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Comparative analysis of the electronic and EPR spectra of copper(II) and nickel(I) complexes; insights into nickel(I) electronic structure

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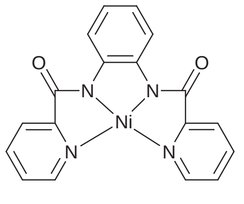
The nickel(I) complex with the ligand 1,2-bis(pyridine-2-carboxamido)benzene (H_2bphen), generated by reduction with sodium amalgam of the homologous nickel(II) complex, has been studied by EPR and electronic spectroscopy. The electronic, structural and bonding properties of the complex were elucidated based on a comparison of the EPR and UV/VIS data of isoelectronic complexes of $^{63}Cu^{II}$ and $^{61}Ni^{I}$ of H_2bphen. Analysis of the spectroscopic data revealed that the complex exhibits low covalency in the σ in-plane bonding and high covalency in the out-of-plane π bonds, and has enabled the assignment of the electronic bands at ≈13 500 and 19 600 cm^{-1} of $[Ni^{I}(bphen)]^-$ to d_{xz}, $d_{yz} \longleftarrow d_{xy}$ and $d_{x^2-y^2} \longleftarrow d_{xy}$ transitions. Implications for the spectral characterization of cofactor F_{430} systems are also presented.

The chemistry of nickel(I) has been of considerable interest in recent years, particularly due to the involvement of this oxidation state of nickel in catalytic reactions. Nickel(I) complexes with porphyrinic ligands, tetraaza macrocycles and tetradentate Schiff-base ligands have been used as catalysts in the reduction of alkyl halides[1–3] and CO_2.[4] Furthermore, methyl-coenzyme M reductase (MCR), an enzyme that catalyses the final step in the reduction of CO_2 to methane[5] and the reductive dehalogenation of chlorinated hydrocarbons in methanogenic bacteria,[6] requires the cofactor F_{430} which in its active form is a nickel(I) hydrocorphinoid complex.[7]

The number of known nickel(I) complexes is low when compared to that of compounds of isoelectronic copper(II). Reduction of low-spin nickel(II) complexes can in principle originate either nickel(I) or π-anion radical nickel(II) complexes.[8–13] Recent studies indicate that reduction to Ni^{I} requires not only the correctly ordered energies of the metal and macrocyclic molecular orbitals, but also ligand framework flexibility to adjust the core size changes (expansion of nickel–ligand distances and distortion of nickel core) that are induced by reduction of the metal ion.[9,12–20] This latter aspect is of paramount importance in stabilizing the σ-antibonding in-plane d orbital, relative to the π* LUMO. Nickel(II) complexes with highly unsaturated ligands are intrinsically rigid systems and are usually reduced to nickel(II) π-anion radicals, due not only to the stabilization of the LUMO ligand orbital, but also to destabilization of the metal orbital promoted by ligand rigidity. By contrast, similar systems, but with more saturated ligands, have greater core size, more ligand flexibility and the combination of both effects results in the stabilization of nickel(I) species. As a consequence the only tetrapyrrolic complexes that allow for stabilization of Ni^{I} upon reduction of the nickel(II) species are nickel isobacteriochlorins[3b,15,16,18] and forms of F_{430},[5d–f,17] a situation to be contrasted with that of tetraaza complexes[2c,d,3c,8,18,20] and polydentate Schiff-base complexes[1e,12,13] for which smaller ligand conjugation and higher structural flexibility afford a large number of nickel(I) complexes. In both cases, the ability of the starting nickel(II) complexes to form nickel(I) species rather than an anion radical is a key point for obtaining efficient catalytic properties.

Metal- *versus* ligand-centred reduction has been studied by combination of UV/VIS and EPR spectroscopy, but despite extensive use of these two techniques in the characterization of nickel(I) complexes, both from biological and synthetic origins, a full description of their electronic structure, and thereby of their catalytic reactivity, is still lacking.

In the present study we used the polydentate 1,2-bis(pyridine-2-carboxamido)benzene (H_2bphen) which may function as a dianionic conjugated ligand with four nitrogen donor atoms, to stabilize the monovalent state of nickel. Upon co-ordination the ligand will provide charge delocalization and ligand framework flexibility, which allows the central metal ion easily to change oxidation state. The approach used to characterize the electronic properties of nickel(I) complexes is based on a comparison of the EPR and electronic spectral properties of isoelectronic complexes of $^{63}Cu^{II}$ and $^{61}Ni^{I}$ with H_2bphen.



[Ni(bphen)]

Experimental

Reagents and solvents

All solvents and chemicals used in synthesis, obtained from Merck, were of reagent grade and used as received. Isotopically enriched ^{61}Ni (88.8%) and ^{63}Cu (99.89%) were obtained as the respective oxides from Oak Ridge National Laboratory.

