

Cobalt(II) Complexes with Nitrogen Donors and Their Dioxygen Affinity in Dimethyl Sulfoxide

Clara Comuzzi,^{*,[a]} Andrea Melchior,^[a] Pierluigi Polese,^[a] Roberto Portanova,^[a] and Marilena Tolazzi^{*,[a]}

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The formation of Co^{II} complexes with differently methylated N-donor ligands ethylenediamine (en), *N,N'*-dimethylethylenediamine (dmen), *N,N,N'*-trimethylethylenediamine (trmen), and *N,N,N',N'*-tetramethylethylenediamine (tmen), has been studied at 298 K in both the aprotic solvent dimethyl sulfoxide (dmsO) and in an ionic medium set to 0.1 mol dm⁻³ with Et₄NClO₄ under anaerobic conditions. UV/Vis spectrophotometric and calorimetric measurements were carried out to obtain the thermodynamic parameters for the systems investigated. Only mononuclear CoL_j²⁺ complexes were formed (*j* = 1–3 for en, *j* = 1, 2 for dmen; and *j* = 1 for trmen and tmen) where the diamines act as bidentate agents.

All the complexes are enthalpy-stabilized whereas the entropy changes counteract the complex formation. The results are discussed in terms of different basicities and steric requirements both of the ligands and the complexes formed. Voltammetric measurements were carried out to correlate the electrochemical properties of the anaerobic complexes with their different dioxygen affinities. The X-ray structure of the starting adduct [Co(dmsO)₆][ClO₄]₂, determined on a monocrystal, is also reported.

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Introduction

A wide variety of cobalt(II) complexes are known to bind dioxygen more or less reversibly and are therefore frequently studied as model compounds for natural oxygen carriers and for their use in O₂ storage, as well as in organic syntheses due to their catalytic properties under mild conditions.^[1–7] In this respect, Co^{II} complexes with N-donor ligands containing binding units suitable either for the coordination of a single metal ion or for assembling dimetallic centres have proven to be particularly useful, and have been extensively investigated especially in aqueous solutions.^[8–14]

Minor attention has been devoted to the behaviour of such complexes in aprotic solvents^[15–21] where their activity as oxidation catalysts can be of great interest. In a previous paper,^[21] as result of an initial study focused on thermodynamics of complex formation of Co^{II} with linear, cyclic polyaza or mixed N–O ligands in aprotic solvents, the interactions of Co^{II} with the monoamine *n*-butylamine (*n*-but) and the triamines diethylenetriamine (dien), *N,N'*-dimethyldiethylenetriamine (dmdien), and *N,N,N',N',N'*-pentamethyldiethylenetriamine (pmdien) were presented in dimethyl sulfoxide (dmsO). In this work it was shown that

the Co^{II} complex stabilities were greatly dependent on the degree of *N*-alkylation of the triamines, and that their dioxygen affinity varied concomitantly; thus, the tertiary pmdien was not able to take up O₂ whilst dmdien and dien were.

Strong σ -donor ligands are known to increase the dioxygen affinity.^[6] In fact, in the oxygenation reaction, the dioxygen donates an electron into the appropriate Co d orbital while the metal centre is thought to donate an electron from the d_{z²} orbital into the π^* orbital of the electrophilic molecular dioxygen, thus forming a complex. This electron transfer should depend on the available electron density at the central metal atom. This density, however, is greatly affected by the electron donor properties of the ligands in the coordination sphere; as the ligand basicity increases, its electron donating ability also increases facilitating such a transfer.^[1]

As an extension of the previous work and with the aim of systematically tuning the influence of the introduction of methyl groups on amino groups we have investigated the Co^{II} complex formation in dimethyl sulfoxide (dmsO) with the following diamines: ethylenediamine (en), *N,N'*-dimethylethylenediamine (dmen), *N,N,N'*-trimethylethylenediamine (trmen), and *N,N,N',N'*-tetramethylethylenediamine (tmen), which are gradually increasingly methylated, so varying the basicity of the amino group in the order –NH₂ > –NHR > –NR₂.^[22] The study presented in this paper refers in detail to the determination of the thermodynamic parameter of Co^{II} complex formation under anaerobic con-

^[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine,
Via Cotonificio 108, 33100 Udine, Italy
Fax: (internat.) + 39-0432/558803
E-mail: comuzzi1@dstc.uniud.it
tolazzi@dstc.uniud.it

ditions, as the knowledge of the properties of the starting complexes are fundamental to extending this investigation to aerobic conditions.

The values of the stability constants of the various systems investigated were determined by UV/Vis spectroscopic measurements using Cd^{II} as auxiliary metal ion,^[23] for the reasons discussed in a previous paper.^[21] The stability constants of this latter ion with the same ligands were previously determined by potentiometric measurements using the ion-selective cadmium electrode.^[24] The enthalpy values were obtained by direct calorimetric titrations.

