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Synthesis, spectroscopic and electrochemical study of nickel-(II) and -(I) complexes with Schiff-base ligands giving a NN′OS co-ordination sphere

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A set of nine new tetradentate ligands were prepared and the corresponding nickel(II) complexes with co-ordination spheres NN′OS synthesized and studied by spectroscopic and electrochemical techniques. The structure of (methyl 2-{[3-(2 hydroxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II) has been determined by X-ray crystallography. The complex has a tetrahedrally distorted square-planar geometry, and spectroscopic results indicated that this structure is retained even in strong co-ordinating solvents. Moreover, as the spectroscopic properties of this complex are very similar to those of the other complexes studied, it can be concluded that the introduction of substituents in the ligand does not induce significant structural changes. Electrochemical and EPR data show that the complexes are typically reduced to four-co-ordinate nickel(I) species although, with some of the ligands, formation of six-co-ordinate nickel(I) complexes was observed and an explanation is put forward to account for these different behaviours. Cyclic voltammetry studies showed that these complexes may also be oxidized but chemically and/or electrochemically oxidized solutions did not show any evidence for the formation of nickel(III) species.

The accessibility of several oxidation states of transition metals is a recurrent theme in co-ordination chemistry, especially due to its importance in catalysis, either in bioinorganic systems or in organometallic chemistry. In particular, the redox chemistry of nickel has received considerable attention in the last few years due to its essential role in several enzymes, where the occurrence of different oxidation states for nickel during the catalytic cycle has been proposed.[1,2] This observation has spurred a great interest in the determination of the electronic and structural factors that contribute to stabilize a particular oxidation state for the nickel centre and several factors have been recognized to be particularly important in the stabilization of the +3 and +1 oxidation states, namely co-ordination number and geometry, type of donor atom and electronic characteristics of the ligand. Optimum co-ordination environments for nickel-(III) and -(I) are different, and while the high oxidation state prefers high co-ordination numbers coupled with hard donors, nickel(I) is known to be stabilized by low co-ordination numbers and soft π-acceptor ligands.

In a systematic study in our laboratory we have designed new polydentate ligands that may be structurally modified in order to change either stereochemical requirements or donor characteristics, and used to evaluate the accessibility of several oxidation states for metal ions. Conformationally flexible ligands with mixed co-ordination spheres containing hard and soft donors seem to be good candidates to stabilize both oxidation states +1 and +3 for nickel. We have synthesized and studied[3] the redox behaviour of nickel(II) complexes with the ligands cdRsalen and cdRnapen (see Scheme 1), which contain a mixed co-ordination sphere NN′OS. This type of ligand proved to be adequate to study the influence of the co-ordination sphere on the redox behaviour of nickel complexes since it is possible to compare their behaviour with that of the related complexes [Ni(salen)] (N_2O_2 co-ordination sphere) and [Ni(cd_2en)] (N_2S_2 co-ordination sphere). Moreover, it was possible to synthesize several ligands containing different substituents, allowing one to assess the effect of small changes in donor ability of the ligand on the spectroscopic and redox properties of the complexes.

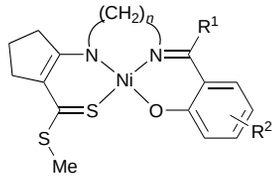
We have now extended the spectroscopic and electrochemical study of nickel(II) complexes with Schiff-base ligands that possess a NN′OS co-ordination sphere to complexes [Ni(cdR^{1}R^{2}salpd)] and [Ni(cdRnappd)] (Scheme 1). The ligands used are identical to those previously reported[3] except in the aliphatic bridge that joins the two nitrogen atoms. The replacement of a dimethylene by a trimethylene bridge is a commonly used strategy in the synthesis of macrocyclic and pseudo-macrocyclic ligands leading to decreased ligand-field and increased stereochemical flexibility of the complexes. Thus, with this new set of ligands it is possible to extend our previous analysis to the effect of stereochemical changes on the accessibility of several oxidation states for nickel.

Results and Discussion

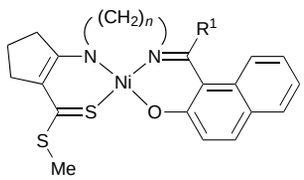
Crystal structure of [Ni(cdsalpd)] 1

Selected bond lengths and bond angles are given in Table 1, and a molecular drawing of the nickel(II) complex with the atomic numbering scheme is presented in Fig. 1. The molecule shows a tetrahedrally distorted square-planar geometry, with a dihedral angle between the planes defined by N(2)–Ni–S(1) and N(1)–Ni–O of 20.79(10)°. The ligand skeleton shows an umbrella configuration, with the trimethylene bridge in a twisted conformation, for which C(6) and C(8) are above and below the co-ordination plane and C(7) is very close to it. Bond lengths and angles within the ligand are indicative that there is a strong π delocalization through the six-membered metallocycles. The delocalization of the π system in the cyclopentene fragment indicates that this co-ordinates in a Schiff-base mode, in accordance with the similarity of the two Ni–N bond lengths and the Ni–S bond length that is typical of anionic sulfur donors in low-spin nickel(II) complexes.[4–6] This kind of co-ordination mode was observed for several complexes containing related ligands,[3,7,8] and contrasts with the behaviour of the free proligand, for which the dithioester/amine form is predominant.[9,10]

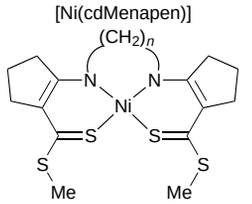
The structure of complex **1** may be compared to those containing the symmetric ligands salpd and cd_2pd. Thus [Ni(salpd)] has a distorted square-planar structure with the two planes defined by NiNO atoms ruffled, with a dihedral angle of 8.9°, and the nickel atom 12 pm out of the co-ordination



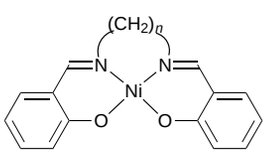
R^1	R^2	$n = 2$	$n = 3$
H	H	[Ni(cdsalen)]	[Ni(cdsalpd)]
Me	H	[Ni(cdMesalen)]	[Ni(cdMesalpd)]
H	3'-MeO	[Ni(cdMeOsalen)]	[Ni(cdMeOsalpd)]
Me	5'-Me	[Ni(cdMe$_2$salen)]	[Ni(cdMe$_2$salpd)]
H	4',6'-(MeO)	[Ni{cd(MeO)$_2$salen}]	[Ni{cd(MeO)$_2$salpd}]
Me	5'-MeO	[Ni(cdMeMeOsalen)]	[Ni(cdMeMeOsalpd)]
H	3',5'-Cl$_2$	[Ni(cdCl$_2$salen)]	[Ni(cdCl$_2$salpd)]