Syntheses

1,2-Bis(pyridine-2-carboxamido)benzene was synthesized as described[21] by condensation of 1,2-phenylenediamine and pyridine-2-carboxylic acid in pyridine and in the presence of triphenyl phosphite. Yield 80%, m.p. 174 °C (Found: C, 67.91; H, 4.46; N, 17.64. Calc. for $C_{18}H_{14}N_4O_2$: C, 67.90; H, 4.44; N, 17.60%). FTIR (KBr): $\tilde{\nu}$ = 3320 and 3255 (N–H band), 1675 and 1667 (amide I band), 1526 and 1517 cm^{-1} (amide II band); lit.,[21] 3320 and 3260, 1675 and 1665, 1525 and 1515 cm^{-1}.

The isotopically enriched metal acetates (^{61}Ni and ^{63}Cu) were prepared by dissolution of the metal oxides in 0.1 mol dm^{-3} sodium hydroxide solution to give a gelatinous precipitate of the respective metal hydroxides, which were filtered off. Subsequent treatment of the solids with acetic acid afforded the desired products.[10]

The nickel(II) complex [Ni(bphen)] was prepared by reaction of stoichiometric amounts of aqueous nickel(II) acetate with an ethanolic solution of H_2bphen.[22] It was recrystallized from acetonitrile. Yield 60% (Found: C, 57.64; H, 3.20; N, 14.90. Calc. for $C_{18}H_{12}N_4NiO_2$: C, 57.64; H, 3.23; N, 14.94%); FTIR (KBr) $\tilde{\nu} = 1640$ (amide I band), 1569 cm^{-1} (amide II band); lit.,[22] 1640 and 1560 cm^{-1}. UV/VIS (dmf) $\nu > 21\,500$ cm^{-1}. The complex [Cu(bphen)] was prepared similarly. Yield 70% (Found: C, 56.87; H, 3.17; N, 14.72. Calc. for $C_{18}H_{12}CuN_4O_2$: C, 56.91; H, 3.19; N, 14.75%). FTIR (KBr): $\tilde{\nu} = 1633$ (amide I band), 1572 cm^{-1} (amide II band); lit.,[22] 1635 and 1585 cm^{-1}. In the preparation of the magnetically diluted Cu complex, [^{63}CuNi(bphen)], nickel(II) acetate was added to a solution of $^{63}Cu(CH_3CO_2)_2$ to achieve a 1 : 100 copper to nickel mole ratio.

The nickel(I) species (both natural abundance and isotopically enriched) were generated under anaerobic conditions by reduction of solutions of [Ni(bphen)] in dimethylformamide, using excess of 5% sodium mercury amalgam. The concentration of the nickel(II) complex was typically 5 mmol dm^{-3} and the solution/amalgam was stirred for 15 min. It changed rapidly from orange to deep purple and the progress of the reduction was followed by UV/VIS and EPR spectroscopy. The reduction was assumed to be complete (15 min) when no changes in EPR signals and the absorbance of electronic bands were detected. The reduced solutions were transferred under anaerobic conditions to EPR tubes and 1 cm cuvettes.

Physical measurements

Elemental analysis (C, H and N) were performed at Instituto de Tecnologia Química e Biológica, Oeiras, Portugal. The EPR spectra were recorded with a Bruker ESP 300E spectrometer, both at 77 K and in fluid solutions at room temperature. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) and the magnetic field was calibrated by the use of Mn^{II} in MgO. The reported EPR parameters were obtained by computer simulation, in the usual manner.[23] Room-temperature electronic spectra were recorded with a Shimadzu UV/3101PC spectrophotometer in the range 1500–200 nm; solutions were typically 5×10^{-3}–10^{-3} mol dm^{-3} in complex. The FTIR spectra were recorded with a Matteson 5000 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets.

Results and Discussion

The synthesis and characterization of nickel(II) and copper(II) complexes with H_2bphen have been reported previously.[22] The spectral data obtained for the compounds prepared in this work are in accordance with the results already published and indicate that bphen^{2-} acts as a N_4-tetradentate dianionic ligand that imposes a square-planar geometry on the complexes, and for which a high electronic π delocalization is implied.[22] Crystal structures of both complexes have also been published[24,25] and reveal the existence of two sets of M–N bonds: those to the amide N atom are always shorter than those to the pyridyl N atom. For the nickel(II) complex[25] two crystallographically independent molecules were observed: for molecule A, Ni–N (amide) 1.847 and Ni–N (pyridyl) 1.948; for B, Ni–N (amide) 1.854 and Ni–N (pyridyl) 1.949 Å. For the copper complex:[24] Cu–N (amide) 1.933 and Cu–N (pyridyl) 2.023 Å. In this latter complex one water molecule is weakly co-ordinated in an axial position but the metal ion is only slightly out of the plane of the four co-ordinated nitrogen atoms (0.19 Å). Reduced nickel species were prepared as described in the Experimental section, and characterized in solution by EPR and electronic spectroscopy.