Also, preliminary remarks concerning dioxygen uptake are reported; in particular voltammetric measurements were carried out in order to obtain a correlation between the electrochemical properties of the anaerobic complexes with the diamines and the triamines previously investigated^[21] and their dioxygen affinity in dmsO.

All the spectrophotometric, calorimetric, and voltammetric measurements were performed at 298 K and in an

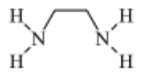
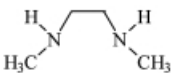
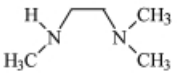
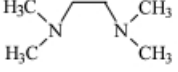
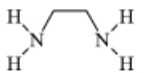
ionic medium adjusted to 0.1 mol dm^{-3} with Et_4NClO_4 as the neutral salt, taking extreme care to obtain and maintain the lowest possible water and oxygen contents in the systems.

The X-ray structure of $[\text{Co}(\text{dmsO})_6][\text{ClO}_4]_2$, determined on a monocrystal, is also reported. This structural study is interesting in itself, taking into account the considerable interest of transition metal complexes with dmsO for their role as possible intermediates in homogeneous catalysis, as antitumoural agents, or radiosensitizers in medicinal chemistry.^[25] Finally, it is important because few X-ray structural evidences are to date available for cobalt–dmsO complexes.^[26–29]

Results and Discussion

The best fit of the spectrophotometric data was obtained when the species reported in Table 1 were taken into ac-

Table 1. Overall stability constants and thermodynamic functions for the reaction $\text{Co}^{2+} + j \text{L} \rightleftharpoons \text{CoL}_j^{2+}$ in dmsO at 298 K and $I = 0.1 \text{ mol dm}^{-3}$ and in water; the errors quoted correspond to three standard deviations.

	Complex	$\log \beta_j$	$-\Delta G^\circ_{\beta j}/\text{kJmol}^{-1}$	$-\Delta H^\circ_{\beta j}/\text{kJmol}^{-1}$	$-T\Delta S^\circ_{\beta j}/\text{kJmol}^{-1}$
n-but ^[a]	CoL	1.91	10.8	23	12.2
	CoL ₂	3.2	18.3	62	43.7
	CoL ₃	4.1	23	88	65
en	CoL	6.41(0.09)	36.5(0.5)	53.5(1.2)	17
	CoL ₂	12.2(0.2)	70.1(0.6)	106.2(1.6)	36.1
	CoL ₃	15.8(0.3)	90(1)	172.0(2.2)	82
dmen	CoL	5.70(0.05)	32.5(0.3)	48.3(1.1)	15.8
	CoL ₂	9.90(0.12)	56.5(0.9)	99.0(0.9)	42.5
trmen	CoL	4.28(0.22)	4.4(0.5)	45.7(0.5)	21.3
					
tmen	CoL	3.07(0.04)	17.5(2)	36(1)	18.5
					
en _{water} ^[b]	CoL	5.94	33.86	28.87	−4.99
	CoL ₂	11.66	60.86	58.37	−2.49
	CoL ₃	14.68	78.06	92.68	14.62

[a] Ref.^[21] [b] Ref.^[32]

count. In Table 1, the overall stability constants and the free energies of formation, with the limits of error indicated, are listed for the reactions $\text{Co}^{2+} + j \text{L} \rightleftharpoons \text{CoL}_j^{2+}$ (where L is the amine concerned and $j = 1-3$). No polynuclear or mixed Co–L–Cd complexes were observed within the concentration range investigated.

As an example, in Figure 1(a) typical UV/Vis spectral changes observed during the reaction of Co^{2+} with dmen are reported in terms of absorbances vs. wavelengths. In Figure 1(b) the spectral modification due to dioxygen uptake is also inserted for the $[\text{Co}(\text{dmen})_2]^{2+}$ system.

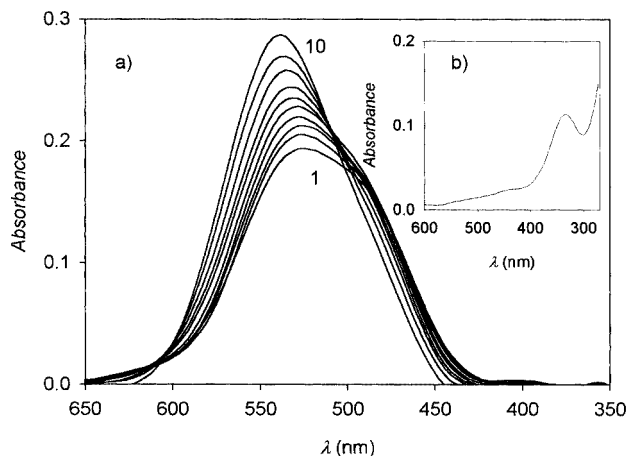


Figure 1. (a) Spectral changes observed during the reaction of Co^{2+} with dmen in dmsO: $C_{\text{Co}}^0 = 25.3$; $C_{\text{Cd}}^0 = 27.7 \text{ mmol dm}^{-3}$ (spectrum 1); C_{dmen}^0 varied from 0 (spectrum 1) to 65.6 (spectrum 10) mmol dm^{-3} ; (b) UV/Vis spectrum of a solution of $[\text{Co}(\text{dmen})_2]^{2+} = 0.4 \text{ mmol dm}^{-3}$ in air after 5 min

