Electronic Spectra of Metal Corrole Anions

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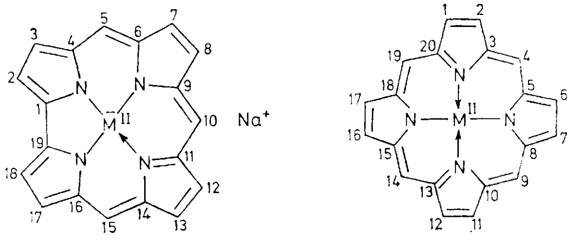
The electronic spectra of copper(II) and nickel(II) corrole anions are described and compared with the corresponding metal porphyrin spectra. The spectra are interpreted with the aid of self-consistent field Pariser–Parr–Pople π-electron calculations, and comparison with similar calculations for the porphin ring allows the origin of the differences between the two types of spectrum to be traced.

THE electronic spectra of porphyrins and their metal derivatives have been studied extensively (refs. 1—3 and references therein), and in general S.C.F. π-electron calculations have been fairly successful in explaining them. However, less attention has been given to conjugated tetrapyrrole complexes having lower symmetry than porphyrins and with partial saturation of the π-system of the ring. Some effort has been made to interpret experimental corrin spectra, but with less success than for porphyrins.[4,5] Recently a variety of macrocyclic conjugated tetrapyrrole complexes having rather lower symmetry than porphyrins has been synthesised by Johnson and his co-workers,[6-8] and these form an interesting series in which to study the effects of change in symmetry and degree of conjugation on the electronic spectra of tetrapyrrole complexes. We now describe the electronic spectra of fully conjugated metal corrole anions and compare them with those of analogous porphyrins. The π-electron framework of these complexes is shown in Figure 1, and has C_{2v} symmetry if the ring system is planar.

As yet, no crystallographic data are available for metal corrole anions, but it is to be expected that the ring system is essentially planar, as in the case of metal porphyrins. The complexes differ from metal porphyrins in having a direct link between two of the pyrrole rings rather than a fourth methine bridge. As a result, the neutral free-base corrole has three of its four pyrrole nitrogens protonated, and bivalent metal corroles have their conjugation interrupted by the presence of an extra hydrogen in the ring system. The fully conjugated metal(II) corrole anions considered here may be formed by treatment of the neutral metal corrole with base.[6] In subsequent papers we will consider the spectra of free-base corroles, neutral-metal corroles, and various corrole derivatives.



(A) (B)

FIGURE 1 (A) Fully conjugated metal(II) corrole anion. (B) Metal(II) porphin

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EXPERIMENTAL

The two samples used were the 8,12-diethyl-2,3,7,13,17,18-hexamethylcopper(II) corrole, and the 2,18-diethyl-3,7,8,12,13,17-hexamethylnickel(II) corrole, both kindly supplied by Professor A. W. Johnson (University of Sussex). Their preparation and purification have been described [6] and the samples were used without further purification.

The corresponding fully conjugated metal(II) corrole anions were prepared by treatment with tetra-n-butylammonium hydroxide in dimethylformamide and by sodium-film reduction in tetrahydrofuran under high vacuum. The spectra recorded for the anions prepared by the two different methods were almost identical, and for convenience therefore we shall only consider those measured in tetrahydrofuran. The solvent purification and reduction technique have been described.[9]

The electronic spectra of the metal corrole anions were recorded on a Beckman DK 2A ratio-recording spectrophotometer at ambient temperatures. They were found to be independent of concentration over the range 10^{-5}—10^{-3}M. Experimental extinction coefficients given are in l mol^{-1} cm^{-1}, and oscillator strengths (f) for various bands in the experimental spectra were calculated from the relationship [10] (1), where ε is the extinction coefficient and ν the transition energy in wavenumbers.