EPR spectra

Chemical reduction of [Ni(bphen)] with sodium amalgam gives a reduced nickel species that exhibits EPR spectra with large g tensor anisotropy and $g_{av} = 2.110$, indicating that chemical reduction is a metal-centred process and the reduced nickel species are effectively nickel(I) complexes.[8–14] Direct inspection of the EPR spectra of [Ni^I(bphen)]$^-$ reveals these to be apparently of axial type which exhibit hyperfine splittings in the perpendicular region due to the interaction of the unpaired electron with the four in-plane N atoms (Fig. 1A). Frozen-solution EPR spectra of the $^{61}Ni^I$-enriched species reveal ^{61}Ni hyperfine splittings ($I = \frac{3}{2}$) in the low-field region, and a broader signal in the high-field region which shows hyperfine splittings due to the interaction of the unpaired electron with the in-plane N atoms (Fig. 1B).

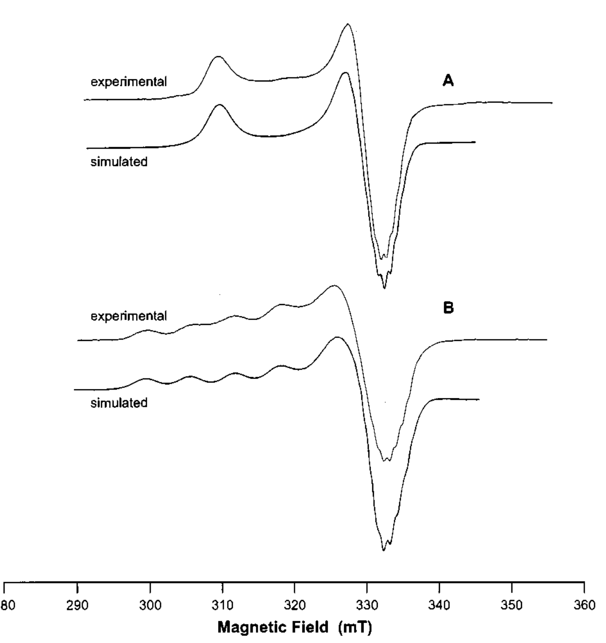


Fig. 1 The EPR spectra (77 K) of: (A) [Ni^I(bphen)]$^-$ and (B) [$^{61}Ni^I$(bphen)]$^-$. EPR conditions: microwave frequency, 9.53 GHz; microwave power, 10 mW; and modulation amplitude, 0.1 mT

Powder EPR spectra [Fig. 2(a)] of the isotropically enriched (99.9%) complex [^{63}Cu(bphen)], obtained from a (dilute) sample coprecipitated with the corresponding nickel(II) complex, are apparently of axial type and show partial overlap of the two g regions. The ^{63}Cu hyperfine splittings and nitrogen hyperfine splitting due to interaction with the four equivalent in-plane N atoms are clearly observed in all g regions. Frozen-solution EPR spectra (77 K) of this complex in dmf exhibit the same g features, albeit with less resolution in the low-field region [Fig. 2(b)]. No significant differences were observed between the g and A values of powder and frozen-solution EPR spectra.

The spectra of the complexes of $^{63}Cu^{II}$ and $^{61}Ni^I$ show very similar features, although the latter exhibits smaller coupling constants and a shift of the whole spectrum to lower magnetic field values.

In the absence of EPR crystal data for our complexes, the observed similarity between their g features and those of Cu^{II} with other tetradentate ligands[26–30] can be further extended to support the following orientation scheme for the tensor axes of the copper(II) and nickel(I) complexes: $g_1 = g_z$, $g_2 = g_x$, $g_3 = g_y$, where g_1 and g_3 refer to the lowest and highest magnetic field g values, respectively (obviously, $A_1 = A_z$, $A_2 = A_x$ and $A_3 = A_y$). All the spectra were simulated using three values for the components of the g tensor. For $^{61}Ni^I$ three values for the A(Ni) tensor were used, whereas for A(Cu) axial symmetry was assumed; furthermore axial symmetry was also assumed for A(N). The EPR parameters for the complexes of Cu^{II} and Ni^I complexes are presented in Table 1.

The absolute values of the A(M)-tensor components, both for $^{63}Cu^{II}$[26–33] and $^{61}Ni^I$,[34–38] are among the largest found in the literature, and support a near square-planar geometry, notwithstanding the possibility of very weak axial interactions. The

Table 1 EPR Parameters for nickel(I) and copper(II) complexes

							Hyperfine coupling[a]			Superhyperfine coupling[a]		
Complex	g_z	g_x	g_y	Δ_{xy}	g_{av}[b]	$\frac{1}{2}(g_x + g_y)$	$-A_z$	$-A_x$	$-A_y$	$A(N)_z$	$A(N)_x$	$A(N)_y$
$[Ni^I(bphen)]$	2.215	2.070	2.044	0.206	2.110	2.057				6.0	9.5	9.5
$[^{61}Ni^I(bphen)]$	2.215	2.071	2.042	0.029	2.109	2.057	68.0	15.0	10.0	6.0	9.5	9.5
$[^{63}CuNi(bphen)]$	2.159	2.040	2.038	0.002	2.079	2.039	211.0	30.0	30.0	12.0	15.0	15.0
$[^{63}Cu(bphen)]$[c]	2.150	2.035	2.030	0.005	2.072	2.033	209.0	27.0	27.0	11.0	15.0	15.0

[a] The values are expressed in 10^{-4} cm^{-1}. [b] $\langle g_{av}\rangle = \frac{1}{3}(g_x + g_y + g_z)$. [c] In dmf solution.

