Luminescence Properties of Some Synthetic Metallocorrins

By **Maureen Gardiner** and **Andrew J. Thomson,*** School of Chemical Sciences, University of East Anglia, Norwich NOR 88C

The luminescence spectra of a series of synthetic metallocorrins, where corrin is 1,2,2,7,7,12,12-heptamethyl-15-cyanocorrin, have been measured. The study has been undertaken to elucidate the mechanism of the photochemical A/D-secocorrin $\longrightarrow$ corrin cyclisation devised by Eschenmoser in the course of the synthesis of vitamin B_{12}. It is found that metal-free, lithium(I), beryllium(II), magnesium(II), zinc(II), and cadmium(II) corrins fluoresce readily, the emission coming from the lowest excited singlet state of the corrin ring. In addition, cadmium(II) corrin emits in the near-i.r. at 11·6 kK at low temperature. This emission is the first location of the triplet state of the corrin chromophore. Nickel(II) and copper(II) corrin show no luminescence whatsoever, whereas a very feeble luminescence of uncertain origin has been seen from dicyanocobalt(III)–corrin. Dicyanorhodium(III) corrin, palladium(II), and platinum(II) corrin show an intense structured luminescence both in glasses at low temperature and in fluid solution. This luminescence is displaced to low energy of the absorption band of corrin by 3000—6000 cm^{-1} and has a lifetime of the order of 10^{-6} s. Mainly on account of the typical corrin chromophore stretching frequency seen in the band system it can be assigned to the phosphorescence of the lowest triplet state of the corrin ring, perturbed by the heavy transition-metal ion. These results lead to the conclusion that in the case of nickel(II), copper(II), and, in all probability, dicyanocobalt(III) corrins metal *d*-states lying below the lowest triplet state of the corrin ring quench the emission of the latter by facilitating rapid radiationless transitions onto the metal ion. On the other hand, in the corrins of palladium, platinum, and rhodium the lowest energy *d*-states are above the lowest triplet state of corrin and, most likely, above the lowest singlet also, so that the lowest corrin states are still populated after excitation of the ring transitions. These results taken together with those of Eschenmoser reveal a striking parallel between those closed ring metal corrins which display corrin luminescence and those secocorrins which undergo a facile photocyclisation. This leads us to conclude that the presence of low-lying metal *d*-states quenches both the emission of the corrin chromophore and the photochemical ring closure of secocorrin.

THE photochemical reactions of corrin compounds have played an unusually significant role in the development of the chemistry of vitamin B_{12}. Thus the extreme photosensitivity of the coenzyme, 5-deoxyadenosylcobalamin, certainly frustrated its discovery for a number of years [1] and it is now known that a great many cobalt(III) corrins undergo photochemical reactions involving the breaking of the bond between the cobalt ion and an axial ligand.[2] Again, during the course of the synthesis of vitamin B_{12} Woodward and Hoffman were led to formulate a set of rules to describe the course of concerted reactions.[3] More recently these very rules were the stimulus for the design, by Eschenmoser,[4] of a novel photochemical ring closure to synthesise the corrin ring. But in spite of this role played by the photochemistry of corrinoid derivatives little work has been carried out to investigate the pathways by which the corrin chromophore can dissipate its excitation energy. This is largely due to the fact that cobalt containing corrinoids have no readily detectable luminescence properties.[5] However, after the discovery of a naturally occurring corrin ring devoid of cobalt [6] it was shown that

---

[1] H. A. Barker, H. Weissbach, and R. D. Smyth, *Proc. Nat. Acad. Sci.*, 1958, **44**, 1093.

[2] For a good review of the photochemical properties of cobalt corrins see J. M. Pratt, 'Inorganic Chemistry of Vitamin B_{12},' Academic Press, New York, 1972, ch. 14.

[3] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395,2511.

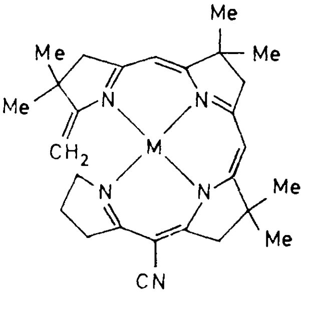
[4] A. Eschenmoser, *Quart. Rev.*, 1970, **24**, 366.

