Solvent Role on Cobalt(II) Dioxygen Carriers Based on Simple Polyamine Ligands

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The kinetics and thermodynamics of O_2 addition to Co^{II} complexes containing the simple triamine ligand (L) diethylenetriamine (=*N*-(2-aminoethyl)ethane-1,2-diamine; dien) or *N,N''*-dimethyldiethylenetriamine (=*N*-methyl-*N'*-[2-(methylamino)ethyl]ethane-1,2-diamine; dmdien) in the aprotic solvent dimethyl sulfoxide (DMSO) were studied by UV/VIS spectrophotometry, potentiometry, and O_2 absorption measurements. A parallel investigation on the anaerobic formation of Co^{II} complexes with dmdien, as well as on their reactivity towards O_2, was carried out in aqueous 0.1M $NaClO_4$ solution. $[CoL]^{2+}$ and $[CoL_2]^{2+}$ were the common species formed under anaerobic conditions in both aqueous and DMSO solutions. Under aerobic conditions, O_2 adducts of different stoichiometry were formed: a superoxo complex $[CoL_2O_2]^{2+}$ in DMSO and dimeric species in H_2O. The role of the reaction medium as well as effects of *N*-alkylation of the triamine ligand in the formation and reactivity of the $[Co^{II}(triamine)]$ complexes are discussed.

1. Introduction. – Over the past few decades, Co^{II} complexes have been widely studied as O_2 carriers and activators in both solid state and solution [1–7]. Although these studies have produced a lot of data, many recent publications on this topic prove that interest continues to focus on the potential application of these adducts in O_2 separation and storage, industrial processes, and oxidation catalysis under mild conditions [5][8–17].

The affinity of Co^{II} complexes for O_2 as well as the stoichiometry of the O_2 adducts formed vary greatly with the solvent and the ligands. Both mononuclear and binuclear oxygenated Co^{II} complexes are in fact known [1][4][5]. The former, usually referred to as superoxo complexes, tend to be formed with sterically hindered ligands, in nonaqueous solvents, and at low temperatures, whereas in aqueous solutions, they are often only transient in the formation of the latter binuclear μ-peroxo species. In fact, it is well-known that in aqueous solution, the formation of a mononuclear Co/O_2 1:1 adduct is immediately followed by a dimerization reaction leading to a binuclear μ-peroxo species in which O_2 bridges two metal ions [4]. The use of different solvent media in studying the same systems would therefore certainly provide a better understanding of the mechanisms involved in O_2 uptake.

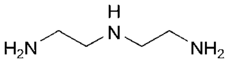
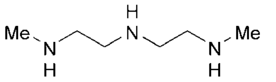
In addition, recent findings show that *N*-alkylation of some polyamine ligands strongly affects the redox properties of their metal complexes, since the oxidation tendency of the metal center is decreased when going from complexes of primary polyamines to complexes of tertiary ones [14–19]. Their subsequent O_2 affinity is largely affected by the charge density on the metal center [1] and, therefore, by the σ-

donor ability of the ligand. Moreover, *N*-alkylation gives a bulky nature to $[Co^{II}(dmdien)]$ complexes (dmdien = *N*,*N*″-dimethyldiethylenetriamine = *N*-methyl-*N*′-[2-(methylamino)ethyl]ethane-1,2-diamine) which should also act by slowing down the evolution of the dioxygenated species towards autoxidation products [15c]. This is one of the most-limiting aspects in the building of a good O_2 carrier.

As an extension of previous work, we present a study on the kinetics and the thermodynamics of O_2 addition to Co^{II} complexes containing the simple triamine ligand diethylenetriamine (= *N*-(2-aminoethyl)ethane-1,2-diamine; dien) or the alkylated *N*,*N*″-dimethyldiethylenetriamine (dmdien) in the aprotic solvent dimethylsulfoxide (DMSO). A parallel study on the anaerobic formation of Co^{II} complexes containing one of the mentioned ligands, *i.e.*, dmdien, as well as on the reactivity of these [Co(dmdien)] species towards O_2 was carried out in H_2O solution. The features of the oxygenated Co^{II} complexes with the ligands in the two solvent media are compared and discussed to show the fundamental role of the medium and of *N*-alkylation of the triamine ligand in the affinity of $[Co^{II}(triamine)]$ complexes for O_2 and in the stoichiometry and nature of the oxygenated adducts.

2. Results. – 2.1. *DMSO Solutions.* As reported in a previous paper [14], the Co^{II} ion in DMSO solution forms two successive mononuclear complexes, $[CoL]^{2+}$ and $[CoL_2]^{2+}$, with dien and dmdien ligands. As their stability constants are known (*Table 1*), it is possible to adjust the reagents concentration to obtain known amounts of the $[CoL_2]^{2+}$ (L = dien or dmdien) species in solution. The O_2 uptake of the 1:1 complex $[CoL]^{2+}$ when L = dien has not been studied as the distribution curves indicate that it coexists with the $[CoL_2]^{2+}$ species, while when L = dmdien, it has already been shown that no O_2 uptake occurred in DMSO [15a].

Table 1. *Overall Stability Constants* [14] *for the* $[Co^{II}(triamine)]$ *Systems in DMSO at 298 K and* I = *0.1*M

Ligand				
Complex	[CoL]	$[CoL_2]$	[CoL]	$[CoL_2]$
log*β*	9.49	18.47	8.3	14.15

On the other hand, $[CoL_2]^{2+}$ complexes of both dien and dmdien were able to bind O_2, as shown by the rising of the characteristic metal-to-ligand charge-transfer (MLCT) bands of the O_2 adducts in the UV/VIS region in *Fig. 1.* The maximum for the $[Co(dien)_2O_2]^{2+}$ complex was localized at *ca.* 310 nm (*Fig. 1,a*) and for the $[Co(dmdien)_2O_2]^{2+}$ at *ca.* 324 nm (*Fig. 1,b*). *Fig. 1* highlights that, after few minutes of exposure to air, the absorbance at 310 nm for the $[Co(dien)_2]^{2+}O_2$ system has already reached a maximum, while for $[Co(dmdien)_2]^{2+}$ the O_2 uptake is much slower. As far as the oxygenated solution of $[Co(dmdien)_2]^{2+}$ is concerned, a decrease in absorbance at 324 nm is observed by bubbling N_2 after only a short time, which indicates a certain reversibility of the O_2 uptake (*Fig. 1,b, inset*). Bubbling N_2 after 24 h does not produce any change in the electronic spectrum, suggesting that an irreversible process has already occurred. When the $[Co(dien)_2]^{2+}$ complex is involved, no change in the