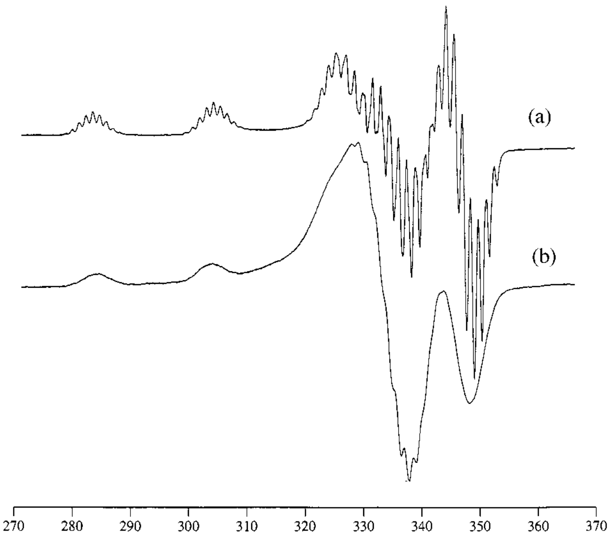


Fig. 2 The EPR spectra (77 K) of $[^{63}CuNi(bphen)]$: (a) powder, and (b) frozen solution. Conditions: microwave frequency, 9.53 GHz; microwave power, 5 (powder) and 10 mW (solution); and modulation amplitude, 0.1 mT

EPR spectra of both complexes can be interpreted by using the conventional perturbation approach developed for square-planar d^9 systems.[26,27,39,40,41] Analysis of the data in Table 1 shows that deviations from axial symmetry are small, providing support for the use of a model developed for D_{4h} symmetry [within this approach $g_{\|} = g_z$ and $g_{\perp} = \frac{1}{2}(g_x + g_y)$, $A_{\|} = A_z$ and $A_{\perp} = \frac{1}{2}(A_x + A_y)$]. The observation that $g_{\|} > g_{\perp}$ and $|A_{\|}| > |A_{\perp}|$ implies a B_{1g} ground state.[26,27] Assuming the molecular axes bisect the xy axes, the relevant molecular orbitals with D_{4h} symmetry can be expressed in forms (1)–(5).[26,27,39,40] The b_{1g} and a_{1g} states

$$b_{1g} = \alpha d_{xy} - \tfrac{1}{2}\alpha'(-\sigma_1 x + \sigma_2 y + \sigma_3 x - \sigma_4 y) \tag{1}$$

$$b_{2g} = \beta d_{x^2-y^2} - \tfrac{1}{2}\beta(\pi_1 y + \pi_2 x - \pi_3 y - \pi_4 x) \tag{2}$$

$$a_{1g} = \gamma d_{z^2} - \tfrac{1}{2}(1 - \gamma^2)^{\frac{1}{2}}(\sigma_1 x + \sigma_2 y - \sigma_3 x - \sigma_4 y) \tag{3}$$

$$e_g = \delta d_{xz} - (\delta/2^{\frac{1}{2}})(\pi_a z - \pi_b z) \tag{4}$$

$$e_g = \delta d_{yz} - (\delta/2^{\frac{1}{2}})(\pi_2 z - \pi_4 z) \tag{5}$$

account for the σ bonding to the metal; b_{2g} represents the in-plane and e_g the out-of-plane π bonding.

The EPR spectra were interpreted in terms of the spin Hamiltonian $\mathcal{H} = \beta_e HgS + I_M A(M)S + I_N A(N)S$, where H is the external field, g the effective g tensor, β_e the Bohr magneton, S the electron spin, I_M and I_N are nuclear spins, and A(M) and A(N) nuclear hyperfine tensors; quadrupole couplings with the metal were neglected. Derivation of g and A(M) values for an unpaired electron in the B_{1g} orbital, assuming the ligand contribution to be negligible, results in equations (6) and (7).[26,27]

$$g_{\|} = 2.0023 - \frac{8\lambda\alpha^2\beta^2}{\Delta(b_{2g} - b_{1g})} \tag{6}$$

$$g_{\perp} = 2.0023 - \frac{2\lambda\alpha^2\delta^2}{\Delta(e_g - b_{1g})} \tag{7}$$

Expressions (8) and (9) were derived for the components of the

$$A_{\|} = P(-\kappa - \tfrac{4}{7}\alpha^2 + \Delta g_{\|} + \tfrac{3}{7}\Delta g_{\perp}) \tag{8}$$

$$A_{\perp} = P(-\kappa + \tfrac{2}{7}\alpha^2 + \tfrac{11}{14}\Delta g_{\perp}) \tag{9}$$

metal hyperfine tensors, $A_{\|}$ and $A_{\perp}$. In these σ, β and δ are the coefficients defined above, λ is the spin–orbit coupling constant of the free ion (−830 cm^{-1} for Cu^{II}[30] and −603 cm^{-1} for Ni^{I}[42]), κ is the isotropic hyperfine coupling constant and $P = \beta_e g_e \beta_N g_N \langle r^{-3}\rangle$ (^{63}Cu^{II}, $P = 0.0388$ cm^{-1};[30] ^{61}Ni^{II}, $P = 0.0102$ cm^{-1}[42]); values of $\Delta g_{\|} = g_{\|} - 2.0023$ and $\Delta g_{\perp} = g_{\perp} - 2.0023$ were obtained from equations (6) and (7).

