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Nickel(II) complexes with N_2OS and N_2S_2 co-ordination spheres: reduction and spectroscopic study of the corresponding Ni(I) complexes

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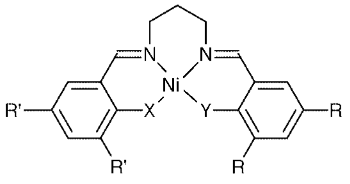
Nickel(II) complexes with Schiff-bases obtained by condensation of 1,3-propanediamine with salicylaldehyde and thiosalicylaldehyde, which present a N_2OS or N_2S_2 co-ordination sphere, were synthesized and studied. The molecular and crystal structure of the asymmetric complex [2-({3-[(3,5-dichloro-2-hydroxyphenyl)methyleneamino]-propyl}iminomethylene)benzenethiolato-*O*,*N*,*N′*,*S*]nickel(II) [Ni(t-salCl$_2$salpd)] has been determined by X-ray crystallography and shows a tetrahedrally distorted square-planar co-ordination geometry for the nickel center. The complexes were characterized by spectroscopic and electrochemical techniques and the results were used to assess the influence of the donor-atoms on their chemical properties. The results obtained show that the compounds may be reduced, either chemically or electrochemically, to Ni(I) complexes. Reduction potentials were found to be strongly dependent on the tetrahedral distortion of the Ni(II) complexes. EPR parameters for Ni(I) complexes, although not very sensitive to ligand substituents, show a regular dependence on the co-ordination set and the tetrahedral distortion of the complexes.

Introduction

In the last years, nickel complexes containing sulfur donors have received considerable attention due to the identification of a sulfur-rich co-ordination environment in biological nickel centres.[1] Several nickel thiolate complexes have been proposed as simple model compounds, and considerable advances have been achieved in nickel–sulfur chemistry, namely in the elucidation of structural aspects, redox chemistry and reactivity.[2–7] The recent crystal structure determination of the hydrogenase from *Desulfovibrio gigas* showed that the nickel is co-ordinated by four sulfur donors and has revealed the hetero-bimetallic nature of the active site.[8] This finding has driven the current investigation on model compounds towards the synthesis of bimetallic complexes.[9] Nevertheless, some important aspects of nickel–sulfur chemistry have remained poorly understood, in particular the role of co-ordinated sulfur donors in the stabilization of unusual oxidation states for nickel.

The purpose of this work is to study the stereochemical and electronic changes induced by replacing oxygen donors by sulfur donors in the co-ordination sphere of nickel(II) four-co-ordinate complexes. Special attention is given to the redox behavior of the complexes, namely the influence of sulfur/oxygen donors in the accessibility of the +1 and +3 oxidation states for the metal ion. Using a strategy developed for N_2O_2 Schiff-base ligands,[10] we have synthesized the asymmetric Ni(II) complexes [Ni(t-salsalpd)] and [Ni(t-salCl$_2$salpd)] depicted in Chart 1, and studied their electrochemical and spectroscopic behavior. We have also synthesized and studied the corresponding symmetric N_2S_2 complex, [Ni(t-salpd)], and compared its physicochemical characteristics with those of [Ni(t-salen)] {t-salen = 2,2′-[ethane-1,2-diylbis(iminomethyl)]dibenzenethiolate},[11] in order to assess chemical changes attributable to different N–(CH$_2$)$_n$–N bridges. The present ligands, in conjunction with [Ni(salpd)],[12] are ideally suited to evaluate the influence of sulfur donors in nickel complexes as they form a complete set of co-ordination spheres N_2O_2, N_2OS and N_2S_2, without any other changes in the ligand skeleton.



Complex	X	Y	R	R'
1 [Ni(salpd)]	O	O	H	H
2 [Ni(t-salsalpd)]	S	O	H	H
3 [Ni(t-salpd)]	S	S	H	H
4 [Ni(Cl$_2$salpd)]	O	O	Cl	Cl
5 [Ni(t-sal-Cl$_2$salpd)	S	O	Cl	H

Chart 1

Results and discussion

Synthesis

The compounds [Ni(t-salsalpd)] and [Ni(t-salCl$_2$salpd)] were prepared using template synthesis with the desired metal ion. The procedure employed was stepwise condensation of 1,3-propanediamine with salicylaldehyde in the presence of nickel(II) acetate followed by condensation of the product obtained with bis(thiosalicylaldehydate)nickel(II) (Scheme 1). Elemental analysis and ^1H NMR spectroscopy agree with the formulae proposed, and the observation of a ^1H NMR signal within the expected diamagnetic region, even in a strong co-ordinating solvent such as $(CD_3)_2SO$, suggests that the complexes retain their square-planar structure in solution.

Attempts to synthesize the free ligand using a similar methodology in the absence of the metal ion yielded in all cases 1 : 2 condensation products, even using a large excess of diamine. Demetalation of the Ni(II) complexes was also attempted, but the reaction was not complete, and the ligand could not be recovered from the reaction medium.