The experimental data obtained from the calorimetric measurements for all the systems investigated are reported in Figure 2 as Δh_r , the total heats of reaction per mol of metal ion, as a function of $R_C = C_L/C_M$, the ratio between the amount (mol) of ligand and the amount (mol) of cobalt(II) in the calorimetric vessel. The enthalpy curves are fully consistent with the information obtained from the analysis of spectrophotometric data. In fact, the curves representing the complexation of Co^{II} –trmen and –tmen indicate formation of complex(es) of relatively low stability(-ies), whereas the Co^{II} –en and –dmen data are consistent with the formation of 3 and 2 complexes, respectively, of relatively high stability.

The lack of evolved heat for $R_C > 2$ for the Co^{II} –dmen system clearly indicates that no more complexes are formed beyond the second one. The fit between experimental and calculated (full lines in Figure 2) curves is quite good.

In Figure 3 the FT-IR spectra of a series of solutions containing the same concentration (about 50 mmol dm^{-3}) of Co^{2+} and different ligand-to-metal ratios R_C , are reported for the Co^{II} –dmen system, chosen as significant example.

In Table 2, the data obtained from electrochemical measurements are summarized in terms of E_{pc} , the cathodic potential at maximum diffusion current, for the $\text{Co}^{\text{II}}/\text{Co}^0$ redox couple, and in terms of $E_{1/2}$ [$E_{1/2} = (E_{\text{pc}} + E_{\text{pa}})/2$] for

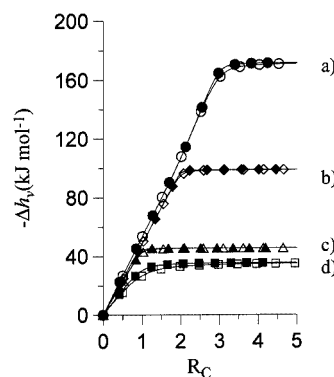


Figure 2. The total molar enthalpy changes, Δh_r , as a function of $R_C = C_L/C_M$ for Co^{II} –diamine systems in dmsO: (a) en: (○) 5.05, (●) 19.91 mmol dm^{-3} in Co^{2+} ; (b) dmen: (◇) 5.12, (◆) 19.96 mmol dm^{-3} in Co^{2+} ; (c) trmen: (△) 5.09, (▲) 19.97 mmol dm^{-3} in Co^{2+} ; (d) tmen: (□) 5.04, (■) 20.01 mmol dm^{-3} in Co^{2+} ; only some of the experimental points, chosen at random, have been plotted; the solid lines were calculated from the values of β_j and $\Delta H^\circ_{\beta_j}$ in Table 1

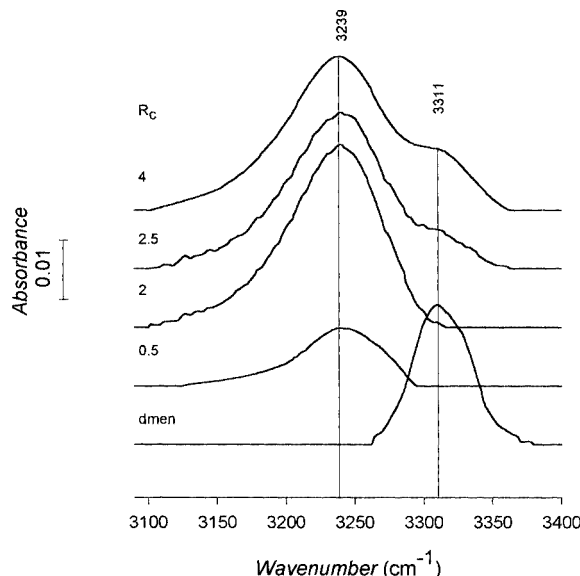


Figure 3. FT-IR spectra of solutions containing 50 mmol dm^{-3} of cobalt(II) and different dmen/metal ratios, R_C

the $\text{Co}^{\text{II}}\text{L}_j/\text{Co}^{\text{III}}\text{L}_j$ couple. The relative reactions [Equations (1) and (2)] are written in the direction in which the experiments were carried out.



