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Cobalt(II) Dioxygen Carriers Based on Simple Diamino Ligands: Kinetic and ab Initio Studies

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The kinetics of the oxygenation reaction of CoL_2^{2+} complexes (L = ethylenediamine (en), *N*,*N*′-dimethylethylenediamnine (dmen)) have been investigated in dimethyl sulfoxide (dmso) at 298 K and in a medium adjused to 0.1 mol dm^{-3} with Et_4NClO_4 by means of a UV–vis spectrophotometric technique. The reaction mechanisms are consistent with the fast formation of superoxo 1:1 initial $CoL_2–O_2$ species (L = en, dmen), whereas the dimeric μ-peroxo $(CoL_2)_2O_2$ adduct is formed only when L = en, in the rate determining step. The kinetic results are discussed taking into account the effects of ligand/solvent substitution. EPR results give information on the electronic structure and the coordination geometry of the Co(II) complexes and further confirm the stoichiometry of the species formed. Ab initio calculations provide insights on the geometrical parameters of all the complexes investigated and allow us to draw some hypotheses about the influence of H···H nonbonded interactions in the eventual formation of the dimeric μ-peroxo $(CoL_2)_2O_2$ complexes. Solvational effects are also considered. The formation of the $(CoL_3)_2O_2$ adduct is also proved when L = en by means of O_2 volumetric absorption.

Introduction

Over the past decades, Co(II) complexes have been widely studied as dioxygen carriers and activators.[1−5] These investigations produced a number of data, and many of the factors affecting affinity and stability of the dioxygen adducts have been studied, understood, and rationalized. The numerous recent publications on this topic prove that the interest is still on and mainly lays on the potential application of these adducts in dioxygen separation and storage, industrial processes, and oxidation catalysis in mild conditions.[6−13] The crucial point to be considered when designing more and more efficient systems is that the dioxygen binds to Co(II) with an oxidative addition occurring with a partial electron-transfer from the metal center toward dioxygen, leading to the formation of a mononuclear superoxo or a dinuclear peroxo species. Thus, the O_2 uptake is favored by any event that brings electronic charge on the metal center:[3−5] the more electron donating the ligand and/or solvent are, the higher the Co(II) complex dioxygen affinity will be. Unfortunately, auto-oxidative irreversible processes often occur, and the complex undergoes rapid deactivation. In order to avoid the degradation process or, at least, to slow it down, the affinity and reversibility toward dioxygen have to be adjusted by tuning the ligand and/or the solvent features. Many data are now available on the link between ligand bulkiness, ligand

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electron-donor ability, solvent, affinity toward O_2, and endurance to auto-oxidation processes.[14−19] The relationship established between the affinity for dioxygen and the characteristic of the whole ligand and solvent system guides the design of Co(II) complexes depending on the application demands. For example, if the main goal is to design Co(II) complexes to be efficient as catalysts in oxidation reaction, the mononuclear superoxo is the active species to be used.[20−24] Then, with the aim of designing a good Co(II) based catalyst, all the system properties have to be tuned in order to build up reversible superoxo mononuclear O_2 adducts, which are able to resist auto-oxidation irreversible reactions as much as possible.

For this purpose, dimethyl sulfoxide (dmso) was then chosen as solvent in order to favor the formation of the polar, highly charge-separated superoxo adduct. Recent findings demonstrate that polyamines bearing different alkylation degrees are able to affect the redox properties of their metal complexes: the oxidation tendency of the metal center decreases on going from complexes of polyamines with primary amino groups to complexes with tertiary ones.[25−28] This finding should parallel the affinity toward dioxygen and then set the possibility to use simple, low cost, and largely available ligands to build up an ideal catalyst.

In this work, we report the first study on the kinetics of the dioxygen adduct formation in the aprotic solvent dmso by Co(II)-complexes with the simple diamine ethylenediamine (en) and the alkylated *N*,*N*′-dimethylethylenediamine (dmen), which were chosen in order to investigate if a simultaneous control of electronic and steric factors was possible and efficient. This characterization, which also allows the determination of the stability constants for the formation of the dioxygenated species, is essential in order to understand the factors at play in the potential performances of oxygenated complexes.[18,19]

Unfortunately, the more alkylated similar diamines, *N*,*N*,*N*′-trimethylethylenediamine (trmen) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen), were not able to bind dioxygen,[28a] therefore limiting this tuning of N-alkylation effects.

In addition, electron paramagnetic resonance (EPR) data have been collected as this spectral technique is a useful tool to investigate the electronic structure and the coordination geometry of Co(II) complexes.

Ab initio calculations have been also performed in order to provide insights into the geometrical parameters of all the complexes investigated. In particular, this approach has been used to draw the hypothetical models for the μ-peroxo dioxygen−Co(II) adducts, focusing the attention on the effects of the methyl functions on their stabilization.

Experimental Section

Chemicals. $Co(ClO_4)_2 \cdot 6dmso$ was prepared and standardized as reported.[27] Dimethyl sulfoxide (Fluka > 99%) was purified by distillation according to the described procedure,[29] degassed by a pumping−freezing procedure, and stored over 4 Å molecular sieves. All the diamines (Aldrich, >97%) were purified by fractional distillation.[30] Cobalt(II) perchlorate stock solutions were prepared by dissolving in anhydrous degassed dmso weighted amounts of the dried $Co(ClO_4)_2 \cdot 6dmso$ adduct, and its concentration was checked by titration with EDTA. The background salt NEt_4ClO_4 was recrystallized twice from methanol and dried at 90 °C. Solutions of the ligands were prepared as described.[27] All standard solutions were prepared and stored in a MB Braun 150 glovebox under controlled atmosphere containing less than 1 ppm of water and less than 1 ppm of dioxygen. The water content in the solutions, typically 10−20 ppm, was determined by a Methrohm 684 KF coulometer.