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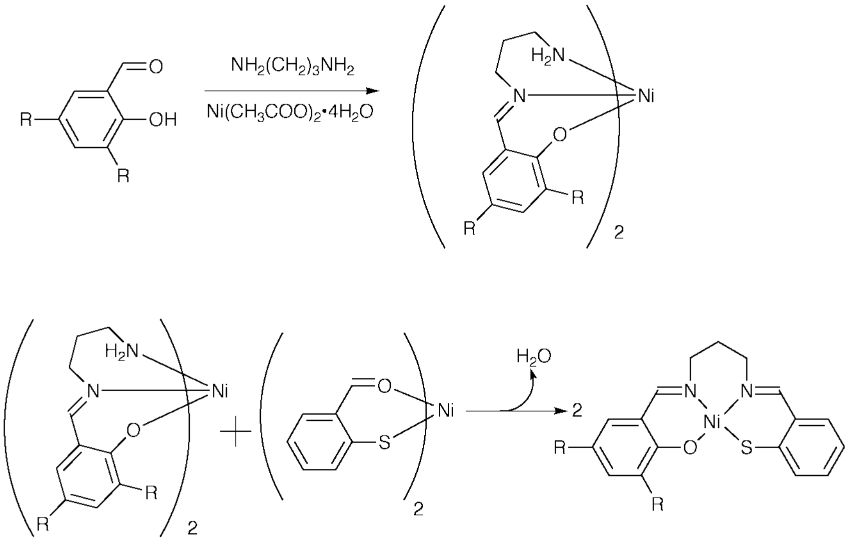
Table 1 Selected bond lengths (Å) and bond angles (°) for [Ni(t-salCl$_2$salpd)] and related complexes

	[Ni(t-salCl$_2$salpd)][a]	[Ni(t-salpd)] A[b]	[Ni(t-salpd)] B[b]	[Ni(salpd)][c]
Ni(1)–N(1)	1.909(6)	1.909(2)	1.913(2)	1.901(4)
Ni(1)–N(2)	1.871(6)	1.916(2)	1.919(2)	
Ni(1)–O(1)	1.856(5)			1.845(3)
Ni(1)–S(1)	2.168(2)	2.1733(9)	2.1686(9)	
Ni(1)–S(2)		2.1454(8)	2.1610(9)	
O(1)–C(17)	1.311(9)			1.309(5)
S(1)–C(1)	1.738(9)	1.708(3)	1.712(3)	
S(2)–C(17)		1.731(3)	1.721(3)	
N(2)–Ni(1)–N(1)	92.0(3)	90.70(10)	90.67(10)	96.39(18)
N(1)–Ni(1)–O(1)	93.7(2)			92.31(16)
N(1)–Ni(1)–S(1)	95.9(2)	90.07(8)	92.36(8)	
O(1)–Ni(1)–S(1)	83.9(2)			
N(2)–Ni(1)–S(2)		96.66(7)	94.36(8)	
S(1)–Ni(1)–S(2)		83.60(3)	83.14(4)	
O(1)–Ni(1)–O(2)				78.31(13)
θ[d]	24.50(10)	10.60(3)	7.64(3)	8.9(1)[e]

[a] This work. [b] Obtained from ref. 13. A and B stand for each of the two crystallographically independent molecules in the unit cell. [c] Obtained from ref. 14. [d] Dihedral angle between co-ordination planes NNiO(S) and NNiS(O), that is a measure of the tetrahedral distortion of the co-ordination sphere. [e] Distortion from planarity is not tetrahedral; the molecule has an umbrella shape with the nickel atom out of the co-ordination plane.



Scheme 1

Structure of the asymmetric complex [Ni(t-salCl$_2$salpd)]

Selected bond distances and bond angles for [Ni(t-salCl$_2$salpd)] and for other related Ni(II) complexes are collected in Table 1. A molecular drawing of the asymmetric Ni(II) complex with atomic numbering scheme is presented in Fig. 1.

[Ni(t-salCl$_2$salpd)] crystallizes in the spatial group $P2_12_12_1$, with four molecules per unit cell. The complex molecules pack in columnar arrangement along the three axes but the distances between neighboring molecules preclude any appreciable interaction between adjacent metal atoms.

The Ni(II) complex has a distorted square-planar geometry with the metal ion bound in a *cis* configuration to the NNOS atoms of the ligand. The geometry around the metal center is tetrahedrally distorted with a dihedral angle between the NiNO and NiNS planes of 24.50(10)°. The two six-membered metallorings show an umbrella-type configuration and the trimethylene bridge a twisted conformation. This type of co-ordination geometry is quite common for nickel(II) complexes with Schiff-base ligands, and may be compared with those of the Ni(II) complexes of the related symmetric ligands t-salpd[13] and salpd.[14] [Ni(t-salpd)] has a similar co-ordination geometry, but with a smaller tetrahedral distortion (dihedral angle between NiNS planes is 10.60° and 7.64° for the two crystallographically independent molecules). The complex [Ni(salpd)] exhibits a distorted square-planar structure with the planes defined by NiNO atoms ruffled, with a dihedral angle of 8.9° and the nickel atom 12 pm out of the co-ordination plane NN′OO′.

