Chemistry of Corphinoids: Structural Properties of Corphinoid Nickel(II) Complexes Related to Coenzyme F430

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An X-ray structure analysis and magnetic as well as electrochemical data for synthetic corrinoid and corphinoid nickel(II) complexes document the pronounced axial electrophilicity of the nickel(II) ion when complexed by ligands of the type occurring in coenzyme F430.
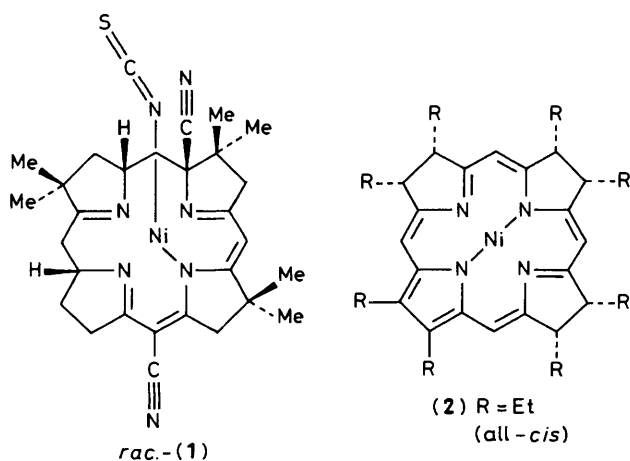
Chemical and magnetic properties of nickel(II) can be strikingly different when the metal ion is complexed to corphinoid as opposed to corrinoid ligands. Two recent discoveries have drawn our attention to these differences: first, the novel type of corphinoid chromophore found in the nickel-containing coenzyme F430 from methanogenic bacteria[1] and, secondly, the pronounced conformational ruffling of the ligand periphery observed in corphinoid nickel(II) complexes recently synthesized in the course of our studies on the porphyrinogen → pyrrocorphin tautomerisation.[2] Here, we report on the solid state structure of the isothiocyanato derivative (1) of the F430 model complex described in the preceding communication,[3] and we also summarize magnetic and electrochemical properties of a series of corphinoid and corrinoid nickel(II) complexes which illustrate the differences referred to above and point to structural factors responsible for them.

All known crystal structures of nickel(II) complexes with hydroporphinoid ligands (chlorins,[4] bacteriochlorins,[2f] iso-bacteriochlorins,[2c] pyrrocorphins,[2d] and isomeric hexahydro-porphyrins[2b]) reveal a characteristic S_4 deformation of the ligand periphery. This conformational ruffling of the ligand system is most pronounced in nickel(II) pyrrocorphinates.[5] Figure 1 (top) shows, as a typical example, a cylindrical projection of the corphinoid nucleus from the crystal structure of the octaethyl pyrrocorphinate (2).[2f] There is considerable new evidence[5] supporting the view† that the ruffling is the

consequence of a contraction of the co-ordination hole of the hydroporphinoid ligand induced by the (small) nickel(II) ion in its tendency to reach saturation of electrophilicity. This interpretation suggests that there should be no such ruffling in nickel(II) complexes in which the residual electrophilicity of the metal ion has become saturated by additional (axial) ligands. This is exactly what is observed in the solid state structure of complex (1).‡
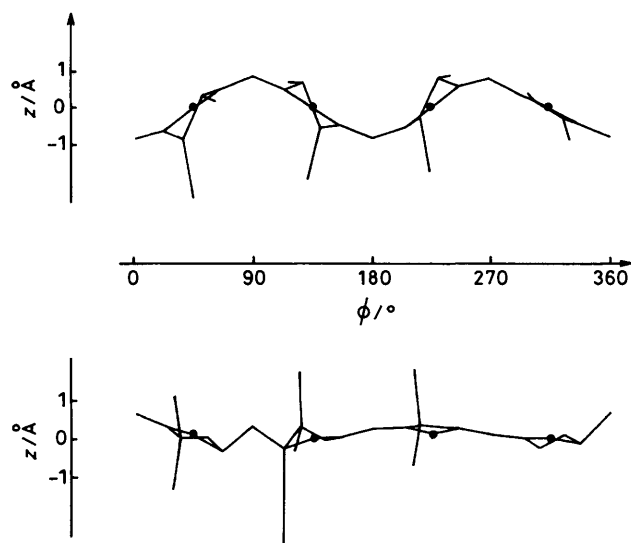
Figure 1. Cylindrical projections of the hydroporphinoid ligand observed in the crystal structures of a typical diamagnetic nickel(II) pyrrocorphinate [top, compound (2)] and of the paramagnetic complex (1) (bottom). Note that in both structures the metal-co-ordinated N-atoms (represented as full circles) are approximately coplanar with the nickel(II) atom. z and φ = cylinder co-ordinates.

rac.-(1)

(2) R = Et
(all-cis)

† Weak ligand ruffling of this type had been first observed for nickel(II) complexes of porphyrins[7] and interpreted by Hoard[8] to result from co-ordination hole contraction as opposed to crystal packing factors (see, e.g., ref. 9). For a recent discussion referring to the ruffling in iron chlorinates and isobacteriochlorinates see ref. 6.