Kinetic Measurements. The kinetics of oxygenation reactions were studied by UV−vis spectroscopy following the appearance of the LMCT band(s) associated with the formation of the dioxygen adduct/s.[18,19] 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 mixture of O_2/N_2 whose composition was finally tuned by means of calibrated mass flow controllers (Alltech Digital Flow Check-HR) and gas mixing valves. Typically, 25 mL of the Co(II) solution at the concentration needed was poured in 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 employed in order to record the spectra, in the range 600−265 nm, at planned time intervals. 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 varying the O_2 partial pressure and at constant O_2 partial pressure varying the complex concentration. The experiments were carried out with O_2 partial pressures ranging from 15.2 to 91.2 Torr; the concentration of the complex ranged from 0.4 to 1 mmol dm^{-3} for both $Co(en)_2$ and $Co(dmen)_2$. The

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concentration of dissolved O_2 in solution was calculated assuming the validity of Henry's law [31] and a value of 2.1×10^{-3} mol dm^{-3} for the equilibrium concentration of O_2 in dmso + TEAP solution at 298 K with a 760 mmHg of partial pressure of O_2 in the gas phase.[32] The data were analyzed with the DYNAFIT program.[33]

Volumetric Absorption. The measurements of the O_2 absorption were performed on the $Co(en)_3^{2+}$ complex as it was the only one for which no results on the stoichiometry of the dioxygenated species could be obtained from UV−vis investigation (see Results section, Kinetics subsection). The gas buret was connected with a vessel containing a known $Co(en)_3^{2+}$ complex concentration ($[Co^{2+}]$ = 30 mmol dm^{-3}, [en] = 120 mmol dm^{-3}) and exposed to pure oxygen or air.

EPR Measurements. EPR spectra were recorded with a Varian E-9 spectrometer working at X-band frequency (9.25 GHz) equipped with an Helium flux cryostat ESR9 from Oxford Instruments. Spectra were recorded either on samples prepared under inert atmosphere and then after air exposition of the same solutions for 5 min. The Co(II) concentration was about 19 mmol dm^{-3} being [en] = 32 mmol dm^{-3} and [dmen] = 41 mmol dm^{-3}, chosen in order to have the maximum amount of the ML_2 species in solution.

Computational Methods. Taking into account that the $[Co(dmen)_2(dmso)_2]^{2+}$ system is rather complicated as it presents a high number (32) of possible isomers, for computational convenience preliminary molecular mechanics (MM) calculations by means of the Hyperchem program[34] were carried out using the in-built mm+ force field parameters, in order to obtain the strain energies of these isomers and identify the most stable one. The same calculations were performed also on the simpler $[Co(en)_2(dmso)_2]^{2+}$ system.

Once the most stable configuration was identified, ab initio calculations were performed on the anaerobic and aerobic complexes using GAMESS-US and PC-GAMESS programs.[35,36]

Self-consistent-field (SCF) calculations were carried out at the Hartree−Fock level of theory using the unrestricted formalism for the open-shell complexes. The anaerobic complexes were optimized in their quartet state, the aerobic CoL_2-O_2 adducts in their doublet state, and the $(CoL_2)_2-O_2$ in their singlet state (see EPR section). The 1:1 oxygenated adducts were optimized simply by substituting a solvent molecule in the anaerobic complex with dioxygen, and so on for the 2:1 adduct.

The 6-31G(d) basis set was employed for all elements with the exception of the dioxygen molecule in the adducts (6-31+G(d)). For the coordinated dioxygen, diffuse functions were added for its anionic character. Geometries were optimized to a final rms gradient of 0.0001 hartree/bohr with the symmetry constrains reported in Table 3.

Results

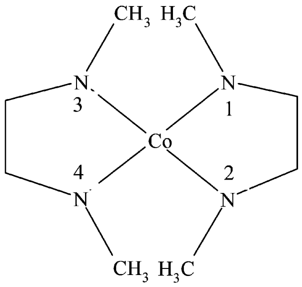
UV−Vis Studies on O_2 Uptake. As the stability constants for the CoL_j complexes (j = 1−3 for L = en; j = 1,2 for L = dmen) were known,[28a] it was possible to adjust the reagents concentration in order to have known amounts of CoL_2 species in solution.

Table 1. Kinetic Parameters for the Oxygenation Reactions Reported in Schemes 1 and 2 and Thermodynamic Overall Stability Constants for the Reaction $iCoL_2 + O_2 \rightarrow (CoL_2)_iO_2$ (L = en, dmen) in Dmso at 298 K and I = 0.1 mol dm^{-3} [a]

system	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	k_2 (M^{-1} s^{-1})	k_{-2} (s^{-1})	i	log K_{O_2}
$Co(en)_2^{2+}$	$1.5(1) \times 10^3$	0.17(2)	$0.102 (6) \times 10^3$	0.00021(2)	1	3.94(6)
					2	9.63(7)
$Co(dmen)_2^{2+}$	$0.083(8) \times 10^3$	0.014(2)			1	3.77(6)

[a] The errors in parentheses are one standard deviation.