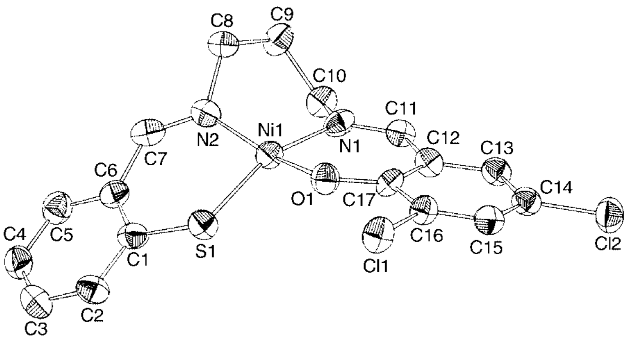


Fig. 1 Molecular structure and crystallographic numbering scheme for [Ni(t-salCl$_2$salpd)].

It is not clear if the larger tetrahedral distortion of the complex [Ni(t-salCl$_2$salpd)], when compared with those of the corresponding symmetric ligands, is related to the asym-

Table 2 Experimental results obtained for nickel-(II) and -(I) complexes

	[Ni(t-salsalpd)][a]	[Ni(t-salCl$_2$salpd)][a]	[Ni(t-salpd)][a]	[Ni(salpd)][b]
Electronic spectra of nickel(II) complexes				
λ/nm (ε/M^{-1} cm^{-1})	614.6(82)	587.0(80)	612.1(87)	500(140)
Cyclic voltammetry				
$E_{1/2}$/V	−1.40	−1.24	−1.28	−1.36
ΔE/mV	77	60	62	56
EPR of nickel(I) complexes				
g_1	2.266	2.268	2.232	2.300
g_2	2.089	2.091	2.079	2.083
g_2	2.057	2.056	2.063	2.055
Electronic spectra of nickel(I) complexes[c]				
λ/nm (ε/M^{-1} cm^{-1})	—	839 sh(370)	894 sh(115)	807(1200)
	726.5(376)	698(1310)	691 sh(503)	672(1500)

[a] This work. [b] Obtained from ref. 23. [c] Molar absorptivities were calculated based on the concentration of the initial nickel(II) complex.

metric nature of the co-ordination sphere, though a similar behavior has been observed previously for other complexes with tetradentate ligands containing NN′OS co-ordination spheres.[15] However, the larger tetrahedral distortion of the co-ordination sphere does not seem to induce significant changes in metal–ligand bond lengths as is evident by inspection of Table 1.

Electronic spectra

Electronic spectra of [Ni(t-salsalpd)], [Ni(t-salCl$_2$salpd)] and [Ni(t-salpd)] were recorded in the interval 300–1200 nm, in several solvents (dmf, dimethyl sulfoxide, acetonitrile, tetrahydrofuran and chloroform) and in Nujol mulls (Table 2). Spectra of the three complexes are very similar, and are practically identical in the solid state and in solution; furthermore, solvent dependence is negligible. One low intensity band at $\lambda_{max} \approx 587$–$615$ nm ($\varepsilon \approx 80$–100 mol^{-1} dm^3 cm^{-1}) is observed, followed by three more intense bands at ≈470, 375 and 345 nm ($\varepsilon \approx 10^2$–10^3 mol^{-1} dm^3 cm^{-1}). At higher energies several high intensity bands ($\varepsilon > 10^4$ mol^{-1} dm^3 cm^{-1}) are also detected, which are typical of ligand based transitions in Schiff-base metal complexes.[1] Similar spectra are commonly observed for low-spin square-planar Ni(II) complexes with N_2OS[15,16] and N_2S_2[11,17,18] co-ordination spheres, for which the low intensity band has been assigned to d–d transitions, and the high energy bands to charge-transfer transitions.

The d–d band maxima are very similar for the three complexes studied, although oxygen and sulfur donors have substantially different donor abilities. Usually, the energy of d–d transitions in square-planar Ni(II) complexes follows the order: $N_2S_2 < N_2OS < N_2O_2$.[19] The irregularity observed in the present case may be explained by the different tetrahedral distortions observed for the NiN_2S_2 and NiN_2OS co-ordination environments. [Ni(t-salpd)][13] has an almost planar co-ordination sphere while [Ni(t-salCl$_2$salpd)] shows a significant tetrahedral distortion of the co-ordination sphere geometry. Since tetrahedral distortion is expected to decrease the ligand field strength, the electronic and the structural effects oppose each other, resulting in very similar d–d transition energies for these two complexes. The effect of increasing tetrahedral distortion in the ligand-field spectra of nickel(II) complexes with N_2S_2 and N_2OS is usually not very strong. On the other hand, the d–d band usually observed for low spin 4-co-ordinated nickel(II) complexes arises from several possible transitions, and the band maximum is only an average value. Thus, in these cases, small differences in band maxima are not usually easily correlated with structural characteristics of these complexes.[15,18]