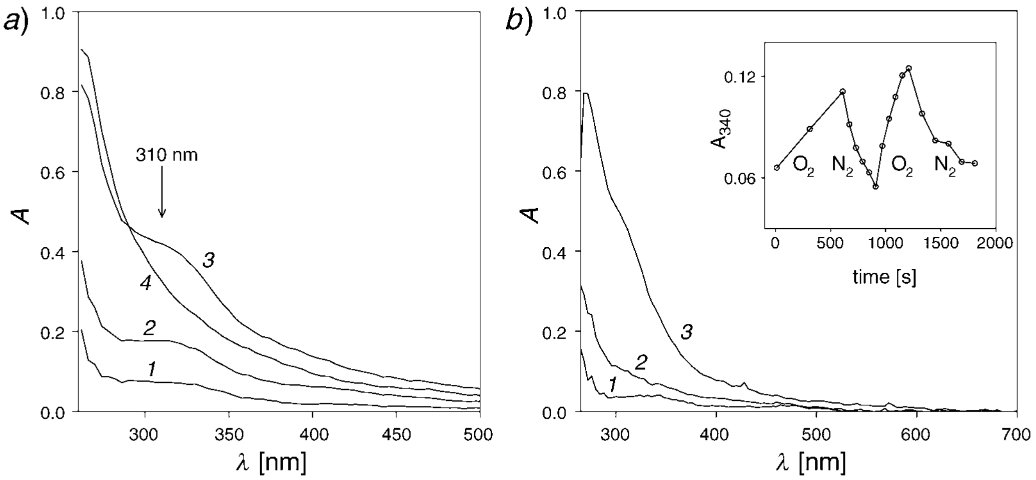


Fig. 1. *Electronic spectra in DMSO of :* a) *[Co(dien)$_2$]$^{2+}$* ([[CoL$_2$]] = 0.2 mM, P_{O_2} = 10 kPa) *after 8s* (*1*), *120s* (*2*), *360s* (*3*), *and 6h* (*4*); b) *[Co(dmdien)$_2$]$^{2+}$* ([[CoL$_2$]] = 0.8 mM, P_{O_2} = 10 kPa) *after 10s* (*1*), *1h* (*2*), *and 6h* (*3*). *Inset:* absorbance at 324 nm of a [Co(dmdien)$_2$]$^{2+}$ solution ([Co] = 0.3 mM, [dmdien] = 0.61 mM) after O_2/N_2 cycles.

spectrum is evident after N_2 bubbling, even after a few minutes of oxygenation. This indicates a quick, irreversible O_2 uptake.

Fig. 2 shows the O_2-binding curves, $R_{O_2} = C_{O_2}/C_{CoL_2}$ *vs.* time, for the [Co(dien)$_2$]$^{2+}$ and [Co(dmdien)$_2$]$^{2+}$ systems. The O_2 absorption of [Co(dien)$_2$]$^{2+}$ reaches a plateau at

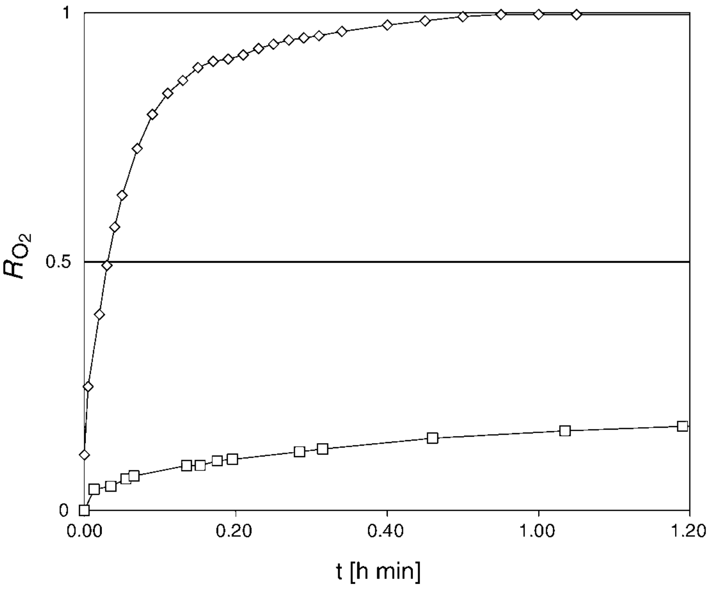


Fig. 2. *Dioxygen-binding curves* ($R_{O_2} = C_{O_2}/C_{CoL_2}$ *vs.* time) *in pure O_2 for [Co(dien)$_2$]$^{2+}$* (Rl) *and [Co(dmdien)$_2$]$^{2+}$* (□)

$R_{O_2} \approx 1.0$, indicating a quantitative final reaction, while for $[Co(dmdien)_2]^{2+}$ complex this is not the case.

The kinetic parameters were calculated by the computer treatment of the absorbance values at 310 and 324 nm for the $[Co(dien)_2]^{2+}$ and $[Co(dmdien)_2]^{2+}$, respectively. The best fit of the experimental data is consistent with the reaction mechanisms (charges omitted) in *Eqns. 1* and *2*. In *Fig. 3*, the experimental points and the calculated curves (solid lines) are reported: note that the experimental and calculated absorbance values are in satisfying agreement. $[Co(dien)_2]^{2+}$ forms a 1:1 adduct that evolves to an oxidation product. In the case of $[Co(dmdien)_2]^{2+}$, the oxidation reaction (*Eqn. 2*) is very slow, and k_2 cannot be determined. The best-fitting kinetic parameters are reported in *Table 2*.

$$[CoL_2]_{(solv)} + O_{2(solv)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [CoL_2O_2]_{(solv)} \tag{1}$$

$$[CoL_2O_2]_{(solv)} \xrightarrow{k_2} \text{ox. product} \tag{2}$$

The equilibrium constants for the overall reactions which lead to the formation of the $[CoL_2O_2]$ species are also calculated, combining the rate constants of direct and inverse reaction at 298 K, and are also entered in *Table 2* (1 mol dm^{-3} standard state for O_2).

Table 2. *Kinetic Parameters for the Oxygenation Reactions Reported in* Eqns. 1 *and* 2 *and Thermodynamic Stability Constants for the Reaction.* $[CoL_2]^{2+}_{(solv)} + O_{2(solv)} \rightleftharpoons [CoL_2O_2]^{2+}_{(solv)}$ (L = dien, dmdien) *in DMSO at 298 K and* I = *0.1*M. The errors in parentheses are one standard deviation.

	k_1 [M^{-1} s^{-1}]	k_{-1} [s^{-1}]	k_2 [s^{-1}]	$\log K_{O_2}$
$[Co(dien)_2]^{2+}$	69(3)	0.0017(3)	$1.6(3) \cdot 10^{-4}$	4.6
$[Co(dien)_2]^{2+}$ [a])	$1.2 \cdot 10^{3}$	–	–	–
$[Co(dmdien)_2]^{2+}$	0.035(6)	$6(2) \cdot 10^{-5}$	–	2.8

[a]) In water, see [22].

2.2. *Aqueous Solutions. Table 3* summarizes the basicity constants of dmdien, determined potentiometrically in aqueous 0.1M $NaClO_4$ solution at 298 K. The $\log K_i$ values for the addition of the first two protons to the neutral species dmdien are very similar in magnitude, while a decrease of *ca.* 6 log*K* units is found for the addition of the third proton. To the best of our knowledge, documented data regarding basicity constants for dmdien are not available; however, the $\log K_i$ values for this system are in line with the trend shown by a series of *N*-methyl-substituted diethylenetriamines [20], whose basicity-constant values are reported in *Table 4*.

Table 3. *Protonation Constants* ($\log K_a$) *of dmdien* (L), *Determined by Means of Potentiometric Measurements in Aqueous 0.1*M *NaClO$_4$ Solution at 298 K.* Values in parentheses are one standard deviation.

