may be a factor in making C2–H---Cl$^-$ a stronger hydrogen bond than those at the 4- and 5-positions. This difference is most evident in the experimental observation[3] that the NMR shift of the C2 proton changes more rapidly with Cl$^-$ concentration than do the NMR shifts of the C4 and C5 protons.[3]

Another factor that must be considered in explaining the NMR results is the relative acidity of the three ring H's. In the isolated MEI$^+$, the C2 hydrogen is predicted by AM1 to have a +0.25 charge while the C4 and C5 hydrogens have +0.23 charges. While this difference is almost insignificant, it is at least in qualitative agreement with the observation that isotopic exchange of ring hydrogens with deuterium occurs more readily at the C2 position for MEI$^+$ in D$_2$O.[15]

While the computational results described above give some insight into the structural causes of the experimental results, it must be kept in mind that predicting the shifted frequencies could only be accomplished by constraining the ring H–Cl$^-$ distances. This required constraint may seem to be a flaw in the model. However, it is reasonable to argue that such constraints are needed when it is desired to simulate the condensed phase with gas-phase clusters. In the condensed phase, the Cl$^-$ ions are constrained from approaching closer to the ring C–H's by the pull of surrounding MEI$^+$ ions. The competing positive charges simulated by the Na$^+$ sparkles are constrained from closer approach to the central MEI$^+$ by the pull of surrounding anions as well as electrostatic repulsion and steric effects.

Conclusions

Semiempirical molecular orbital calculations using the MOPAC program have correctly predicted the shifts in ring C–H stretching frequencies observed for MEI$^+$ due to interaction with Cl$^-$ counterions. The interaction can best be classified as hydrogen bonding of Cl$^-$ at the three ring C–H positions. The stronger interaction observed at the C2–H position (on the basis of proton NMR shift dependence on Cl$^-$ concentration) can likely be attributed to structural factors involving the two alkyl groups and, more significantly, the nonequilateral triangular shape of the three ring C–H positions. These factors allow Cl$^-$ to interact with C2–H at a C2–H---Cl$^-$ angle approaching 180° while influencing the C4–H---Cl$^-$ and C5–H---Cl$^-$ angles to optimize at smaller angles and larger H---Cl$^-$ distances.

Registry No. AlCl$_3$, 7446-70-0; 1-methyl-3-ethylimidazolium chloride, 65039-09-0.

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Contribution from the Department of Chemistry,
University of Florence, Florence, Italy

Electronic and CD Spectra of Catecholate and Semiquinonate Adducts of Zinc(II) and Nickel(II) Tetraaza Macrocyclic Complexes

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The synthesis, the electrochemical properties, and the electronic and CD spectra of dioxolene adducts of the nickel(II) and zinc(II) complexes with the racemic and the (–)-*SS* isomer of the macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, CTH, are reported. The spectra of the catecholate adducts show d–d (nickel) and ligand transitions but no charge transfer. The spectra of the semiquinonate derivatives show a band in the range 11 000–13 000 cm^{-1} that is internal to the ligand and is suggested to be diagnostic of the nature of the dioxolene. A complete assignment is proposed and used to rationalize the relative stability of catecholate and semiquinonate derivatives.

Introduction

In the recent past a significant amount of work has been devoted to the ligand properties of catechol and its oxidation products (semiquinone and quinone) with transition-metal ions.[1-18] The noninnocent character of these ligands has often created ambiguity in assessing the oxidation state of the metal ion. X-ray structural analysis, magnetic measurements, and ESR and vibrational spectroscopy have shown to be powerful tools of investigation. Electronic spectroscopy is not frequently used, the spectra being complicated by the intense absorptions of the dioxolene ligand and by the existence of charge-transfer transitions of different origin. In short, the electronic spectra of the complexes are poorly understood because of the ambiguity in the assignment of the transitions. To date only one work concerning the detailed assignment of the spectra of a series of ruthenium(II)–polypyridine or –bipyridine complexes with variously substituted dioxolene ligands has been reported.[15]

As a part of an effort to explore the electronic properties of molecules containing a paramagnetic metal ion and an organic radical, we have synthesized a number of dioxolene adducts of the type ML(diox)$^{n+}$ (M = Cr, Mn, Fe, Co, Ni, Cu), where diox is a variously substituted dioxolene ligand, either catecholate or semiquinonate, and L is a polyazamacrocyclic ligand.[19] In particular the chemical and physical properties of solid compounds containing the Ni(CTH)DTBSQ$^+$ cation (CTH = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; DTBSQ = anion of 3,5-di-*tert*-butylbenzo-*o*-semiquinone) have

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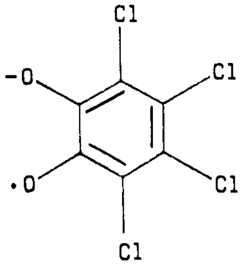
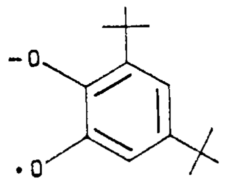
been recently reported.[20] X-ray crystal structural data indicate that this compound is six-coordinate, the DTBSQ ligand acting as bidentate and the tetradentate macrocycle being coordinated in a folded configuration.