It must be pointed out that the EPR data suggest that the nickel(I) complexes have at best D_{2h} symmetry, however as has been shown for several copper(II) complexes[39,40] this lowering in symmetry only affects the out-of-plane π bonding parameter; all other parameters are obtained from the equations derived for D_{4h} symmetry. This observation supports the use of equations (6)–(9) for both nickel(I) and copper(II) complexes.

From the A(M)-tensor components this model allows for the calculation of κ and of α^2, where α^2 is a covalency parameter which describes the in-plane metal–ligand σ bonding; its value is 1 for pure ionic bonding and <1 for covalent bonding. The signs of $A_{\|}$ and $A_{\perp}$ could not be determined experimentally in the present study, but assuming negative signs for both $A_{\|}$ and $A_{\perp}$ (see below) and using the spin Hamiltonian parameters for the copper(II) complex (Table 1) the values $\kappa = 0.31$ and $\alpha^2 = 0.71$ were obtained, comparable to those reported for other square-planar copper(II) complexes with tetradentate ligands.[9–12] The choice of negative signs for $A_{\|}$ and $A_{\perp}$ was dictated by the observation that the other combinations yielded unrealistic values for κ and α^2: [$A_{\|}$, $A_{\perp}$] {κ, α^2} [+,+] −0.16, −0.38; [+,−], −0.05, −0.56; [−,+] +0.21, +0.89; furthermore, as the value of A_{iso} (86.5×10^{-4} cm^{-1}) is very similar to $A_{av} = \frac{1}{3}(A_{\|} + 2A_{\perp})$, $A_{\|}$ and $A_{\perp}$ must have the same sign.

No fluid-phase EPR spectra could be observed for the nickel(I) complex; but similar calculations also using negative signs for $A_{\|}$ and $A_{\perp}$ yielded $\kappa = 0.41$ and $\alpha^2 = 0.86$. Other combinations are: [$A_{\|}$, $A_{\perp}$] {κ, α^2} [+,+] −0.20, −0.41; [+,−] −0.03, −0.70; [−,+] +0.25, +1.15. The EPR studies using ^{61}Ni^{I} are scarce and refer to complexes with ligands that have different donor atom sets, hence with different electronic properties, thus making difficult the comparison of their α^2 values or equivalent bonding parameters with those reported here. Nevertheless, in all cases the reported values are indicative of little covalency in the σ metal–ligand bonds.[34–38]

The copper(II) complex exhibits lower α^2 values than the related nickel(I) complex, as has been found previously for other

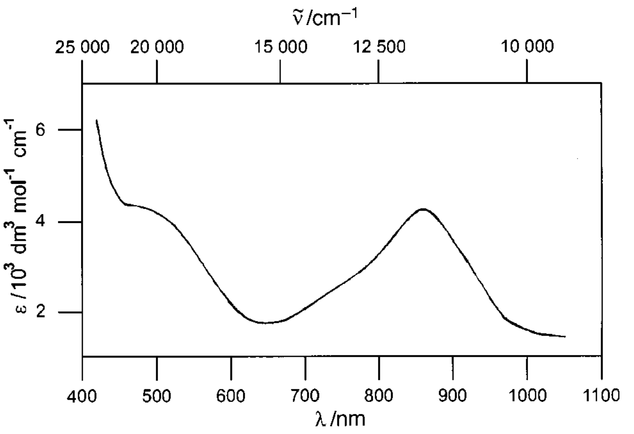


Fig. 3 Electronic spectrum of [Ni^I(bphen)]$^-$ in dmf

complexes of Cu^{II} and Ni^I which have a common ligand,[34–36] which implies that σ M–N bonds are more covalent in the copper(II) complex.

Electronic spectra

Nickel(I) complexes are usually deeply coloured and their electronic spectra are dominated by low-energy charge-transfer bands with high intensities. In the case of four-co-ordinate complexes medium-intensity bands are observed in the range 17 000 to 20 000 cm^{-1} and have been assigned to d–d transitions on the basis of their absorption coefficients.[9,14,18,19,43,44] The assignment of d–d bands in the range referred to above is also consistent with the assumption of an energy red shift in the corresponding d–d bands of the precursor nickel(II) four-co-ordinate complex, due to a decrease in ligand-field strength induced by the reduction process.[43,44]

The solution spectrum of the nickel(I) complex in dmf (Fig. 3) compares with those described in the literature; it shows a medium-intensity band at 11 700 cm^{-1} (ε = 4200 dm^3 mol^{-1} cm^{-1}) with a shoulder in the high-energy side at 13 510 cm^{-1} (ε = 200 dm^3 mol^{-1} cm^{-1}), and high-intensity bands in the UV region with a shoulder at 19 600 cm^{-1} (ε < 1000 dm^3 mol^{-1} cm^{-1}).