Table 2. Calculated Strain Energies for the Isomers of *trans*-$[Co(dmen)_2(dmso)_2]^{2+}$



configuration (1,2,3,4)	strain energy (kJ/mol)	ΔE (kJ/mol)
R,S,R,S	236.3	0.0
R,S,S,S	253.9	17.6
R,R,R,R	257.1	20.8
R,R,S,S	267.0	30.7
S,R,S,S	269.4	33.1
R,R,R,S	272.3	35.9
S,R,S,S	277.9	41.6
S,R,R,S	281.8	45.5

Table 3. Calculated Bond Lengths (Å) and Angles (deg) for the Complexes Studied

complex	point group	r(M−N)[a]	r(O−O)	r(Co−O)	Co−O−O
$[Co(en)_2(dmso)_2]^{2+}$	C_2	2.220			
$[Co(en)_2(dmso)O_2]^{2+}$	C_s	2.000	1.331 (1.17)[a]	1.850	114.5
$[Co(dmen)_2(dmso)_2]^{2+}$	C_i	2.250			
$[Co(dmen)_2(dmso)O_2]^{2+}$	C_1	2.098	1.322	1.865	124.4
$[Co_2(en)_4(dmso)_2O_2]^{4+}$	C_{2h}	1.994	1.434	1.891	114.4
$[Co_2(dmen)_4(dmso)_2O_2]^{4+}$	C_i	2.035	1.431	1.898	119.1

[a] Calculated value for free O_2 molecule.

Only CoL_2 (L = en, dmen) and $Co(en)_3$ were able to bind dioxygen as shown by the rapid rising of the characteristic LMCT bands of the dioxygen adducts in the UV−vis region in Figure 1a. Their maxima were localized at 313, 328, and 314 nm, respectively, after an exposure to air of about 30 s. These bands are absent when the 1:1 complexes are considered.

It is notable that the similarity between the stepwise constants for the Co(II)−en system do not allow us to obtain a solution where only the $Co(en)_2$ complex is present. In particular, in Figure 1a the $Co(en)_2$ concentration is 76% of the total Co(II) concentration, the rest being the Co(en) species. However, since Co(en) is unable to bind dioxygen, we could safely assume that all the changes occurring in the UV−vis region upon oxygenation of a solution containing

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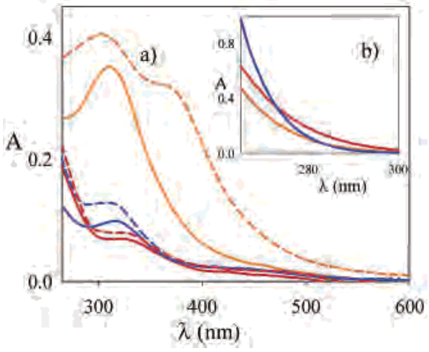

Figure 1. (a) Electronic spectra of $Co(en)_2^{2+}$ (orange), $Co(dmen)_2^{2+}$ (red), and $Co(en)_3^{2+}$ (blue) solutions after 30 s (—) and after 6 min (- - -) of exposure to O_2. (b) The same as in part a after 3 h (blue) and 24 h.

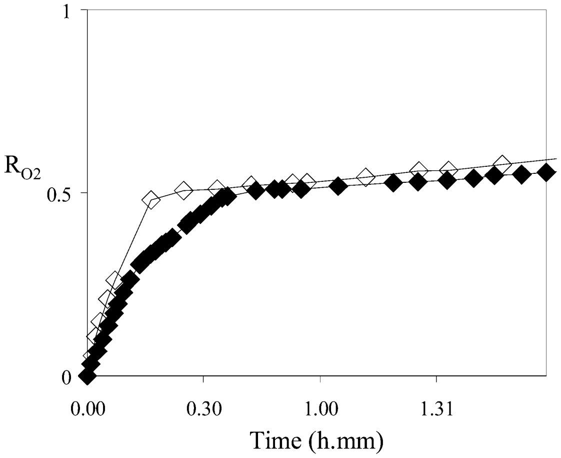

Figure 2. Dioxygen binding curves $R_{O_2} = n_{O_2}/n_{Co(en)_3}$ vs time, in pure O_2 (◇) and in air (◆), for the $Co(en)_3$ system.

both the Co(en) and $Co(en)_2$ species are to be ascribed to O_2 binding to $Co(en)_2$ species.

In Figure 1a (- - -), it is evident that, after 6 min of exposure to air, the maxima of both $Co(en)_3$ and $Co(dmen)_2$ dioxygen adducts raised in absorption while the $Co(en)_2$ spectrum showed, in addition to the maximum at 313 nm, a new band at 370 nm. As far as the oxygenated solution of $Co(dmen)_2$ is concerned, a decrease in absorbance at 328 nm is observed by bubbling Ar, pointing out a certain reversibility of the system.

A complete disappearance of the characteristic adduct bands in the UV−vis region is evident in Figure 1b: this is achieved after 3 h of exposure to air for $Co(en)_3$ and after at least 24 h for $Co(en)_2$ and $Co(dmen)_2$ and suggests the formation of an irreversible auto-oxidation product.

Volumetric Absorption. Figure 2 shows the dioxygen binding curves, $R_{O_2} = n_{O_2}/n_{CoLj}$ versus time, for the $Co(en)_3$ system. From the values of the stability constants relative to the anaerobic complex,[28a] it can be inferred that this is the only species initially present in solution. Its O_2 absorption reaches a rough plateau at $R_{O_2} = 0.5$ both in pure dioxygen (a) and in air (b), thus indicating a quantitative reaction. This allows the unambiguous determination of the dioxygen complex stoichiometry, which therefore can be safely described as a 2:1 adduct. The absorption of O_2 continues then very slowly indicating that irreversible processes are likely at play.