Table 1.

| Ni^II complex | R | dia = diamagnetic[a] para = paramagnetic (μ, ± 0.2 μ_B[b]) | | | $E_{\frac{1}{2}}$/V[c] | |
		CH$_2$Cl$_2$ or CDCl$_3$	CD$_3$OD	CD$_3$CN	MeCN	Other solvents
(3)	H	dia	dia	dia	−1.47[d]	
(4)	CN	dia	dia	dia	−1.19[d]	
(5)	CN	dia	dia	dia	−0.97[d]/−1.05[e]/−0.92[f]	−0.86[f] (CH$_2$Cl$_2$)
(6)	H	dia	para	dia	−1.03[d]	
(7)	H	dia	dia	dia	−1.20[d]	
(8)	CN	dia	para (2.27)	dia	−1.05[e,g]	
(9)	H	dia	dia			
(10)	CN	dia	para			
(11)	CN	dia	para (2.50)	para (2.73)	−1.05[e]	−0.51[h](THF)
(12) F430M		dia	para (1.84)	dia (<0.3)	−1.07[e] (irreversible)[i]	−0.63[h](THF)

[a] According to [1]H n.m.r. spectrum. [b] Determined by the Evans–Scheffold[12] method in MeOH and MeCN; reference signal tetramethylsilane (5%), concentrations determined from u.v.–visible spectra. [c] Half-wave potential in volts of (reversible) first one-electron reduction wave determined by cyclic voltammetry, vs. 0.1 M calomel electrode, scan rate 0.1–1.0 V/s, 25 °C, Pt and/or Hg electrode, supporting electrolyte d or e; exptl. details see ref. 13. [d] 0.1 M Bu$_4$NClO$_4$. [e] 0.1 M LiClO$_4$. [f] vs. 1.0 M calomel electrode, 20°C, 0.5 M Bu$_4$NClO$_4$. [g] Reversible only at scan rates > 5 V/s. [h] 0.2 M LiClO$_4$, 'glassy carbon' electrode. [i] Irreversible up to a scan rate of 1000 V/s; peak potential −1.10 V (0.1 V/s) ($E_{\frac{1}{2}}$ estimated −1.07 V).

The nickel(II) ion in (1) is pentaco-ordinated when the complex is in (dilute) CH$_2$Cl$_2$ solution§,[3] but hexaco-ordinated in the solid state after crystallisation of (1) from methylene chloride–ethyl acetate. The octahedral co-ordination is achieved in a remarkable way (see Figure 2): one axial co-ordination position is occupied by the isothiocyanate nitrogen, and the other by the nitrogen of the ligand-bound nitrile group of a centrosymmetrically related (enantiomorphic) molecule. The latter interaction amounts to the formation of centrosymmetric dimers whose constituent molecules mutually supply each other with their covalently bound ring B nitrile group as the sixth ligand for the nickel(II) ion. The complex does not show the wave-shaped cylindrical projection (Figure 1, bottom) characteristic of conformationally ruffled, hydroporphinoid nickel(II) complexes,[5] and the diameter of the co-ordination hole of (1) (4.18 Å = average of the two transannular N,N distances) is distinctly larger than the corresponding average value of 3.85 ± 0.02 Å for the latter complexes[5] in which the co-ordination of the nickel(II) ion is square-planar (see also ref. 10).