The copper(II) complex exhibits electronic spectra that are similar both in Nujol mulls and in dmf; spectra in solution show two main features that are typical of square-planar complexes: a band at 18 190 cm^{-1} (ε = 180 dm^3 mol^{-1} cm^{-1}) that is assigned to d–d transitions, and high-intensity charge-transfer (CT) bands at higher energies.[28–31] No effective axial solvent co-ordination occurs, as can be inferred from the similarity of spectra in solid and solution. Using the splitting scheme proposed by Nishida *et al.*[28,29] for d orbitals in square-planar copper(II) complexes with dinegatively charged tetradentate ligands ($d_{xy} > d_{xz}$, $d_{yz} > d_{z^2} > d_{x^2-y^2}$), the lower-energy band can be thus assigned to the following d–d transitions: d_{xz}, $d_{yz} \longleftarrow d_{xy}$.

Assuming the same d-splitting scheme used for Cu^{II} still holds for the isoelectronic Ni^I, the ratios $\Delta g_\parallel^{Cu}:\Delta g_\parallel^{Ni}$ and $\Delta g_\perp^{Cu}:\Delta g_\perp^{Ni}$ [equations (10) and (11)] can be used to estimate the

$$\frac{\Delta g_\parallel^{Cu}}{\Delta g_\parallel^{Ni}} = \frac{\Delta^{Ni}(b_{2g} \longleftarrow b_{1g})\lambda_{Cu}\alpha_{Cu}{}^2\beta_{Cu}{}^2}{\Delta^{Cu}(b_{2g} \longleftarrow b_{1g})\lambda_{Ni}\alpha_{Ni}{}^2\beta_{Ni}{}^2} \tag{10}$$

$$\frac{\Delta g_\perp^{Cu}}{\Delta g_\perp^{Ni}} = \frac{\Delta^{Ni}(e_g \longleftarrow b_{1g})\lambda_{Cu}\alpha_{Cu}{}^2\delta_{Cu}{}^2}{\Delta^{Cu}(e_g \longleftarrow b_{1g})\lambda_{Ni}\alpha_{Ni}{}^2\delta_{Ni}{}^2} \tag{11}$$

energy of electronic bands for the nickel(I) complex, once the corresponding values for Cu^{II} are known. Using the energy of the transitions d_{xz}, $d_{yz} \longleftarrow d_{xy}$ (18 190 cm^{-1}) for Cu^{II} in equation (11), and assuming, as a first estimate, that the value of the ratio $\delta_{Cu}{}^2:\delta_{Ni}{}^2$ is 1 : 1; the energy of the corresponding transitions for Ni^I is predicted to occur at *ca.* 10 840 cm^{-1}. This calculated energy compares roughly with the two low-energy bands observed for [Ni^I(bphen)]$^-$ and we note that the band at 11 700 cm^{-1} is due to a CT transition, whereas that at 13 510 cm^{-1} is a d–d band, as the experimental ε values suggest.

The assignment of the transitions d_{xz}, $d_{yz} \longleftarrow d_{xy}$ for Ni^I is not unambiguous: they may occur at 13 510 cm^{-1}, or be hidden under the CT band, in which case the band at 13 510 cm^{-1} should be associated with the transition $d_{z^2} \longleftarrow d_{xy}$. This ambiguity cannot be resolved by calculation of the out-of-plane π-bonding parameter δ^2 in D_{4h} symmetry, as insertion in equation (7) of the two possible values for the energy of d_{xz}, $d_{yz} \longleftarrow d_{xy}$ transitions for Ni^I (13 510 and ≈11 700 cm^{-1}) and that observed for Cu^{II} (18 190 cm^{-1}) yields $\delta^2 = 0.53$ for Cu^{II} and either 0.71 in the first case and 0.62 in the second for Ni^I. As there are no reported values of δ^2, not even by similarity one of the values can be preferred.