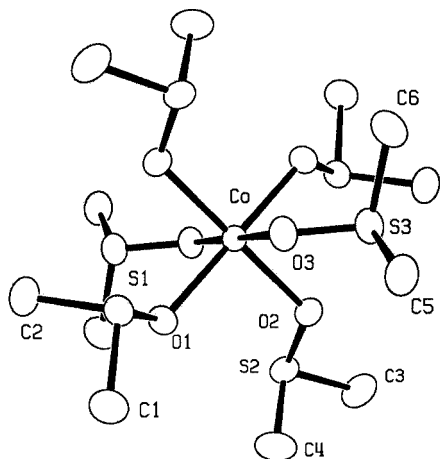
For comparison, the measurements have been extended to the triamines dien, dmdien, and pmdien, and the data obtained are also inserted in Table 2. The signals relative to Equation (2) consisted of a pair of irreversible oxidation/reduction waves, but were only detected for some of the systems investigated; no better results could be obtained by

Table 2. Redox potentials [V] of the cobalt(II) complexes vs. sat. Ag/AgCl electrode

	E_{pc} Reaction 1	$E_{1/2}$ Reaction 2
Co(en) ²⁺	−1.50	
Co(en) ₂ ²⁺	−1.56	
Co(en) ₃ ²⁺	−1.62	−0.44
Co(dmen) ²⁺	−1.46	
Co(dmen) ₂ ²⁺	−1.58	
Co(trmen) ²⁺	−1.42	
Co(tmen) ²⁺	−1.38	
Co(dien) ²⁺	−1.54	
Co(dien) ₂ ²⁺	−1.70	−0.34
Co(dmdien) ²⁺	−1.53	
Co(dmdien) ₂ ²⁺	−1.63	0.25
Co(pmdien) ²⁺	−1.44	

working with different electrodes, Au or glassy carbon. The cyclic voltammograms related to the Co^{II}/Co⁰ couple show only the reduction peak corresponding to reaction (1).

Figure 4 shows an arbitrary view of the crystal unit of the cationic [Co(dmsO)₆]²⁺ unit along with the labelling scheme. Selected interatomic distances and angles are listed in Table 3. Crystal data and data collection summary are reported in Table 4.

Figure 4. ORTEP view of the asymmetric unit of the [Co(dmsO)₆]²⁺; perchlorate anions and hydrogen atoms are omitted

Equilibrium Studies under Anaerobic Conditions

The complexes listed in Table 1 are all characterized by negative enthalpy and entropy values, which is typical of reactions involving complexation of metal ions by neutral ligands in aprotic solvents.^[30,31] The desolvation of the species is here rather small and, given the relatively weak ligand–solvent interactions, the enthalpy change associated with the complex formation is therefore essentially a measure of the difference in bond energy toward the metal ion between the ligand and the coordinated molecules of the solvent. Thus, the enthalpy stabilization found here em-

Table 3. Selected bond lengths [Å] and angles [°] for [Co(dmsO)₆][ClO₄]₂

Bonds	[Å]	Angles	[°]
Co–O(1)	2.0934(15)	O(1)–Co–O(2)	92.31(6)
Co–O(2)	2.0887(15)	O(2)–Co–O(3)	90.11(6)
Co–O(3)	2.0833(17)	O(1)–Co–O(3)	90.72(6)
S(1)–O(1)	1.5203(16)	S(1)–O(1)–Co	117.26(8)
S(2)–O(2)	1.5352(17)	S(2)–O(2)–Co	118.95(9)
S(3)–O(3)	1.5304(16)	S(3)–O(3)–Co	117.42(9)
S(1)–C(1)	1.787(2)	O(1)–S(1)–C(1)]	104.15(11)
S(1)–C(2)	1.785(3)	O(1)–S(1)–C(2)	105.27(12)
S(2)–C(3)	1.780(3)	O(2)–S(2)–C(3)	102.83(12)
S(2)–C(4)	1.786(3)	O(2)–S(2)–C(4)	104.36(14)
S(3)–C(5)	1.784(2)	O(3)–S(3)–C(5)	104.01(10)
S(3)–C(6)	1.780(3)	O(3)–S(3)–C(6)	105.19(12)
		C(1)–S(1)–C(2)	99.03(14)
		C(3)–S(2)–C(4)	99.36(15)
		C(5)–S(3)–C(6)	98.89(14)

Table 4. Crystal data and data collection summary

Empirical formula	C _{17.32} H ₄₈ Cl ₂ CoO ₁₆ S _{6.68}
Formula mass [g mol ^{−1}]	856.39
Crystal dimensions [mm]	0.45 × 0.3 × 0.3
<i>T</i> [K]	120.0
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	8.606(4)
<i>b</i> [Å]	15.147(4)
<i>c</i> [Å]	15.230(3)
β [°]	76.05(2)
<i>V</i> [Å ³]	1985.3(12)
<i>Z</i>	2
<i>D</i> _{calcd.} [g cm ^{−3}]	1.433
μ [mm ^{−1}]	0.974
Limiting indices	<i>h</i> = −12/12, <i>k</i> = −21/21, <i>l</i> = −21/21.
<i>R</i> _{int}	0.0366
<i>R</i>	0.0496
<i>wR</i> ₂	0.1363
GOF	1.032
Parameters	232
Reflections/unique reflections/ <i>I</i> > 2σ(<i>I</i>)	10771/5933/5160
ρ _{max} , ρ _{min}	0.848, −0.848

phasizes the importance of the Co^{II}–nitrogen interaction in the aprotic solvent dmsO.

