiperazyl}$) were prepared by reaction of anhydrous cobalt(II) acetate with deoxygenated methylene chloride solutions of **I** at molar ratio 1:1 under dinitrogen. Complexes **II** ($M = \text{Co(II)}$) are air sensitive and their freshly prepared reddish brown solutions turn dark brown when exposed to air. The μ -peroxodicobalt(III) complexes **III** ($R = \text{piperidyl, morpholyl and } N\text{-methylpiperazyl}$) were prepared either by passing dry dioxygen through a methylene chloride solution of **II** ($M = \text{Co(II)}$) or by reaction of methanolic solutions of cobalt(II) acetate tetrahydrate with an equimolar methanolic solution of **I** at room temperature. Elemental analyses, cryoscopic data and the magnetic moments of the cobalt(II) and cobalt(III) complexes are given in Table 1. The compounds do not possess sharp melting points and appear to decompose above 250 °C.

The IR spectra of the free ligands **I** ($R = \text{piperidyl, morpholyl and } N\text{-methylpiperazyl}$) exhibit absorption bands at *c.* 3200 and 3050 cm^{-1} due to $\nu(\text{N-H})$ for free and intramolecularly hydrogen-bonded N-H groups, in common with other diketone-bis-hydrazones [18]. However, the cobalt(II) and cobalt(III) complexes lack any absorption due to $\nu(\text{N-H})$, which implies deprotonation of the bis-thiosemicarbazone ligands **I** on coordination. The strong band at *c.* 1590 cm^{-1} in the IR spectra of **I** is assigned to the combination of $\nu(\text{C=N})$ and $\nu(\text{C=C})$ modes [19]. The bands around 1320 and 790 cm^{-1} observed in the free ligand **I** may be assigned to $\nu(\text{C=S})$ vi-

brations. These vibrations are not isolated from the other vibrations, especially C=N vibrations [20].

The IR spectra of peroxodicobalt(III) complexes **III** exhibit a medium intensity band at *c.* 860 cm^{-1} . The corresponding cobalt(II) complexes **II** ($M = \text{Co(II)}$) have no such bands in this region. Thus, the bands at *c.* 860 cm^{-1} of the cobalt(III) complexes can be assigned to the O-O stretching vibration. These frequencies are in the range of the reported values for peroxides [21–24]. Except for the $\nu(\text{O-O})$ band, the IR spectra of **II** ($M = \text{Ni(II), Cu(II)}$) [15] and **III** are reasonably similar. They exhibit bands at *c.* 1580 and 1600 cm^{-1} attributed to free and coordinated azomethine $\nu(\text{C=N})$, respectively. Bands at *c.* 785 and 765 cm^{-1} are assigned to free $\nu(\text{C=S})$ (thione) and coordinated $\nu(\text{C-S})$ (thiol) sulfur, respectively [15]. IR evidence for this unusual coordination mode of ligand **I** was substantiated by X-ray structural data for **II** ($M = \text{Cu and Ni}$; $R = \text{morpholyl}$) [15] and ^1H NMR spectral data for **II** ($M = \text{Ni and Pd}$ [15]) and **III** (see below).

The room temperature magnetic moments of complexes **II** ($M = \text{Co(II)}$; $R = \text{piperidyl, morpholyl and } N\text{-methylpiperazyl}$) vary from 1.89 to 2.03 BM. These values fall in the range expected for low-spin, square planar cobalt(II) complexes [25–28]. Methylene chloride solution electronic spectra of the cobalt(II) complexes **II** (Table 2) and their magnetic moments (Table 1) are consistent with a square planar structure **II** [29].

Since all the oxygenated complexes **III** are intensely brown colored, the oxidation of **II** can be easily followed by spectrophotometry. Representative spec-

TABLE 1. Elemental analyses, cryoscopic data and magnetic moments of **II** ($M = \text{Co}$) and their corresponding peroxodicobalt(III) complexes **III**

Compound	Elemental analysis ^a (%)			Molecular weight ^b	μ_{eff} (BM)
	N	S	Co		
[(DAPP)Co]	19.33 (19.52)	12.62 (12.75)	11.58 (11.75)	490 ± 20 (502)	2.03
[(DAPM)Co]	19.26 (19.37)	12.44 (12.65)	11.51 (11.66)	495 ± 20 (506)	1.89
[(DAPN)Co]	23.32 (23.68)	11.89 (12.03)	10.93 (11.09)	510 ± 20 (532)	1.98
[(DAPP)Co] ₂ O ₂	19.27 (19.22)	12.43 (12.55)	11.38 (11.57)	1015 ± 20 (1020)	diamagnetic
[(DAPM)Co] ₂ O ₂	18.91 (19.07)	12.25 (12.45)	11.35 (11.48)	1010 ± 20 (1028)	diamagnetic
[(DAPN)Co] ₂ O ₂	23.11 (23.33)	11.64 (11.85)	10.90 (10.93)	1070 ± 20 (1080)	diamagnetic

^aAnalytical methods are described in the text; calculated values are given in parentheses. ^bIn nitrobenzene: typical molal concentration 2×10^{-2} .