The UV/vis data may also be taken as evidence of similar structures for the two complexes with asymmetric co-ordination spheres, since d–d transitions in these types of complexes are expected to be more sensitive to the geometry of the co-ordination sphere than to the introduction of substituents in the aromatic rings of the ligands.[15,16]

Cyclic voltammetry

Cyclic voltammetric experiments were performed at room temperature, under strictly anaerobic conditions, in dmf, $(CH_3)_2SO$ and CH_3CN, and in the potential range +1.5 to −2.4 V. The three complexes show one irreversible oxidation process at ≈0.75 V for [Ni(t-salsalpd)] and [Ni(t-salCl$_2$salpd)], and at ≈0.76 V for [Ni(t-salpd)]. Irreversible oxidation behavior is typically found in thiolate containing complexes,[20–22] and has been attributed to the oxidation of thiolate to disulfide species. For the asymmetric complexes, however, thiolate oxidation is not the only possible oxidation process, since for the corresponding N_2O_2 complex [Ni(salpd)] a similar voltammetric behavior was also observed.[23] For Ni(II) complexes with N_2O_2 Schiff-bases the oxidation may take place at the ligand or at the metal center, and the oxidation product is strongly influenced by the stereochemical and electronic properties of the ligand and the donor ability of the solvent.[23–25]

Voltammograms of solutions of the three complexes studied in $(CH_3)_2SO$/0.1 mol dm^{-3} TBAP (tetrabutylammonium perchlorate), obtained in the potential range 0.0 to −2.4 V, show one electrochemically reversible redox process. Reversibility of the redox process was inferred by (a) $i_{pa},i_{pc}/v^{1/2}$ constant at all scan rates studies; (b) i_{pa}/i_{pc} ratios close to 1; (c) ΔE values similar to those found for the Fc$^+$/Fc couple under the same experimental conditions. For the remaining solvents used the electrochemical behavior is similar with the following exceptions: [Ni(t-salCl$_2$salpd)] in dmf and in CH_3CN and [Ni(t-salsalpd)] in CH_3CN show i_{pa}/i_{pc} values less than 1 for scan rates lower than 100 mV s^{-1}, an indication of the occurrence of a slow chemical reaction following heterogeneous electron transfer.

Electrolytic reduction of [Ni(t-salsalpd)] and [Ni(t-salCl$_2$salpd)] at potentials 50 mV more negative than E_{pc} was followed by coulometry. The solutions changed from brown to dark-green, and the spectroscopic studies show that Ni(I) complexes are formed (see EPR results in the following section). Current intensity decreased exponentially in the region corresponding to one-electron reduction to 70% of the initial quantity of Ni(II) complex, remaining constant thereafter. This latter behavior may be explained by a catalytic reaction involving the Ni(I) species and probably corresponds to electrocatalyzed reduction

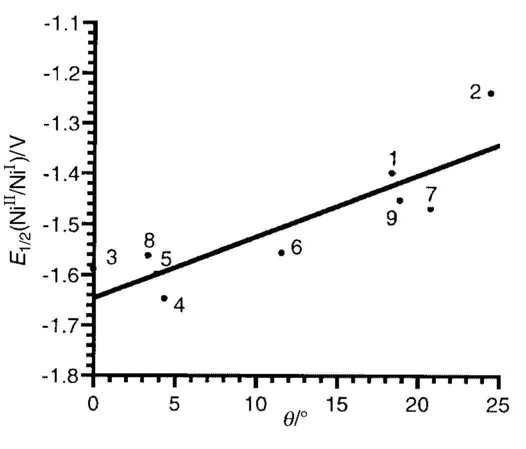


Fig. 2 Plot of $E_{1/2}$ for Ni(II)/Ni(I) process *vs.* the dihedral angle, θ, between the NNiX (X = O, S) planes. (1) [Ni(t-salsalpd)],[36] (2) [Ni(t-salCl$_2$salpd)], (3) [Ni(salen)],[24] (4) [Ni(cdsalen)],[16] (5) [Ni(napen)],[16] (6) [Ni(cdMeOsalen)],[16] (7) [Ni(cdsalpd)],[15] (8) [Ni(cd$_2$en)][16] and (9) [Ni(cd$_2$pd)].[15]

of residual water.[27] Cyclic voltammograms of the resulting electrolyzed solutions in the region from 0.0 to −2.4 V are identical to those obtained for the initial Ni(II) complexes except for a small decrease in current intensity of the voltammetric waves. This decrease is less than 10% of the initial current even when the total charge consumed corresponds to 4 electrons per Ni complex, and provides an indication that there is a small quantity of Ni(I) complex that decomposes in solution.

[Ni(t-salpd)] exhibits a different electrochemical behavior, and its EPR spectra show that electrochemical reduction yields radical species, an indication that the reduction process is ligand based. In view of the results it is not possible to compare directly $E_{1/2}$ values for this complex with those determined for the asymmetric complexes studied, since the electrochemical redox processes are different.