$$f = 4{\cdot}319 \times 10^{-9}\int \varepsilon \, d\nu \qquad (1)$$

π-Electron Calculations.—Since the electronic spectra of metal corrole anions are determined largely by $\pi \rightarrow \pi^*$ transitions of the corrole ring, as in the case of porphyrins, it is appropriate to use S.C.F. π-electron calculations as a starting point for their interpretation. The calculations discussed in this paper utilized a π-electron Hamiltonian simplified by the approximations of Pariser, Parr, and Pople (P.P.P.).[11,12] The basic procedure has been discussed at length.[13-16]

The calculation of the spectra of the corrole systems was performed with allowance of configuration interaction between the lowest 20 singly excited configurations. The oscillator strengths f_1 and f_2 of the transitions were calculated by use of the length and velocity forms respectively of the transition moment matrix element. Expressions for the primitive integrals of these operators over the homo- and hetero-nuclear atomic orbitals have been given by Hush and Williams.[17]

In all the calculations a planar skeleton was assumed for the corrole ring. The atomic co-ordinates employed were those calculated by us [18] using the bond length–bond order relationships of Nishimoto and Forster.[14,15] The full skeleton possesses C_{2v} symmetry and the values of the co-ordinates are given in Table 1, together with corresponding co-ordinates for the porphin ring system. The porphin molecular geometry is an adaptation of that of Hoard *et al.*,[19] the slight non-planarity and non-square symmetry being ignored by forcing the molecule into a plane and averaging symmetrically related bond distances and angles. The resulting skeleton therefore possesses D_{4h} symmetry.

TABLE 1

(a) Atomic co-ordinates * for the corrole ring

Atom	x	y	Atom	x	y
1	0·000	0·729	7	4·630	3·486
2	−1·025	1·714	8	5·509	2·436
3	0·357	2·927	9	4·721	1·231
4	1·026	2·584	10	5·429	0·000
5	2·120	3·498	20	1·224	1·251
6	3·352	2·820	21	3·406	1·471

(b) Atomic co-ordinates * for the porphin ring

Atom	x	y	Atom	x	y
2	0·681	4·217	21	0·000	2·054
3	1·098	2·839	22	2·054	0·000
4	2·444	2·444			
5	2·839	1·098			
6	4·217	0·681			

* All values in Å, numbering as in Figure 1.

RESULTS AND DISCUSSION

The electronic spectra of the copper and nickel corrole anions obtained in tetrahydrofuran by the method previously described are shown in Figures 2 and 3. Acid–base titrations in dimethylformamide [20] have confirmed that the formation of the metal corrole anion is due to the removal of a single proton from the neutral-metal corrole, so that the spectra observed for these species arise from a fully conjugated corrole ring, having 26 π-electrons. The spectra of the nickel and copper complexes are very similar to one another and also to those of the corresponding nickel and copper octa-alkylporphins.[2]