R^1	$n = 2$	$n = 3$
H	[Ni(cdnapen)]	[Ni(cdnappd)]
Me	[Ni(cdMenapen)]	[Ni[cdMenappd)]



$n = 2$	$n = 3$	$n = 4$
[Ni(cd$_2$en)]	[Ni(cd$_2$pd)]	[Ni(cd$_2$bd)]



$n = 2$	$n = 3$
[Ni(salen)]	[Ni(salpd)]

Scheme 1

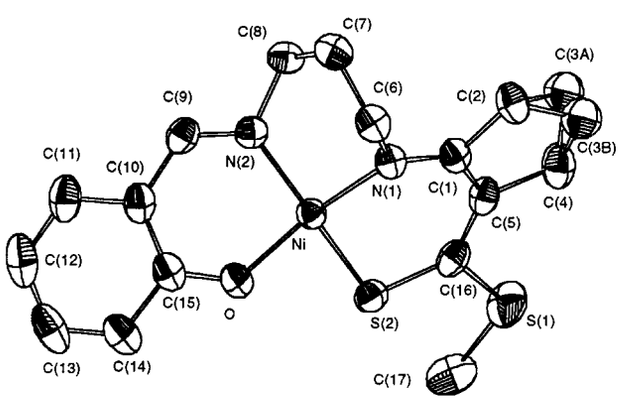


Fig. 1 Molecular structure and crystallographic numbering scheme for [Ni(cdsalpd)]

plane.[11] Nevertheless, bond lengths and angles between atoms of the salicylate fragment of **1** are very similar to those of [Ni(salpd)], the only significant differences occurring in the metal–ligand bond lengths that are slightly longer in **1**. The complex [Ni(cd$_2$pd)] shows also a tetrahedrally distorted square-planar structure,[12] but with a smaller dihedral angle (13.3°). Metal–ligand bond lengths are very similar in both

Table 1 Selected bond lengths (Å) and angles (°) for the complex [Ni(cdsalpd)]

Ni–O	1.887(2)	N(1)–C(6)	1.487(3)
Ni–N(1)	1.904(2)	N(2)–C(9)	1.293(2)
Ni–N(2)	1.930(2)	N(2)–C(8)	1.521(3)
Ni–S(2)	2.187(1)	C(1)–C(5)	1.439(3)
S(2)–C(16)	1.736(2)	C(5)–C(16)	1.398(3)
S(1)–C(16)	1.773(2)	C(9)–C(10)	1.478(3)
S(1)–C(17)	1.824(3)	C(10)–C(15)	1.434(3)
N(1)–C(1)	1.313(2)	C(15)–O	1.312(2)
O–Ni–N(1)	165.81(7)	O–Ni–S(2)	81.58(5)
O–Ni–N(2)	95.87(7)	N(1)–Ni–S(2)	96.97(6)
N(1)–Ni–N(2)	89.66(7)	N(2)–Ni–S(2)	162.38(5)

[Ni(cd$_2$pd)] and **1**, with Ni–N approximately 1 pm smaller in the asymmetric complex while Ni–S is approximately 1 pm longer.

The stereochemical effect of replacing a dimethylene by a trimethylene bridge may be evaluated by comparing the structure of complex **1** with that of [Ni(cdsalen)].[13] The two complexes have similar molecular structures but exhibit different tetrahedral distortions, [Ni(cdsalen)] being almost planar (dihedral angle between NiNO and NiNS planes of 4.4°). Bond lengths and angles between atoms of the ligand skeleton do not show significant differences, but metal–ligand bonds are approximately 3 pm longer in the complex with the trimethylene bridge, as expected due to the decreasing metal–ligand interaction with the extent of tetrahedral distortion.

Our results are to be contrasted with those reported for the series of symmetric NiN_2S_2 complexes [Ni(cd$_2$en)], [Ni(cd$_2$pd)] and [Ni(cd$_2$bd)], for which Bereman and co-workers[12] have reported a shortening of the Ni–S bonds with increasing tetrahedral distortion. These authors have argued that an increase in the number of carbon atoms of the polymethylene bridge forces the two nitrogens out of the co-ordination plane, thus allowing for increased covalency in the Ni–S bonds. This explanation contradicts what is usually observed for tetrahedrally distorted metal complexes, and does not account for the observed increase of Ni–S bond lengths in the asymmetric complexes [Ni(cdRsalen)][13] and **1**.

However, a closer analysis of the molecular structures of the NiN_2S_2 complexes [Ni(cd$_2$en)], [Ni(cd$_2$pd)] and [Ni(cd$_2$bd)] shows that: (i) distances between two neighbouring co-ordinated sulfur atoms are remarkably short, and approximately constant for the three complexes (2.81, 2.84 and 2.83 Å, respectively), and (ii) S–Ni–S bond angles are small (81–82°) when compared with what is usually found in complexes with similar tetrahedral distortions. The invariance of S···S distances and S–Ni–S bond angles is remarkable, especially taking into account that the dihedral angle between the N–Ni–N and S–Ni–S planes varies from 3.4 to 38.6°. We propose that these results may be explained by the existence of weak bonding interactions between nominally non-bonded sulfur atoms and that these interactions constrain to a large extent the Ni–S bond lengths. Examples of close contacts, due to weak bonding interactions between sulfur atoms, in co-ordination complexes and in other molecular species are known, and typically S···S distances are intermediate between the sum of the van der Waals radii of two sulfur atoms (3.7 Å) and S–S bond lengths in disulfide species (≈2.04–2.06 Å).[14] There is also evidence that this kind of interaction may impose significant distortions from regular geometries in co-ordination complexes.[14] Such interactions are obviously inoperative in the case of the asymmetric NiNN′OS complexes, for which the expected increase of Ni–S bond length with tetrahedral distortion is observed.