Reduction potentials of Ni(II) complexes are expected to be strongly dependent on stereochemical factors. For a geometry intermediate between square-planar and tetrahedral, an increase in tetrahedral distortion is expected to reduce metal–ligand interaction and thus to reduce the energy difference between the corresponding Ni(II) and Ni(I) complexes. In order to verify this stereochemical dependence in the present complexes we have plotted $E_{1/2}$ values *vs.* the dihedral angle between NiNO and NiNS co-ordination planes, θ (Fig. 2). In addition to the reported complexes, we have included data of other related Schiff base complexes with NiN$_2$O$_2$, NiN$_2$OS and NiN$_2$S$_2$ co-ordination spheres. Except for [Ni(salpd)], there is a fairly good correlation between these parameters, showing that the tetrahedral distortion of the Ni(II) complexes is the most important factor contributing to the reduction potential of Ni(II) complexes. Previous reports on the reduction of N$_2$OS Schiff-base Ni(II) complexes indicated that reduction potentials are very sensitive to the introduction of chloride substituents on the salicylate moiety,[15,16] but the present results show that this dependence may be mainly a consequence of a higher tetrahedral distortion induced by these substituents.

The reduction potential of [Ni(salpd)] was not included in the graph shown in Fig. 2 since in this case the distortion from planarity is different from the other complexes and there is evidence that solvation induces significant structural changes,[23] making meaningless any correlation between solution and solid state data.

Chemical reduction

Chemical reduction of the three Ni(II) complexes was performed using Na–Hg amalgam (5%) and yielded Ni(I) complexes, as assessed by EPR spectroscopy. For [Ni(t-salpd)] this result was unexpected since electrochemically reduced solutions contained only radical products. This different behavior may be due to: (i) stabilization of the Ni(I) species by alkaline metal ions, as has been previously reported for [Ni(salen)];[28] or to (ii) further reduction of the Ni(II) radical species to a Ni(I) complex with the reduced ligand.

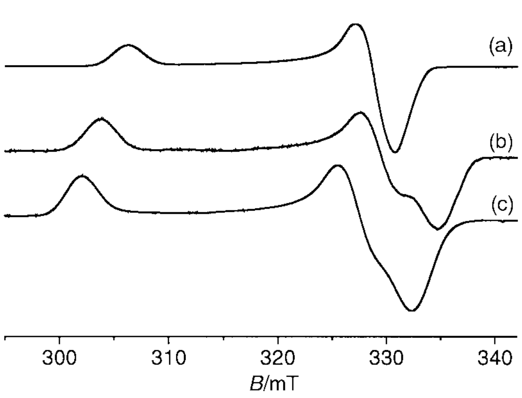


Fig. 3 X-Band EPR spectra of reduced dmf solutions of (a) [Ni(t-salpd)], (b) [Ni(t-salCl$_2$salpd)] and (c) [Ni(t-salsalpd)].

We have tried to solve this problem by studying the electrochemical behavior of [Ni(t-salpd)] solutions using NaClO$_4$ and LiClO$_4$ as supporting electrolytes. In both cases it was not possible to detect any voltammetric wave before the solvent discharge, in contrast with the results obtained using TBAP (tetrabutylammonium perchlorate) as the supporting electrolyte, which suggests that alkaline cations somehow interfere with the electrochemical reduction process. Efforts are being made in order to understand the electrolyte effect and the differences observed between electrochemical and chemical reduction for [Ni(t-salpd)].

Spectroscopic studies of reduced solutions of the nickel(II) complexes

Frozen solution EPR spectra in dmf, (CH$_3$)$_2$SO and CH$_3$CN at 77 K (Fig. 3) of chemically and electrochemically reduced solutions of [Ni(t-salsalpd)] and [Ni(t-salCl$_2$salpd)], and of chemically reduced solutions of [Ni(t-salpd)] were found to be independent of the solvent used and are typical of Ni(I) complexes with a $d_{x^2-y^2}$ or a d_{xy} ground state.[15,16,29–32] All spectra are anisotropic, with $g_1 \gg g_2 \approx g_3$, and do not show any resolved hyperfine structure.

As can be gathered by analysis of the values presented in Table 2, g values are not very sensitive to substituents of the ligand: g values for [Ni(t-salsalpd)] and [Ni(t-salCl$_2$salpd)] are almost the same within experimental error, showing that the influence of the chloride substituents on the Ni(I) electronic structure is insignificant. On the other hand, EPR parameters are more dependent on the co-ordinating atoms. Comparison of our g_1 values with those obtained for [Ni(salpd)] and similar NiN$_2$O$_2$ complexes,[29] reveals that replacement of one oxygen donor by a sulfur donor results in a decrease of ≈0.03 in g_1. This type of behavior was previously observed for other Ni(I) Schiff-base complexes,[15,16] and was attributed mainly to two non-independent factors: (i) higher covalency of Ni–S bonds compared to Ni–O bonds, and (ii) higher spin–orbit coupling constants for S than for O. Both factors reduce the spin–orbit contribution of the metal ion to the g tensor, thus decreasing the values of g.