Nevertheless, recognizing that the nickel(I) complexes are at best of D_{2h} symmetry and using the equations obtained for this symmetry, the unambiguity can be removed and will allow for the assignment of the band at 13 510 cm^{-1} to the d_{xz}, $d_{yz} \longleftarrow d_{xy}$ transitions. The reduction in symmetry implies that equation (7) has to be replaced by $g_x = 2.0023 - [2\lambda\alpha^2/\Delta(b_{2g} \longleftarrow b_{1g})]$ and $g_y = 2.0023 - [2\lambda\alpha^2\delta'^2/\Delta(b_{3g} \longleftarrow b_{1g})]$ where the molecular orbital $b_{2g} = d_{xz}$ and $b_{3g} = \delta' d_{yz} - \frac{1}{2}(1 - \delta'^2)^{\frac{1}{2}}(\pi_1 z + \pi_2 z - \pi_3 z - \pi_4 z)$ and δ'^2 is the out-of-plane π-bonding parameter in this symmetry.[40] As g_x depends only on α^2, the value of $\Delta(b_{2g} - b_{1g})$ can be estimated and was found to be 15 300 cm^{-1}; furthermore, because only one broad band is detected at 13 510 cm^{-1}, we propose that it is associated with the two transitions $\Delta(b_{2g} - b_{1g})$ and $\Delta(b_{3g} - b_{1g})$, which have similar energies and these observations provide support for assigning the band at 13 510 cm^{-1} to the d_{xz}, $d_{yz} \longleftarrow d_{xy}$ transitions in D_{4h} symmetry. Using 13 510 cm^{-1} as an estimate for $\Delta(b_{3g} - b_{1g})$ and inserting the value of g_y in the equation above, the value of δ'^2 is 0.54. The value of δ^2 (D_{4h}) is always larger than δ'^2 (D_{2h}) [in fact $\delta^2 = (1 + \delta'^2)/2$], and from the calculated value for δ'^2, one obtains $\delta^2 = 0.72$, in good agreement with the value calculated above (D_{4h} symmetry) when the band at 13 510 cm^{-1} was assumed to be associated with the d_{xz}, $d_{yz} \longleftarrow d_{xy}$ transitions.

The δ^2 values, 0.53 for Cu^{II} and 0.71 for Ni^I, taken together with those of α^2, suggest that for both complexes the out-of-plane π bonding is more covalent than σ bonding and indicate extensive π interaction of the metal ions with the π system of the ligand. Again, the copper(II) complex shows greater covalence than the homologous nickel(I) complex.

An internal check for the assignment made above can be provided by calculating the energy of the $d_{x^2-y^2} \longleftarrow d_{xy}$ transition for the nickel(I) complex using the ratio $\Delta g_\parallel^{Ni}:\Delta g_\perp^{Ni}$ [equation (12)], and the energy of the d_{xz}, $d_{yz} \longleftarrow d_{xy}$ transitions and using $\beta^2 = 1$, as a small in-plane π bonding is expected for these complexes.

$$\frac{\Delta g_\parallel^{M}}{\Delta g_\perp^{M}} = 4\,\frac{\Delta^{M}(e_g \longleftarrow b_{1g})\beta_M{}^2}{\Delta^{M}(b_{2g} \longleftarrow b_{1g})\delta_M{}^2} \tag{12}$$

That the calculated value, 19 500 cm^{-1}, is in close agreement with the observed value, 19 600 cm^{-1}, has two important consequences: first, it supports the assignment of this band to the $d_{z^2-y^2} \longleftarrow d_{xy}$ transition and secondly gives plausibility to the model used.

Applying the same equation (12) to the copper complex, the $d_{x^2-y^2} \longleftarrow d_{xy}$ transition is estimated to occur at 31 970 cm^{-1}, a value that precludes comparison with experimental values as the band must lie in the UV where it is masked by high-intensity CT bands. However, the internal consistency of the model can be checked by estimating the energy of this latter transition using the energy of the corresponding nickel(I) transition in equation (10). The obtained value, 30 420 cm^{-1}, compares well with that calculated from equation (12).

The remaining electronic transition, $d_{z^2} \longleftarrow d_{xy}$, could not be assigned, as only two d–d bands are observed in these spectra and our model has identified them as the other d–d transitions. Furthermore, as its energy does not explicitly appear in the expression for g and A(M), EPR data do not provide any information concerning its energy. However, as in the framework of the results of Nishida *et al.*[28,29] this transition must be associated with any of the two d–d bands.

Structural implications from the spectroscopic data

The combination of EPR and UV/VIS studies of isoelectronic square-planar complexes of $^{63}Cu^{II}$ and $^{61}Ni^{I}$ with the ligand bphen^{2-} has allowed what we believe is the first assignment of visible electronic bands of a nickel(I) complex, and provided insights into its structural and bonding properties.

The EPR spectra of [Ni^{I}(bphen)]$^{-}$ exhibit higher g values than does the homologous copper(II) complex, as is usually observed for complexes of Ni^{I} and Cu^{II} which have ligands in common. This general observation cannot be rationalized in terms of the relative metal spin–orbit couplings, as it can be seen from equations (6) and (7) and considering that $\lambda_{Cu(II)}$ is larger. Instead, this behaviour is thought to be a consequence of the lower charge/lower electronegativity of the nickel(I) ion, and the data obtained for our complexes provide direct evidence that Ni^{I}: (i) has lower σ and π covalency in M–N bonding (higher values for α^2, δ^2) and (ii) lower d–d orbital separation [smaller values for the energy difference E ($d_{x^2-y^2} \longleftarrow d_{xy}$) and E(d_{xz}, $d_{yz} \longleftarrow d_{xy}$)].