	$L + H^+ \rightleftharpoons HL^+$	$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$
$\log K_a$	9.73(2)	9.22(2)	3.64(3)

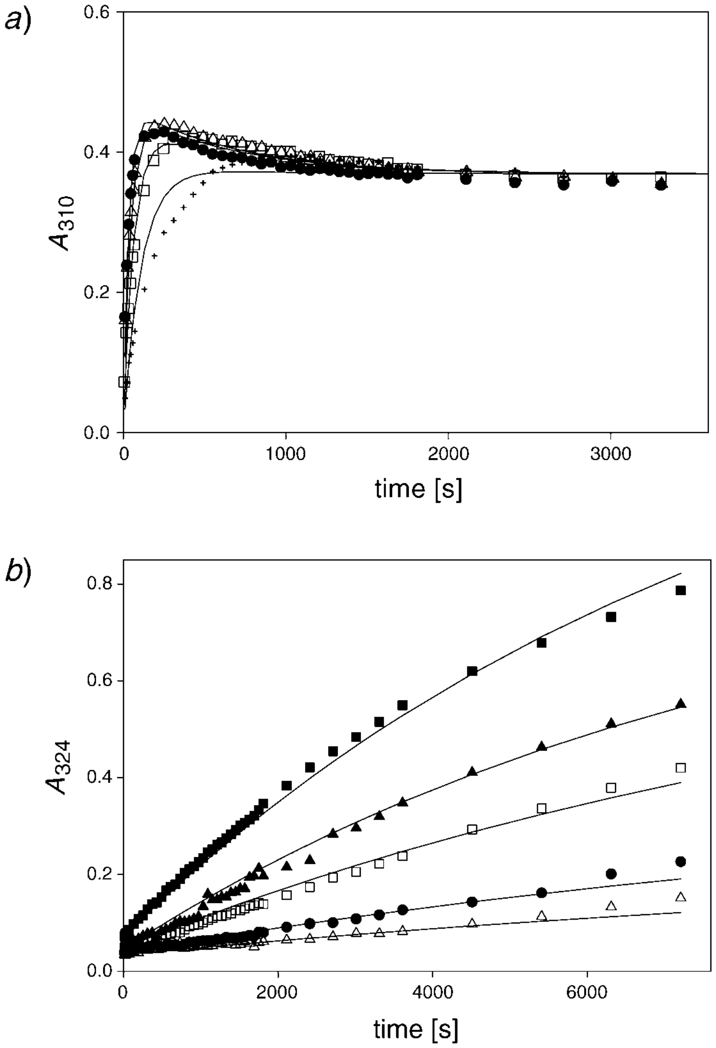


Fig. 3. *Experimental data and fitting curves for the oxygenation of* a) *[Co(dien)$_2$]$^{2+}$* (+: P_{O_2} = 5 kPa, [Co^{2+}] = 0.20 mM, [dien] = 0.41 mM; □: P_{O_2} = 10 kPa, [Co^{2+}] = 0.20 mM, [dien] = 0.41 mM; •: P_{O_2} = 15 kPa, [Co^{2+}] = 0.20 mM, [dien] = 0.41 mM; △: P_{O_2} = 20 kPa, [Co^{2+}] = 0.20 mM, [dien] = 0.41 mM; calc. molar absorbances at 310 nm, ε_{MLO_2} = 2.43(7) · 10^3 mol^{-1} dm^3 cm^{-1}) *and* b) *[Co(dmdien)$_2$]$^{2+}$* (△: P_{O_2} = 10 kPa, [Co^{2+}] = 0.82 mM, [dmdien] = 1.69 mM; •: P_{O_2} = 20 kPa, [Co^{2+}] = 0.82 mM, [dmdien] = 1.69 mM; □: P_{O_2} = 51 kPa, [Co^{2+}] = 0.82 mM, [dmdien] = 1.69 mM; ▲: P_{O_2} = 101 kPa, [Co^{2+}] = 0.66 mM, [dmdien] = 1.44 mM; ■: P_{O_2} = 101 kPa, [Co^{2+}] = 0.99 mM, [dmdien] = 2.06 mM; calc. molar absorbance at 324 nm: ε_{MLO_2} = 2.7(2) · 10^3 mol^{-1} dm^3 cm^{-1})

The coordination properties of dmdien towards Co^{II} were studied in aqueous 0.1M $NaClO_4$ solutions at 298 K at different metal/ligand molar ratios. The best fit of the potentiometric data is consistent with the formation of mono-ligand mononuclear $[CoL]^{2+}$, $[CoLOH]^+$, and $[CoL(OH)_2]$ complexes and bis-ligand mononuclear $[CoL_2H]^{3+}$ and $[CoL_2]^{2+}$ complexes. The stability constants of all these species are

Table 4. *Reported [20] Protonation Constants log*K$_i$ ($i=1,2,3$) *of dmdien and Different* N-*Methyl-Substituted Diethylenetriamines*

	logK_1	logK_2	logK_3
Diethylenetriamine (dien; $H_2NCH_2CH_2NHCH_2CH_2NH_2$)	9.89(1)	9.06(1)	4.27(1)
N-Methyldiethylenetriamine ($MeNHCH_2CH_2NHCH_2CH_2NH_2$)	9.86(6)	9.18(2)	3.30(3)
N,N″-Dimethyldiethylenetriamine (dmdien; $MeNHCH_2CH_2NHCH_2CH_2NHMe$)	9.73(2)	9.22(2)	3.64(3)
N,N-Dimethyldiethylenetriamine ($Me_2NCH_2CH_2NHCH_2CH_2NH_2$)	9.62(6)	8.63(5)	3.62(4)
N,N,N′,N″,N″-Pentamethyldiethylenetriamine ($Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$)	9.22(1)	8.41(3)	2.09(3)

reported in *Table 5*, while *Fig. 4* shows distribution diagrams of the species as a function of pH for the Co^{II}/L molar ratios 1:1 and 1:2. It is worth noting that the mono-dmdien Co^{II} complex shows a clear tendency to form stable hydroxo species. In this complex, in fact, only three N donor atoms bind to the metal ion, and the deprotonation of coordinated H_2O molecules occurs easily, producing mono- and dihydroxylated complexes.

Table 5. *Logarithm of the Equilibrium Constants Determined in 0.1*M *NaClO$_4$ at 298 K for the Complexation Reactions of dmdien* (L) *with Co^{II}*

	log$K$
$Co^{2+} + L \rightleftharpoons [CoL]^{2+}$	7.04(1)
$Co^{2+} + L + H_2O \rightleftharpoons [CoLOH]^{+} + H^{+}$	– 2.93(3)
$Co^{2+} + L + 2\,H_2O \rightleftharpoons [CoL(OH)_2] + 2\,H^{+}$	– 13.56(3)
$Co^{2+} + 2L + H^{+} \rightleftharpoons [CoL_2H]^{3+}$	20.70(4)
$Co^{2+} + 2L \rightleftharpoons [CoL_2]^{2+}$	10.71(7)
$CoL^{2+} + OH^{-} \rightleftharpoons [CoL(OH)]^{+}$	3.77
$[CoL(OH)]^{+} + OH^{-} \rightleftharpoons [CoL(OH)]_2$	3.11

2.3. *Dioxygen Binding.* The ability of [Co^{II}(dmdien)] complexes to bind molecular O_2 was studied by means of potentiometric measurements (see *Exper. Part*) at Co^{II}/L molar ratios ranging from 1:1 to 1:2. However, while the mono-ligand Co^{II}/dmdien complexes display a marked tendency to add molecular O_2, giving rise to stable oxygenated complexes, the bis-ligand Co^{II}/dmdien precursor species does not. When the Co^{II}/L ratio is lower than 1, a slow reaction is observed, and it is not possible to attain the equilibrium conditions. For this reason, only the EMF data obtained at Co^{II}/L 1:1 were considered in the fitting procedure. The analysis of the experimental potentiometric data is consistent with the formation of three dimeric μ-peroxo hydroxo species of formula $[Co_2L_2(\mu\text{-}O_2)(OH)_j]$, with $j=1,2,3$ depending on the pH of the solution. The overall equilibrium stability constants determined for the oxygenated complexes are reported in *Table 6*, while *Fig. 5* displays the distribution diagrams of the complexed species as a function of pH.