The data for the analogous complexes formed by the Co^{II}–en system in aqueous solution have also been inserted in Table 1;^[32] no data in water are available in the literature for the other diamine systems.^[33] Lower stabilities are observed in water than in dmsO; in a previous work,^[21] as no information concerning the heat of transfer of Co²⁺ from water to any other solvent were available,^[34] we reasonably supposed that this ion would be more strongly solvated by dmsO than by water on the basis of some comparisons between Zn²⁺ and Co²⁺, characterized by similar charge density.^[35] The X-ray structural data reported here for the [Co(dmsO)₆]²⁺ species show that, in the solid state, interactions more akin to Co–dmsO than to Zn–dmsO are at play;

this seems to confirm our previous hypothesis. Therefore, the trend in the complexes stabilities in water and dmsO, at variance with what might be expected on the basis of Co^{II} solvation in the two solvents, is to be attributed to a greater solvation of amines in water than in dmsO^[30] through hydrogen bonding.

The electronic spectra of CoL_j complexes are similar to those observed for the octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex^[35] and to those previously reported for octahedral $[\text{Co}(\text{dmsO})_6]^{2+}$ and Co^{II} –triamine systems^[21] in dmsO [see (a) in Figure 1] and clearly indicate that also for Co^{II} –diamine systems the octahedral structure is retained after the coordination of the ligands. Thermodynamic data confirm that no change of coordination occurs at any step of complexation. If the change occurred, in fact, abnormally less unfavourable entropy and less favourable enthalpy values would be expected.^[30]

A comparison between the stability constant associated with the first complexation step for the Co^{II} –en and –n-but systems (Table 1) shows that it is much higher for the former ligand, indicating that the en ligand behaves as bidentate; the very exothermic value of the $\Delta H^\circ_{\beta_1}$ and the unfavourable entropy terms are in line with this hypothesis, which is further confirmed by FT-IR spectra run on solutions containing Co^{II} –en in a molar ratio 1:0.5 where no bands typical of free $-\text{NH}_2$ groups^[36,37] were detected.

Similar considerations can be applied for the successive complexation steps; coming to the conclusion that hexacoordination is saturated by nitrogen groups when the $[\text{Co}(\text{en})_3]^{2+}$ species is formed. It is interesting to note that the third stepwise complexation step is slightly more exothermic than the preceding ones and that the stepwise entropy term is more unfavourable: the coordination of the third en ligand evidently has no great effects on the desolvation of the central metal ion. The data for the other diamines investigated also indicate that bidentation is achieved for all the systems investigated.

The $\log \beta_1$ values decrease smoothly for Co^{II} –dmen system with respect to the primary en, whereas this decrease is much more evident when one (trmen) or two (tmen) tertiary groups are present. The trend in thermodynamic stabilities primarily reflects the different basicities of the N atoms, which decrease in the order $-\text{NH}_2 > -\text{NHR} > -\text{NR}_2$,^[22] whereas, when tertiary amino groups are involved, the greater steric crowding also contributes to a marked elongation of the M–N bonds.^[38] In addition, *N*-methylation inhibits the formation of hydrogen bonds of the type M–N–H–O, decreasing the outer-sphere solvation energy of the complexes.^[38] It is to note that *N*-alkylation strongly influences not only the stabilities but also the stoichiometry of the species formed; in fact, despite the borderline acid character, cobalt(II) is expected to become harder in dmsO,^[30] enhancing its affinity for the hard N atom, no more complexes beyond ML_2 or even ML could be detected when dmen or trmen and tmen, respectively, were concerned. In addition to the steric requirements of the more bulky ligands, certainly a role is also played by the small ionic radius of Co^{II} ^[35] as for example dmen and trmen

ligands were found to be able to form three and two complexes, respectively, when octahedral Cd^{II} complexes were considered in dmsO. Likely, large metal ions such as Cd^{II} can better minimize steric hindrances and repulsions when more than two bulky $-\text{N}(\text{CH}_3)_2$ moieties are involved in the complex formation. This is confirmed by the observation that the drop in complex stability by methylation is indeed more evident for Co^{II} – than for Cd^{II} –diamino complexes^[24] ($\Delta \log K_{1[\text{Co}(\text{en})] \rightarrow [\text{Co}(\text{trmen})]} = 2.13$; $\Delta \log K_{1[\text{Co}(\text{en})] \rightarrow [\text{Co}(\text{tmen})]} = 3.34$; $\Delta \log K_{1[\text{Cd}(\text{en})] \rightarrow [\text{Cd}(\text{trmen})]} = 1.76$; $\Delta \log K_{1[\text{Cd}(\text{en})] \rightarrow [\text{Cd}(\text{tmen})]} = 2.78$). Also, the increasing soft nature of the nitrogen donors should be responsible of this behaviour in this latter case.^[38] The same trend was found for Co^{II} and Cd^{II} complexes with 1,4,8,11-tetraazacyclotetradecane (cyclam) and tetramethylcyclam.^[39]