To assess the importance of the co-ordination sphere on g_1 values we present in Fig. 4 a graphical representation of g_1 values *vs.* the number of sulfur atoms in the co-ordination sphere for several Schiff-base Ni(I) complexes with NiN$_2$O$_2$, NiN$_2$OS and NiN$_2$S$_2$ chromophores. As revealed by this graph there are essentially two main properties of the ligand that clearly influence the g_1 values: (i) the number of S donor atoms in the co-ordination sphere and (ii) the number of carbon atoms of the aliphatic bridge that link the two nitrogen donors.

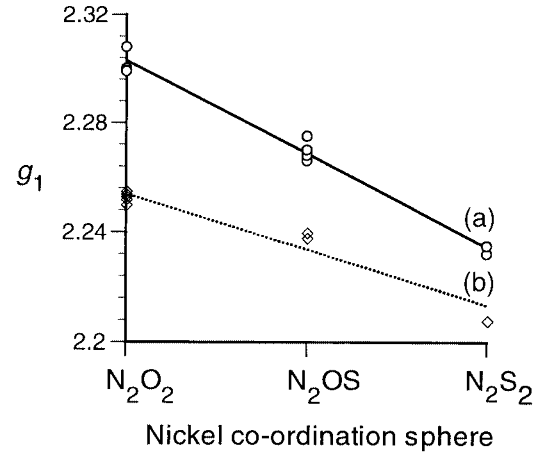


Fig. 4 Plot of g_1 values *vs.* type of co-ordination sphere for several Ni(I) complexes (a) with trimethylene bridges (N_2O_2 co-ordination spheres: [Ni(salpd)]$^-$;[24] [Ni(Mesalpd)]$^-$;[24] [Ni(nappd)]$^-$;[24] N_2OS co-ordination spheres: [Ni(t-salsalpd)]$^-$; [Ni(t-salCl$_2$salpd)]$^-$; [Ni(cdsalpd)]$^-$;[15] [Ni(cdCl$_2$salpd)]$^-$;[15] [Ni(salpd)]$^-$ and with N_2S_2 co-ordination spheres: [Ni(t-salpd)]$^-$; [Ni(cd$_2$pd)]$^-$ [15]) and (b) with dimethylene bridges (N_2O_2 co-ordination spheres: [Ni(salen)]$^-$;[24] [Ni(Mesalen)]$^-$;[24] [Ni(saltMe)]$^-$;[24] N_2OS co-ordination spheres: [Ni(cdsalen)]$^-$;[16] [Ni(cdCl$_2$salen)]$^-$ [16] and with N_2S_2 co-ordination spheres: [Ni(cd$_2$en)]$^-$ [16]). All values were obtained from this work and from references 15, 16 and 24.

Several studies on Schiff-base metal complexes with aliphatic bridges of increasing length have been reported,[33] and essentially two different effects were observed: complexes of metal ions that have a strong electronic preference for square-planar structures, such as Ni(II), show only minor structural differences, but spectroscopic studies show a significant decrease of the ligand-field strength; for metal ions with lower electronic preferences for a square-planar geometry, as for example copper(II), the increase in the length of the aliphatic bridge induces significant tetrahedral distortion of the complex. For Ni(I) complexes, the electronic preference for a square-planar geometry is expected to be even lower than that for copper(II), due to the weaker metal–ligand interaction caused by the lower charge of the metal ion. Thus, for Ni(I) complexes, the increase of the aliphatic bridge length most probably results in larger tetrahedral distortions, leading to an increase of g_1 values.

Electronic spectra of electrochemically and chemically reduced solutions of the N_2OS Ni(II) complexes were obtained and the results are presented in Table 2. Data for chemically reduced solutions of [Ni(t-salpd)] are also presented. All spectra are very similar, with two intense bands, one at $\lambda \approx 700$ nm, and the other at $\lambda < 500$ nm, with molar absorption coefficients in the range 400–1300 mol^{-1} dm^3 cm^{-1}, probably attributable to MLCT transitions. In addition, for [Ni(t-salsalpd)] and [Ni(t-salpd)], a low-intensity shoulder in the lower-energy band is observed at $\lambda \approx 895$ nm ($\varepsilon = 100$–300 mol^{-1} dm^3 cm^{-1}), probably corresponding to d–d transitions. The vis/NIR spectrum of reduced solutions of [Ni(salpd)] is also similar,[29] with a d–d band at $\lambda \approx 807$ nm; in this case, however, the high absorption coefficient reported seems to indicate some CT character for this band. This hypothesis is not excluded for [Ni(t-salCl$_2$salpd)] and [Ni(t-salpd)], since the uncertainty in absorption coefficients is expected to be high, due to partial decomposition of the Ni(I) complexes. On the other hand, since d–d bands are observed as weak shoulders on more intense CT bands, any small differences in band maxima may be due to errors on the experimental values, thus excluding any further interpretation of our results.