TABLE 2. Spectral data for cobalt(II) and their corresponding peroxocobalt(III) complexes

Compound	Infrared (cm ⁻¹)		Band maxima (nm) (log ϵ (mol ⁻¹ cm ⁻¹))	¹ H NMR spectra, δ (ppm)				
	ν (C=N)	ν (C=S)		ν (O-O)	C-CH ₃	N-CH ₃	-CH ₂	pyridinic-H
H ₂ DAPP ^c	1560	800		334, 410 (4.37) (4.35)	2.58		4.00 ^a 1.80 ^b	7.31–8.62
[(DAPP)Co]	1580 1595	790 760		370, 415sh, 490, 620 (4.52) (4.05) (2.69) (3.10)				
[(DAPP)Co] ₂ O ₂	1585 1600	795 770	860	390, 500, 580 (4.72) (2.66) (2.93)	2.35 2.58		4.95 ^a 1.85 ^b	7.40–8.30
H ₂ DAPM ^c	1560	785		336, 410 (4.27) (4.15)	2.60		3.76 ^a 4.10 ^c	7.40–8.40
[(DAPM)Co]	1580 1600	780 770		375, 415sh, 495, 625 (4.63) (4.16) (2.78) (3.24)				
[(DAPM)Co] ₂ O ₂	1580 1610	780 775	865	400, 510, 590 (4.64) (2.71) (2.98)	2.41 2.62		3.75 ^d	7.45–8.09
H ₂ DAPN ^c	1558	790		338, 412 (4.30) (4.27)	2.58	2.61	4.10 ^a 2.50 ^c	7.62–7.94
[(DAPN)Co]	1600 1615	785 765		375, 420sh, 500, 630 (4.69) (4.18) (2.83) (3.27)				
[(DAPN)Co] ₂ O ₂	1600 1620	780 775	860	405, 515, 580 (4.76) (2.84) (2.99)	2.23 2.47	2.49	3.79 ^a 2.63 ^c	7.18–8.13

^a α -CH₂ protons. ^b β , γ -CH protons. ^c β -CH₂ protons. ^d α , β -CH₂ protons. ^eRef. 15.

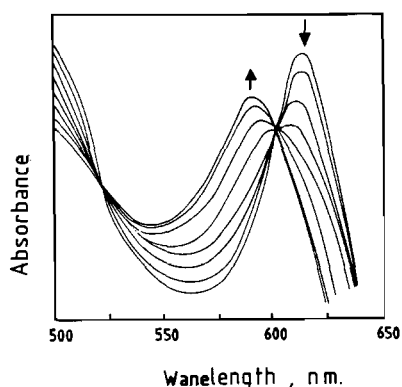


Fig. 1. Absorption spectral changes as a function of time for the oxidation of **II** ($M = \text{Co(II)}$, $R = \text{piperidyl}$) ($1 \times 10^{-4} M$) in methylene chloride at 24.6°C ; $\Delta t = 35$ min.

trah changes upon oxidation are given in Fig. 1. Sharp isosbestic points at 520 and 600 nm indicate the presence of only two absorbing species, namely **II** ($M = \text{Co(II)}$) and **III**.

The isolated μ -peroxodicobalt(III) complexes are diamagnetic (Table 1). Their electronic spectra contain medium intensity bands at *c.* 580 and 510 nm. This spectral pattern resembles those of many μ -peroxodicobalt(III) complexes [22, 30–33] and can be assigned to the two ligand-field transitions of cobalt(III). The brown colours of **III** are due to charge transfer from peroxide to cobalt, which results in shoulders at *c.* 400 nm [22].

The chemical shifts, δ , of the methyl, methylene, pyridyl and NH hydrogen atoms in ligands **I** and their diamagnetic peroxodicobalt(III) complexes **III** in CDCl_3 are listed in Table 2. The ^1H NMR spectra of ligands **I** show a downfield signal at *c.* 15.0 ppm due to N–H protons which disappear either upon deuteration or upon complex formation [15]. The spectrum of **I** ($R = \text{piperidyl}$) (Table 2) shows a broad signal at 4.0 ppm due to the α - CH_2 protons of the piperidyl moiety, while the β - and γ - CH_2 protons appear in a single broad peak at 1.8 ppm. The chemical shifts for α -, β - and γ - CH_2 protons in **III** ($R = \text{piperidyl}$) are about the same as for the parent ligand **I**. The spectrum of ligand **I** ($R = \text{morpholyl}$) shows two poorly resolved multiplets at 3.7 and 4.1 ppm for the α - CH_2 and β - CH_2 protons, respectively, while in **III** ($R = \text{morpholyl}$) the α - CH_2 and β - CH_2 protons appear together as one poorly resolved multiplet centered at 3.75 ppm. A more complex spectral pattern is observed for **I** ($R = N$ -methylpiperazyl) due to the overlap of N– CH_3 and β -N– CH_2 signals with the CH_3 -C=N signals at 2.5–2.6 ppm.