[5] A. J. Thomson, *J. Amer. Chem. Soc.*, 1969, **91**, 2780.

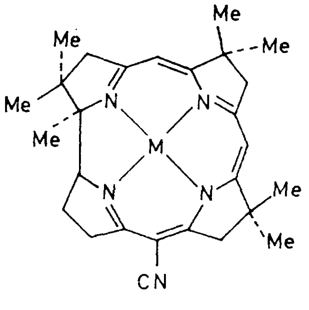
[6] J. I. Toohey, *Proc. Nat. Acad. Sci.*, 1965, **54**, 934.

the corrin ring itself has an intense fluorescence.[5] Now a series of corrins containing a range of metal ions have been produced by the elegant synthetic work of Eschenmoser [7] so that it has become possible for the first time to study the influence of the metal ion upon radiationless pathways in the corrin chromophore. Here we present the results of luminescence studies on a series of metallocorrins with a wide range of metal ion. These materials were made by Eschenmoser and his collaborators and generously supplied to us.

The primary goal of our study has been to contribute towards the elucidation of the mechanism of the photochemical A/D-secocorrin to corrin cycloisomerisation designed by Eschenmoser.[4] This synthesis involved the construction of an open ring precursor secocorrin (I) containing a metal ion and its subsequent photocyclisation to yield the corrin ring (II).



(I)



(II)

The process is a thermally forbidden antarafacial sigmatropic 1,16-hydrogen transfer followed by a thermally allowed 1,15 ($\pi \longrightarrow \sigma$) isomerisation. Since the secocorrin coils in a helical sense the cyclisation can only take place to yield the desired *trans*-configuration of the cyclised product. Eschenmoser found an intriguing dependence of this cyclisation process upon the nature of the central metal ion.[7] Thus cyclisation proceeded smoothly and cleanly in the presence of lithium(I), sodium(I), magnesium(II), calcium(II), zinc(II), and cadmium(II), but not in the presence of cobalt(III) or copper(II). Also in a most significant set of compounds it was found that whereas palladium(II) and platinum(II) secocorrins readily cyclise, no trace of cyclised product was produced from nickel(II) secocorrin. The original suspicion [8] that stereochemical factors were responsible for these striking differences in reactivity was shown to be ill founded by *X*-ray analysis,[9] which revealed that the ground state structures of the three secocorrins of nickel(II), palladium(II), and platinum(II) are almost identical and appear ideal for a photochemical hydrogen transfer. This led naturally to the view that the metal ion, in some cases, was quenching the photochemistry, a possibility that was already suggested by the observation that the fluorescence of the metal-free corrin ring is quenched by cobalt ion.[5] Hence it became imperative to search for emission from as wide a range of metallocorrins as possible. The results of this work are reported here. We had two primary aims; first to locate by emission spectroscopy the positions of the excited states of the corrin ring and the metal ions, and secondly to obtain estimates for the efficiency with which such states are populated after excitation of the corrin ring. All experiments have been carried out with the cyclised product (II). We refer throughout to this as corrin.

EXPERIMENTAL

All the corrinoid materials were supplied by Professor A. Eschenmoser, H. Wild, H. U. Blaser and B. Hardegger of the E.T.H., Zurich. The derivative supplied was 1,2,2,7,7,-12,12-heptamethyl-15-cyanocorrin (II). The metal-free salt was available as the bromide. The following metallocorrins were used: Li^{I}, Be^{II}, Mg^{II}, Cu^{II}, Pd^{II}, Pt^{II}, Zn^{II}, and Cd^{II}. In addition, samples of the dicyano-cobalt(III) and -rhodium(III) compounds were received. Those compounds requiring an anion possessed perchlorate except for the Zn^{II}, Mg^{II}, and Cd^{II} salts which were the chlorides. All samples were dissolved in an ethanol–methanol mixture except for Li^{I} and Be^{II} which were made up in cyclohexane. Solutions were degassed using standard techniques of several freeze–thaw cycles on a vacuum line.