Independent FT-IR measurements were carried out in order to ascertain both the maximum stoichiometry and the coordination mode of the dmen ligand. Figure 3 shows the spectra of a series of solutions containing Co^{II} and different dmen-to-metal ratios, R_C . It can be observed that up to $R_C = 2$, only the band due to the bonded secondary amine (at 3239 cm^{-1}) is present, whereas the band due to the free amino groups (at 3311 cm^{-1}) is also present when $R_C > 2$. This confirms both the bidentation in the ML_2 complex and the absence of higher species beyond the ML_2 one, as evidenced also by calorimetry studies.

As mentioned in the introduction, particular interest was devoted to the tuning of the behaviour of different methylated diamines in Co^{II} complexation under anaerobic conditions, in order to clarify their successive role in the affinities for molecular dioxygen. As a matter of fact, it was found^[21] that in the case of the Co^{II} complexes with the triamines dien, dmdien, and pmdien, the affinity for dioxygen varied with the number of methyl groups present in the ligands; pmdien was in fact not able to promote dioxygen binding, dmdien promoted a certain amount of binding and release, and dien caused an irreversible dioxygen uptake.^[21,40]

A similar behaviour is shown by en, dmen, and tmen; CoL_j complexes with en and dmen ($j \geq 2$) were able to take up dioxygen (see also Electrochemical and UV/Vis Data), with a certain degree of reversibility ascertained for the secondary dmen system, whereas $[\text{Co}(\text{tmen})]^{2+}$ was not able to do the same. Unfortunately, the trmen ligand, chosen for its σ -donor properties (intermediate between that of dmen and tmen), was unexpectedly unable to form higher complexes beyond the first one, thus not reaching a minimum of three nitrogen donors per cobalt ion which appears to be necessary to form an oxygenated species as supposed in a previous work^[41] and suggested by a comprehensive view of the results reported here and previously.^[21] Therefore, we systematically searched for a correlation between the electron density of the metal ion in the complexes and the dioxygen uptake, by means of cyclic voltammetry.

Electrochemical and UV/Vis Data

The signals relative to the $\text{Co}^{\text{II}}\text{L}_j/\text{Co}^{\text{III}}\text{L}_j$ couples were visible only for the $[\text{Co}(\text{en})_3]^{2+}/[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{L})_2]^{2+}/[\text{Co}(\text{L})_2]^{3+}$ ($\text{L} = \text{dien}$ or dmdien) systems (Table 2). Con-

sidering the basicity order of the amino groups,^[22] one should expect that the electron density on the cobalt ion decreases in the order $\text{Co}(\text{en})_3 > \text{Co}(\text{dien})_2 > \text{Co}(\text{dmdien})_2$, which is reflected (see Table 2) in the concomitant increase in the $E_{1/2}$ values of the corresponding $\text{CoL}_j^{2+}/\text{CoL}_j^{3+}$ couples.^[38,42,43] This finding agrees with previous reports that *N*-alkylation of amine ligands shifts the redox potentials of the couples $\text{M}^{n+1/n}\text{L}_m$ anodically relative to those of the corresponding non-alkylated systems.^[38] The voltammograms for the other di- and triamine systems should be, according to this trend in electron density, shifted anodically,^[38] likely in the potential range where the solvent signals overcome those of the investigated couples.

The values of E_{pc} for reaction (2) are, on the other hand, easily evaluated for all the systems investigated; taking into account that the reaction for the uptake of dioxygen by a given Co^{II} complex is a charge-transfer process, a correlation between E_{pc} values for reaction (1) and Co^{II} charge density, and therefore the $\text{Co}^{\text{II}}\text{L}_j$ dioxygen affinity, should be observed. The higher the charge density is, the more difficult the reduction process to Co^0 should be and the more negative the expected E_{pc} values should be. The E_{pc} values for reaction (1) are in fact shifted anodically as secondary or, even more, tertiary diamines and triamines are considered.