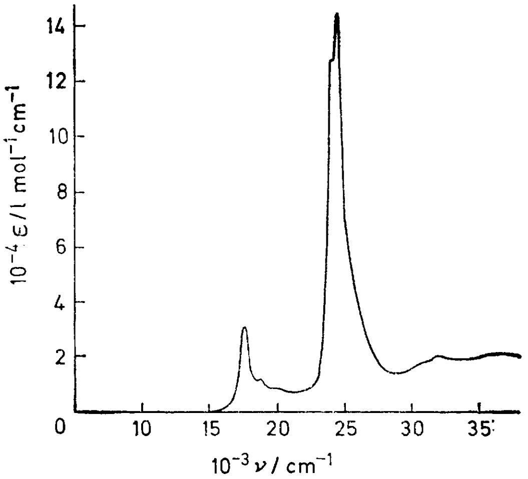

FIGURE 2 Electronic spectrum of copper corrole anion in tetrahydrofuran

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An intense absorption is observed in the near-u.v. region (24 000—26 000 cm^{-1}), and a weaker system of bands is seen in the visible region (16 000—20 000 cm^{-1}), analogous to the Soret (or B) and visible (Q) bands in porphin spectra. In discussing corrole spectra, therefore, we shall refer to these as the Soret and visible bands. Assuming D_{4h} symmetry for metal porphins, we predict the Q and B bands to be doubly degenerate, and to arise largely from transitions between the two highest occupied molecular orbitals ($3a_{2u}$ and $1a_{1u}$) [1] and the lowest vacant molecular orbitals, the e_g pair. The appearance of several peaks in the visible region of porphin spectra has therefore been interpreted as vibrational fine structure of the electronic transitions.[21,22] Typically two peaks are observed in the visible region with a separation of *ca.* 1250 cm^{-1}. The lower-energy peak is in general the more intense, and has been assigned to the 0–0 vibrational component of the first singlet $\pi \rightarrow \pi^*$ transition, and the second to the 0–1 vibrational component of the same electronic transition.[2] In contrast, the Soret band does not normally exhibit any fine structure.

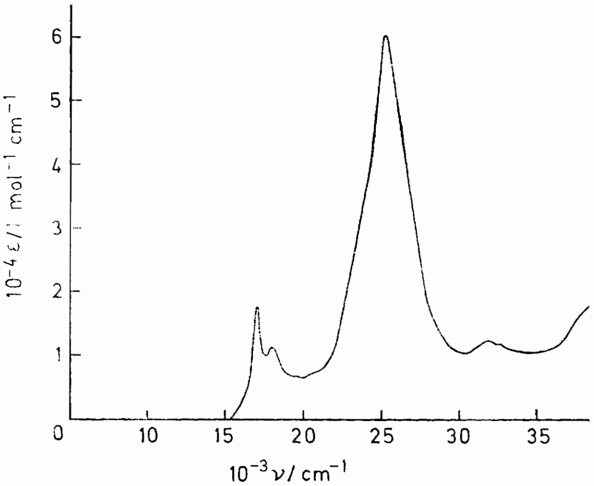

FIGURE 3 Electronic spectrum of nickel corrole anion in tetrahydrofuran

The observed corrole spectra are not markedly different from those of a typical porphin. However, the lower symmetry of corroles requires that some modification of the assignment used for porphin spectra is necessary in discussing corrole spectra; in particular we no longer expect degenerate transitions.

Table 2 shows the calculated π-molecular orbital energies and symmetries for the fully conjugated corrole and porphin rings. Even with the lower symmetry of the corrole ring, the relationship between the orbitals is clear. The calculated $7a_2$ and $8b_1$ corrole orbitals are separated by only 0·46 eV, whilst the next higher orbital, $9b_1$, is almost 3 eV higher in energy. The $7a_2$ and $8b_1$ levels correspond to the two components of the lowest vacant orbitals in porphins, the $4e_g$ pair. Similarly the $6a_2$ and $7b_1$ corrole orbitals correspond to the highest filled porphin orbitals $1a_{1u}$ and $3a_{2u}$ respectively, the charge distributions within corresponding orbitals being fairly similar. The correlation between other orbitals is less obvious, but since the visible and Soret bands in porphins arise mainly from transitions between the $1a_{1u}$, $3a_{2u}$, and $4e_g$ pair, it is not surprising that the visible and Soret bands of the corrole anions closely resemble those of the corresponding porphins.