With the aim of understanding the optical properties of these systems, we have synthesized some nickel(II)- and zinc(II)-dioxolene adducts with the optically active (−)-*SS* isomer of the macrocyclic ligand CTH, in order to also record CD spectra, which provide useful information complementary to that of electronic spectra. For instance, the narrow circular dichroism absorptions have greatly facilitated the detection of transitions that are not readily observed in the absorption spectra of the considered chromophores and the comparison of the relative intensities in the two types of spectra provided information on the symmetry of the transition. We wish to report here the analysis of the electronic spectra of nickel(II) and zinc(II) adducts with tetrachlorocatecholate (TCCat), tetrachlorosemiquinonate (TCSQ) (I), and 3,5-di-*tert*-butylbenzo-*o*-semiquinonate (DTBSQ) (II) and to assign some transitions that appear to be diagnostic of the semiquinone nature of the ligand.



(I)



(II)

Experimental Section

Materials. Ni(*SS*-CTH)(ClO$_4$)$_2$. The α-isomer of the optically active Ni(*SS*-CTH)(ClO$_4$)$_2$ was obtained by using a previously reported procedure.[21]

***SS*-CTH.** A 5-g sample of this compound was suspended in 100 mL of methanol, and 2.7 g of potassium cyanide was added. The suspension was stirred and gently warmed for 20 min and cooled at room temperature, and after the addition of 100 mL of diethyl ether, the mixture was placed in a refrigerator for 2 h. The solid potassium tetracyanonickelate and potassium perchlorate were removed by filtration, and the filtrate was concentrated to 20 mL under reduced pressure. The addition of an equal volume of aqueous sodium hydroxide led to the precipitation of 2.3 g of the *SS*-CTH enantiomer as monohydrate.

Zn(*SS*-CTH)(PF$_6$)$_2$·2H$_2$O. The bis(hexafluorophosphate) zinc(II) derivative of this ligand was obtained as follows. Equimolar amounts of zinc(II) acetate and *SS*-CTH (2 mmol) were allowed to react for 10 min in refluxing ethanol (20 mL). A slight excess of hexafluorophosphoric acid (70%) was then added, leading to the precipitation of white crystals.

TCCatH$_2$. Tetrachlorocatechol was synthesized by mixing wet diethyl ether solutions of tetrachloro-1,2-benzoquinone and triphenylphosphine in stoichiometric ratio 1/1.[22] The triphenylphosphine oxide–tetrachlorocatechol adduct precipitated in few minutes and was used directly in the synthesis of the complexes.

Synthesis of the Dioxolene Adducts. In the following we describe the procedures for synthesizing the optically active compounds. The same procedures may be applied also to the syntheses of the racemic derivatives. It is worthwhile to note that the latter complexes exhibit a solubility significantly lower than that of the corresponding single enantiomers.

Ni(*SS*-CTH)(DTBSQ)ClO$_4$. This compound was obtained in a similar way as reported for the racemic complex.[20] (Anal. Calcd for C$_{30}$H$_{56}$ClN$_4$NiO$_6$: C, 54.35; H, 8.51; N, 8.45. Found: C, 54.40; H, 8.85; N, 8.23.)

Ni(SS-CTH)(TCCat)·H$_2$O. A 2-mmol portion of α-Ni(*SS*-CTH)(ClO$_4$)$_2$ was suspended in 30 mL of warm methanol containing an equimolar amount of the triphenylphosphine oxide–tetrachlorocatechol adduct. The suspension was warmed under stirring, and 4 mmol of sodium hydroxide in the same solvent was added. After some minutes the yellow diperchlorate disappeared and light blue-green crystals separated from the solution. They were filtered, washed with methanol, and recrystallized from an acetone–methanol solution. (Anal. Calcd for C$_{22}$H$_{38}$Cl$_4$N$_4$NiO$_3$: C, 43.52; H, 6.31; N, 9.21. Found C, 43.66; H, 6.35; N, 9.08.)