These data are combined with UV/Vis results, obtained both for the Co^{II} –diamine systems studied in this paper and for previously investigated Co^{II} –triamine systems, dien, dmdien, and pmdien,^[21] which show that: (i) no changes are observed in the spectra of deaerated and aerated solutions of all the 1:1 Co^{II} –diamine and Co^{II} –triamine (except dien) species in the range 650–300 nm; (ii) all the aerated spectra of the other complexes show the origin of a charge-transfer band in the range 380–300 nm as shown in Figure 1(b) for the $[\text{Co}(\text{dmen})_2]^{2+}$ system. The species mentioned in (i) are clearly not able to bind dioxygen whereas the others are. Therefore, the data reported in Table 2 for reaction (1) suggest an interesting correlation between the E_{pc} values of the Co^{II} complexes related to Equation (1) and their dioxygen affinity; one can in fact foresee that when $E_{\text{pc}} \geq -1.54$ V for the $\text{Co}^{\text{II}}\text{L}_j/\text{Co}^0$ couple the uptake of dioxygen is not possible in dmso.

Structural Data

Few crystal structures of cobalt(II)–dmso solvates are available in the literature,^[26–29] due to the difficulty of obtaining single crystals suitable for X-ray investigation. Despite numerous attempts to improve their quality, also the crystals here investigated show a relative degree of disorder that does not in any case invalidate the overall features of the structure.

Co^{II} is a hard acceptor in dmso preferring hard donor atoms like oxygen, the bonds being mainly of electrostatic character.^[30] In the solid-state structure reported in Figure 4, six solvent molecules are coordinated to the metal centre through the oxygen atom in a distorted octahedral geometry. The mean Co–O distance of 2.088(5) Å (Table 3)

is consistent with the value found for an octahedral Co^{II} –oxygen coordination^[25] and a little shorter than the analogous distance found for the Zn^{II} ion (Zn–O 2.11 Å) in $[\text{Zn}(\text{dmso})_6][\text{ClO}_4]_2$,^[44] shown for comparison for the similar charge density values of these ions. This datum indicates that slightly stronger interactions exist in the solid state between Co and dmso than between Zn and dmso.

Sulfur–oxygen average bond lengths [1.5286(16) Å], are in agreement with those present in the literature^[25] for metal–sulfoxide complexes and greater than the S–O bond length in free dmso [1.495(4) Å]. The O–S–C angles [104.08(20)°] are also average for corresponding angles found in the literature for 400 related metal–sulfoxide complexes and less than that in free dmso [105.7(2)°], whereas the C–S–C bond angles (Table 3) are almost similar to the corresponding values in free dmso (98.6°).^[25] The perchlorate anions are not coordinated to the central Co^{II} ion and therefore they are not reported in Figure 4. This feature is also maintained in dmso solution as $\text{Co}(\text{ClO}_4)_2$ has been found to be completely dissociated in dmso.^[21]

Concluding Remarks

Important information have been obtained on how different donor properties of the ligands influence the stability and stoichiometry of the Co^{II} complexes; in fact the addition of only one $-\text{CH}_3$ group to dmen is shown to cause a drastic change in the number of complexes formed and strongly influence their dioxygen affinity. This result should be taken into account to suitably modify N-donors in order to obtain Co^{II} complexes able to promote a more or less reversible dioxygen binding.

The electrochemical properties, correlated with the number of methyl substituents, point to an interesting result, i.e. that an E_{pc} value of -1.54 V, related to reaction (1), should be at least overcome by the Co^{II} –amino complexes to be able to bind dioxygen. Finally, the structural data of the $[\text{Co}(\text{dmso})_6][\text{ClO}_4]_2$ adduct are fully consistent with a distorted octahedral geometry of the hexasolvate and provide additional data on cobalt(II)–dmso complexes.

Experimental Section

Warning: Although metal perchlorates solvated by dmso are generally explosive under certain conditions,^[45] no problems were encountered when handling $\text{M}(\text{ClO}_4)_2 \cdot 6\text{dmso}$ ($\text{M} = \text{Co}$ or Cd). Anyway, as a precaution, only small quantities of the salts should be prepared each time. Great caution was exercised when handling dmso solutions of poisonous cadmium salts, since they are easily carried through the skin by dmso, which penetrates lipid tissues at an astonishing rate.

Chemicals: $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{dmso}$ and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{dmso}$ were prepared and standardised as before.^[21,24] Dimethyl sulfoxide (Fluka; > 99%) was purified by distillation according to the described procedures,^[46] degassed by a pumping-freezing procedure and stored over 4-Å molecular sieves. The ligands en, dmen, trmen, and tmen (Aldrich; > 97%) were purified by fractional distillation.^[47] Perchlorate

stock solutions of Cd^{II} and Co^{II} ions were prepared by dissolving weighed amounts of the adducts in anhydrous degassed dmso, and their concentrations were checked by titration with EDTA.^[48]

The background salt Et_4NClO_4 was recrystallised twice from methanol and dried at 110 °C. Solutions of the ligands were prepared as described.^[24] All standard solutions were prepared and stored in an MB Braun 150 glove box under a controlled atmosphere containing less than 1 ppm of water and less than 1 ppm of oxygen. The water content in the solutions, typically 10–20 ppm, was determined by a Metrohm 684 KF Coulometer.