To confirm our potentiometric results, we carried out separate experiments in which the formation of the oxygenated complexes was monitored by measuring the consumption of O_2 as a function of pH. Oxygenated solutions containing Co^{II}/L in a 1:1 molar ratio were titrated (in a cell filled without leaving vapor space) from acid to alkaline pH, allowing the formation of the oxygenated species. The concentration ratio

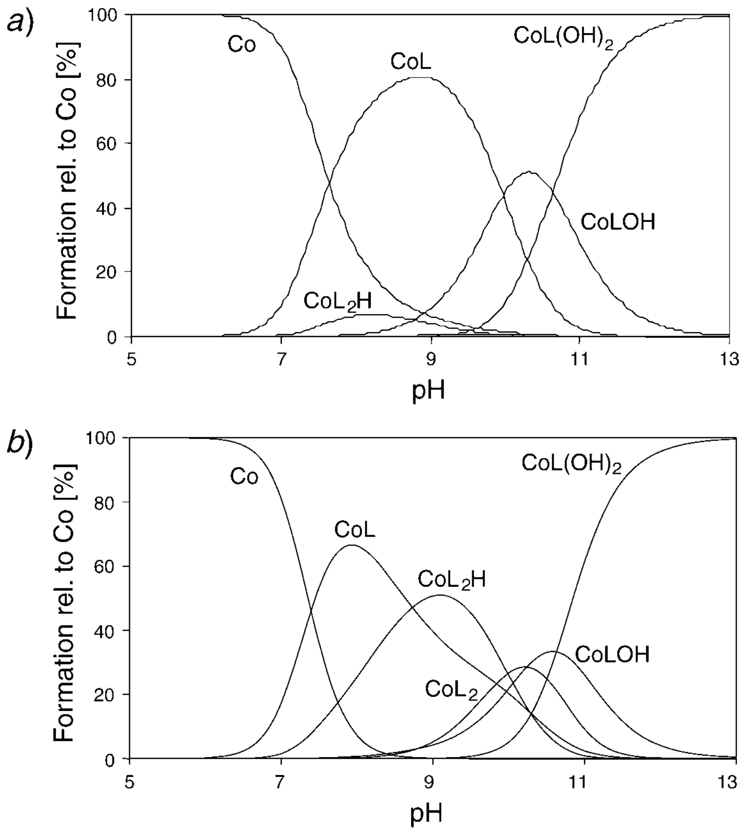


Fig. 4. *Distribution diagram of the species for the system* Co^{II}*/dmdien* (= L) *as a function of pH in 0.1*M *$NaClO_4$ at 298 K:* a) *[L] = 1* mM *and* $[Co^{2+}]$ *= 1* mM *and* b) *[L] = 1* mM *and* $[Co^{2+}]$ *= 0.5* mM. For convenience, complex formulae are not enclosed in brackets and charges are omitted.

Table 6. *Logarithm of the Equilibrium Constants Determined in 0.1*M *$NaClO_4$ at 298 K for the Formation of the Oxygenated Cobalt Complexes*

	log*K*
$2\,Co^{2+} + 2L + O_2 + H_2O \rightleftharpoons [Co_2L_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+} + H^+$	12.87(4)
$2\,Co^{2+} + 2L + O_2 + 2\,H_2O \rightleftharpoons [Co_2L_2(\mu\text{-}OH)_2(\mu\text{-}O_2)]^{2+} + 2\,H^+$	4.50(4)
$2\,Co^{2+} + 2L + O_2 + 3\,H_2O \rightleftharpoons [Co_2L_2(\mu\text{-}OH)_3(\mu\text{-}O_2]^{+} + 3\,H^+$	− 5.60(5)
$2\,CoL^{2+} + O_2 + OH^- \rightleftharpoons [Co_2L_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$	12.53
$[Co_2L_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+} + OH^- \rightleftharpoons [Co_2L_2(\mu\text{-}OH)_2(\mu\text{-}O_2)]^{2+}$	5.37
$[Co_2L_2(\mu\text{-}OH)_2(\mu\text{-}O_2)]^{2+} + OH^- \rightleftharpoons [Co_2L_2(\mu\text{-}OH)_3(\mu\text{-}O_2)]^{+}$	3.66

of bound O_2/Co^{II} as a function of pH, R_{O_2} (pH), was calculated as $R_{O_2}(pH) = (C^\circ_{O_2} - C^\circ_{O_2}(pH))/C^\circ_{Co}$, where $C^\circ_{O_2}$ and C°_{Co} are the initial concentration of O_2 and Co^{II}, respectively, and where $C^\circ_{O_2}$ (pH) is the O_2 concentration in solution during the titration. R_{O_2} (pH) reaches a limit value of *ca.* 0.46, indicative of the almost complete

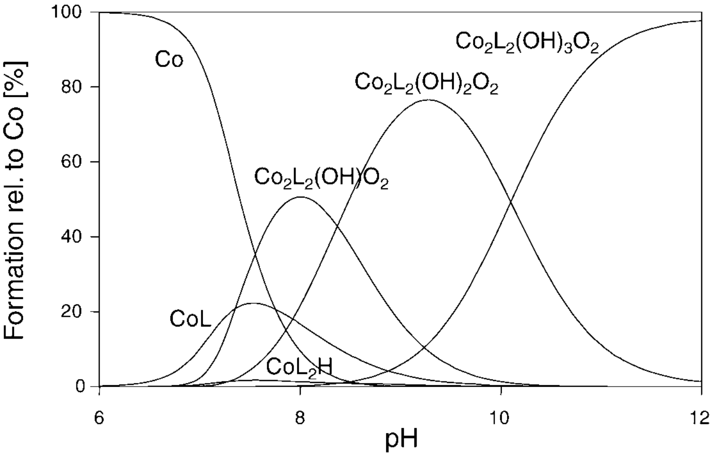


Fig. 5. *Distribution diagram of the species for the system $Co^{II}/L/O_2$ as a function of pH in 0.1*M *$NaClO_4$ at 298 K: [L] = 1* mM, *$[Co^{2+}]$ = 1* mM, *and $[O_2]$ = 1.85* mM. For convenience, complex formulae are not enclosed in brackets and charges are omitted.

formation of a μ-peroxo complex. *Fig. 6* shows the agreement between the O_2-binding curves, calculated on the basis of the equilibrium constants given in *Tables 3*, *5*, and *6*, and the experimental ones obtained through independent measurements of consumed O_2.

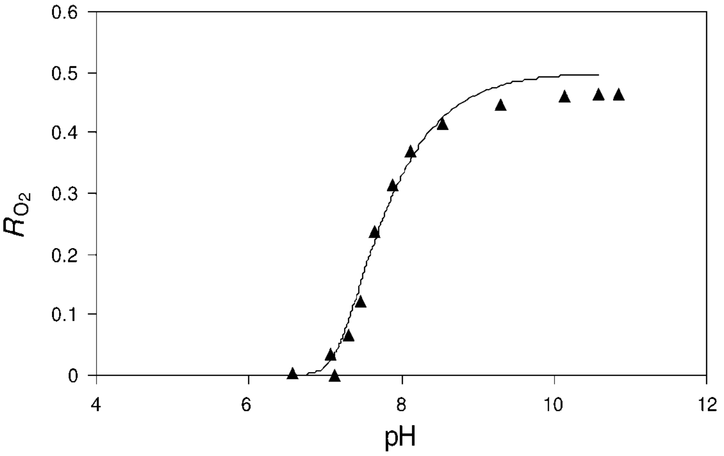


Fig. 6. *Comparison between experimental points* (▲) *and calculated O_2-binding curve* (—) *for the Co^{II}/dmdien/ O_2 system in aqueous 0.1*M *$NaClO_4$ solution at 298 K, starting from pH 6.5.* [dmdien] = 1.08 mM, [Co] = 1.036 mM, and $[O_2]$ = 1.056 mM.