Ni(*SS*-CTH)(TCSQ)ClO$_4$. A solution of silver perchlorate (1 mmol) in 10 mL of acetonitrile was added to a solution of Ni(*SS*-CTH)(TCCa) (1 mmol) in the same solvent. The resulting suspension was stirred for 20 min and filtered through a sintered glass funnel. Dark violet crystals were obtained after careful addition of water to the filtrate. They were collected, washed several times with an acetonitrile–water mixture, and dried in vacuo. (Anal. Calcd for C$_{22}$H$_{36}$Cl$_5$N$_4$NiO$_6$: C, 38.37; H, 5.27; N, 8.14. Found: C, 38.53; H, 5.38; N, 8.41.)

Zn(*SS*-CTH)(DTBSQ)PF$_6$. This compound was obtained by aerial oxidation of a basic methanolic solution containing equimolar amounts of the bis(hexafluorophosphate) zinc(II) derivative and 3,5-di-*tert*-butyl-1,2-dihydroxybenzene. An excess of sodium hydroxide with respect to the stoichiometric amount is required. A 1-mmol sample of Zn(*S*-*S*-CTH)(PF$_6$)$_2$ was suspended in 20 mL of a solution of the catechol (1 mmol) in methanol, and then 5 mmol of sodium hydroxide in the same solvent was added. The color of the solution turned slowly to blue. Addition of water induced the precipitation of an impure blue-green product. Recrystallization from dichloromethane–pentane mixtures led to the isolation of blue crystals. (Anal. Calcd for C$_{30}$H$_{56}$F$_6$N$_4$O$_2$PZn: C, 50.38; H, 7.89; N, 7.46. Found: C, 50.01; H, 8.07; N, 7.63.)

Zn(SS-CTH)(TCCat)·H$_2$O. This compound was prepared in a similar way as the nickel(II) derivative. (Anal. Calcd for C$_{22}$H$_{38}$Cl$_4$N$_4$O$_3$Zn: C, 43.05; H, 6.24; N, 9.13. Found: C, 43.31; H, 6.42; N, 8.80.)

Physical Measurements. Polycrystalline powder ESR spectra were recorded with a Bruker ER200 spectrometer working at X-band frequency. Electronic spectra were recorded in the range 5000–40 000 cm^{-1} on a Perkin-Elmer Lambda 6 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. The circular dichroism spectra were carried out by using a Jasco J-500 C spectropolarimeter in the range 12 500–40 000 cm^{-1}. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel Model 553 potentiostat equipped with Amel 863, 560/Å, and 568 elements) and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl (SCE). Before each experiment the solution was carefully deaerated with a nitrogen flow. All potentials here reported are referenced against SCE, and the observed potentials were not corrected for junction potentials and/or *iR* potential drops due to the internal resistance of the system. Under these conditions the couple ferrocenium/ferrocene lies at +0.35 V vs SCE in acetonitrile–0.1 M NBu$_4$PF$_6$.

Variable-temperature magnetic susceptibility data were measured by using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF1200S continuous-flow cryostat and a Bruker B-E15 electromagnet. The apparatus was calibrated by measuring the magnetic susceptibilities of a pure sample of manganese Tutton salt at several temperatures between 4.2 and 300 K. Diamagnetic corrections were estimated from Pascal's constants.

Results and Discussion

Synthesis, Magnetic Properties, and Electrochemistry. Catecholate adducts of M(*SS*-CTH)$^{2+}$ (M = Ni, Zn) were obtained with both TCCat and DTBCat, but the latter were found to be highly unstable and were not used for spectral characterization. Semiquinone adducts were formed with both metal ions and ligands, but Zn(*SS*-CTH)(TCSQ)$^+$ was found to be stable only in solution, while all the others yielded stable solid derivatives.

The nature of the coordinate dioxolene ligands in our compounds is confirmed by the IR spectra, according to the previously suggested rules.[3,15] Both the racemic and the *SS* enantiomer of Zn(CTH)(DTBSQ)PF$_6$ are characterized by an effective magnetic moment of 1.73 μ_B at room temperature, in agreement with the presence of a semiquinone ligand. Similar conclusions can be reached from the polycrystalline powder ESR spectra, which show an isotropic feature at g = 2.00. The spectrum of a CHCl$_3$ solution is a doublet with a splitting of ca. 3 G, due to the coupling with the ring protons of the dioxolene ligand.[17,23] In the solid state, intermolecular exchange interactions are operative, as shown by the temperature dependence of the magnetic susceptibility of