The emission measurements were made with an instrument constructed in this laboratory and designed to have a good near-i.r. response. The exciting light was generated either from a 500 W a.c. or 150 W a.c. xenon arc lamp and passed through a double grating monochromator (Hilger–Watts D 331) to produce a high intensity of high spectral purity light. The emission was gathered with a 600 mm grating monochromator (Hilger–Engis Monospek). The grating was blazed at 7500 Å. The light was detected with a cooled photomultiplier tube with extended S 20 response or with an S 1 response. Phase-sensitive detection (Aim Electronics) was used.

Quantum yield measurements were made by comparing the emission under identical conditions of geometry, of excitation wavelength, and of sensitivity with rhodamine B solution in ethanol. Emission spectra have been corrected for the response of the instrument to yield intensities in terms of relative numbers of photons per unit frequency bandwidth. The method is fully described by Parker and Rees [10] and Melhuish.[11] The spectral distribution of the lamp and monochromator output was measured with a Hilger–Watts Schwartz thermopile.

Lifetime measurements were made with the collaboration of Dr. F. Wilkinson using laser flash photolysis equipment built by D. Adams and a photon counting apparatus assembled by Dr. A. Thornton.

Closed-shell-metal Corrins.—The luminescence spectra and lowest energy absorption bands of metal-free corrin and the metallocorrins lithium(I), beryllium(II), magnesium(II), and zinc(II) are shown in Figure 1. The quantum yields of this emission, ϕ_f, which are quoted in Table 1, were estimated by comparison with a solution of rhodamine B assuming a value of 0·69 for the quantum yield of the

---

[7] A. Eschenmoser, XXIIIrd International Congress of Pure and Applied Chemistry, 1971, vol. 2, p. 69.

[8] Y. Yamada, D. Miljkowic, P. Wehrli, B. Golding, P. Löliger, R. Keese, K. Müller, and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1969, **8**, 343.

[9] M. Currie and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 98.

[10] C. A. Parker and W. T. Rees, *Analyst*, 1960, **85**, 587.

[11] W. H. Melhuish, *J. Opt. Soc. Amer.*, 1962, **57**, 1256.

standard. There is an uncertainty in the values of ϕ_f because the sensitivity of the photomultiplier is falling rapidly in the low energy region of the luminescence. Rather high correction factors are therefore needed to obtain an emission spectrum plotted in units of relative numbers of photons per unit frequency interval. Figure 1(b) illustrates the difficulty with an uncorrected spectrum of the room temperature luminescence of lithium(I) corrin and a plot of $S(\nu)$, the correction factor. The resultant corrected spectrum appears as Figure 1(c).

TABLE 1

Quantum efficiencies and estimates of fluorescence lifetimes of closed-shell-metal corrins

Corrin	ϕ_f [a]	Excitation wavelength/nm	Absorbance	Solvent	Calculated radiative lifetime τ_{rad}/ns	Calculated $\tau_M = \tau_{rad}\cdot\phi_f$
Metal-free	0·08	510	0·04	EtOH	18·15	1·49
Lithium(I)	0·07	500	0·035	Cyclohexane		
Beryllium(II)	0·03	500	0·025	Cyclohexane		
Zinc(II)	0·05	510	0·045	EtOH	12·92	0·68

[a] Determined assuming a value of ϕ_f for rhodamine B of 0·69.