The UV/VIS electronic spectra of the oxygenated species, recorded in aqueous solution at different pH values, show similar features and only minor differences at all values of pH in the range 8 – 11.6. At pH 8.5, two absorption bands are present: the first at λ_{max} 370 nm, which shifts to 358 nm at pH 11.5, and the second at λ_{max} 290 nm. The presence of the band at 360–370 nm indicates a dibridged oxygenated structure [21] and suggests a bridge disposition of the O_2 molecule and of the OH group.

A decrease in absorbance was observed by N_2 bubbling for 30 min in an oxygenated Co^{II}/dmdien solution at pH 8.5 which indicates that the oxygenation reaction is reversible at this pH value. *Fig. 7* shows a cycle of oxygenation–deoxygenation–oxygenation and highlights the reversibility of the O_2 uptake, similarly to that found in DMSO. No changes in the electronic spectra are evident at higher pHs after Ar bubbling.

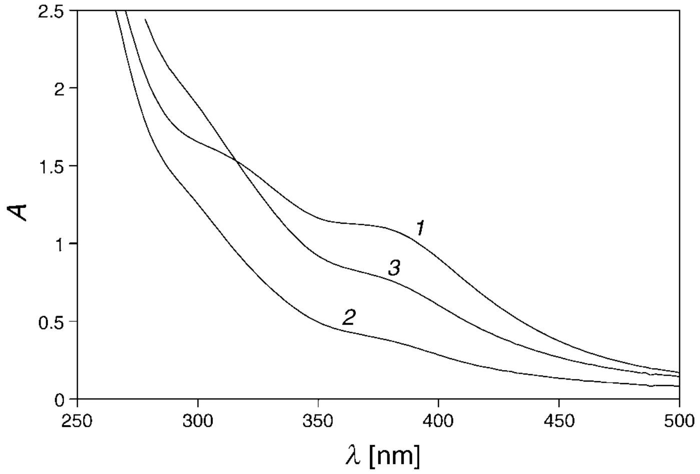


Fig. 7. *Reversibility experiment performed with an aqueous 0.1*M *$NaClO_4$ solution, adjusted to pH 8.5, containing Co^{II} and dmdien in a 1:1 molar ratio* ([dmdien] = 1.0 mM, [Co] = 0.9 mM): *under O_2* (*1*), *after bubbling N_2* (*2*), *and after bubbling O_2* (*3*)

3. Discussion. – 3.1. *O_2 Uptake in DMSO.* The formation of the superoxo adduct $[Co(dien)_2O_2]^{2+}$ in DMSO is characterized by $k_1 = 69$ M^{-1} s^{-1} which is lower than that previously found in aqueous solution (*ca.* $1 \cdot 10^3$ M^{-1} s^{-1}) [22a] and in agreement with previous reported trends observed for polyamine systems in the two solvents [17]. The lower value found here in DMSO should indicate a minor stabilization of the transition state involved in the O_2 coordination, likely due to solvation effects, which suggests an interesting role for DMSO in the study of oxygenation reactions. The k_1 value is indeed lower than that found for the formation of the superoxo adducts starting from the similar coordinatively unsaturated $[Co(en)_2]^{2+}$ complex (en = ethane-1,2-diamine, $k_1 = 1.5 \cdot 10^3$ M^{-1} s^{-1} [15c]. Note that in this last case, two coordinating positions are occupied by DMSO molecules in the anaerobic complexes, and one is still retained in the oxygenated adduct. The trend in k_1 values is, therefore, in agreement with a dissociative mechanism [23] where certainly a higher activation energy is required for the Co–N bond break due to O_2 coordination in the $[Co(dien)_2]^{2+}$ complex than for the $Co-O_{(DMSO)}$ bond break in coordinatively unsaturated $[CoL_2]^{2+}$ complexes, the Co–N interaction being stronger than the $Co-O_{(DMSO)}$ one.

The k_1 value of 0.035 $\text{M}^{-1}\,\text{s}^{-1}$ for the formation of $[\text{Co(dmdien)}_2\text{O}_2]^{2+}$ is three orders of magnitude lower than that of $[\text{Co(dien)}_2\text{O}_2]^{2+}$ (*Table 2*). The presence of steric interactions due to the Me groups makes the dissociative mechanism slower [22b]. Unfortunately, no similar species are found in H_2O and, therefore, no comparisons can be made within these systems.

The stability constants for the mononuclear species (*Table 2*) are $\log K_{\text{O}_2}{}^{\text{Co(dien)}_2} = 4.6$ and $\log K_{\text{O}_2}{}^{\text{Co(dmdien)}_2} = 2.8$. The significant difference of these stability constants should be explained by taking into account the following: *i*) in $[\text{Co(dmdien)}_2]^{2+}$, the amino groups are all secondary, thus slightly poorer σ-donors than those in $[\text{Co(dien)}_2]^{2+}$, and the electron density on the metal center is slightly lower in the former case; *ii*) on the other hand, the value of $\log K_{\text{O}_2}$ has been related [4] to the sum of $\log K_\text{a}$ of the ligands (which is a measure of the simple σ-donor ability of a ligand) that are reported here in H_2O for dmdien ($\Sigma\log K_\text{a} = 22.59$) and available for dien ($\Sigma\log K_\text{a} = 23.22$) [24]. As this trend is not expected to be affected very differently in DMSO, the large difference in the $\log K_{\text{O}_2}$ values for dien and dmdien does not seem to be accounted for by these arguments alone, as $\Delta\Sigma\log K_\text{a}$ is only *ca.* 0.6. Thus, this difference should be explained by taking into account that both starting anaerobic octahedral complexes are coordinatively saturated by the ligands. Therefore, it can safely be assumed that the adducts formed in the reaction of *Eqn. 1* are bearing the O_2 ligand opposite to an amino group. The dien ligand in the $[\text{Co(dien)}_2\text{O}_2]^{2+}$ species possesses two primary and one secondary amino group, while the dmdien in the $[\text{Co(dmdien)}_2\text{O}_2]^{2+}$ species possesses only disubstituted N-atoms. In the latter case, the coordinated O_2 in *trans* position always statistically supports a secondary amino group which is a poorer σ-donor than a primary one [18][25]. This is not the case when the $[\text{Co(dien)}_2\text{O}_2]^{2+}$ species is involved. As generally found [4], for a σ-donor ligand, the axial position is the most efficient in promoting O_2 binding to an octahedral Co^{II} complex, as it favors the electron back donation from the metal to the O_2: this back bonding should be much more sensitive to the different σ-donor ability in *trans* position than to the total $\Sigma\log K_\text{a}$ of the ligands. This also seems to be in agreement with the quite similar values [15c] of $\log K_{\text{O}_2}$ obtained for the oxygenation of the $[\text{Co(en)}_2]^{2+}$ (3.94) and $[\text{Co(dmen)}_2]^{2+}$ (3.77) complexes (dmen = *N*,*N*′-dimethylethanamine), where, in the hypothesis that the same DMSO ligand is present in the two complexes in *trans* position to the bound O_2, a similar affinity towards O_2 should be expected, and indeed it is. In addition, the steric repulsions of the Me groups in $[\text{Co(dmdien)}_2]^{2+}$ should play a role in lowering the outer-sphere solvation energy of the adduct and limiting stabilizing interactions, such as intramolecular H-bonding [18][25].