Spectrophotometric Measurements: UV/Vis spectra were recorded with a Varian Cary 50 Spectrophotometer directly inside the glove box using optic fibre probes and a quartz cuvette with a pathlength of 1 cm (117.100 Bracco cell). The data were recorded over the wavelength range 300–650 nm. Different types of titrations were carried out in order to obtain the best competition between Cd^{II} and Co^{II} for the same ligand and/or to evidence possible formation of mixed or polynuclear species. The absorption maximum for $\text{Co}(\text{ClO}_4)_2$ in dmso occurs at 535 nm with an extinction molar coefficients $\epsilon = 11.9 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The absorption maximum of CoL_j complexes are shifted to lower wavelengths, in line with an increase in the ligand field strength, with the maximum ϵ values being of the same order of magnitude as that of the starting salt; therefore the dmso solutions always contained at least 20.00 mmol dm^{-3} of the $\text{Co}(\text{ClO}_4)_2$ starting salt in order to obtain reliable values for absorbance data.^[23] The fact that equilibrium was attained was supported by the observation that addition of a titrant solution produced an immediate spectral change with no further change noted after several hours. The absorbance data at about 20 different wavelengths in the range 450–550 nm were analysed and the formation constants of the CoL_j complexes ($j = 1\text{--}3$) were determined, together with the molar extinction coefficients of the complexes at each relevant wavelength, using the Hyperquad program.^[49]

Calorimetric Measurements: A Tronac model 87-558 precision calorimeter was employed to measure the heats of reaction. The cover of the titration vessel and its connection to the calorimeter were modified in order to make a gas-proof closure. To be sure of operating in absence of O_2 , both the vessel and the burette were filled inside the glove box, joined together, taken out of the glove box and connected to the calorimeter for the measurements. The calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (tham) with a standard solution of HCl in water. The experimental value of the heat of neutralization of tham was found to be $\Delta H^\circ = -47.48 \text{ kJ mol}^{-1}$, in good agreement with the accepted value of $-47.53 \pm 0.13 \text{ kJ mol}^{-1}$.^[33] The procedure for the calorimetric titration was described before.^[46] The heats of dilution of the reactants, determined in separate runs, were found to be negligible. The least-squares computer program Letagrop Kalle^[50] was used for the calculation of the enthalpy changes.

FT-IR Spectroscopy: The FT-IR spectra were obtained using a Bio-Rad FTS 40 spectrometer (maximum resolution 4 cm^{-1} ; 16 scans). A cell with barium fluoride windows (thickness of $25 \mu\text{m}$) was used. The cells were filled and closed in a glove box and quickly transferred to the spectrometer. The C_{60} in the dmso solutions was about 50 mmol dm^{-3} .

Cyclic Voltammetry: The cyclic voltammograms of CoL_j complexes were carried out using an EG&G Princeton Applied Research Model 263A potentiostat controlled by a Win/PC based program. A saturated Ag/AgCl electrode was employed as reference and a Pt electrode was used as working electrode, being a Pt wire present as

auxiliary electrode. The measurements were carried out with a scan rate of 100 mV/s.

X-ray Crystallography: Small violet crystals of the $[\text{Co}(\text{dmso})_6][\text{ClO}_4]_2$ adduct were obtained from an anhydrous dmso solution of $\text{Co}(\text{ClO}_4)_2$ by the solvent-diffusion method with acetone. Data collection was carried out on a crystal of dimensions $0.45 \times 0.30 \times 0.30 \text{ mm}$ by using a Nonius DIP-1030H system with Mo-K_α radiation, at 120 K by a nitrogen stream cryo-cooler. A total of 30 frames were collected, each with an exposure time of 10 min, over half of the reciprocal space with a rotation of 6° about the detector being at a distance of 80 mm from the crystal. Data reduction and cell refinement was carried out by using the program Mosflm.^[51] The structure was solved by Patterson and Fourier analyses^[52] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.^[53] Of three crystallographic independent dmso ligands, two were found to be disordered, and the S–C moiety refined over two positions (occupancies of 88 and 12%, respectively, with hydrogen atoms omitted for the methyl group at lower occupancy). A solvent molecule of dmso and of acetone, sharing the methyl groups and the oxygen atom, were disordered on the same site. Occupancy factor of the S atom (dmso) and of the central C atom (acetone) refined to 0.68 and 0.32, respectively. All the calculations were performed using the WinGX System, Ver 1.64.^[54] Additional material is available from the Cambridge Crystallographic Data Center as supplementary material comprising H-atom coordinates, thermal parameters, and remaining bond lengths and angles. CCDC-178439 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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