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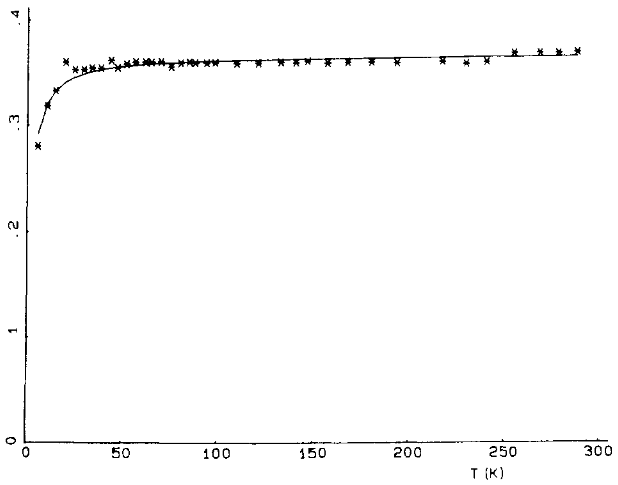

Figure 1. Variation of χT product with temperature in the range 4–300 K for Zn(CTH)(DTBSQ)PF$_6$. The curve represents the best fit (see text).

Zn(*dl*-CTH)(DTBSQ)PF$_6$ (Figure 1). A simple molecular field model nicely fits the experimental data with $nzJ' = 4.1$ cm^{-1}.

Ni(*SS*-CTH)(TCCat)·H$_2$O is characterized by an effective magnetic moment of 3.16 μ_B, in agreement with a pseudooctahedral coordination. Both the racemate and the *SS* enantiomer of Ni(CTH)(TCSQ)ClO$_4$ are characterized by a magnetic behavior similar to that previously reported for Ni(*dl*-CTH)(DTBSQ)PF$_6$.[20] The effective magnetic moment of the racemate is practically temperature independent in range 77–300 K with $\mu_{eff} = 4.38$ μ_B. The polycrystalline ESR powder spectra at X-band frequency are typical of a Kramers doublet with $g_1 = 5.8$, $g_2 = 2.4$, and $g_3 = 1.7$. These data clearly indicate that the nickel(II) is strongly ferromagnetically coupled to the TCSQ radical to yield a quartet ground state.[20]

The cyclic voltammograms of 1,2-dichloroethane solutions of Ni(CTH)(DTBSQ)PF$_6$ show a reversible redox process at −0.58 V and a nonreversible one at +0.48 V, which have been attributed to the catecholate–semiquinonate and semiquinonate–quinone couples, respectively.[20] Similar voltammograms are obtained for Ni(*SS*-CTH)(TCCat), Zn(*SS*-CTH)(DTBSQ)PF$_6$, and Zn(*SS*-CTH)(TCCat). The values of the observed redox potentials in 1,2-dichloroethane and acetonitrile are listed in Table I. In all of the observed cases the semiquinonate–catecholate process shows the typical features of reversible one-electron charge transfer. The semiquinonate–quinone couple is a nonreversible process, and only oxidation potentials can be obtained. The lack of reversibility can be attributed to the low stability of the quinone adducts, as supported by the presence in the reverse scans of the voltammograms of peaks attributable to the free quinone.

Electronic and CD Spectra. The spectral parameters of the complexes are shown in Table II. The electronic and CD spectra of acetonitrile solutions of Zn(*SS*-CTH)(DTBSQ)PF$_6$ and of Ni(*SS*-CTH)(DTBSQ)PF$_6$ are shown in Figures 2 and 3, respectively. The reported spectral data of the [Zn(*SS*-CTH)(TCSQ)]$^+$ chromophore were obtained by oxidizing the parent catecholate with a stoichiometric amount of silver(I) perchlorate.

Table I. Electrochemical Potentials of the M(*SS*-CTH)(diox)$^{n+}$ Complexes (n = 0, 1)[a,b]

compd	SQ/Cat D	SQ/Cat AN	Q/SQ[c] D	Q/SQ[c] AN
Ni(*SS*-CTH)(DTBSQ)PF$_6$	−0.58	−0.64	0.48	0.35
Zn(*SS*-CTH)(DTBSQ)PF$_6$	−0.58	−0.59	0.38	0.33
Ni(*SS*-CTH)(TCCat)	−0.02	0.05	0.87	0.75
Zn(*SS*-CTH)(TCCat)	0.09	0.09	0.79	0.73

[a] All potentials are reported in volts with respect to SCE in 1,2-dichloroethane (D) and acetonitrile (AN) solutions of 0.1 M NBu$_4$PF$_6$. The potentials are the average anodic and cathodic peak potentials for reversible processes and half-height peak anodic potentials for irreversible couples in cyclic voltammograms recorded at 100 mV s^{-1}. [b] At 25 °C for solutions ca. 10^{-3} M. [c] Irreversible.