The spectra of organic ligands **I** show only one signal due to the CH_3 -C=N group centred at *c.* 2.6 ppm. As found for the structurally characterized nickel(II) complex **II** ($M = \text{Ni(II)}$) [15], the ^1H NMR

spectra of **III** (Table 2) exhibit resonances for the methyl protons of the 2,6-diacetylpyridine moiety (CH_3 -C=N) at *c.* 2.2 and 2.6 ppm. This indicates that the two methyl groups are chemically shifted inequivalent. This is explained by the crystal structure of **II** ($M = \text{Ni(II)}$), which shows that only one imino nitrogen is coordinated to the nickel while the other remains free [15]. The similarities of the IR spectra of **II** ($M = \text{Co(II)}$) and **III** and of the ^1H NMR spectra of **III** and **II** ($M = \text{Ni(II)}$) suggest the same coordination behaviour of ligands **I** towards cobalt(II) and cobalt(III).

Stoichiometry and products of oxidation of **II** ($M = \text{Co}$) with dioxygen

Cobalt(II) complexes normally form 2:1, μ -peroxo-bridged complexes on oxidation with dioxygen [23, 34, 35]. When the chelating agent has an insufficient number of coordinating groups or is present in insufficient concentration to completely saturate the coordination sites available on the cobalt ion, a second bridge may form [36–38]. Formation of the second bridge is precluded when only one coordination site is available on each cobalt centre.

Exposure of reddish brown solutions of cobalt(II) complexes **II** in methylene chloride or nitrobenzene to dioxygen causes rapid colour changes to brown. Manometric dioxygen uptake and cryoscopic measurements in nitrobenzene and product analyses (Table 1) support the stoichiometry of eqn. (1), which indicates dioxygen reduction by monomeric **II** to give dimeric μ -peroxodicobalt(III) products.



No liberation of dioxygen from **III** was observed on degassing solutions of **III** at reduced pressure or on bubbling dinitrogen through such solutions. Reaction (1) are thus irreversible.

Kinetics of oxidation of **II** ($M = \text{Co(II)}$) by dioxygen

With **II** in large excess, plots of $\ln(A_\infty - A_t)$ versus time, where A_t is the absorbance at time t , were linear for at least four half-lives in the reactions of **II** with dioxygen. This shows that the oxidations are first-order in $[\text{O}_2]$. The kinetic data provided no spectrophotometric evidence for any reaction precursors or intermediates under the conditions of this study. Plots of the observed pseudo-first-order rate constants for the reaction of **II** with dioxygen at fixed temperature, k_{obs} versus $[\text{II}]^2$ ($M = \text{Co(II)}$; $R = \text{piperidyl}$, morpholyl and N -methylpiperazyl) were linear and passed through the origin (Fig. 2), consistent with third-order rate law (2) for an irreversible process, where k_2 is the experimental third-order rate constant. This same high reaction order was previously observed in the oxidation of dimeric

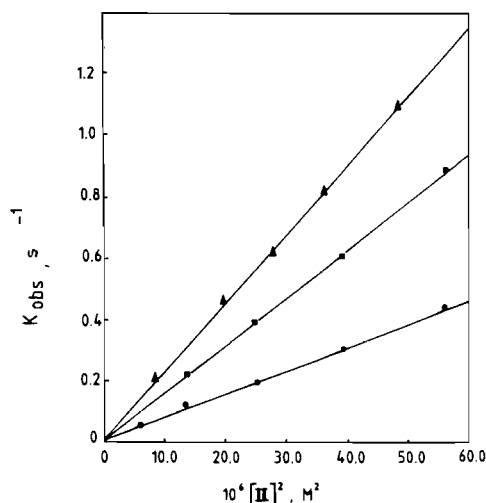


Fig. 2. Dependence of the observed pseudo-first-order rate constant k_{obs} on $[\text{II}]^2$ ($M = \text{Co(II)}$; $R = \text{piperidyl}$ ●; morpholyl ■; N -methylpiperazyl ▲) in methylene chloride at 23 °C.