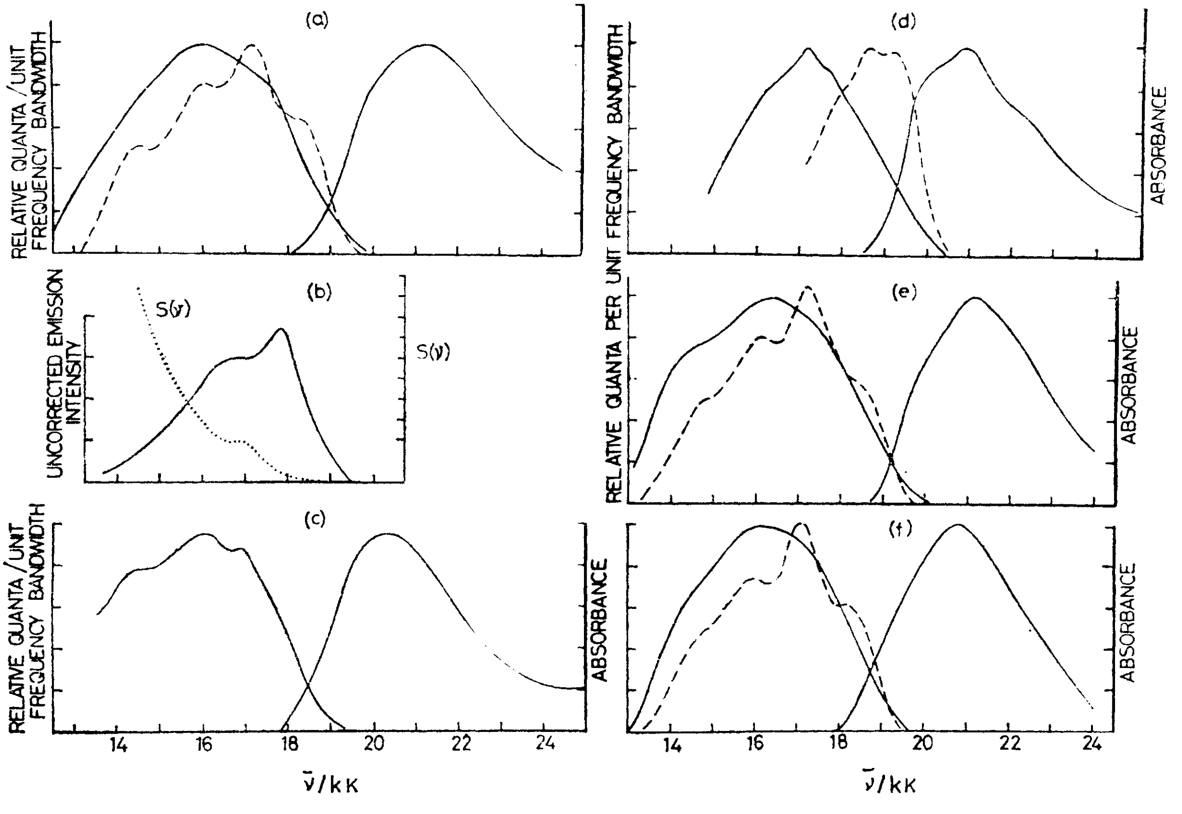


FIGURE 1 Luminescence and absorption spectra of (a) metal-free, (c) lithium(I), (d) beryllium(II), (e) magnesium(II), and (f) zinc(II) 1,2,2,7,7,12,12-heptamethyl-15-cyanocorrin at room temperature (—) and 77 K (- - -). The luminescence spectra, on the left-hand side of each diagram, have been corrected for the response of the detection system; (b) illustrates the uncorrected spectrum of lithium(I) corrin at room temperature, and the experimentally determined correction factor, $S(\nu)$, for the detection system using photomultiplier EMI 9558 Q. Spectra (a)—(c) were measured in cyclohexane, (d)—(f) in MeOH–EtOH (2 : 1)

An attempt was made to measure the radiative decay time, τ_M, directly. This was not possible since the decay of the emission is more rapid than the width of the exciting flash lamp available. However, we are able to place a lower limit on this lifetime of 10 ns. In view of this, the radiative lifetimes of the metal-free and zinc(II) corrin were estimated from this absorption spectrum using the procedure given by Bowen and Wokes.[12] These results, given in Table 1, in conjunction with ϕ_f were used to calculate the measured lifetime, τ_M. The values obtained, final column Table 1, are close to 1 ns and hence at the limit of the resolving time of the lifetime equipment available.