Scheme 1

$$Co(en)_{2(solv)} + O_{2(solv)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{A}}{[Co(en)_2O_2]_{(solv)}} \qquad (1)$$

$$[Co(en)_2O_2]_{(solv)} + Co(en)_{2(solv)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\mathbf{B}}{[Co(en)_2O_2Co(en)_2]_{(solv)}} \qquad (2)$$

Scheme 2

$$Co(dmen)_{2(solv)} + O_{2(solv)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{C}}{[\ Co(dmen)_2O_2]_{(solv)}} \qquad (3)$$

Unfortunately, no further results could be obtained on this latter system because of some limits in our experimental conditions (see Kinetics subsection).

Kinetics. The kinetic parameters have been calculated by the computer treatement of the absorbance values at 313 and 328 nm for Co−en and −dmen systems, respectively. The best fit of the experimental data is consistent with the reaction mechanisms shown in Schemes 1 and 2.

In Figure 3, the experimental points and the calculated curves (—) are reported: a good agreement exists between experimental and calculated absorbance values.

The kinetic parameters are reported in Table 1 for $Co(en)_2$ and $Co(dmen)_2$ systems and refer to the reaction mechanisms reported in Schemes 1 and 2, respectively.

The equilibrium constants for the overall reactions which lead to the formation of species **A**, **B**, and **C** are also calculated, combining the rate constants of direct and inverse reaction at 298 K, being the standard state for O_2 in solution at 1 mol dm^{-3}, and are also entered in Table 1.

As far as $Co(en)_2$ is concerned, the data suggest a first step where a 1:1 dioxygenated adduct is formed which is slowly converted in a μ-peroxo dimeric adduct, as further confirmed by EPR results (see below). On the other hand, all the attempts to fit the experimental data introducing an additional 2:1 species failed when the $Co(dmen)_2$ system was considered.

In order to investigate $Co(en)_3^{2+}$ behavior, a large excess of en was used to avoid the presence of $Co(en)_2^{2+}$ species. Unfortunately, the volatile free en was moved away by the gas flow: thus, the kinetics of the formation of the hypotesized μ-peroxo dioxygen adduct were impossible to follow.

EPR Measurements. The EPR spectra recorded at 4.2 K for the anaerobic CoL_2 complexes are shown in Figure 4a,b (—) for L = en and dmen, respectively. The spectra are characterized by a broad axial signal with $g_{per} = 4.4$ and $g_{par} = 2.4$ and 2.2 for en and dmen, which can be reasonably attributed to a high spin Co(II) ion in an octahedral environment.[37] The temperature dependence of the spectra confirms the high spin state of the Co(II) ion. In fact, on increasing temperature, the signal rapidly becomes broader and disappears above the liquid nitrogen temperature due to the very short spin−lattice relaxation time which character-

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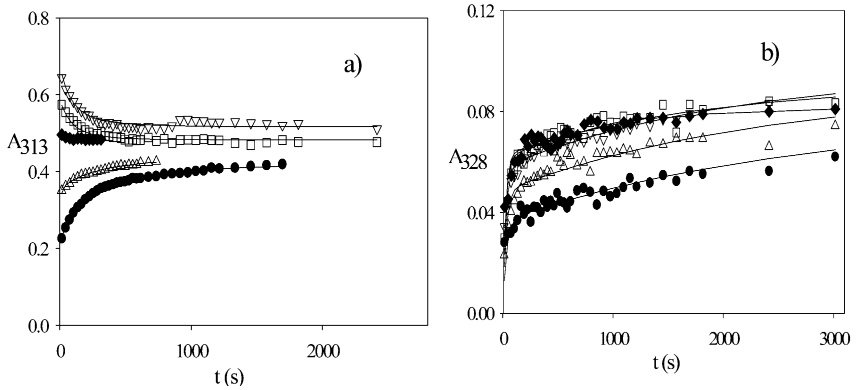

Figure 3. (a) Experimental data and fitting curves for the oxygenation of $Co(en)_2^{2+}$: ● $P_{O_2} = 16$, $[Co^{2+}] = 0.44$, $[en] = 0.57$; △ $P_{O_2} = 30$, $[Co^{2+}] = 0.47$, $[en] = 0.56$; ◆ $P_{O_2} = 46$, $[Co^{2+}] = 0.47$, $[en] = 0.59$; □ $P_{O_2} = 60$, $[Co^{2+}] = 0.40$, $[en] = 0.54$; ▽ $P_{O_2} = 75$, $[Co^{2+}] = 0.44$, $[en] = 0.57$. P_{O_2} in Torr and concentrations (in brackets) in mmol dm^{-3}. Calculated molar absorbances at 313 nm: $\epsilon_{ML_2O_2} = 7.0(4) \times 10^3$ mol^{-1} dm^3 cm^{-1} and $\epsilon_{(ML_2)_2O_2} = 5.1(3) \times 10^3$ mol^{-1} dm^3 cm^{-1}. (b) Experimental data and fitting curves for the oxygenation of $Co(dmen)_2^{2+}$: ● $P_{O_2} = 61$, $[Co^{2+}] = 0.40$, $[dmen] = 1.30$; △ $P_{O_2} = 30$, $[Co^{2+}] = 0.45$, $[dmen] = 1.59$; ◆ $P_{O_2} = 91$, $[Co^{2+}] = 0.49$, $[dmen] = 1.6$; □ $P_{O_2} = 106$, $[Co^{2+}] = 0.48$, $[dmen] = 1.38$; ▽ $P_{O_2} = 122$, $[Co^{2+}] = 0.46$, $[dmen] = 1.3$. P_{O_2} in Torr and concentrations (in brackets) in mmol dm^{-3} Calculated molar absorbance at 328 nm: $\epsilon_{ML_2O_2} = 1.87(2) \times 10^2$ mol^{-1} dm^3 cm^{-1}.