3.2. *Complexation Equilibria in Water.* The stepwise protonation constants for the addition of the first two protons to the neutral species dmdien are very similar in magnitude ($\log K_1 = 9.73$, $\log K_2 = 9.22$), while a decrease of *ca.* 6 $\log K$ units is found (*Table 3*) for the addition of the third proton. The reason for this difference is the minimization of electrostatic repulsion between positive charges in protonated species. In fact, the first two protonation steps involve terminal N-atoms located far from each other, while the third protonation reaction occurs at the central N-atom, leading to an increased *Coulomb* repulsion between protonated amine groups. The $\log K_i$ values reported in *Table 4* for the basicity constants of a series of polyamines clearly indicate that basicity decreases with increasing degree of *N*-methylation. Note that monomethylation slightly affects the values of the first two protonation constants, while it has a more-pronounced effect on the third one.

The decrease in the basicity of dmdien with respect to dien is also reflected in its coordinative ability towards Co^{II}. It has already been observed [18][19] that the stability of the (amine)metal complexes decreases regularly with increasing substitutions at the terminal N-atoms. Dmdien forms rather stable mono-ligand $[CoL]^{2+}$ and bis-ligand $[CoL_2]^{2+}$ complexes. However, the addition of one metal ion to dmdien gives a lower value of the stability constant ($\log K = 7.04$) than the value reported for the addition of Co^{II} to dien ($\log K_1 = 8.00$) [24]. A more dramatic decrease in the stability constant is observed when the formation of the bis-ligand complexes of dmdien ($\log K_2 = 3.67$) and dien ($\log K_2 = 5.90$) [24] are compared. This matches the result obtained for the same triamines in DMSO, where a lower stability (*Table 1*) and a less exothermic value for the complexation reaction was also measured in going from dien to dmdien [14]. The lower complexation ability of the *N*-methylated dmdien with respect to dien has been attributed to a minor strength of the M–N bonds due to both the decreased basicity of the N-atoms and the steric crowding produced by the *N*-alkyl groups, which causes an elongation of M–N bonds [18].

In a mono-ligand $[Co(dmdien)]^{2+}$ complex, the coordination sphere of the metal is not saturated by the ligand donors and, therefore, this complex is a potential receptor for secondary ligands. In fact, the $[Co(dmdien)]^{2+}$ complex shows a good tendency to coordinate additional species from the medium giving rise to mono- and dihydroxylated species (see *Table 5* and *Fig. 4*). A value of 3.77 and 3.11 logarithmic units can be calculated for the addition of the OH^- anion to the $[Co(dmdien)]^{2+}$ and $[Co(dmdien)OH]^{2+}$ complexes, respectively.

3.3. *O_2 Uptake in Water.* It is well-known that in aqueous solution, mononuclear complexes bind O_2, leading to dimeric μ-peroxo species in which the O_2 molecule bridges the metals of two different complexes [1–4]. Whenever the chelating agent has an insufficient number of coordinating groups, as is the case in dmdien, a secondary ligand may coordinate to the Co^{2+} ion. In the present case, only hydroxylated μ-peroxo-bridged Co^{II}/dmdien complexes are formed, demonstrating a cooperative binding of OH^- and O_2 in the formation of the O_2 adducts. The synergic effect of OH^- coordination to Co^{II} also explains why the Co^{II}/dmdien 1:1 system was able to bind O_2 in H_2O, whereas the $[Co(dmdien)]^{2+}$ species was not able to do so in DMSO. This result certainly constitutes a very interesting example of the fundamental role of the solvent in the formation and nature of O_2 carriers.

The presence of two absorption bands at λ_{max} 290 and 370 nm in the UV/VIS spectra indicates the formation of a μ-dioxygen-μ-hydroxo structure with a bridge disposition of both the O_2 molecule and the OH^- group [21], thus accounting for the cooperativity in the binding of O_2 and OH^-. The $[Co_2(dmdien)_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$ complex starts to form at pH > 7 and is the prevalent species at pH 8, while the di- and trihydroxo forms prevail at higher pHs. We can calculate, from data reported in *Tables 5* and *6*, a value of $\log K = 12.53$ for the simultaneous binding of O_2 and OH^- to two $[Co(dmdien)]^{2+}$ precursor complexes. This value is lower than the one for the same reaction which gives rise to $[Co_2(dien)_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$ ($\log K = 14.88$) [26]. As already found in DMSO, the *N*-alkylation of the polyamine not only reduces the stability of the Co^{II}/dmdien complexes, but also their affinity to O_2 which is significantly affected by the charge density on the metal centre and, therefore, by the σ-donor ability of the ligand.

It is evident from the equilibrium diagram in *Fig. 5* that the oxygenated $[Co_2(dmdien)_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$ complex is in equilibrium with deoxygenated precursors. The equilibrium pressure of O_2 at half oxygenation, $(P_{O_2})_{1/2}$, in a μ-peroxo-μ-hydroxo dinuclear complex depends on the pH and on the initial molar concentration of the $[CoL]^{2+}$ complex [27]. A value of $(P_{O_2})_{1/2} = 4.3$ kPa can be calculated for $[Co_2(dmdien)_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$ at pH 8.5 and [[CoL]] = 1 mM. The presence of only disubstituted N-atoms in dmdien, which are poorer σ-donors than monosubstituted ones, leads evidently to a reversible O_2 binding.

At higher pH values $[Co_2(dmdien)_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$ displays a good tendency to add one or two more OH^- groups thus fulfilling the Co^{II} coordination sphere. $\log K = 5.37$ and $\log K = 3.66$ are obtained for the addition of OH^- to $[Co_2(dmdien)_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$ and to $[Co_2(dmdien)_2(\mu\text{-}OH)_2(\mu\text{-}O_2)]^{2+}$, respectively (see *Table 6*). These values are higher than those found for the OH^- binding in nonoxygenated Co^{II} complexes. They account for the more-hydrophilic nature of the Co^{II} ion in a μ-peroxo complex and closely agree with the equilibrium-constant values for the addition of nonbridged OH^- groups in dibridged Co^{II}/O_2 structures. The ligands 10,22-dioxa-1,4,7,13,16,19-hexaazacyclotetracosane (O-bisdien) [28] and 2,6-bis{[bis-(2-aminoethyl)-amino]methyl}phenol (diden) [29] were found to form dinuclear dibridged O_2 complexes with Co^{II}. At alkaline pH, these complexes are able to coordinate two more OH^- ligands. The equilibrium constants for the addition of the OH^- groups have the $\log K$ values 5.48 and 4.37 for *O*-bisdien and 5.67 and 3.32 for diden, in close agreement with our values of 5.37 and 3.66.

3.4. *Comparison of Data from Different Reaction Media.* Lower stabilities for the anaerobic $[CoL]^{2+}$ species are observed in H_2O [20] than in DMSO [14]: as no data concerning the heat of transfer of Co^{2+} from H_2O to any other solvent was available [30], it was previously [14] assumed that this ion would be more strongly solvated by DMSO than by H_2O on the basis of some comparisons between Zn^{2+} and Co^{2+}, characterized by similar charge density [31], and by the analysis of X-ray data of solvated derivatives [15b]. Therefore, the trend in the stability of the complexes in H_2O and DMSO, unlike what might be expected on the basis of Co^{II} solvation in the two solvents, is due to greater solvation of amines in H_2O than in DMSO [24] through H-bonding.

The drop in stability is much more marked when the $[CoL_2]^{2+}$ complex is formed. Likely, in H_2O the desolvation of the species is still important when the $[ML_2]^{2+}$ complex is formed, whereas it was shown to have finished at the first step of complexation in DMSO.

Dioxygen complexes of different stoichiometry are formed in aqueous solution and in DMSO. In the aprotic DMSO, a Co^{II}/O_2 1:1 superoxo complex is formed, while a Co^{II}/O_2 2:1 μ-peroxo complex is formed in aqueous solution. The formation of a μ-peroxo binuclear Co^{II} complex gives more-polar coordinate bonds and an increased charge separation between the metal ion and the O_2 ligand [4]. H_2O is the best solvent for stabilizing charge separation, and this is probably the reason why μ-peroxo-bridged dicobalt species are more stable in aqueous solution, whereas mononuclear superoxo cobalt species are favored in DMSO.