Electronic spectra

Band maxima of the nickel(II) complexes reported and of some related compounds are presented in Table 2. The UV/VIS/NIR

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

	UV/VIS, λ/nm (log, ε/dm^{3}mol^{-1}cm^{-1})		Cyclic voltammetry[a]		EPR of reduced solutions[b]		
Complex	dmf	Nujol	$E_{\frac{1}{2}}$	ΔE	g_1	g_2	g_3
[Ni(cdsalpd)]	442 (3.41), 646 (1.96)	454, 668	−1470	95	2.275	2.096	2.054
[Ni(cdMesalpd)][c]	432 (3.24), 628 (1.96)[d]	435, 542,[d] 615[d]	−1555	100	2.375	2.124	2.062
					2.279	2.090	2.062
[Ni(cdMeOsalpd)]	451 (3.38), 652 (2.02)	451, 668	−1440	85	2.281	2.093	2.056
[Ni(cdMe$_2$salpd)][c]	434 (3.11), 611 (2.03)[d]	436, 463,[d] 542, 620[d]	−1599	88	2.338	2.123	2.060
					2.282	2.085	2.060
[Ni{cd(MeO)$_2$salpd}]	433 (3.46), 468 (2.95), 640 (1.97)	445, 498,[d] 546,[d] 682	−1508	67	2.281	2.095	2.057
[Ni(cdMeMeOsalpd)]	431 (3.71), 608 (2.10)[d]	441, 544	−1580	90	2.378	2.115	2.083
[Ni(cdCl$_2$salpd)]	439 (3.29), 651 (1.89)	452, 504,[d] 559,[d] 662	−1333	70	2.270	2.099	2.054
[Ni(cdnappd)]	438 (3.72), 638 (2.04)	454, 482,[d] 664	−1464	88	2.280	2.096	2.060
[Ni(cdMenappd)][c]	417 (3.25), 590 (2.10)[d]	421, 566	−1526	85	2.373	2.128	2.057
					2.276	2.099	2.057
[Ni(cdsalen)][e]	428 (3.41), 461 (3.37), 607 (2.00)	435, 487, 622	−1649	88	2.238	2.086	2.041
[Ni(cd$_2$pd)][f]	452 (3.78), 671 (2.23)	457, 667	−1454	80	2.235	2.076[g]	2.076[g]
[Ni(salpd)][h]	595 (1.90)				2.304	2.085	2.058

[a] Potentials reported in mV, relative to Ag–AgCl (1 mol dm^{-3} NaCl) and corrected to the ferrocenium–ferrocene couple; $E_{\frac{1}{2}}$ was taken as $\frac{1}{2}(E_{pa} + E_{pc})$. [b] Obtained in dmf at 77 K. [c] The EPR spectrum of the reduced complex shows two different signals. [d] Inflection. [e] Obtained from ref. 3. [f] The UV/VIS results were from ref. 7, in CH_2Cl_2; voltammetric and EPR results from this work. [g] Axial signal with $g_2 = g_3$. [h] The UV/VIS results were from ref. 15, in $CHCl_3$; EPR results obtained from ref. 16, in Me_2SO.

spectra recorded in dmf, dichloromethane and Nujol mulls are virtually identical, and show one low-energy band at 600–650 nm with absorption coefficients of approximately 10^2 dm^3 mol^{-1} cm^{-1}, followed by three more intense bands (ε ≈ 10^3 dm^3 mol^{-1} cm^{-1}) in the region 400–500 nm. At higher energy several absorption bands are detected which, by comparison with the electronic spectra of the free proligands, may be assigned to ligand-based transitions. The low-energy band observed in the electronic spectra is characteristic of low-spin square-planar nickel(II) complexes, with co-ordination spheres N_2O_2,[15,17–19] and N_2S_2,[17,20] while the next three bands have been assigned to S→Ni charge-transfer transitions in related NiN_2S_2 complexes.[7,8]

Analysis of Table 2 reveals that the position of both the d–d band and the MLCT bands is only slightly affected by the substituents of the ligand; the larger variations for [Ni(cdMe$_2$salpd)], [Ni(cdMeMeOsalpd)] and [Ni(cdnappd)] are probably due to poor determination of band maxima as they are masked by the MLCT bands. Nevertheless, these small changes cannot be correlated directly with the electron-donor or -acceptor ability of the substituents, since they may be caused by different tetrahedral distortions. In fact, for complexes of general formula [Ni(cdRsalen)], X-ray crystallographic studies have revealed that the extent of tetrahedral distortion may depend on the substituents of the phenolate ring,[3] and a clear-cut distinction between these two factors is not possible in the absence of structural data.

Electronic spectra of the present complexes are very similar to those reported for [Ni(cdRsalen)] and [Ni(cdRnapen)],[3] but with all the bands shifted towards lower energies. This shift may be explained by the stronger tetrahedral distortion of the present complexes that is imposed by the trimethylene bridge. Moreover, as can be gathered from the data shown in Fig. 2, d–d band maxima for all the complexes with NN′OS co-ordination spheres with known structures vary linearly with the dihedral angle between the two co-ordination planes NiNO and NiNS, thus supporting the previous statement that changes in d–d band maxima with different substituents on the ligands may be related with the extent of tetrahedral distortion.[3]

Cyclic voltammetry

Cyclic voltammograms of the nickel(II) complexes were obtained in dmf–0.1 mol dm^{-3} NBu_4ClO_4 within the potential range +1.6 to −2.4 V (Fig. 3, Table 2). At potentials from +0.71 to +0.89 V one anodic wave is detected with one or two

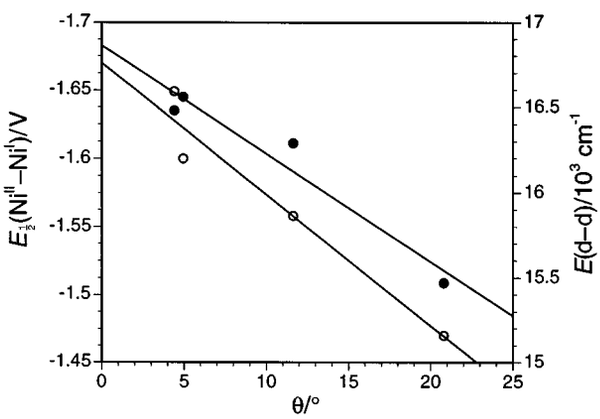


Fig. 2 Plots of $E_{\frac{1}{2}}$ (○) and d–d (●) band maxima for nickel(II) complexes *vs*. the dihedral angle, θ, between the NNiO and NNiS planes

coupled cathodic waves of lower intensity at ≈−0.5 and ≈−1.1 V. Repeated scanning in the potential range +1.6 to −1.3 V results in a current intensity decrease in subsequent cycles, and in electrode fouling at the end of the voltammetric experiment. Electrochemical or chemical oxidation of the present complexes was performed, but it was not possible to detect the formation of nickel(III) complexes. In addition, the spectroscopic characteristics of the oxidized solutions are indicative that a complex mixture of products is formed, indicating that probably decomposition of the complexes occurs after electron transfer. This behaviour is similar to that reported for nickel(II) complexes with ligands containing the dithioester fragment,[3,7,8] showing that, as commonly observed for unhindered thiolate ligands, the dithiocarboxylate moiety is a non-innocent redox ligand. In contrast, chemical or electrochemical oxidation of [Ni(salen)] and derivatives in co-ordinating solvents was found to yield nickel(III) species,[16] although oxygen-based ligands are not expected to be as efficient as thiolate donors in the stabilization of high oxidation states.