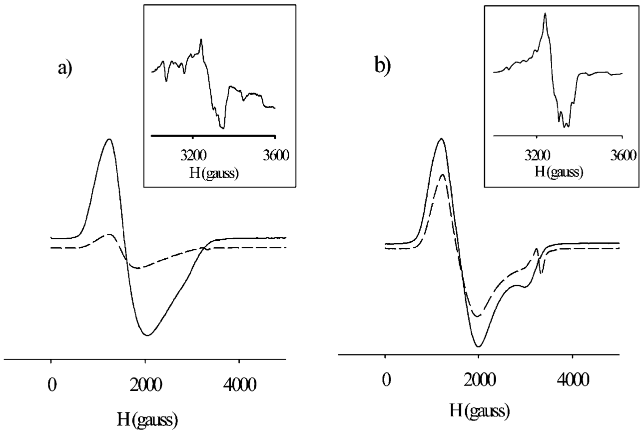

Figure 4. EPR spectra, collected at 4 K, of frozen solutions of $Co(en)_2^{2+}$ (a) and $Co(dmen)_2^{2+}$ (b) in anaerobic conditions (—) and after 30 min bubbling with pure O_2 (- - -). In the frames: the same as previous dashed spectra, collected at 90 K.

izes Co(II) in the high spin.[37] The broadness of the signals observed for the two systems can be ascribed to the presence of more than one anaerobic complex (i.e., CoL and CoL_2) present in both systems.

Upon oxygenation of the solutions, a more (en) or less (dmen) pronounced decrease in the intensity of the signals is observed, and a weak, broad signal appears at g ≃2.0 as clearly shown in Figure 4a,b (- - -). In the frames, where the EPR spectra at 90 K are reported, this appears to be the hyperfine-splitting signals with low intensity due to ^{59}Co($I = {}^{7}/_{2}$) typical of octahedral low spin 1:1 cobalt superoxo complex.[4,38]

Ab Initio Calculations. Theoretical ab initio studies on metal compleses and their dioxygen adducts are reported in the literature mainly on Cu(I) complexes,[39] Schiff's bases, and porphyrin Co(II) complexes.[40-42] To the best of our knowledge, no similar theoretical studies appeared both on Co(II) anaerobic and aerobic complexes with differently methylated polyaza ligands, probably for the lack of crystallographic data.

The preliminary MM study on the $Co(dmen)_2(dmso)_2$ complex identifies the most stable isomer as the *trans* one, where the methyl groups of a coordinated dmen are both in the same side of the plane, i.e., the R,S,R,S isomer reported in Table 2. This is in agreement with X-ray data for $M(dmen)_2X_2$ (M = Cu(II), Ni(II), X = Br^-, SCN^-, NO_3^-, H_2O)[43] which point out that the *trans* configuration of the amine ligands is the only one present in the solid state and that the methyl groups of the same dmen ligand are both above or under the plane of the nitrogen atoms, as in the R,S,R,S isomer in Table 2. This also fits with recent assumptions which hypothesize the *trans*-conformation of the methyl groups to be the most stable when similar nitrogen ligands are bonded to Co(II).[44] The *trans* isomer is also favored as far as the $[Co(en)_2(dmso)_2]^{2+}$ complex is concerned.

Ab initio calculations were then run for the trans isomers of the two anaerobic Co(II)−en and − dmen complexes: the optimized structures are reported in Figure 5a,d. In order to find a correlation between structural calculated parameters and the inability of $Co(dmen)_2^{2+}$ to form the 2:1 adduct, also the structures of monomeric 1:1 (Figure 5b,e) and

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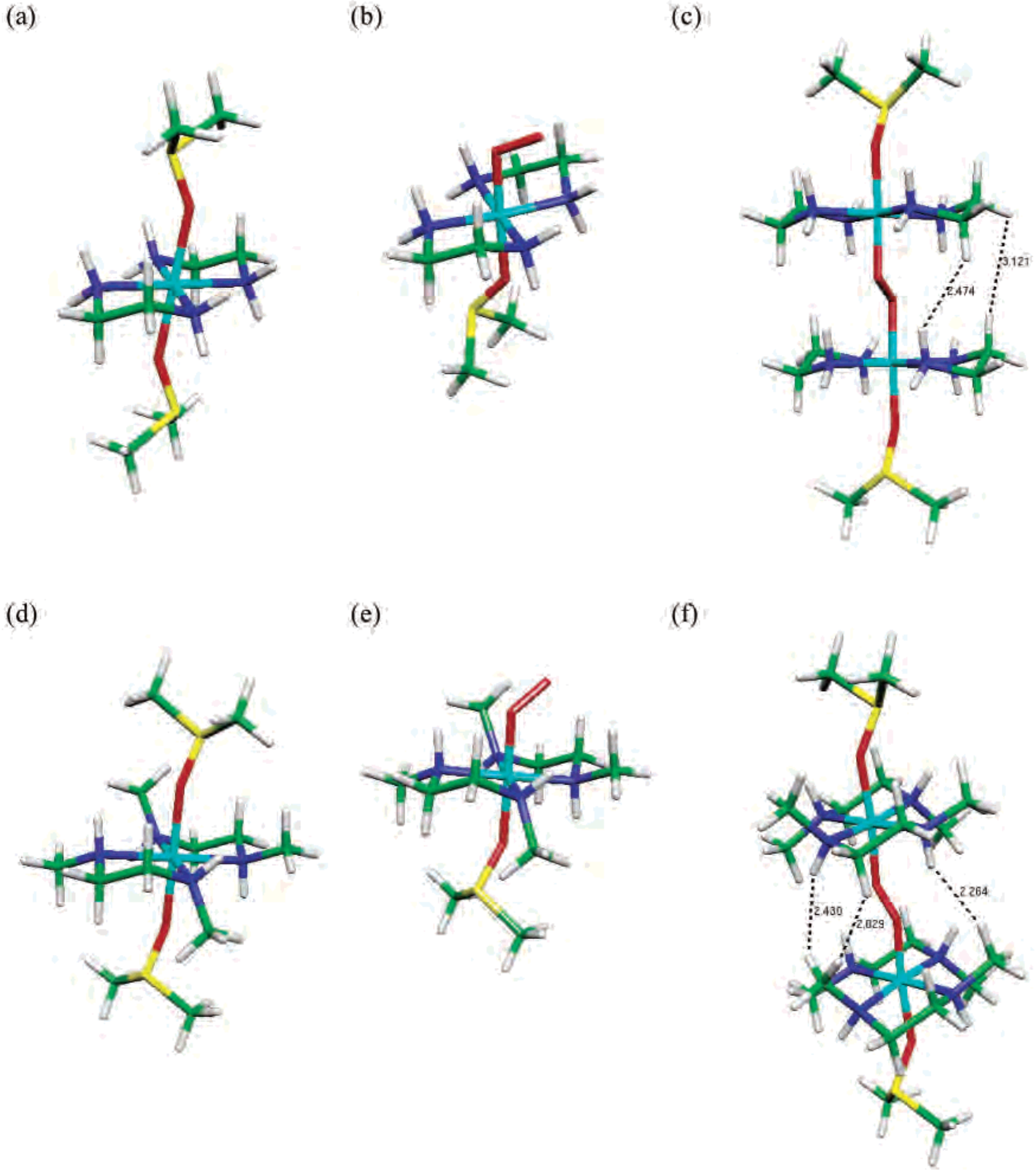