In addition, the synergic effect of OH^- coordination is very important in making the mono-ligand species able to uptake O_2 in H_2O, when dmdien is involved.

Conclusions. – Interesting results have been obtained which show that both in H_2O and DMSO a reversible O_2 uptake can be achieved by different oxygenated Co^{II}/dmdien-based species, which is not achieved for Co^{II}/dien adducts. This highlights that the simple *N*-methylation of primary amino groups acts on steric and σ-donor properties of the ligand in such a way that its Co^{II} complexes become better O_2 carriers in both solvent media.

The kinetic parameters of the Co^{II}/dien system found here for DMSO and available for H_2O solutions, as well as the different nature of the species reacting with O_2 of the Co^{II}/dmdien system in the two solvents indicate an important, interesting role of the solvent in governing the affinities of the Co^{II} complexes for O_2. This is particularly reflected in the different behavior of the mononuclear $[Co(dmdien)]^{2+}$ species towards O_2 uptake in the two solvents, the synergic action of OH^- being fundamental in H_2O to achieve O_2 coordination.

The values of the kinetic constants reported here are in line with other results in DMSO for the coordinatively unsaturated complexes $[Co(en)_2]^{2+}$ and $[Co(dmen)_2]^{2+}$ and highlight that the opening of a Co–N bond rather than of a $Co-O_{(DMSO)}$ bond is very important in determining the reaction rate.

Finally, the large difference in the thermodynamic O_2 affinity of the two $[CoL_2]^{2+}$ complexes (L = dien, dmdien) in DMSO is not rationalized only on the basis of the total basicity of the ligand as done previously, but seen as being mainly dependent on the structural features of the dioxygenated adduct.

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Experimental Part

General. $[Co(ClO_4)_2] \cdot 6$ DMSO was prepared and standardized as reported [14]. DMSO (*Fluka*; > 99%) was purified by distillation according to [14], degassed by a pumping-freezing procedure, and stored over 4 Å molecular sieves. Dien (*Aldrich*; > 97%) and dmdien, whose synthesis is described in [32][33], were purified by fractional distillation [34]. Their purity (> 99%) was checked by ^1H- and ^{13}C-NMR techniques. A 0.5M $Co(ClO_4)_2$ stock soln. in H_2O was prepared by dissolving $Co(ClO_4)_2 \cdot 6\,H_2O$ in bidistilled H_2O. $Co(ClO_4)_2$ stock solns. in DMSO were prepared by dissolving in anh. degassed DMSO weighted amounts of the dried $Co(ClO_4)_2 \cdot 6$ DMSO adduct. The Co^{II} concentration was checked by titration with EDTA both in H_2O and in DMSO. All other chemicals were reagent-grade products and were used without further purification. All standard DMSO solns. were prepared and stored in a *MB-Braun 150* glove box, under a controlled atmosphere containing less than 1 ppm of H_2O and less than 1 ppm of O_2. The H_2O content in the solns., typically 10–20 ppm was determined with a *Methrohm 684-KF* coulometer.

Kinetic Measurements. The kinetics of oxygenation reactions in DMSO were studied by UV/VIS spectroscopy following the appearance of the LMCT band(s) associated with the formation of the O_2 adduct(s) [27]. The apparatus employed for these measurements consisted of a three-necked flask connected to the gas inlet and outlet and, through an optical-fiber immersion probe (1-cm optical path), to a *Varian Cary-50* spectrophotometer. The gas supplied to the reaction flask was a O_2/N_2 mixture whose composition was tuned by means of calibrated mass-flow controllers (*Alltech Digital Flow Check-HR*) and gas-mixing valves. Typically, 25 ml of the Co^{II} soln. at the concentration needed were poured into the reaction flask and conditioned for at least 30 min with the gas mixture. Then an aliquot of ligand was added and the spectra collection started. An automatic procedure was used to record the spectra, in the range 700–260 nm, at planned interval times. At least 50 data points were collected in each kinetic run. A continuous bubbling of the gas mixture was maintained during the experiments. The measurements were performed at constant complex concentration by varying the O_2 partial pressure from 4 to 101 kPa. The concentration of the complex was 0.2 or 0.5 mM for $[Co(dien)_2]^{2+}$ and 0.5 mM $[Co(dmdien)_2]^{2+}$. The concentration of dissolved O_2 in soln. was calculated assuming the validity of *Henry*'s law [35] and a value of 2.1 mM for the equilibrium concentration of O_2 in DMSO + $Et_4N(ClO_4)$ soln. at 298 K with a partial pressure of O_2 of 101 kPa in the gas phase [36]. The data was fitted with the DYNAFIT program [37] by numerically solving *Eqns. 3–5* (for convenience, brackets and charges in complex formulae are omitted).

$$d[ML_2]/dt = -k_1[O_2][ML_2] + k_{-1}[ML_2O_2] \quad (3)$$

$$d[ML_2O_2]/dt = k_1[O_2][ML_2] - k_{-1}[ML_2O_2] - k_2[ML_2O_2] \quad (4)$$

$$d[\text{ox. prod}]/dt = k_2[ML_2O_2] \quad (5)$$

Potentiometric Measurements. Equilibrium constants for protonation and complexation reactions with dmdien in H_2O were determinated by pH-metric measurements ($pH = -\log[H^+]$), carried out in 0.1M $NaClO_4$ at 298.0 ± 0.1 K, with the automatic equipment described earlier [38]. The combined glass electrode, *Crison 52.21*, was calibrated as a H^+ concentration probe by titrating known amounts of HCl with CO_2-free NaOH solns. and determining the equivalent point by *Gran*'s method [39] which gives the standard potential E°. A value of $pK_w = 13.75$ at 298.0 ± 0.1 K in 0.1M $NaClO_4$ was used [40]. At least three potentiometric titrations (*ca.* 90 data points each one) were performed for each system in the pH range 2.5–11. Measurements performed to determine the equilibrium constants for the formation of O_2 complexes were carried out, maintaining a constant pressure (101 kPa) of O_2 in the potentiometric cell. The concentration of O_2 in soln. (1.185 mM), at the operating pressure, temp., and ionic strength, was obtained from published data [41]. The dmdien concentration was varied in the range 0.9 – 2 mM, while the metal ion concentration [M] was varied from $[M] = 0.5 \cdot [\text{dmdien}]$ to $[M] = [\text{dmdien}]$ in the complexation experiments under both aerobic and anaerobic conditions. The equilibrium constants for both protonation and metal binding were determined by means of the Hyperquad program [42]. A modified version of this program was used to calculate the equilibrium constants of the oxygenated complexes from the EMF data. This modification was made to consider the presence of a chemical species (O_2) involved in the complexation equilibria whose free concentration was kept constant during the measurement. All titration curves were treated either as a single set or as separated entities without significant variation in the value of the stability constant.

Dioxygen Binding Measurements in Water. The O_2 concentration was measured with a *WTW* oxygen sensor (*Oxi 340/set*) equipped with an oxygen electrode (*CellOx 325*) capable of measuring O_2 concentrations up to a maximum of 100.0 ppm. The electrode was calibrated in air-saturated aq. 0.1M $NaClO_4$ solns. The cell was designed to contain the oxygen sensor, a glass electrode, and two openings through which the reagents were introduced by microsyringes or titration microburettes. The cell was filled, leaving no vapor space, with the oxygenated soln. of the ligand in aq. 0.1M $NaClO_4$ adjusted to the selected pH value. The soln. was thermostatted at 298 K. Known amounts of $Co(ClO_4)_2$ stock soln. were added, and the concentration of O_2, C_{O_2}, was measured as a function of pH or time.