In the potential range 0.0 to −2.4 V one electrochemically reversible reduction process is detected (Fig. 3), with i_{pa}/i_{pc} close to unity, and ΔE values similar to that observed for the ferrocenium–ferrocene couple. Electrolysis of these solutions at potentials 50 mV more negative than the corresponding E_{pc} values yields nickel(I) species, as evidenced by their EPR spectra (see following section).

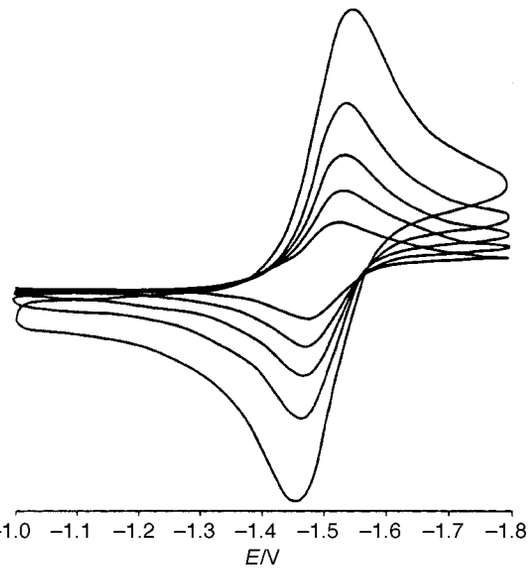


Fig. 3 Cyclic voltammogram of [Ni{cd(MeO)$_2$salpd}] in dmf solutions at 25 °C (scan rate = 500, 200, 100, 50 and 20 mV s^{-1})

Comparison of voltammetric data of [Ni(cdRsalpd)] and [Ni(cdRnappd)] with those of [Ni(cdRsalen)] and [Ni(cdRnapen)][3] shows that the complexes with the trimethylene bridge have values of $E_{\frac{1}{2}}$ that are on average 0.12 V higher than those with dimethylene bridges. For several nickel complexes with tetraazamacrocyclic ligands it has been observed that an increase in chelate ring size is associated with more positive reduction potentials,[21,22] a behaviour that has been attributed to a better fit of the ligand hole to the larger reduced metal ion and/or to a higher tetrahedral distortion of the metal complex that would favour the lower oxidation state. In macrocyclic complexes the former effect is usually believed to be more important, since this kind of ligand usually imposes square-planar geometry upon the complexes in both oxidation states.[23–25] For the present complexes, crystallographic and spectroscopic data suggest that the complexes with the trimethylene bridge are clearly more tetrahedrally distorted than those with the dimethylene bridge, suggesting that this effect may be more important in the stabilization of nickel(I) species. This is supported by the good correlation found between $E_{\frac{1}{2}}$ values and the dihedral angle between the co-ordination planes NNiO and NNiS in [Ni(cdsalpd)], [Ni(cdsalen)], [Ni(cdnapen)] and [Ni(cdMeOsalen)] (Fig. 2), for which the molecular structures are known.[3,13,16]

On the other hand, analysis of voltammetric data presented in Table 2 shows that, as was previously found for [Ni(cdRsalen)] and [Ni(cdRnapen)], there is a strong dependence of $E_{\frac{1}{2}}$ values on the substituents of the ligand, with the expected stabilization of the lower oxidation state by electron-withdrawing substituents. Comparison of voltammetric results for [Ni(cdRsalen)] and [Ni(cdRnapen)] shows that increased aromaticity of the ligand shifts the Ni^{II}–Ni^{I} process toward more positive potentials. Nevertheless, this latter effect does not seem to be so important for [Ni(cdRnappd)], as expected for the lower metal–ligand π interactions in the more distorted complexes.

Another aspect to stress in our results is the similarity between the reduction potentials of [Ni(cdsalpd)] and [Ni(cd$_2$pd)], which are ≈0.14 V more positive than $E_{\frac{1}{2}}$ of [Ni(salpd)]. This result contrasts with the dependence observed for similar complexes with dimethylene bridges, for which the change of oxygen for softer sulfur donors in the co-ordination sphere was found to play a key role in the stabilization of nickel(I) species.[3] For these latter complexes values of $E_{\frac{1}{2}}$ were found to increase by ≈0.07 V in the order NiN_2O_2 < NiNN′OS < NiN_2S_2. The different behaviour can be accounted for by the larger tetrahedral distortion of [Ni(cdsalpd)] compared with that of [Ni(cd$_2$pd)] and [Ni(salpd)]. In fact, while the complexes [Ni(cdsalen)], [Ni(cd$_2$en)] and [Ni(salen)] are almost planar, those with trimethylene bridges show very different structures: [Ni(salpd)] is practically square planar,[11] whereas [Ni(cdsalpd)] and [Ni(cd$_2$pd)] are tetrahedrally distorted, although the latter has a dihedral angle between co-ordination planes that is 7.5° smaller than that of the former.[12] These results imply that both the co-ordination sphere and the extent of tetrahedral distortion are important factors in the relative stabilization of nickel(I) species.

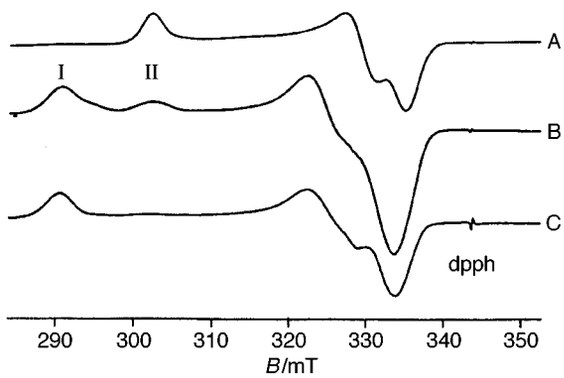


Fig. 4 X-Band EPR spectra of reduced dmf solutions of [Ni(cdMeOsalpd)] (A), [Ni(cdMe$_2$salpd)] (B) and [Ni(cdMeMeOsalpd)] (C) at 77 K; dpph = diphenylpicrylhylrazyl

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

Electrolysis of the nickel(II) complexes in dmf were performed under strictly anaerobic conditions and using previously dried solvents. The total charge at the end of the electrolysis corresponds in all cases to one-electron reductions. Frozen electrolysed solutions exhibit rhombic EPR spectra (Table 2 and Fig. 4), with g values typical of nickel(I) complexes with a $d_{x^2-y^2}$ or a d_{xy} ground state.[23–27] Chemical reduction of nickel(II) complexes using Na/Hg amalgam yielded solutions with similar EPR and UV/VIS/NIR spectra. Electrolysis of [Ni(cd$_2$pd)] was also performed, for which previous electrochemical studies indicated the possible formation of nickel(I) species,[7] although no EPR studies were published.