Figure 5. Optimized structures of the complexes (a) $[Co(en)_2(dmso)_2]^{2+}$, (b) $[Co(en)_2(dmso)O_2]^{2+}$, (c) $[Co_2(en)_4(dmso)_2O_2]^{4+}$, (d) $[Co(dmen)_2(dmso)_2]^{2+}$, (e) $[Co(dmen)_2(dmso)O_2]^{2+}$, and (f) $[Co_2(dmen)_4(dmso)_2O_2]^{4+}$.

dimeric 2:1 (Figure 5c,f) dioxygenated complexes were optimized.

Some calculated geometrical parameters of the investigated complexes are in Table 3. For the complex $[Co(en)_2(dmso)_2]^{2+}$, the Co−N bond length of 2.22 Å is a bit longer than usual values of 2.14−2.19 Å found for some Co(II)−$N_{primary}$ complexes.[45a] In the 1:1 dioxygen adduct, the Co−N bond length is 2.00 Å which is closer to 1.95−1.99 Å for Co(III)−$N_{primary}$ bond distances.[45b] Both in $[Co(dmen)_2(dmso)_2]^{2+}$ and in the 1:1 adduct the Co−N bond distances are a little bit longer than those found when $[Co(en)_2(dmso)_2]^{2+}$ is concerned.

The O−O distances of 1.331 and 1.322 Å calculated for the two monomeric adducts are both longer than 1.17 Å, calculated at the same level of theory for the free dioxygen molecule,[3] and are typical of the monomeric μ-superoxo cobalt adducts. The O−O distance is in the range between O_2^- and O_2^{2-} measured in the solid state[3] confirming its superoxide character. The r(O−O) and r(Co−O) values in Table 3 indicate a slightly weaker interaction with dioxygen in the case of the $Co(dmen)_2(dmso)O_2^{2+}$ complex.

The calculated charges (q's) obtained using Mulliken population analysis and the spin densities (ρ's) are reported in Table 4. The results show that the substitution of a dmso molecule with O_2 causes a shift in negative charge primarily from the metal center to the coordinated dioxygen. This is consistent with similar results obtained for other systems

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Table 4. Partial Charges (q's) and Calculated Spin Densities (ρ's, in au) for the Optimized Geometries of the Model Compounds

complex	$q_{(Co)}$	$q_{(N)}{}^a$	$q_{(O1)}{}^b$	$q_{(O2)}{}^b$	$\rho_{(Co)}$	$\rho_{(N)}{}^a$	$\rho_{(O1)}$	$\rho_{(O2)}$
$[Co(en)_2(dmso)_2]^{2+}$	1.40	−1.012			0.320	0.027		
$[Co(en)_2(dmso)O_2]^{2+}$	1.743	−1.073	−0.530	−0.122	0.065	−0.001	0.046	0.218
$[Co(dmen)_2(dmso_2)]^{2+}$	1.393	−0.872			0.312	0.026		
$[Co(dmen)_2(dmso)O_2]^{2+}$	1.742	−0.929	−0.614	−0.034	0.175	−0.005	0.019	−0.220

[a] Averaged. [b] Co−O1−O2.

using density functional approach,[40] ab initio,[42] and semiempirical methods.[41]

The calculated spin densities in the anaerobic complexes agree with the unpaired electrons confined on the cobalt ion, being only a small fraction of unpaired electrons localized on the other nuclei. When the dioxygen adduct is formed, the unpaired spin is transferred to the dioxygen moiety with small residuals remaining on the cobalt atom. This is in accord with a general model for the end-on binding of O_2 in which the interaction is viewed as a spin pairing of one of the unpaired antibonding electrons of O_2 with an unpaired electron in the d_{z^2} orbital of Co(II).[4] The calculated parameters are in good agreement with existing structural data, and therefore, the models well describe the species concerned.