TABLE 2

Calculated π-molecular orbital energies/eV and symmetries for the fully conjugated corrole and porphin rings

Corrole			Porphin		
Orbital number and symmetry		Energy/eV	Orbital number and symmetry		Energy/eV
20	$11b_1$	10·981	22, 23	$6e_g$	8·097
19	$9a_2$	10·156	21	$3b_{1u}$	7·273
18	$10b_1$	9·788	20	$3b_{2u}$	7·093
17	$8a_2$	9·423	18, 19	$5e_g$	6·498
16	$9b_1$	9·320	17	$2a_{1u}$	6·310
15	$8b_1$	6·375	16	$2b_{1u}$	3·779
14	$7a_2$	5·919	14, 15	$4e_g$	2·712
13	$7b_1$	2·347	13	$3a_{2u}$	−1·362
12	$6a_2$	1·346	12	$1a_{1u}$	−2·139
11	$6b_1$	−0·315	10, 11	$3e_g$	−3·967
10	$5a_2$	−0·408	9	$2b_{2u}$	−4·195
9	$5b_1$	−0·733	8	$2a_{2u}$	−4·359
8	$4a_2$	−0·856	6, 7	$2e_g$	−4·575
7	$3a_2$	−1·318			

Both the corrole and porphin rings have 26 π-electrons. Their net charges are 3— and 2— respectively.

The orbitals reduce as follows on going from D_{4h} (porphin) to C_{2v} (corrole) symmetry with the present axis system.

$$e_g \longrightarrow b_1 + a_2 \qquad b_{2u} \longrightarrow a_2$$
$$a_{2u} \longrightarrow b_1 \qquad b_{1u} \longrightarrow b_1$$
$$a_{1u} \longrightarrow a_2$$

Table 3 gives the calculated π-electronic spectra of the fully conjugated 26 π-electron corrole and porphin rings.

Two transitions are predicted to appear in the visible region at 12 460 cm^{-1} and 15 210 cm^{-1} in the case of corroles compared with the doubly degenerate transition predicted at 14 090 cm^{-1} for porphins. The two bands corresponding to the degenerate component transitions of the porphin Soret band are predicted at 21 680 cm^{-1} and 23 130 cm^{-1} for corroles, while the porphin transitions are calculated to be at 25 090 cm^{-1}.

The lowest $\pi \rightarrow \pi^*$ transition in the corrole ring is predicted to be quite intense and 2700 cm^{-1} lower in energy than the second $\pi \rightarrow \pi^*$ transition. It seems reasonable therefore to assign the bands observed at 16 960 cm^{-1} and 17 510 cm^{-1} for the nickel and copper corrole anions respectively, as the 0–0 vibronic component of the lowest singlet $\pi \rightarrow \pi^*$ transition, and those at 17 950 cm^{-1} and 18 720 cm^{-1} as the 0–1 vibronic components of the same transition. With this assignment the vibrational separations are 990 cm^{-1} for the nickel corrole anion and 1210 cm^{-1} for the copper corrole anion, compared with 1230 and 1260 cm^{-1} in the case of nickel and copper octaethylporphins.[2]

For both corroles and porphins, we predict the lowest $\pi \rightarrow \pi^*$ transition to be *ca.* 4000 cm^{-1} lower in energy than is observed experimentally. This deficiency of the

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calculations has also been encountered in other P.P.P. π-electron calculations on porphins.[1,2] The second π→π* transition in the corrole anions is not resolved, but seems to contribute to the overall absorption in the region between 19 000 and 22 000 cm^{-1}, which is greater than in the case of porphins. The absorption in this region is thus considered to arise from a combination of the second π→π* transition and further vibronic components of the first π→π* transition.

would therefore correspond to the second Soret band transition.

The situation in the case of the nickel corrole anion Soret band is less clear owing to the rather broader profile of the band.† However, it is evident that it is composed of several components as predicted.

The calculated and experimental transition energies are in reasonable agreement for the Soret bands, although the calculated values are *ca.* 2000 cm^{-1} too low in energy.