Analysis of the EPR spectra of reduced solutions of [Ni(cdRsalpd)] (Fig. 4) and [Ni(cdRnappd)] shows that the results obtained may be divided into three groups: (i) nickel complexes with ligands that do not contain a methyl substituent in the −C=N group of the salicylate fragment, for which very similar EPR spectra were obtained with g values of 2.28, 2.10 and 2.06 (Fig. 4, spectrum A); (ii) reduced solutions of [Ni(cdMeMeOsalpd)] which show a different pattern of g values with $g_1 = 2.378$, $g_2 = 2.115$ and $g_3 = 2.083$ (Fig. 4, spectrum C); and (iii) nickel complexes with ligands containing a methyl substituent at the −C=N group, the EPR spectra of which may be described as two superimposed signals, one with g values close to those of type (i) complexes and the other with g values close to that observed for [Ni(cdMeMeOsalpd)] (Fig. 4; spectrum B). A reduced solution of [Ni(cd$_2$pd)] shows an axial EPR spectrum, with $g_{\|}$ similar to g_1 of signal A and $g_{\perp}$ similar to the average of g_2 and g_3.

Spectrum A shows g values close to those found for square-planar nickel(I) complexes with tetraazamacrocyclic ligands,[23–25] which probably correspond to four-co-ordinate nickel(I) complexes with geometries close to those of the parent nickel(II) complexes. The higher g values in spectrum C may be assigned either to four-co-ordinate nickel(I) complexes with a more severe tetrahedral distortion or to complexes with co-ordinated solvent molecules, with formation of either five- or six-co-ordinate species. Of these latter two hypotheses, the formation of five-co-ordinate species does not seem acceptable,

since five-co-ordinate nickel(I) species usually show more rhombic spectra than corresponding four- or six-co-ordinate complexes,[28,29] and $g_1 - g_2 < g_2 - g_3$, in opposition to what is observed for spectra A and C.

In order to distinguish between distorted tetrahedral or distorted octahedral geometries for the nickel(I) species exhibiting spectrum C (or B), we have recorded the VIS/NIR spectra of the reduced solutions in the range 500–1600 nm. All spectra exhibit one high-intensity broad band centred at ≈620 nm ($\varepsilon > 2000$ dm^3 mol^{-1} cm^{-1}). In addition, reduced solutions of [Ni{cd(MeO)$_2$salpd)}], [Ni(cdCl$_2$salpd)] and [Ni(cdMeMeOsalpd)] show a shoulder in the low-energy range of the ≈620 nm band, at 834 ($\varepsilon \approx 40$), 938 ($\varepsilon \approx 200$), and 682 nm ($\varepsilon \approx 110$ dm^3 mol^{-1} cm^{-1}), respectively.† The low-intensity band may be assigned to d–d transitions of the nickel(I) species,[24,25] while the band at ≈620 nm probably corresponds to MLCT transitions. Analysis of these results in conjunction with the EPR spectra shows that [Ni(cdMeMeOsalpd)], (EPR spectrum C) has a significant deviation of the d–d band towards high energy, compared with those of the other complexes (EPR spectra A), which strongly suggests that spectrum C is due to a six-co-ordinate species.

Conclusion

Our previous work on the synthesis and characterization of nickel(II) complexes with co-ordination spheres NN′OS with the ligands cdRsalen and cdRnapen led us to extend our work to the present complexes, which differ only in the number of carbon atoms of the bridge between the two nitrogen donors. This synthetic strategy has been commonly used to impose a larger tetrahedral distortion in complexes of metal ions that show a structural preference for square-planar geometry. Although it has not proved successful in every case, sometimes leading to different kinds of distortion, for the Schiff bases reported here this substitution induces a significant tetrahedral distortion, allowing one to study the influence of this factor on the spectroscopic and electrochemical behaviour of the present complexes. Moreover, the results for the two series of nickel complexes with different bridges provide an extended set of spectroscopic and electrochemical data, which may be used to rationalize the relative contributions of electronic and stereochemical factors that control the physical/chemical properties of these complexes.

Nickel(II) complexes

The extent of tetrahedral distortion of nickel(II) complexes has a strong influence on their spectroscopic and voltammetric properties. Nevertheless, the spectroscopic properties of the complexes studied are primarily dependent on the co-ordination sphere, secondly on the degree of tetrahedral distortion and finally on the electronic characteristics of the ligand substituents. In contrast, the electrochemical characteristics are more sensitive to the electronic characteristics of the ligand substituents. From the set of complexes studied it can be concluded that the energy of the d–d band falls within well defined intervals that can be associated with each set of co-ordination sphere and N–N bridge (N_2OS/en; 600–615; N_2OS/pd; 640–650; N_2S_2/en, 660; N_2S_2/pd, 670; N_2O_2/en, 530–560; N_2O_2/pd, 550–590 nm)]. In contrast, $E_{\frac{1}{2}}$ values when grouped by these same characteristics lead to superimposed intervals.

Nickel(I) complexes

Spectroscopic characterization of reduced nickel(I) complexes revealed that four- and/or six-co-ordinate species may be formed. This result contrasts with those found for [Ni(cdRsalen)] and [Ni(cdRnapen)], for which only four-co-ordinate nickel(I) species were detected. Whether the co-ordination of solvent molecules in some of the complexes studied is explained by stereochemical or electronic differences is an unsolved problem. The decrease in metal–ligand interaction upon reduction of the metal centre and change of electron configuration from d^8 to d^9 is expected to decrease the preference for square-planar structure shown by the corresponding nickel(II) complexes; furthermore, the lower oxidation state of nickel is expected to induce a more tetrahedrally distorted structure. The observation that only those complexes that contain a trimethylene bridge and a methyl substituent on the azomethine carbon form six-co-ordinate species suggests that the methyl group may stereochemically interact with the methylene bridge, thus favouring the formation of less tetrahedrally distorted complexes, which are able to bind solvent molecules at the axial positions. Nevertheless, in the absence of structural data for the nickel(I) complexes, it is not possible to rule out completely the hypothesis that the formation of six-co-ordinate nickel(I) species may be imposed by changes in N donor ability.

Another important aspect to stress is that EPR spectra of nickel(I) four-co-ordinate species are almost independent of the substituents on the ligand skeleton, and show only a minor dependence on both co-ordination sphere and tetrahedral distortion, with g values decreasing in the order N_2O_2, N_2OS, N_2S_2 and increasing with the extent of tetrahedral distortion. A decrease in g values associated with O/S replacement is usually observed for isoelectronic copper(II) complexes,[30,31] and has been shown to be a consequence of the high spin–orbit constant of sulfur and higher covalent character of the M–S bond compared with M–O bond. On the other hand, the observed increase in g values with the tetrahedral distortion reflects the decrease in metal–ligand interaction for the more distorted complexes.