A striking difference in EPR parameters of these complexes lies in the values of Δ_{xy}: nickel(I) complexes exhibit values that are ten times larger than those of the copper(II) complex (Table 1). This difference must be related to structural modifications concomitant with the reduction Ni$^{II} \longrightarrow$ Ni^{I}. In the absence of crystallographic data for the nickel(I) complex the explanation cannot be ascertained directly, but some clues can be provided by spectroscopic data.

As has been referred to above, both the nickel(II) and copper(II) complexes reveal two sets of M–N bond distances, M–N (amide) and M–N (pyridyl), which are larger for the copper(II) complex. However, their differences, Δ_{bond} = (M–N$_{amide}$) − (M–N$_{pyridyl}$), are slightly larger for the nickel(II) complex, (Cu^{II}, 0.090; Ni$^{II}_{A}$, 0.101 or Ni$^{II}_{B}$, 0.095), but this difference is insufficient to account for the difference in Δ_{xy} of the copper(II) and nickel(I) EPR spectra, unless we propose that reduction of [Ni^{II}(bphen)] to [Ni^{I}(bphen)]$^{-}$ induces an alteration of the nickel core: either its distortion and/or unequal expansion of the Ni–N bond distances. Such changes are known to occur with macrocyclic ligands:[14,17–20,44] flexible saturated systems show expansion of Ni–N bond lengths, whereas rigid unsaturated ligands impose mainly distortions on the core without an expansion of the hole. The ligand used in the present work when bound to the metal ion allows some π-electron delocalization, but forms a non-closed ring that can easily accommodate changes in metal-ion size without necessarily imposing a distortion on the nickel core.

With the experimental data available we cannot distinguish unequivocally between the two types of structural changes, but we propose that both effects are present and that the difference in the two sets of bond lengths increases on reducing Ni^{II} to Ni^{I}. A similar behaviour has been observed in several nickel-(II), -(I) complexes with macrocyclic ligands with Ni–N$_{amine}$ and Ni–N$_{imine}$ bonds, where upon reduction of the metal centre the difference between the two sets of bonds increased.[44]

Biological relevance of the [Ni^{I}(bphen)]$^{-}$ spectroscopic properties

Identification of the monovalent state of nickel in the catalytic cycle of MCR was based on EPR studies,[5] and two distinct EPR signals have been identified for the active forms of MCR, MCR-red1(axial) and MCR-red2 (rhombic), that can be interconverted by the action of substrates. Both the characterization of these EPR signals and the co-ordination chemistry of the nickel cofactor are still not settled, thus making the use of models for F$_{430}$ an area of current interest.

Spectroscopic characterization of [Ni^{I}(bphen)]$^{-}$ shows that the tetradentate ligand induces two sets of Ni–N bonds (Ni–N$_{amide}$ and Ni–N$_{pyridyl}$) and behaves as a flexible ligand that allows some π-electronic delocalization. Furthermore, the g values of [Ni^{I}(bphen)]$^{-}$ compare well with those of the 12,13 diepimer of the reduced factor F$_{430}$ pentacarboxylic acid (aqueous solution),[5f] and are similar to those of the reduced factor F$_{430}$ pentacarboxylic acid (aqueous solution)[5f] and of the pentamethyl ester F$_{430}$M.[5d,e] These observations may suggest that the electronic structure of the Ni^{I} of our complex is similar to that of the nickel(I) in F$_{430}$, and led us to compare their electronic spectra.

Analysis of the electronic spectra of reduced factor F$_{430}$ pentacarboxylic acid and its 12,13 diepimer and of the pentamethyl ester F$_{430}$M shows that the electronic bands can be grouped based on their absorption coefficient: (i) one band in the range 13 300–14 100 cm^{-1} with the medium ε values, and (ii) two bands in the range 26 300–37 700 cm^{-1} with high ε values. The band at low energy compares well with the low-energy medium-intensity electronic band (at 13 510 cm^{-1}) of our complex which has been assigned to the d_{xz}, $d_{yz} \longleftarrow d_{xy}$ electronic transition, thus allowing us to propose the assignment of the electronic band at 13 300–14 410 cm^{-1} in the electronic spectra of F$_{430}$ pentacarboxylic acid, of its 12,13 diepimer and of the pentamethyl ester F$_{430}$M to the d_{xz}, $d_{yz} \longleftarrow d_{xy}$ electronic transitions. The other d–d transition observed in our spectra and which is not detected in the spectra of F$_{430}$ pentacarboxylic acid and of pentamethyl ester F$_{430}$M may be masked by the high-energy charge-transfer bands. Support for this statement can be gained by noting that in the spectra of the 12,13 diepimer of the reduced factor F$_{430}$ pentacarboxylic acid (aqueous solution)[5f] a medium-intensity shoulder is observed at 20 830 cm^{-1} and must be associated with the $d_{x^2-y^2} \longleftarrow d_{xy}$ transition.

Finally, our nickel(I) complex may act as a potential model for F$_{430}$, and reactions of [Ni^{I}(bphen)]$^{-}$ with several Lewis bases and substrates are now under investigation.

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