TABLE 3

Calculated π-electronic spectra for the fully conjugated corrole and porphin rings

Transition energy $10^{-3}\nu/\mathrm{cm}^{-1}$ and polarisation		Corrole Oscillator strength		Main components of transition
		f_1	f_2	
12·46	(y)	0·285	0·010	13 → 14 (0·88), 12 → 15 (0·09)
15·21	(x)	0·019	0·003	13 → 15 (0·71), 12 → 14 (0·28)
21·68	(x)	1·632	0·309	13 → 15 (0·26), 12 → 14 (0·68)
23·12	(y)	0·658	0·116	12 → 15 (0·84), 13 → 14 (0·08)
28·22	(y)	0·000	0·001	11 → 14 (0·83), 8 → 15 (0·09)
28·33	(x)	0·294	0·089	10 → 14 (0·85), 11 → 15 (0·04)
31·23	(y)	0·306	0·118	9 → 14 (0·64), 10 → 15 (0·28)
32·83	(x)	0·101	0·046	11 → 15 (0·59), 8 → 14 (0·32)
33·02	(y)	0·336	0·107	13 → 17 (0·91), 11 → 14 (0·03)
34·83	(x)	0·168	0·056	8 → 14 (0·58), 11 → 15 (0·29)
34·95	(y)	0·000	0·000	10 → 15 (0·39), 8 → 15 (0·31)
35·99	(x)	0·007	0·006	13 → 16 (0·88), 13 → 18 (0·05)
37·65	(x)	0·445	0·106	13 → 18 (0·86), 13 → 16 (0·03)
38·11	(y)	0·012	0·004	8 → 15 (0·57), 10 → 15 (0·31)
39·76	(x)	0·089	0·025	9 → 15 (0·88), 10 → 14 (0·03)

Transition energy $10^{-3}\nu/\mathrm{cm}^{-1}$		Porphin Oscillator strength		Main components of transition *
		f_1	f_2	
14·09	(Q)	0·052	0·018	13 → 15 (0·67), 12 → 4(0·30)
25·09	(B)	3·938	0·674	12 → 14 (0·66), 13 → 15 (0·26)
33·26	(N)	1·106	0·410	9 → 14 (0·69), 10 → 16 (0·13)
37·23	(L)	0·762	0·260	8 → 14 (0·77), 9 → 14 (0·11)
41·18		1·223	0·374	13 → 18 (0·42), 13 → 19 (0·44)
43·94		0·040	0·002	11 → 16 (0·71), 9 → 15 (0·08)
50·01		0·075	0·000	12 → 18 (0·97)
63·01		0·324	0·050	11 → 17 (0·98)

Polarisations of corrole transitions are parallel (x) and perpendicular (y) to the C_2 axis. Figures in parentheses after the main components of transitions are the *squares* of the C.I. vector coefficients. The configuration interaction in the case of porphin involved the following 16 allowed transitions: 13 → 14, 15, 18, 19; 12 → 14, 15, 18, 19; 11 → 16, 18; 10 → 16, 17; 9 → 14, 15, and 8 → 14, 15.

* All transitions are doubly degenerate. The component transitions are for one of the degenerate pair, the f_1 and f_2 values are the total oscillator strengths for the degenerate transitions.

The integrated absorption intensities of the observed visible bands of the corrole anions (Table 4) are more than twice those of the corresponding porphins. This is qualitatively predicted by the f_1 values, but not by the f_2 values, the former being in reasonable agreement with the absolute experimental values.

The Soret bands observed for nickel and copper corrole anions differ somewhat from those of the analogous porphins, being composed of several components, whereas metal porphin Soret bands exhibit no structure.[2]

The Soret band of the copper complex appears to show vibrational structure (peaks were observed at 23 840 and 24 200 cm^{-1}) and it seems reasonable to assign these as vibrational components of the first Soret band transition, since the calculations predict the second electronic transition in the Soret band to occur 1440 cm^{-1} higher in energy than the first, and to have a smaller absorption intensity than the first. The shoulder on the high-energy side of the observed Soret band around 25 500 cm^{-1}

A similar result occurs in the porphin calculations, where the Soret band is predicted to lie some 500 cm^{-1} lower in energy than is observed. This is in contrast to the earlier results of Gouterman *et al.*[1,2] who calculated the energy of the porphin Soret band to be *ca.* 3000 cm^{-1} higher than the experimental value.