Experimental

Materials

All solvents and reagents in the synthesis of ligands and nickel(II) complexes were reagent grade used without further purification. Electrochemical measurements were performed in dimethylformamide (dmf) (Merck, *proanalisi*); tetrabutylammonium perchlorate was prepared by published methods.[32] **CAUTION:** perchlorates are hazardous and may explode.

Instrumentation

Elemental analysis (C, H and N) were performed at the Micro Analytical Laboratory, University of Manchester and at the Chemical Department, University of Porto. The UV/VIS/NIR spectra were recorded on a Shimadzu UV-3101PC spectrometer and NMR spectra on a Brüker AMX300 spectrometer, using deuteriochloroform as solvent and tetramethylsilane as internal standard. Electrochemical studies were performed with a EG&G PAR 362 instrument using solutions $\approx 1 \times 10^{-3}$ mol dm^{-3} in complex and 0.1 mol dm^{-3} in NBu_4ClO_4. Cyclic voltammetry was performed in dmf using a three-electrode cell, with a platinum microsphere as working electrode, a platinum foil as counter electrode and a Ag–AgCl (1 mol dm^{-3} NaCl) reference electrode (Metrohm, ref. 6.0724.140). In all cases, ferrocene was used as an internal standard. Under the experimental conditions employed $E_{\frac{1}{2}}$ of the ferrocenium–ferrocene couple is 485 mV. All potentials are reported relative to Ag–AgCl (1 mol dm^{-3} NaCl). Current intensities measured were baseline corrected.[32]

Controlled-potential electrolyses of the nickel(II) complexes were performed under strictly anaerobic conditions in a three-electrode cell, using a platinum-gauze working electrode, a

† Molar absorption coefficients estimated assuming the concentration of Ni^{I} to be equal to that of Ni^{II} in the original solution, since the determination of Ni^{I} proved to be unreliable due to its high sensitivity towards oxygen.

platinum-foil counter electrode and a Ag–AgCl (1 mol dm^{-3} NaCl) reference electrode. The potential applied was approximately 50 mV more negative than the cathodic peak potential determined in the voltammetric experiments.

The EPR spectra were obtained with a Brüker ESP300E spectrometer (9 GHz) in a dual cavity, using diphenylpicrylhydrazyl ($g = 2.0037$) as an external standard; the magnetic field was calibrated by use of Mn^{2+} in MgO. Spectra were obtained at 77 K, using sealed quartz tubes.

General procedure for the synthesis of the ligands $H_2cdR^1R^2salpd$ and $H_2cdRnappd$

Methyl 2-(3-aminopropylamino)cyclopent-1-ene-1-dithiocarboxylate (Hcdpd) was prepared by published methods.[9,10] All the ligands used in this work were prepared as described previously.[3] Typically, Hcdpd (2.0 mmol, 0.44 g) in methanol was added to a methanolic solution containing the stoichiometric amount of the appropriate salicylaldehyde. The resultant yellow powder was recrystallized from methanol–chloroform (2 : 1 v/v).

Methyl 2-{[3-(2-hydroxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdsalpd. Yield 53.0%. λ_{max}(dmf)/nm 314 (log ε_{max} 4.14) and 397 (4.40); δ_H(300 MHz, $CDCl_3$) 1.87 (2 H, m), 2.08 (2 H, m), 2.60 (3 H, s), 2.68 (2 H, t), 2.81 (2 H, t), 3.49 (2 H, m), 3.77 (2 H, t), 6.87–6.98 (2 H, m), 7.28–7.35 (2 H, m), 8.43 (1 H, s, CH=N), 12.46 (1 H, br s, NH) and 13.24 (1 H, br s, OH) (Found: C, 61.1; H, 6.57; N, 8.58; S, 18.6. $C_{17}H_{22}N_2OS_2$ requires C, 61.0; H, 6.63; N, 8.37; S, 19.2%).

Methyl 2-{[3-(2-hydroxyphenyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdMesalpd. Yield 61.2%. λ_{max}(dmf)/nm 314 (log ε_{max} 4.57) and 397 (4.84); δ_H(300 MHz, $CDCl_3$) 1.88 (2 H, m), 2.14 (2 H, m), 2.37 (3 H, s), 2.60 (3 H, s), 2.71 (2 H, t), 2.81 (2 H, t), 3.58 (2 H, m), 3.73 (2 H, t), 6.81 (1 H, t), 6.93 (1 H, d), 7.30 (1 H, t), 7.53 (1 H, d), 12.46 (1 H, br s, NH) and 16.16 (1 H, br s, OH) (Found: C, 62.0; H, 6.83; N, 8.31; S, 18.7. $C_{18}H_{24}N_2OS_2$ requires C, 62.0; H, 6.94; N, 8.31; S, 18.4%).

Methyl 2-{[3-(2-hydroxy-3-methoxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdMeOsalpd. Yield 78.1%. λ_{max}(dmf)/nm 313 (log ε_{max} 4.06) and 397 (4.34); δ_H(300 MHz, $CDCl_3$) 1.86 (2 H, m), 2.06 (2 H, m), 2.60 (3 H, s), 2.67 (2 H, t), 2.80 (2 H, t), 3.49 (2 H, m), 3.77 (2 H, t), 3.91 (3 H, s, OCH_3), 6.80–6.95 (3 H, m), 8.41 (1 H, s, CH=N), 12.45 (1 H, br s, NH) and 13.69 (1 H, br s, OH) (Found: C, 59.7; H, 6.90; N, 7.58. $C_{18}H_{24}N_2O_2S_2$ requires C, 59.3; H, 6.64; N, 7.68%).

Methyl 2-{[3-(2-hydroxy-5-methylphenyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdMe$_2$salen. Yield 82.2%. λ_{max}(dmf)/nm 313 (log ε_{max} 4.09) and 397 (4.42); δ_H(300 MHz, $CDCl_3$) 1.88 (2 H, m), 2.14 (2 H, m), 2.30 (3 H, s), 2.36 (3 H, s), 2.60 (3 H, s), 2.71 (2 H, t), 2.81 (2 H, t), 3.58 (2 H, m), 3.71 (2 H, t), 6.84 (1 H, d), 7.12 (1 H, d), 7.33 (1 H, s), 12.46 (1 H, br s, NH) and 15.8 (1 H, br s, OH) (Found: C, 62.7; H, 7.21; N, 7.60. $C_{19}H_{26}N_2OS_2$ requires C, 62.9; H, 7.23; N, 7.73%).