Table II. Electronic and CD Spectra of M(*SS*-CTH)(diox)$^{n+}$ (n = 0, 1) in Acetonitrile Solution

complex	electronic abs[b]	CD abs[c]
Ni(*SS*-CTH)(TCCat)	9900 (1.38)	
	12 100 sh	
	17 500 (1.41)	17 500 (−0.32)
	27 500 sh	27 750 (−0.36)
	31 700 (3.83)	31 550 (−1.67)
	35 600 (3.77)	35 500 (+2.08)
Zn(*SS*-CTH)(TCCat)	27 600 sh	
	32 100 (3.81)	31 750 (−1.01)
	35 700 (3.82)	35 600 (+1,54)
Ni(*SS*-CTH)(TCSQ)ClO$_4$	11 400 (2.66)	
	17 200 sh	17 700 sh
	19 200 (3.11)	19 500 (−1.40)
	24 760 (3.13)	23 150 sh
	26 000 sh	24 630 (+0.44)
	27 200 sh	26 000 sh
	29 700 (3.97)	29 100 (−2.46)
	31 400 sh	
	35 000 sh	35 100 (+4.43)
Ni(*SS*-CTH)(DTBSQ)PF$_6$	11 600 sh	
	12 950 (2.65)	
	14 300 sh	
	21 200 (3.10)	20 800 (−3.78)
	23 500 sh	
	28 500 sh	26 450 (+1.43)
	32 380 (4.01)	30 700 (+1.48)
	33 500 sh	32 700 (−1.17)
	36 600 sh	36 900 (+3.35)
Zn(*SS*-CTH)(TCSQ)$^+$	10 200 sh	
	11 500 (2.57)	
	12 700 sh	
	14 200 sh	
		22 000 (−0.20)
	24 250 (3.27)	24 200 (+0.49)
	25 600 sh	25 400 sh
	26 900 sh	27 500 (+0.65)
	29 600 (3.83)	29 800 (−2.70)
	31 100 sh	31 100 sh
	35 450 (3.56)	36 000 (+4.82)
Zn(*SS*-CTH)(DTBSQ)PF$_6$	11 700 sh	
	12 950 (2.59)	
	14 200 sh	
		22 550 (−0.43)
	26 600 (3.17)	26 600 (+0.27)
	27 800 sh	
	29 000 sh	
	32 150 (4.05)	31 150 (+1.07)
		33 200 (−1.18)
	36 700 sh	33 400 (+1.56)

[a] In cm^{-1}; sh = shoulder. [b] log ϵ in parentheses. [c] $\Delta\epsilon$ in parentheses.

Catecholate Derivatives. The spectra of Zn(*SS*-CTH)(TCCat) and Ni(*SS*-CTH)(TCCat) are strictly similar in the UV region, while the bands of the nickel(II) derivative in the visible and in the near infrared regions show the expected pattern of energies and intensities characterizing a cis-octahedral nickel(II) chromophore.[24] Also the CD spectra of the two complexes are quite similar in the UV region, with two absorptions characterized by different differential intensity ($\Delta\epsilon$) and dissymmetry factors ($\Delta\epsilon/\epsilon$), the band at lower energy being less intense than the other. Since the transition moments of the electronic absorptions are similar, it should be concluded that they are characterized by different magnetic dipole allowedness. The dissymmetry factors of the bands of the nickel(II) chromophore in the visible region are similar to those reported for similar cis-octahedral derivatives of Ni(*SS*-CTH)$^{2+}$.[21]

The striking similarity of the spectral behavior of the two chromophores in the UV region suggests that these transitions involve only the electronic levels primarily of the ligand. In order to discuss these results, a qualitative energy-level diagram has been constructed by means of an extended Hückel calculation (Figure