TABLE 3. Kinetic data for oxidation of complexes **II** ($M = \text{Co(II)}$; $R = \text{piperidyl}$ [(DAPP)Co], morpholyl [(DAPM)Co] and N -methylpiperazyl [(DAPN)Co]) by dioxygen in aprotic solvents

Cobalt(II) reactant	Solvent ^a	$10^{-3} \times k_2^b$	$\Delta H_2^{\ddagger c}$	$-\Delta S_2^{\ddagger d}$
[(DAPP)Co]	MC	370	9.1	35
	NB	410	6.8	40
[(DAPM)Co]	MC	625	8.2	37
	NB	690	5.5	44
[(DAPN)Co]	MC	910	7.8	38
	NB	970	4.1	46

^aMC=methylene chloride, NB=nitrobenzene. ^bUnits are $\text{M}^{-2} \text{s}^{-1}$ at 21 °C; typical precision = $\pm 5\%$. ^cUnits are kcal mol^{-1} (typical error is $\pm 0.4 \text{ Kcal mol}^{-1}$). ^dUnits are $\text{cal deg}^{-1} \text{ mol}^{-1}$ at 25 °C (typical error is $\pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$).

copper(I) complexes with dioxygen [17] and is indicative of reactant preassociation. Third-order rate constants k_2 and their associated activation parameters are collected in Table 3.

$$\text{rate} = k_2 [\text{O}_2][\text{II}]^2 \quad (2)$$

Plots of $\log k_2$ versus $1/T$ were linear in each system, showing that eqn. (2) is obeyed under all experimental conditions; thus, there is no evidence for changes in cobalt(II) reactant molecularity in any of the systems investigated. The rate law for oxidation of monomeric **II** ($M = \text{Co(II)}$) is, in fact, a direct reflection of their molecularity because reduction of dioxygen to peroxide occurs in the presence of a large excess of cobalt(II).

The major features of the kinetic data for oxidation of **II** ($M = \text{Co(II)}$) by dioxygen in aprotic solvents (Table 3) are as follows.

(i) Variation of the ligand in **II** has only a small effect on k_2 .

(ii) The rate constants k_2 at 21 °C are somewhat larger in nitrobenzene than in methylene chloride.

(iii) Oxidation of **II** is fastest with $R = N$ -methylpiperazyl and slowest with $R = \text{piperidyl}$.

(iv) ΔS_2^{\ddagger} is in the narrow range -35 to $-46 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for these oxidation reactions.

(v) A plot of ΔH_2^{\ddagger} versus ΔS_2^{\ddagger} (not shown) is linear, within experimental error, for all systems investigated. This suggests similar activation requirements [39].

Interpretation of the kinetic data

Reaction (1) requires the transfer of two electrons from cobalt(II) to dioxygen. Rate law (2) indicates that there are two monomeric cobalt(II) complexes **II** and one dioxygen molecule in the activated complex. Possible rate-determining steps are (i) activated complex assembly and (ii) electron transfer.

Previous work on the oxidation of dimeric copper(I) complexes $\text{L}_2\text{Cu}_2\text{X}_2$ ($L = N, N', N', N'$ -tetraalkyldiamines; $X = \text{Cl}$ or Br) by dioxygen indicates, on the basis of low ΔH^{\ddagger} , very negative ΔS^{\ddagger} and minimal solvent effects, that assembly of the activated complex is rate-determining [17]. Since assembly appears to be rate-determining, it must result in effective donor-acceptor orbital overlap so that electron transfer is very rapid.

The reaction of a complex with dioxygen generally involves a large negative entropy change, which must be offset by a favourable enthalpy change if the free energy change is to be negative. The large negative entropy results primarily from loss of rotational, vibrational and translational freedom of the dioxygen molecule in the activated complex [40, 41]. Other factors also contribute. The increase of effective oxidation state of the metal ion on bonding of dioxygen increases the strength of bonds to the other ligands, decreasing their freedom. This results in a further negative entropy contribution. Increased charge separation between the metal ion and the dioxygen ligand increases interaction with polar solvents, which is another entropically unfavourable process. Because the coordinate bonds in binuclear dioxygen complexes **III** are polar, they tend to be formed to a larger extent in polar solvents [42].

This explains larger rate constant k_2 in nitrobenzene (dielectric constant = 34.8 at 20 °C) than in methylene chloride (dielectric constant = 8.9 at 20 °C) (Table 3). Favourable enthalpy of activation for the dioxygen binding reaction is assisted by increasing the strength

of the metal–ligand bonds. The dioxygen ligand receives electron density from donor atoms in its coordination sphere. Binding of dioxygen is thus a redox process, albeit an incomplete one. An increase in the donor ability of the ligands about the central metal ion will increase the electron-donating ability of the metal ion towards dioxygen and would thus be expected to strengthen the M–O₂ bond [23].

The molecular structure of these formed μ -peroxo species is of central importance in all this chemistry and attempts to grow crystals of these oxygenated materials for a definitive X-ray structural study have been quite encouraging.

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