Methyl 2-{[3-(2-hydroxy-4,6-dimethoxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cd(MeO)$_2$salpd. Yield 48.7%. λ_{max}(dmf)/nm 294 (log ε_{max} 4.17), 312 (sh) and 397 (4.36); δ_H(300 MHz, $CDCl_3$) 1.88 (2 H, m), 2.02 (2 H, m), 2.59 (3 H, s), 2.66 (2 H, t), 2.80 (2 H, t), 3.49 (2 H, m), 3.65 (2 H, t), 3.77 (6 H, s, OCH_3), 5.68 (1 H, s), 5.92 (1 H, s), 8.44 (1 H, s, CH=N), 12.42 (1 H, br s, NH) and 14.37 (1 H, br s, OH) (Found: C, 58.7; H, 6.77; N, 7.32; S, 15.9. $C_{19}H_{26}N_2O_3S_2$ requires C, 57.8; H, 6.64; N, 7.10; S, 16.2%).

Methyl 2-{[3-(2-hydroxy-5-methoxyphenyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdMeMeOsalpd. Yield 42.8%. λ_{max}(dmf)/nm 314 (log ε_{max} 4.04) and 397 (4.39); δ_H(300 MHz, $CDCl_3$) 1.87 (2 H, m), 2.13 (2 H, m), 2.34 (3 H, s), 2.59 (3 H, s), 2.70 (2 H, t), 2.80 (2 H, t), 3.58 (2 H, m), 3.71 (2 H, t), 3.79 (3 H, s, OCH_3), 6.86–6.96 (2 H, m), 7.05 (1 H, d), 12.46 (1 H, br s, NH) and 15.41 (1 H, br s, OH) (Found: C, 60.3; H, 6.94; N, 7.40. $C_{19}H_{26}N_2O_2S_2$ requires C, 60.3; H, 6.94; N, 7.40%).

Methyl 2-{[3-(3,5-dichloro-2-hydroxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdCl$_2$salpd. Yield 15.3%. λ_{max}(dmf)/nm 285 (log ε_{max} 5.01), 315 (3.94), 398 (4.27) and 435 (3.60); δ_H(300 MHz, $CDCl_3$) 1.89 (2 H, m), 2.13 (2 H, m), 2.61 (3 H, s), 2.69 (2 H, t), 2.81 (2 H, t), 3.50 (2 H, m), 3.84 (2 H, t), 7.18 (1 H, s), 7.42 (1 H, s), 8.33 (1 H, s, CH=N), 12.46 (1 H, br s, NH) and 14.33 (1 H, br s, OH) (Found: C, 49.6; H, 4.98; N, 6.88. $C_{17}H_{20}Cl_2N_2OS_2$ requires C, 50.6; H, 5.00; N, 6.94%).

Methyl 2-{[3-(2-hydroxynaphthyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdnappd. Yield 37.7%. λ_{max}(dmf)/nm 309 (log ε_{max} 4.58), 398 (4.70) and 427 (sh); δ_H(300 MHz, $CDCl_3$) 1.80 (2 H, m), 2.14 (2 H, m), 2.61 (3 H, s), 2.63 (2 H, t), 2.76 (2 H, t), 3.52 (2 H, m), 3.86 (2 H, t), 6.97 (1 H, d), 7.24 (1 H, t), 7.46 (1 H, t), 7.64 (1 H, d), 7.72 (1 H, d), 7.89 (1 H, d), 12.50 (1 H, br s, NH) and 14.62 (1 H, br s, OH) (Found: C, 65.6; H, 6.21; N, 7.12. $C_{21}H_{24}N_2OS_2$ requires C, 65.6; H, 6.29; N, 7.28%).

Methyl 2-{[3-(2-hydroxynaphthyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylate, H_2cdMenappd. Yield 46.6%. λ_{max}(dmf)/nm 292 (log ε_{max} 3.42), 312 (4.06) and 397 (4.36); δ_H(300 MHz, $CDCl_3$) 1.88 (2 H, m), 2.20 (2 H, m), 2.61 (3 H, s), 2.65 (3 H, s), 2.74 (2 H, t), 2.82 (2 H, t), 3.66 (2 H, m), 3.76 (2 H, t), 6.96 (1 H, d), 7.24 (1 H, t), 7.41 (1 H, t), 7.64–7.70 (3 H, m), 12.50 (1 H, br s, NH) and 15.5 (1 H, br s, OH) (Found: C, 65.9; H, 6.54; N, 6.90. $C_{22}H_{26}N_2OS_2$ requires C, 66.3; H, 6.57; N, 7.03%).

General procedure for the synthesis of nickel(II) complexes

The complexes [NiL], with L = cdR^1R^2salpd or cdR^1nappd were synthesized as described previously.[3] Typically, Ni(O$_2$CMe)$_2$·4H$_2$O (1.0 mmol) in methanol was added to the stoichiometric amount of the desired ligand in methanol–chloroform (1 : 1, v/v). The resulting brown powder was recrystallized from acetonitrile.

(Methyl 2-{[3-(2-hydroxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdsalpd)]. Yield 53.0%. δ_H(300 MHz, $CDCl_3$) 1.79–1.92 (4 H, m), 2.40 (2H, t), 2.58 (2 H, t), 2.67 (3 H, s), 3.63 (2 H, t), 3.70 (2 H, t), 6.49 (1 H, t), 6.76 (1 H, d), 7.05–7.14 (2 H, m) and 7.60 (1 H, s, CH=N) (Found: C, 52.2; H, 5.19; N, 7.17. $C_{17}H_{20}N_2NiOS_2$ requires C, 52.2; H, 5.15; N, 7.16%). Single crystals were obtained by recrystallization from 1,4-dioxane.

(Methyl 2-{[3-(2-hydroxyphenyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdMesalpd)]. Yield 61.2%. δ_H(300 MHz, $CDCl_3$) 1.77 (2 H, m), 2.26–2.39 (7 H, m), 2.53 (2H, t), 2.64 (3 H, s), 3.08 (2 H, t), 3.69 (2 H, t), 6.60 (1 H, t), 6.78 (1 H, d), 7.10 (1 H, t) and 7.38 (1 H, d) (Found: C, 52.8; H, 5.50; N, 6.98. $C_{18}H_{22}N_2NiOS_2$ requires C, 53.4; H, 5.47; N, 6.91%).

(Methyl 2-{[3-(2-hydroxy-3-methoxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)-nickel(II), [Ni(cdMeOsalpd)]. Yield 78.1%. δ_H(300 MHz, $CDCl_3$) 1.79–1.93 (4 H, m), 2.41 (2H, t), 2.59 (2 H, t), 2.68 (3 H, s), 3.62

(2 H, t), 3.71 (2 H, t), 3.74 (3 H, s OCH_3), 6.43 (1 H, t), 6.64–6.72 (2 H, m) and 7.61 (1 H, s, CH=N) (Found: C, 51.5; H, 5.30; N, 6.72. $C_{18}H_{22}N_2NiO_2S_2$ requires C, 51.3; H, 5.26; N, 6.65%).