Our calculated visible–Soret band separation for porphins is 11 000 cm^{-1} compared with the experimental value of *ca.* 8000 cm^{-1}. This represents a slight improvement on Gouterman's work [2] where the separation was predicted to be 12 500 cm^{-1}. In the case of corroles, the lower-energy visible and Soret band transitions are calculated to have a separation of 9220 cm^{-1}, a decrease of 1780 cm^{-1} compared with the porphins. The experi-

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† The general broadening of the spectrum of the nickel corrole anion compared with the copper corrole anion may result from greater buckling of the corrole ring due to steric interactions of the 2,18-ethyl substituents in the nickel corrole anion. In the copper corrole anion the 2,18-substituents are less bulky methyl groups.

mental value is 6330 cm^{-1} in the case of the copper corrole anion, a decrease of 1010 cm^{-1} compared with the copper octaethylporphin.[2] The calculated decrease in the visible–Soret band separation of corroles compared with porphins is thus in reasonable agreement with experiment.

TABLE 4

(*a*) Peak positions and intensities for the electronic spectrum of copper corrole anion

Peak position $10^{-3}\nu/\text{cm}^{-1}$	Intensity $10^{-4}\varepsilon$
17·51	3·10
18·72	1·21
19·97	0·84
23·84	12·77
24·20	14·44
31·64	2·05
36·00	2·18

Integrated absorption intensity, *f* (oscillator strength)	Limits of integration
0·283 (visible)	$\nu < 22\cdot00$
1·180 (Soret)	$22\cdot00 < \nu < 27\cdot50$
0·506	$27\cdot50 < \nu < 34\cdot00$

(*b*) Peak positions and intensities for the electronic spectrum of nickel corrole anion

Peak position $10^{-3}\nu/\text{cm}^{-1}$	Intensity $10^{-4}\varepsilon$
16·96	1·79
17·95	1·15
19·06	0·72
24·30	4·26
25·14	6·02
31·78	1·24
39·22	2·14

Integrated absorption intensity, *f* (oscillator strength)	Limits of integration
0·205 (visible)	$\nu < 21\cdot00$
1·053 (Soret)	$21\cdot00 < \nu < 29\cdot00$
0·273	$29\cdot00 < \nu < 34\cdot50$

The decreased visible–Soret band separation in the case of corroles arises from changes in the amount of configuration interaction between the transitions responsible for these bands. Also, the increased intensity of the visible bands and decrease in intensity of the Soret band of corroles, compared with porphins, is a further manifestation of the reduced configuration interaction between the transitions. This effect also occurs in the tetra-azaporphins and phthalocyanines,[1] and has also been considered in the description of corrin spectra.[5]

The lower symmetry of corroles means that many more transitions are allowed than in porphins, and this is reflected in the appearance of the corrole anion spectra at energies higher than the Soret band. In particular, the first two predicted transitions above the Soret band correspond to forbidden transitions in porphins, and occur at 28 220 and 28 330 cm^{-1}, the latter being the more intense of the pair. The configurational excitations in corroles corresponding to the N and L bands in porphins are $4a_2 \rightarrow 7a_2, 8b_1$ and $5b_1 \rightarrow 7a_2, 8b_1$. The splitting of their degeneracy and the introduction of further transitions forbidden in porphins is presumably responsible for the general broadening of the spectra at high energies, so that no firm assignment of bands in this region is possible.

In conclusion we add that while the π-electron calculations do not give an exact description of the observed corrole spectra, they do give reasonable semiquantitative predictions, and their deficiencies are known. They also show rather clearly how the spectra differ from those of analogous porphyrins, and consequently we may hopefully expect to be able to use them to trace the changes in the π-electronic spectra of other related conjugated tetrapyrrolic rings systems.

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