Conclusions

The present work allows some conclusions to be advanced about the consequences of O/S replacement in the co-ordination sphere of Ni complexes. We have found that one of the most important factors for the reduction potentials for Ni(II) is the extent of tetrahedral distortion. Although, softer donors are expected to contribute to the stabilization of metal ions in low oxidation states, we have found no evidence for this effect in our complexes, and the differences in $E_{1/2}$ values for the complexes with N_2O_2, N_2OS and N_2S_2 co-ordination spheres have been shown to be mainly related to differences in the tetrahedral distortion of the Ni(II) complexes. Moreover, the dependence of reduction potentials with the substituents of the salicylate moiety is probably due to significant structural changes induced by the substituents and are not of an electronic nature.

On the other hand, spectroscopic data for Ni(I) complexes are almost independent of ligand substituents, thus implying that Ni(I) is not so sensitive as Ni(II) to structural changes induced by ligand substituents. EPR data show that g values are very sensitive both to the co-ordination sphere and to the extent of tetrahedral distortion, but show little dependence on the substituents of the ligand skeleton. This behavior parallels what is commonly observed for isoelectronic copper(II) complexes, but allowing for a weaker metal–ligand interaction of Ni(I) complexes, due to the lower charge of the nickel(I) center.

All our results point to a weak interaction between nickel(I) and thiolate donors, implying that the presence of sulfur donors in the co-ordination sphere of nickel is not very important to the accessibility of Ni(I) complexes. The only relevant factor that contributes to higher reduction potentials for nickel complexes with sulfur donors is an indirect effect, since sulfur donors show a higher tendency than oxygen donors towards tetrahedral distortion, probably due to the lower ligand-field strength of sulfur-donors. Our results seem to imply that the thiolate rich co-ordination sphere of nickel in hydrogenase is not a particularly relevant factor to the stabilization of low oxidation states for this metal ion, at least in what concerns electronic effects.

Experimental

Reagents and solvents

All solvents and reagents used in the preparation of ligands and metal complexes were of reagent grade and used as received. Solvents for electrochemical studies (Merck, *pro analysi*) were dried by standard methods.[34] The following compounds were prepared by published methods: 2-aminobenzaldehyde,[35] bis{2-[*N*-(3-aminopropyl)methyleneamino]phenolato-*O*,*N*,*N*′}nickel(II), [Ni(salap)$_2$],[10] bis{2-[*N*-(3-aminopropyl)methyleneamino]-3,5-dichlorophenolato-*O*,*N*,*N*′}-nickel(II), [Ni(Cl$_2$salap)],[10] and tetra(*n*-butyl)ammonium perchlorate, TBAP.[36] **CAUTION:** perchlorates are hazardous and may explode.

Physical measurements

Elemental analyses (C, H and N) were performed at the Departamento de Química, Faculdade de Ciências do Porto. UV/Vis/NIR spectra were recorded with a Shimadzu UV-3101PC and FTIR spectra with a Mattson 5000 (KBr pellets), all at room temperature. ^{1}H NMR spectra were obtained with a Bruker AMX300, at room temperature using deuterochloroform as solvent and tetramethylsilane as internal standard. EPR spectra at 77 K were recorded with a Bruker ESP300E (9 GHz) equipped with a dual cavity; spectra were calibrated with diphenylpicrylhydrazyl (DPPH, $g = 2.0037$) and the magnetic field was calibrated using Mn^{2+} in MgO. EPR parameters were obtained by computer simulation of the experimental spectra in the usual manner.[37] Cyclic voltammetry was carried out at room temperature, under nitrogen, using a EG&G PAR 273A potentiostat. A three-electrode cell was used, with a platinum microsphere as working electrode, a platinum wire counter electrode and a Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode (Metrohm, ref. 6.0724.140). All potentials were corrected for the ferrocenium/ferrocene couple [$E_{1/2}$ (Fc$^+$/Fc) = 0.493 V *vs.* Ag/AgCl (1 mol dm^{-3} NaCl)], used as an internal standard. All complexes were studied at scan rates from 20 to 500 mV s^{-1}. Electrolysis was performed at room temperature, under strictly anaerobic conditions and at constant potential; a three electrode cell with a platinum gauze working electrode, a platinum foil counter electrode and a Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode was used.