(Methyl 2-{[3-(2-hydroxy-5-methylphenyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdMe$_2$salpd)]. Yield 82.2%. δ_H(300 MHz, $CDCl_3$) 1.76 (2 H, m), 2.23 (3 H, s), 2.28–2.37 (7 H, m), 2.52 (2 H, t), 2.63 (3 H, s), 3.05 (2 H, t), 3.66 (2 H, t), 6.70 (1 H, d), 6.93 (1 H, d) and 7.16 (1 H, s) (Found: C, 54.7; H, 5.69; N, 6.75. $C_{19}H_{24}N_2NiOS_2$ requires C, 54.4; H, 5.77; N, 6.68%).

(Methyl 2-{[3-(2-hydroxy-4,6-dimethoxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni{cd(MeO)$_2$salpd}]. Yield 48.7%. δ_H(300 MHz, $CDCl_3$) 1.79–1.89 (4 H, m), 2.39 (2H, t), 2.56 (2 H, t), 2.66 (3 H, s), 3.56 (2 H, t), 3.64 (2 H, t), 3.68 (3 H, s, OCH_3), 3.73 (3 H, s, OCH_3), 5.58 (1 H, s), 5.90 (1 H, s) and 7.83 (1 H, s, CH=N) (Found: C, 49.4; H, 5.40; N, 6.03. $C_{19}H_{24}N_2NiO_3S_2$ requires C, 50.6; H, 5.36; N, 6.21%).

(Methyl 2-{[3-(2-hydroxy-5-methoxyphenyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdMeMeOsalpd)]. Yield 42.8%. δ_H(300 MHz, $CDCl_3$) 1.76 (2 H, m), 2.31 (3 H, s), 2.32–2.40 (4 H, m), 2.52 (2 H, t), 2.63 (3 H, s), 3.04 (2 H, t), 3.65 (2 H, t), 3.76 (3 H, s, OCH_3), 6.70–6.81 (2 H, m) and 6.88 (1 H, d) (Found: C, 52.5; H, 5.60; N, 6.43. $C_{19}H_{24}N_2NiO_2S_2$ requires C, 52.4; H, 5.56; N, 6.44%).

(Methyl 2-{[3-(3,5-dichloro-2-hydroxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdCl$_2$salpd)]. Yield 15.3%. δ_H(300 MHz, $CDCl_3$) 1.84–1.93 (4 H, m), 2.43 (2 H, t), 2.60 (2 H, t), 2.69 (3 H, s), 3.61 (2 H, t), 3.73 (2 H, t), 6.91 (1 H, s), 6.95 (1 H, s) and 7.59 (1 H, s, CH=N) (Found: C, 44.6; H, 3.95; N, 6.11. $C_{17}H_{18}Cl_2N_2NiOS_2Cl_2$ requires C, 44.4; H, 3.94; N, 6.09%).

(Methyl 2-{[3-(2-hydroxynaphthyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdnappd)]. Yield 37.3%. δ_H(300 MHz, $CDCl_3$) 1.80 (2 H, m), 2.00 (2 H, m), 2.47–2.58 (4 H, m), 2.61 (3 H, s), 3.63 (2 H, t), 3.92 (2 H, t), 6.76 (1 H, d), 7.21 (1 H, t), 7.44 (1 H, t), 7.64 (1 H, d), 7.71 (1 H, d), 8.12 (1 H, d) and 8.69 (1 H, s, CH=N) (Found: C, 57.6; H, 5.10; N, 6.36. $C_{21}H_{22}N_2NiOS_2$ requires C, 58.0; H, 5.31; N, 6.15%).

(Methyl 2-{[3-(2-hydroxynaphthyl)(methyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato)nickel(II), [Ni(cdMenappd)]. Yield 46.6%. δ_H(300 MHz, $CDCl_3$) 1.58 (2 H, m), 1.74 (2 H, t), 2.37 (2 H, t), 2.49 (2 H, t), 2.45 (3 H, s), 2.60 (3 H, s), 2.89 (2 H, t), 3.50 (2 H, t), 6.92 (1 H, d), 7.21 (1 H, t), 7.40 (1 H, t), 7.51–7.56 (2 H, m) and 7.67 (1 H, d) (Found: C, 57.8; H, 5.30; N, 6.04. $C_{22}H_{24}N_2NiOS_2$ requires C, 58.0; H, 5.31; N, 6.15%).

Chemical reduction of the nickel(II) complexes

Solutions of the nickel(II) complexes ($c \approx 1 \times 10^{-3}$ mol dm^{-3}) in dmf were reduced with a large excess of sodium amalgam (1% Na/Hg) under strictly anaerobic conditions.

Crystallography

Crystal data and data collection parameters. [Ni(cdsalpd)], $C_{17}H_{20}N_2NiOS_2$, $M = 391.16$, monoclinic, space group $P2_1/n$, $a = 8.924(5)$, $b = 16.889(8)$, $c = 12.051(6)$ Å, $\beta = 97.94(2)°$, $U = 1799(2)$ Å^3 (by least-squares refinement on diffractometer angles from 23 centred reflections, $13.71 < \theta < 25.03$), $T = 203$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 1.444$ Mg m^{-3}, $F(000) = 816$, brown prism with dimensions $0.40 \times 0.20 \times 0.10$ mm, μ(Mo-Kα) = 1.287 mm^{-1}, empirical absorption correction based on ψ scans, transmission factors 0.3354–0.3727, STOE STADI IV diffractometer, 2θ–ω scans, data collection range $3.41 < 2\theta < 54.00°$, $\pm h$, $\pm k$, $\pm l$, three standard reflections measured every 90 min showed no significant variation in intensity; 4091 reflections measured, 3713 unique ($R_{int} = 0.0233$) which were used in all calculations.

Structure solution and refinement. The structure was solved by direct methods and subsequent Fourier-difference techniques, and refined anisotropically, by full-matrix least squares, on F^2 (program SHELXL 93).[33] Hydrogen atoms were located in the Fourier-difference map, except those corresponding to C(3) which were calculated for idealized positions. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0340P)^2 + 0.6495P]$ where $P = (F_o^2 + 2F_c^2)/3$. The final $wR2(F^2)$ was 0.0688, with $R1$ 0.0272 (R factors defined in ref. 33), for 280 parameters with no restraints, goodness of fit = 1.058, maximum $\Delta/\sigma = 0.003$, maximum $\Delta\rho = 0.77$ e Å^{-3}.

CCDC reference number 186/827.

See http://www.rsc.org/suppdata/dt/1998/629/ for crystallographic files in .cif format.

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