For the optimized structures of the $[Co_2(en)_4(dmso)_2O_2]^{4+}$ and $[Co_2(dmen)_4(dmso)_2O_2]^{4+}$, the calculated O_2 bond lengths (Table 4) are higher than those in the monomeric adduct and close to the 1.49 Å value found in the solid state[3] for $O_2{}^{2-}$ pointing out its peroxide nature. In addition, the calculated structural parameters in Table 4 are in good agreement with the values found for μ-peroxo adducts of some Co−amine complexes.[46] As evidenced in Figure 5c,f, for the two dimeric species the distances between the hydrogens of methyls and of the amino and ethylenic groups are also reported.

Discussion

The study here presented points out some very interesting results, such as that the final dioxygenated adducts of both $Co(en)_2$ and $Co(dmen)_2$ systems are quite resistant to autooxidation reaction (at least 24 h) making them very promising for practical applications.

On the other hand, a simple variation in alkylation makes the two systems behave in a different way: in fact, while a mononuclear adduct is formed in a second-order reaction by both systems, $Co(en)_2$ also gives a successive dimeric species (Scheme 1) whereas $Co(dmen)_2$ does not (Scheme 2).

This behavior is rather unusual: in fact, in water, the formation of end-on oxygenated complexes requires superstructured ligands,[18,19] whereas μ-peroxo (and μ-hydroxo) complexes are always formed when polyamines are considered.[47] In aprotic solvents of low dielectric constants, such as butirronitrile ($\epsilon = 20$), similar CoL_2 complexes (L = diamines) form; on the other hand, they are only 1:1 species.[38] Dmso's dielectric constant ($\epsilon = 46$) does not prevent in such a way the formation of dinuclear adducts[48] as also evidenced by the fact that $[Co(en)_2]_2O_2$ does exist. In addition, both $Co(en)_2$ and $Co(dmen)_2$ present an insufficient number of coordination groups so that, in principle, one or even two bridges may be formed.

The literature data reported in dmso until now mainly refer to Schiff's bases[4,49] so this paper represents the first report on the formation of Co(II)L (L = simple diamines) dioxygen adducts. Therefore, careful investigations on the species formed are fundamental, despite the shape of UV−vis spectra (Figure 1a) unambiguously detecting different behaviors of en and dmen described above.

EPR measurements show the presence of high spin octahedral Co(II) complexes in anaerobic conditions. Upon oxygenation, a decrease in the intensity of these signals occurs, and a weak signal relative to low spin 1:1 cobalt superoxo complex appears (Figure 4a,b). Though the way in which these spectra are recorded in principle do not allow any quantitative evaluation, nevertheless the qualitative comparison of the spectra of the two solutions before and after oxygenation shows that the drop in the intensity of the anaerobic signal is significant for the $Co(en)_2$ system (Figure 4a, - - -) whereas this is not the case when the $Co(dmen)_2$ system is concerned (Figure 4b, - - -). This clearly confirms the formation of an additional species, namely the dimeric, diamagnetic EPR silent μ-peroxo species for the Co(II)−en system, whereas no detectable amount of dimeric species is present in the other system. An attempt to rationalize the whole of the experimental results is reported as follows.

1:1 Superoxo Adducts. It must be remembered that the reaction with O_2 is related to the tendency for the complex to undergo the oxidation reaction $CoL_2{}^{2+} \rightarrow CoL_2{}^{3+} + e^-$ and that N-alkylation causes the stabilization of the lower oxidation state as a result of different effects:[25,43] (i) the inductive effect of methyl groups increases the σ-donating properties of the N atoms; (ii) N-alkylation decreases the outer sphere solvation energy making then the total electron density on the metal decrease; (iii) nonbonding interactions between alkyl groups and/or hydrogen atoms are also to be considered as they might cause M−N elongation and steric strain affecting the total transfer, as pointed out by reliable X-ray and MM studies.[26]

On these bases, a different affinity of the two amine systems toward O_2 should be expected, whereas the values of the stability constants are, respectively, log $K_{O_2}{}^{Co(en)_2} =$

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3.94(6), log $K_{O_2}^{Co(dmen)_2} = 3.77(6)$. Thus, the two complexes show a surprisingly quite similar affinity for dioxygen suggesting that the monomethylation does not imply huge differences in the CoL_2/O_2 1:1 stability. This result can be explained with the reasonable hypothesis that the effects i–iii are balancing each other.

On the other hand, effects ii and iii become certainly more relevant when additional tertiary amino groups are present, as shown also by the inability of trmen and tmen to form anaerobic 1:2 CoL_2 complexes.[28a] These are therefore not reaching the minimum of three coordinated nitrogen atoms, which are at least necessary to be able to bind dioxygen.[50]

The O_2 uptake by Co(II)L (L = polyamines) complexes has been demonstrated to be a dissociative process (I_d) in water,[51] and a similar I_d process seems to occur in dmso as well. In fact, the value of k_1 determined in aqueous solution for the $Co(en)_2$ system[52] is 4.7×10^5 M^{-1} s^{-1}, higher than the value of k_1 (1.5×10^3 M^{-1} s^{-1}) found here in dmso: this agrees with structural evidence which suggests that Co(II) is more strongly solvated by dmso than by water,[28a,53] thus causing a higher activation energy for the I_d process.