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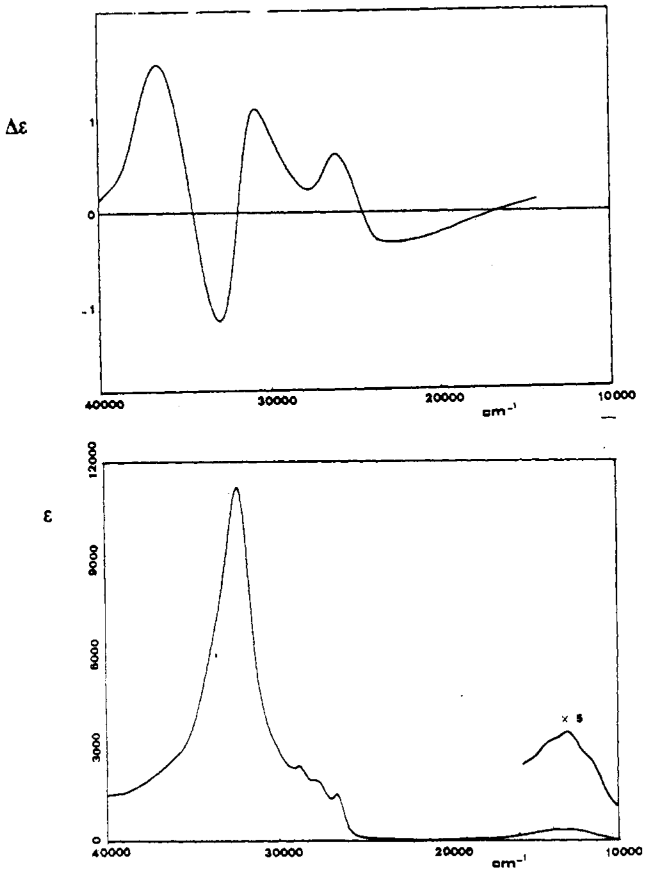

Figure 2. CD and electronic spectra of Zn(*SS*-CTH)(DTBSQ)PF_6 in acetonitrile solution.

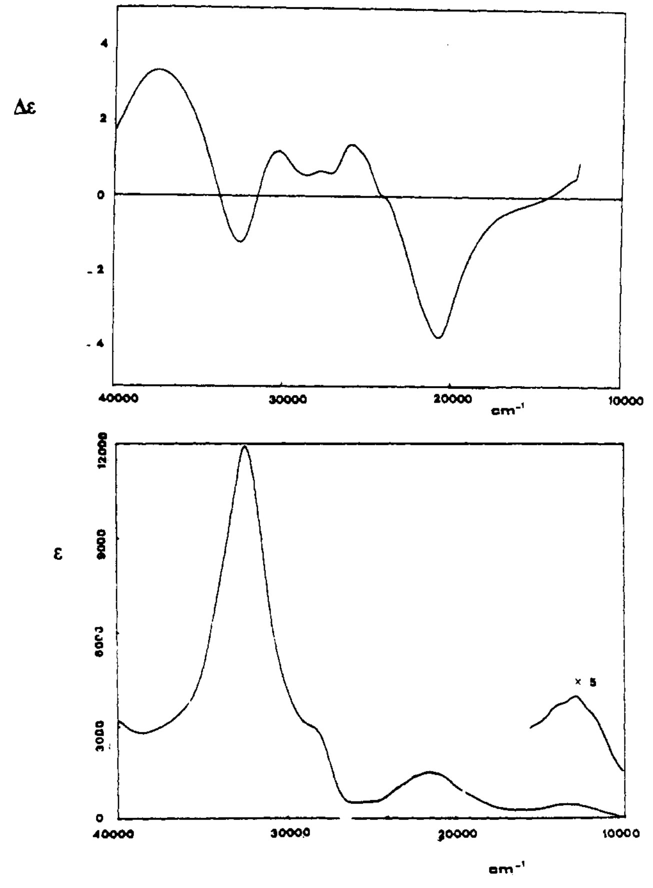

Figure 3. CD and electronic spectra of Ni(*SS*-CTH)(DTBSQ)PF_6 in acetonitrile solution.

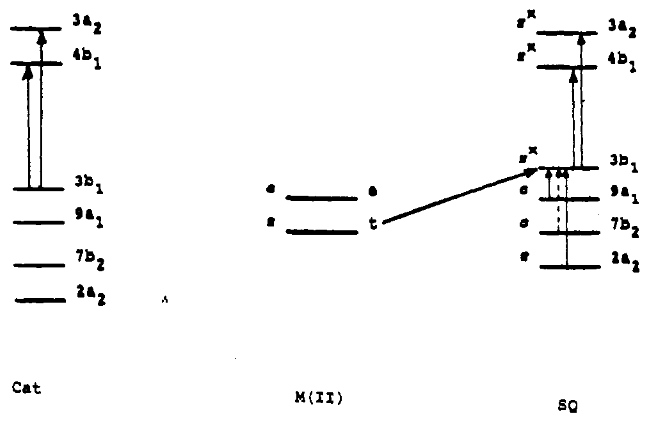

Figure 4. Scheme of the electronic transitions of catecholate (Cat) and semiquinonate (SQ) in M(*SS*-CTH)(diox)$^{n+}$ chromophores (M = Ni, Zn).