Table 1 summarizes magnetic properties (in solution) of a series of corphinoid and corrinoid nickel(II) complexes, all of which are mono-positively charged and possess ligand chromophores that are constitutionally closely related. Whereas in the non-nucleophilic solvent CH$_2$Cl$_2$ (or CHCl$_3$) all the complexes are diamagnetic, in the (moderately) nucleophilic solvents methanol (or ethanol) and acetonitrile this is not true. The trend which these data reveal supports the view that the higher electrophilicity of the nickel(II) ion in corphinoid complexes [see magnetic properties of (6) to (10) in methanol] is a reflection of the size difference between the co-ordination holes of the (larger) corphinoid and the (smaller) corrinoid ligands.¶ Axial electrophilicity that is sufficiently high to
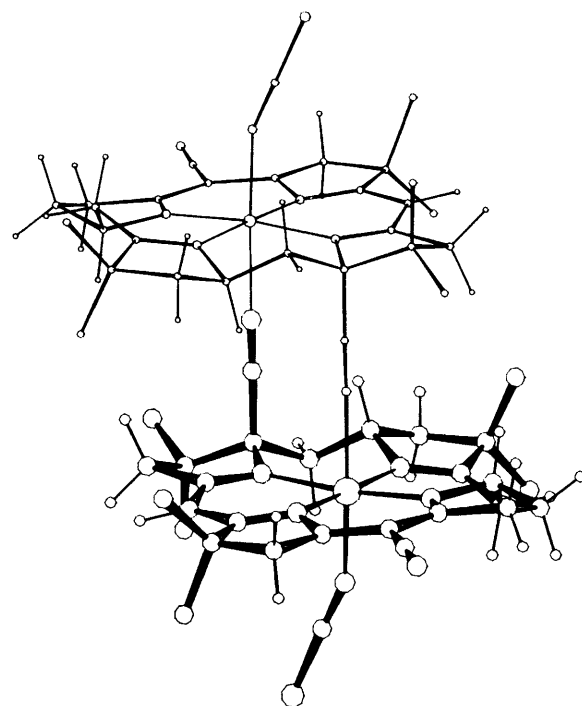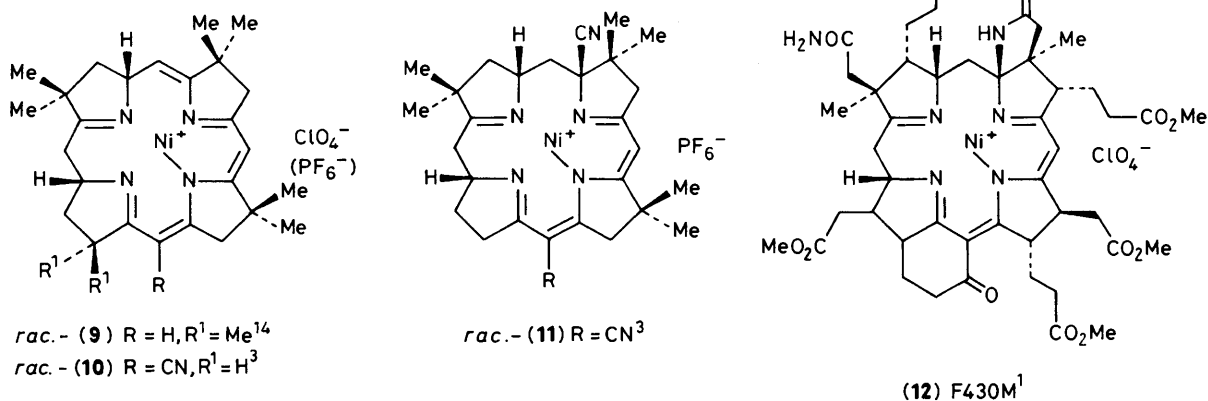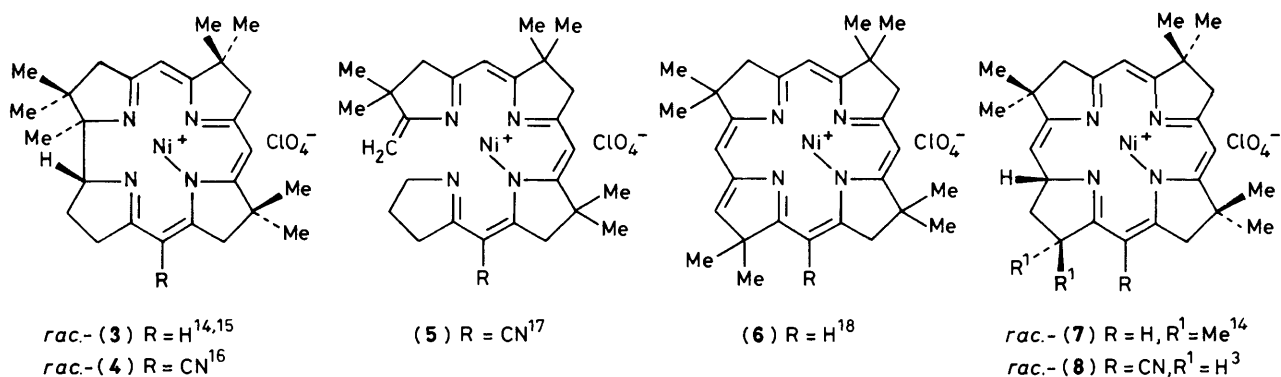