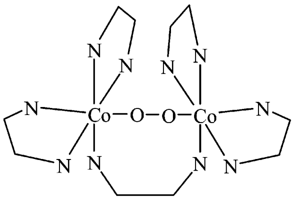
The value of the rate constant k_1 for reaction 1 is higher than k_1 for reaction 3. The steric hindrance of methyl groups should play an important role, inhibiting the dmso exchange, thus slowing the oxygenation of the N-alkylated chelate.[54]

2:1 Peroxo Adducts. The huge difference between the two systems lies in the stoichiometry of the final O_2 adduct.

A possible explanation may be related to nonbonding interactions due to the presence of methyl groups,[26] which become more and more important, when a dinuclear species is formed. The geometrical parameters found in the models reported in Figure 5c,f seem to reveal some interesting features of the H···H nonbonded interactions. In fact, the dashed distances between the hydrogens of methyls and of the amino and ethylenic groups in the Co–dmen system are quite shorter (2.029–2.430 Å) than those found in the Co–en system (2.471–3.121 Å). Despite ab initio calculations neglecting environmental effects, nevertheless it can be safely assumed that these geometric features should be retained, or even enhanced, also in dmso solution.

In a reported molecular mechanics (MM3) approach, a function was proposed from which one can calculate the van der Waals potential energy between two atoms of hydrocarbons.[55] When H atoms are concerned, and taking the R_{vdW} (vdW = van der Waals radius) value of 1.62 Å proposed, it can be found that the minimum potential energy is located at about 3.24 Å, becoming more and more positive below ~2.8 Å. The H···H distances evidenced for the Co–dmen system therefore all belong to highly positive vdW energies, and this should mainly account for the absence of the dimeric $[Co(dmen)_2]_2O_2$ species.

Chart 1



Solvational effects should also play a role, as effect ii is expected to become much effective when the dimeric species is concerned.

The binuclear adduct formation reported in reaction 2 for the $Co(en)_2$ system is the rate determining step ($k_2 = 0.102 \times 10^3$ s^{-1}, $k_1 = 1.5 \times 10^3$ M^{-1} s^{-1}), as found in water for open chain polyamine systems[3] and as shown by the Co(II)–trien system in dmso.[53] The k_{-2} value here reported is similar to the one found for $[Co_2(trien)_2O_2]^{4+}$ complex formation in dmso and suggests that Co–O breakage in the peroxo species (represented by k_{-2}) appears to be only slightly dependent on the chelating ligands coordinated to Co(II) in dmso.

The stepwise stability constant for the formation of the binuclear **B** adduct is 4.9×10^5, indicating that this species, with more polar Co–O bonds, is more thermodynamically favored than the superoxo A. Due to its high polarity and relatively high dielectric constant, dmso likely shows the same ability, also displayed by water, to stabilize highly charged centers, regardless of the balancing dipoles through molecular symmetry.[4]

The overall stability constant for **B** is close to the value of 1.3×10^9 previously reported for the monobridged μ-peroxo $[Co_2(trien)_2O_2]^{4+}$ adduct.[53] Evidently, in the absence of methyl groups a mononuclear species containing secondary and primary amino groups is able to react with another molecule of nonoxygenated complex to give the dimeric species. It should be observed that the stabilities of $[Co_2(trien)_2O_2]^{4+}$ and $[Co_2(en)_4O_2]^{4+}$ dinuclear adducts are independent of the type of nitrogen atoms when they are primary or secondary ones. This is in agreement with the above discussion on the stability of 1:1 dioxygen complexes where the effects i, ii, and iii have been regarded as balancing each other.

$Co(en)_3$ forms a bridged 2:1 μ-peroxo adduct despite the initial saturation of the metal coordination sites. Previous reported data[56] in aqueous solution on the same system pointed out the formation of a $[Co_2(en)_5O_2]^{4+}$ species with the hypothesized structure reported in Chart 1.

It is difficult to draw a hypothesis about the coordination features of the species found in dmso as NMR and EPR approaches did not provide a clear structural characterization. Therefore, a structure similar to that reported in Chart 1 should be taken as a reasonable hypothesis also in this case.

Seven-coordination of the metal ion is here discarded as this is rather unusual also in the solid state for Co(II) ion as

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shown by the evidence that Mn^{2+} and Fe^{2+} can form seven-coordinated complexes with nitrogen donor macrocyclic polyamines whereas Co^{2+} does not. To detect this coordination mode in Co(II), very highly preorganized ligands are needed.[57,58]

Conclusions

Interesting results have been obtained which point out that the two CoL_2 dioxygenated systems here investigated are very promising for practical applications, due to their quite good resistance to auto-oxidation processes and to their simplicity.

In addition, the insertion of a methyl group on each nitrogen group, while not highly influencing the thermodynamic stability of the 1:1 superoxo dioxygenated adduct, causes a different behavior mainly for what concerns the nature of the species formed.

It is clearly shown, in fact, that the dimeric μ-peroxo adduct is not formed when Co(II)−dmen system has been considered, as evidenced by UV−vis and EPR results. This quite surprising result, which is very promising taking into account that the 1:1 species is active in catalytic processes, has been explained by considering the influence of H···H nonbonded repulsions and outer-sphere decreased solvational effects. For this purpose, ab initio calculations provide useful insights on the geometrical features of all the complexes investigated and are especially enlightening when applied to the hypothetical dimeric adducts.

As far as the kinetics are concerned, the N-alkylation should inhibit the dmso exchange, thus slowing down the oxygenation rate in the formation of the **C** adduct. The low k_1 value for reaction 1 as compared to the similar k_1 in water suggests an interesting role of the dmso solvent in the oxygenation reaction.

Finally, $Co(en)_3$ reveals the interesting peculiarity of forming a 2:1 μ-peroxo adduct, despite the saturation of the anaerobic initial metal coordination sites.

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