Synthesis

[2-({3-[(2-Hydroxyphenyl)methyleneamino]propyl}iminomethyl)benzenethiolato-*O*,*N*,*N′*,*S*]nickel(II), [Ni(t-salsalpd)]. [Ni(CH$_3$COO)$_2$]·4H$_2$O (4.9 g, 20 mmol) was suspended in a solution of thiosalicylaldehyde (2.1 mmol) in diethyl ether (10 mL), and was stirred at room temperature for 2 h. The resulting dark red powder was recovered by filtration and partially solubilized in 100 mL of dichloromethane. Evaporation of this solution, in vacuum, yielded a red powder, [Ni(t-sal)$_2$] that was recrystallized from methanol–dichloromethane (1 : 1 v/v). Yield 0.42 g, 60%, δ_H(300 MHz; CDCl$_3$) 7.05 (2 H, t, arom), 7.26 (2 H, t, arom), 7.55 (2 H, d, arom), 7.62 (2 H, d, arom), 8.99 (2 H, s, CHO). [Ni(t-sal)$_2$] (1.7 g, 5.1 mmol) in dichloromethane was added to a solution of [Ni(salap)$_2$] (2.1 g, 5.1 mmol) in 10 mL of methanol. The resulting brown solution was stirred overnight at room temperature. Addition of methanol was added to precipitate a brown powder, that was collected, recrystallized from methanol–dichloromethane (1 : 10 v/v), and chromatographed on silica gel 60 (70–230 mesh) with methanol–dichloromethane (1 : 4 v/v). Yield 0.80 g, 44%; δ_H(300 MHz; CDCl$_3$) 1.98 (2 H, m, CH$_2$), 3.69 (2 H, t, CH$_2$), 4.00 (2 H, t, CH$_2$), 6.51 (1 H, t, arom), 6.89 (1 H, d, arom), 6.95 (1 H, t, arom), 7.05–7.17 (4 H, m, arom), 7.44 (1H, s, CHN), 7.73 (1 H, d, CHN); ν_{max}/cm^{-1}: 1450 (benzene stretch), 1618, 1602 (C=N) (Found: C, 56.9; H, 4.5; N, 7.8%. $C_{17}H_{16}N_2NiOS$ requires C, 57.5; H, 4.6; N, 7.9%).

[2-({3-[(3,5-Dichloro-2-hydroxyphenyl)methyleneamino]propyl}iminomethyl)benzenethiolato-*O*,*N*,*N′*,*S*]nickel(II), [Ni(t-salCl$_2$salpd)]. A procedure analogous to the previous one was used. Crystals of suitable quality for X-ray diffraction studies were obtained by slow evaporation of a dichloromethane–methanol solution. Yield 1.17 g, 54.1%; δ_H(300 MHz; CDCl$_3$) 1.92 (2 H, m, CH$_2$), 3.97 (2 H, t, CH$_2$), 4.29 (2 H, t, CH$_2$), 6.96 (1 H, t, arom), 7.20 (1 H, t, arom), 7.34–7.46 (3 H, m, arom), 7.50 (1 H. d, arom), 8.79 (1 H, s, CHN), 9.06 (1 H, s, CHN); ν_{max}/cm^{-1}: 1450 (benzene stretch), 1613, 1625 (C=N) (Found: C, 48.1; H, 3.4; N, 6.6%. $C_{17}Cl_2H_{14}N_2NiOS$ requires C, 48.3; H, 3.3; N, 6.6%).

{2,2′-[Propane-1,3-diylbis(iminomethyl)]dibenzenethiolato-*N*,*N′*,*S*,*S′*}nickel(II), [Ni(t-salpd)]. To a dichloromethane solution of [Ni(t-sal)$_2$] (0.67 g, 2.0 mmol) was added a stoichiometric amount of 1,3-propanediamine in methanol. After stirring for 2 h at room temperature, approximately one-half of the solvent was vacuum evaporated. Addition of methanol yields a brown solid that was chromatographed on silica gel 60 (70–230 mesh) with dichloromethane. Yield 70%; δ_H(300 MHz; CDCl$_3$) 2.05 (2 H, m, CH$_2$), 3.93–3.98 (4 H, m, CH$_2$), 6.98 (2 H, t, arom), 7.11–7.1 (2 H, m, arom), 7.20–7.23 (2 H, m, arom), 7.82 (2 H, s, CHN); ν_{max}/cm^{-1}: 1450 (benzene stretch), 1613, 1625 (C=N) (Found: C, 54.4; H, 4.6; N, 7.4%. $C_{17}H_{16}N_2NiS_2$ requires C, 55.0; H, 4.4; N, 7.5%).

Crystal structure determination of complex [Ni(t-salCl$_2$salpd]

Crystal data and data collection parameters. $C_{17}H_{14}Cl_2N_2NiOS$, $M = 423.95$, orthorhombic, $a = 7.511(2)$, $b = 11.616(4)$, $c = 19.228(6)$ Å, $V = 1677.6(9)$ Å^3 ($T = 298$ K), space group $P2_12_12_1$, $Z = 4$, μ(Mo-Kα) = 1.576 mm^{-1}; 12282 reflections measured, 4011 unique ($R_{int} = 0.1252$) which were used in all calculations.

Structure solution and refinement. Hydrogen atoms were calculated for idealized positions. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.01064\,P)^2 + 0.005\,P]$ where $P = (F_o^2 + 2F_c^2)/3$. The final $wR_2(F^2)$ was 0.1562, with R_1 0.0656 (R factors defined as usual), for 218 parameters with no restraints.

CCDC reference number 186/1876.

See http://www.rsc.org/suppdata/dt/a9/a908330h/ for crystallographic files in .cif format.

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