4). The obtained scheme is very similar to that reported by Gordon and Fenske,[25] who consider only the levels up to the HOMO. We found that the two first excited states behave as b_1 and a_2, in agreement with other published calculations.[17] All of the considerations that follow have been formulated by assuming a C_{2v} symmetry for our chromophores (the C_2 axis bisecting the dioxolene ligand).

We assign the observed maxima at 31 700 and 35 000 cm^{-1} to $3b_1 \rightarrow 4b_1$ and $3b_1 \rightarrow 3a_2$ in order of increasing energy. Both transitions are electronically allowed, but the first is magnetically forbidden. This assignment predicts similar intensities of the two transitions in the electronic spectra and different dissymmetry factors in the CD spectra, as experimentally observed.

The two transitions are, if we use the organic chemistry nomenclature, the secondary and primary bands that characterize any benzenoid system.[26] As a relevant point for the following discussion, it should be noted that no charge transfers involving the electronic levels of the metal ion are observed for the nickel(II) derivative.

Semiquinone Derivatives. The spectra of the semiquinone complexes are very similar to each other both as regards the absorption energies and the intensities. Furthermore, similarities exist between the observed spectra and that reported[12] for the free DTBSQ ligand, at least in the spectral range 12 000–33 000 cm^{-1}. The bands of the TCSQ derivatives show a decrease in energy of about 1500 cm^{-1} with respect to the DTBSQ complexes.

Both the zinc(II) and the nickel(II) chromophores are characterized by a band in the red region of the spectrum, which shows a vibronic progression of about 1200–1300 cm^{-1}, both in the TCSQ and in DTBSQ derivatives. A similar vibronic progression is observed also in the near-UV region.

Two very intense broad bands occur at higher energies, the first being constituted by at least two main components, as evidenced by the CD spectrum. Again, the dissymmetry factors of the group of bands in this region are significantly different. The CD spectra of the zinc(II) complexes show a broad band in the visible region at ca. 22 000 cm^{-1}, which has negligible intensity in the electronic spectrum.

The oxidation of the catecholate ligand removes one electron from the $3b_1$ level, which has both C–O π^* antibonding and C–C bonding character. The highest doubly occupied molecular orbital is the $9a_1$, which is localized mainly on the ortho oxygen atoms and interacts in a σ fashion with metal orbitals. The energy separation between these two levels increases in the order Cat $\leq$ SQ $\leq$ Q according to the increased antibonding character of the $3b_1$ orbital.[25] The transition $9a_1 \rightarrow 3b_1$ has $n \rightarrow \pi^*$ character and involves a significant charge redistribution; therefore, one may expect that the ground and the excited state show a marked geometrical difference, and consequently, this transition should be characterized by a high probability of vibrational excitation. The bands observed in the red region of the electronic and CD

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spectra can be attributed to transitions involving these two electronic levels. The value of the separation of the vibrational structure of 1200–1300 cm^{-1} also supports this assignment, since the C–O stretching vibration mode occurs at ca. 1250 cm^{-1}. We suggest that the presence of this band at ca. 10000–13000 cm^{-1} is diagnostic of the semiquinone character of a coordinated dioxolene ligand. Although this criterion cannot be exploited in all of the cases, due to the possible presence of other more intense bands, it is extremely useful and simple to apply. A scan of the literature showed for instance that in $M_4(DTBSQ)_8$ complexes (M = Co, Ni, Mn),[14] where the semiquinone nature of the ligands was established by X-ray crystal structure, bands are present at ca 13000 cm^{-1} thus confirming our assignment.

The determination of the origin of the pattern of bands occurring in the UV region is not straightforward. On the basis of the relative intensities and the values of the dissymmetry factors, we assign the bands at highest energy to the same transitions occurring in the catecholate derivatives, i.e. $3b_1 \rightarrow 4b_1$ and $3b_1 \rightarrow 3a_2$. The band with a vibronic progression observed in the near-UV region is tentatively assigned to the $2a_2 \rightarrow 3b_1$ transition, which has $\pi \rightarrow \pi^*$ character, on the basis of its absence in the spectra of catecholate complexes and of its intensity.

Finally, the broad band in the visible region of the CD spectrum is tentatively assigned to the $n \rightarrow \pi^*$ electric dipole forbidden and magnetic dipole allowed $7b_2 \rightarrow 3b_1$ transition.