Spectrophotometric Measurements. UV/VIS spectra were recorded on a *Perkin-Elmer Lambda-6* UV/VIS spectrophotometer, or on a *Hewlett-Packard 8452A* diode-array spectrophotometer. The samples were prepared by adding $Co(ClO_4)_2$ stock soln. to oxygenated solns. containing dmdien and adjusted at various pH values or by bubbling O_2 into solns. containing the preformed deoxygenated complexes.

Volumetric Absorption in DMSO. The measurements of the O_2 absorption were performed on the $[Co(dien)_2]^{2+}$ and $[Co(dmdien)_2]^{2+}$ systems. The thermostatted gas burette was connected with a vessel containing a known complex concentration ($[CoL_2] = 30$ mM) and exposed to pure O_2 under stirring.

REFERENCES

[1] A. E. Martell, D. T. Sawyer, 'Oxygen Complexes and Oxygen Activation by Transition Metals', Plenum Press, New York, 1988.

[2] H. Sugimoto, T. Nagayama, S. Maruyama, S. Fujinami, Y. Yasuda, M. Suzuki, A. Uehara, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2267.

[3] R. D. Jones, D. A. Summerville, F. Basolo, *Chem. Rev.* **1979**, *79*, 139.

[4] E. C. Niederhoffer, J. H. Timmons, A. E. Martell, *Chem. Rev.* **1984**, *84*, 137.

[5] L. I. Simandi, 'Dioxygen Activation and Homogeneous Catalytic Oxidation', Elsevier, Amsterdam, 1991; 'Advances in Catalytic Activation of Dioxygen by Metal Complexes', 'Catalysis by Metal Complexes', Ed. L. I. Simandi, Kluwer Academic, Boston, 2003.

[6] S. Fallab, *Angew. Chem., Int. Ed.* **1967**, *6*, 496.

[7] H. Maecke, M. Zehnder, U. Thewalt, S. Fallab, *Helv. Chim. Acta* **1979**, *62*, 1804.

[8] T. Watanabe, R. D. Archer, *J. Mol. Catal.* **1994**, *93*, 253.

[9] E. Bolzacchini, C. Canevali, F. Morazzoni, B. Rindone, M. Orlandi, R. Scotti, *J. Chem. Soc., Dalton Trans* **1997**, *24*, 4695.

[10] B. Steiger, F. C. Anson, *Inorg. Chem.* **2000**, *39*, 4579.

[11] P. Mastrorilli, F. Muscio, G. P. Suranna, C. F. Nobile, M. Latronico, *J. Mol. Catal. A* **2001**, *165*, 81.

[12] H. Tang, C. Shen, M. Lin, A. Sen, *Inorg. Chim. Acta* **2000**, *300–302*, 1109.

[13] D. D. Hu, Q. Z. Shi, Z. X. Tang, Y. Fang, J. F. Kennedy, *Carbohydr. Polym.* **2001**, *45*, 385.

[14] C. Comuzzi, M. Grespan, P. Polese, R. Portanova, M. Tolazzi, *Inorg. Chim. Acta* **2001**, *321*, 49.

[15] a) C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Eur. J. Inorg. Chem.* **2002**, *8*, 2194; b) C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Eur. J. Inorg. Chem.* **2003**, *10*, 1948; c) C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Inorg. Chem.* **2003**, *42*, 8214.

[16] A. Melchior, S. Peressini, R. Portanova, C. Sangregorio, C. Tavagnacco, M. Tolazzi, *Inorg. Chim. Acta* **2004**, *357*, 3473.

[17] S. Del Piero, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Dalton Trans.* **2004**, 1358.

[18] D. Meyerstein, *Coord. Chem. Rev.* **1999**, *185–186*, 141; T. Clark, M. Hennemann, R. van Eldik, D. Meyerstein, *Inorg. Chem.* **2002**, *41*, 2927.

[19] P. V. Bernhardt, *J. Am. Chem. Soc.* **1997**, *119*, 771; P. V. Bernhardt, A. Jones, *J. Chem. Soc., Dalton Trans* **1998**, *11*, 1757; P. Comba, *Coord. Chem. Rev.* **1999**, *182*, 343; P. Comba, *Coord. Chem. Rev.* **1999**, *185–186*, 81; P. V. Bernhardt, G. A. Lawrence, M. Napitupulu, G. Wei, *Inorg. Chim. Acta* **2000**, *300–302*, 604.

[20] J. W. Allison, R. J. Angelici, *Inorg. Chem.* **1971**, *10*, 2233.

[21] A. B. P. Lever, H. B. Gray, *Acc. Chem. Res.* **1978**, *11*, 348; E. I. Solomon, F. Tuczek, D. E. Root, C. A. Brown, *Chem. Rev.* **1994**, *94*, 827.

[22] F. Miller, J. Simplicio, R. G. Wilkins, *J. Am. Chem. Soc.* **1969**, *91*, 1962; M. Kodama, E. Kimura, *J. Chem. Soc., Dalton Trans* **1980**, 327.

[23] R. van Eldik, *Coord. Chem. Rev.* **1999**, *182*, 373.

[24] M. Ciampolini, P. Paoletti, L. Sacconi, *J. Chem. Soc.* **1961**, 2294.

[25] A. Mucci, R. Domain, R. L. Benoit, *Can. J. Chem.* **1980**, *58,* 953; R. L. Benoit, M. J. Mackinnon, L. Bergeron, *Can. J. Chem*. **1981**, *59*, 1501.

[26] R. Nakon, A. E. Martell, *J. Inorg. Nucl. Chem*. **1972**, *34*, 1365.

[27] S. Cabani, *React. Funct. Polym.* **1996**, *28*, 167.

[28] A. E. Martell, R. J. Motekaitis, D. Chen, I. Murase, *Pure Appl. Chem.* **1993**, *65*, 959.

[29] N. Ceccanti, M. Formica, V. Fusi, L. Giorgi, M. Micheloni, R. Pardini, R. Pontellini, M. R. Tiné, *Inorg. Chim. Acta* **2001**, *321*, 153.

[30] C. Kalidas, G. Hefter, Y. Marcus, *Chem. Rev.* **2000**, *100*, 819.

[31] F. A. Cotton, G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley, New York, 1980.

[32] R. M. Clay, S. Corr, M. Micheloni, P. Paoletti, *Inorg. Chem.* **1985**, *24*, 3330.

[33] D. W. White, B. A. Karcher, R. A. Jacobson, J. G. Verkade, *J. Am. Chem. Soc.* **1979**, *101*, 4921.

[34] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, Oxford, 1980.

[35] H. J. James, R. F. Broman, *Anal. Chim. Acta* **1969**, *48*, 411.

[36] D. T. Sawyer, G. Chiericato, C. T. Angelis, E. J. Nanni, T. Tsuchiya, *Anal. Chem.* **1982**, *54*, 1720.

[37] P. Kuzmic, *Anal. Biochem.* **1996**, *237*, 260.

[38] S. Cabani, N. Ceccanti, R. Pardini, M. R. Tinè, *Polyhedron* **1999**, *18*, 3295.

[39] F. J. C. Rossotti, H. Rossotti, *J. Chem. Educ.* **1965**, *42*, 375.

[40] G. Carpeni, E. Boitard, R. Pilard, S. Poize, N. Sabiani, *J. Chim. Phys.* **1963**, *69*, 1445.

[41] 'Oxygen and Ozone', 'Solubility Data Series', Ed. R. Battino, Elsevier-Science, New York, 1981, Vol. 7.

[42] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739.

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