Figure 2. The centrosymmetric dimers observed in the crystal structure of (1). The axial (Ni–N) distances are 2.04 Å (to isothiocyanate group) and 2.12 Å (to nitrile group). For the equatorial (Ni–N) distances see text.‡

§ Molecular weight of (1) found (osmometrically, in CH$_2$Cl$_2$ at 30 °C) 589 ± 15 at concentrations up to 2.6 × 10^{-3} M (calcd. for monomer 572.4); at c = 8.6 × 10^{-2} M (solubility limit) 779 ± 15, K(dimer/monomer) = 6.7 (CH$_2$Cl$_2$, 30 °C).

¶ For X-ray data of corrin and A/D-secocorrin nickel complexes see ref. 11. The average of the (Ni–N)-bond lengths in a nickel(II)-corrinate of structural type (3) is 1.87 Å; [11a] in the (size-adjustable) secocorrinate (5) 1.88 Å.[11c]

induce penta- (or hexa-) co-ordination in alcoholic solvents is regularly observed with corphinoid complexes which bear a nitrile group at the meso position between rings C and D. In the corrin series, however, electron withdrawal from the chromophore's enaminoid π-system by a similar nitrile substituent seems to be insufficient to lower the equatorial ligand field strength enough for an observable axial electrophilicity of the nickel ion to ensue. Strain release due to release of the ligand's ruffling in the event of axial co-ordination may be a

rac.- (3) R = H[14,15]
rac.-(4) R = CN[16]

(5) R = CN[17]

(6) R = H[18]

rac.- (7) R = H, R^1=Me[14]
rac.- (8) R = CN, R^1 = H[3]

rac.- (9) R = H, R^1 = Me[14]
rac. - (10) R = CN, R^1 = H[3]

rac.- (11) R = CN[3]

(12) F430M[1]

contributing factor for the high electrophilicity of nickel(II) in corphinoid ligands.

The occurrence of axial co-ordination in nucleophilic solvents is also recognizable by u.v.–visible spectroscopy. Paramagnetism of corphinoid complexes in nucleophilic solvents is paralleled by pronounced differences in the u.v.–visible spectrum (especially in the u.v. region) as compared to the spectrum in CH_2Cl_2 (for an example, see preceding communication[3]). In contrast, the electronic spectra of nickel(II) corrin and A/D-secocorrin complexes are essentially solvent independent.

In Table 1, values for one-electron half-wave reduction potentials of the F430 model complex (11)[3] and the pentamethyl ester F430M[1] are compared with corresponding values from earlier investigations[13] on synthetic corrin and corphin[18] nickel(II) complexes. The pair of nickel(II) corrinates (3) and (4) in acetonitrile shows a potential difference of 0.28 V which one might expect[19] to result from a constitutional difference of a nitrile substituent at a *meso* position. Since in acetonitrile the complex (11) is paramagnetic and (4) is diamagnetic, the observed difference in reduction potential (0.14 V) between these two complexes in this solvent reflects less than the inherent difference in electron affinity of a nickel(II) corrin complex and a complex containing a tetraco-

ordinated nickel(II) ion in a ligand of the type occurring in F430. The F430 model complex (11) and the pentamethyl ester (12) of the natural coenzyme closely resemble each other in their exceptionally low reduction potential in tetrahydrofuran (THF), a solvent in which the latter complex is diamagnetic and the former on the brink of it.** The nickel(II) ion complexed in a tetrahydrocorphinoid ligand of the type occurring in coenzyme F430 is the most axially electrophilic metal centre yet encountered among synthetic hydroporphinoid nickel(II) complexes. This property may well be related to the nickel ion's coenzymic task in factor F430 (see also ref. 1c).

** This low value for $E_{\frac{1}{2}}$ of (11) in THF points to a metal-centred reduction process. For $E_{\frac{1}{2}}$ of a zinc(II) tosylate complex of the secocorrin ligand (5) (−1.23 V in MeCN, 0.1 M LiClO$_4$^{c}), see ref. 13, p. 162. For data in the porphyrin series see ref. 20.

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