We assign to charge-transfer transitions the bands observed at 21200 and 19200 cm^{-1} for the nickel(II)–DTBSQ and –TCSQ derivatives, respectively. These bands show a red shift on passing from the DTBSQ to the TCSQ derivative, consistent with a MLCT character of the electronic excitation. It appears reasonable to assign this transition to the spin-allowed $t_{2g} \rightarrow \pi^*$ quartet transition, taking into account its intensity and dissymmetry factor. This assignment requires a difference of optical electronegativity between the nickel(II) and the semiquinone ligand of about 1.[27] Other assignments involving doublet terms appear less probable, taking into account the energy difference between the ground state and the first doublet excited states.

The proposed assignment for both catecholates and semiquinonates agrees well with the observed chemical properties of these systems. Oxidation of divalent metal–catecholate adducts can occur either on the metal, yielding metal(III) catecholates, or on the ligand, yielding metal(II) semiquinonates. We have found[19] that for CTH complexes the former process occurs with chromium–, manganese–, iron–, and cobalt–catecholate adducts, in agreement with the results of previous investigations on other chemically related systems.[1,2] Nickel(II) represents the crossover and together with copper(II) and zinc(II) forms stable semiquinonate adducts.

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Registry No. *SS*-CTH, 53187-81-8; α-Ni(*SS*-CTH)$(ClO_4)_2$, 80531-86-8; Zn(*SS*-CTH)$(PF_6)_2$, 119565-86-5; Ni(*SS*-CTH)(DTBSQ)ClO_4, 119565-88-7; Ni(*SS*-CTH)(TCCat), 119480-47-6; Ni(*SS*-CTH)(TCSQ)ClO_4, 119480-49-8; Zn(*SS*-CTH)(DTBSQ)PF_6, 119480-51-2; Zn(*SS*-CTH)(TCCat), 119480-52-3; Ni(*SS*-CTH)(DTBSQ)PF_6, 119615-74-6; 3,5-di-*tert*-butyl-1,2-dihydroxybenzene, 1020-31-1.

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Stability and Structure of Xanthosine–Metal Ion Complexes in Aqueous Solution, Together with Intramolecular Adenosine–Metal Ion Equilibria

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The stability constants of the 1:1 complexes formed between Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cu(2,2′-bipyridyl)$^{2+}$, or Cu(1,10-phenanthroline)$^{2+}$ and xanthosine (Xao) were determined by potentiometric pH titration in aqueous solution (I = 0.1 ($NaNO_3$); 25 °C). Xanthosine is deprotonated at N-1 with $pK^{H}_{Xao} = 5.47$, and in accord herewith M(Xao-H)$^+$ complexes are formed. The anion (Xao-H)$^-$ displays a dichotomy between metal ion binding at N-1 and binding at N-7. The ratios for the metal ion distribution between these two sites are estimated: Cu^{2+}, like the proton, strongly favors binding at N-1; Ni^{2+} also binds about 70% at this site; Mn^{2+} and Cd^{2+} prefer N-7 binding by about 75%; Co^{2+} and Zn^{2+} are more equally distributed between the two sites. In connection with these structural evaluations previous conclusions regarding metal ion binding in M(adenosine)$^{2+}$ complexes are reconsidered; it is suggested that the amino group next to N-1 in adenosine gives rise to steric hindrance in the case of N-1 metal ion coordination. When this and some other effects are taken into account, it is concluded that Ni^{2+}, Cu^{2+}, and Zn^{2+} coordinate to adenosine preferably via the N-7 site. From the relationships obtained for N-1 and N-7 coordination between the log K stability constants and the ligand pK_a values, other stability constants may be estimated, provided the ligand pK_a is known. This procedure is applied to calculate with $pK^{H}_{H(Xao)} = 0.74$ and the indicated relationships the stability constants of the complexes formed between Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, or Cd^{2+} and neutral xanthosine; the resulting constants are compared with some experimentally obtained estimations. Metal ion coordination occurs in these M(Xao)$^{2+}$ complexes at the N-7 site. Finally it is emphasized that the indicated relationships may be used to judge the validity of published stability constants for nucleoside–metal ion complexes; this is an important aspect, as here many pitfalls are buried.

Enzymes utilizing nucleotides as substrates are in general also metal ion dependent (e.g. ref 2–4). This explains why great efforts are being made to understand and to quantify the interactions between metal ions and nucleotides in the solid state (e.g. ref 5 and 6) and in solution (e.g. ref 7–11).

Our own efforts are presently concentrated on the stability and structure of the complexes between nucleoside monophosphates and the divalent alkaline-earth or 3d transition-metal ions.[12,13]

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