These results show that the luminescence recorded is the prompt fluorescence of the corrin chromophore coming from the lowest singlet (π—π^*) state of the corrin ring. Although there is a good mirror image relationship between

---

[12] E. J. Bowen and J. Wokes, 'Fluorescence of Solutions,' Longman, Green and Co., London, 1970.

the absorption and emission spectra there is a large Stokes shift, amounting to 2650 cm^{-1} for metal-free corrin at room temperature. Since the luminescence maximum undergoes a shift to the blue of 1200 cm^{-1} on immobilising the molecules in a rigid solvent at 77 K (Figure 1a) part of the Stokes shift must be due to a significant difference in polarity between the ground and excited states. The remainder of the shift then arises from vibrational relaxation in the excited state of the corrin ring. This contrasts with the situation found in the luminescence of the naturally occurring red metal-free corrin which has a Stokes shift of only 250 cm^{-1}. The chromophores carry different substituents; in the case of red corrin methyl groups at positions 5 and 15 and in the synthetic corrin a cyano-group at position 15. There are also differences between the groups attached to the exocyclic positions which may influence the conformation adopted by the ring and hence the luminescence. The difference in geometry between the ground and excited states is further reflected in the nature of the vibrational progression in the fluorescence spectrum at 77 K, the most intense member of the progression being a high member. We return to this question of the way in which the geometry of the corrin ring affects the fluorescence spectrum when we consider the important question of why none of Eschenmoser's secocorrins luminesce. But it is of interest to notice that when a transition-metal ion occupies the centre of the ring, particularly an ion which will dictate a coplanar geometry on the four axial nitrogen atoms, such as the dicyanocobalt(III) derivative, Figure 4, the absorption spectrum of the lowest energy band displays a pronounced vibrational progression with a relatively intense 0–0 band. Clearly in this instance vibrational relaxation in the excited state is less pronounced.

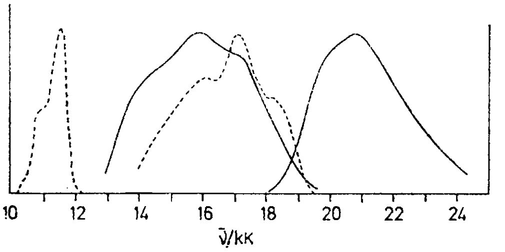


FIGURE 2 Absorption and emission spectra of cadmium(II) 1,2,2,7,7,12,12-heptamethyl-15-cyanocorrin at room temperature (—) and 77 K (– – –) dissolved in MeOH–EtOH (2 : 1)

The absorption and emission spectra of the cadmium(II) corrin is given in Figure 2. In common with the corrins of other closed-shell-metal ions a broad fluorescence spectrum is readily detected at room temperature and 77 K. But in addition a second weak luminescence could be detected, at 77 K only, at 11 500 cm^{-1}. The excitation spectrum of this luminescence matched the absorption spectrum of the cadmium(II) corrin. The spectrum could also be recorded with appropriate filters positioned to remove the fluorescence in second order. The luminescence was not detectable at room temperature. The spectrum shown in Figure 2 is uncorrected for the photomultiplier response since there is a large uncertainty in the correction factors at this energy. This weak emission we assign to the phosphorescence of the corrin ring, that is, to the emission from the lowest triplet state.

A search was carried out for weak emissions at low energy from the other closed-shell-metal corrins studied. Samples were degassed and cooled to 77 K. The search was carried out with both S-1 and S-20 photomultipliers but no emission could be positively identified. This result constitutes the first unambiguous location of the triplet state of the corrin chromophore. Undoubtedly the high atomic number of cadmium increases the rate of intersystem crossing sufficiently to provide a good population of the triplet and hence a detectable phosphorescence.

Transition-metal Corrins.—In this section are presented the results for those corrins containing a transition-metal ion, that is, nickel(II), palladium(II), platinum(II), cobalt(III), rhodium(III), and copper(II). The compounds are divided into three groups according to the number of *d*-electrons possessed by the metal ion. Thus nickel(II), palladium(II), and platinum(II), with configuration d^8, are presented as a group and so are cobalt(III) and rhodium(III), d^6. Copper(II), d^9, is treated separately. After the results the assignments are discussed in a separate section.

d^8 *Metal ions.* The luminescence and absorption spectra of palladium(II) and platinum(II) corrins are shown in Figure 3. No luminescence has been detected from nickel(II) in spite of careful searches at 77 K with degassed samples and using the full sensitivity of the fluorimeter. The apparatus has some sensitivity down to 10 000 cm^{-1}. By

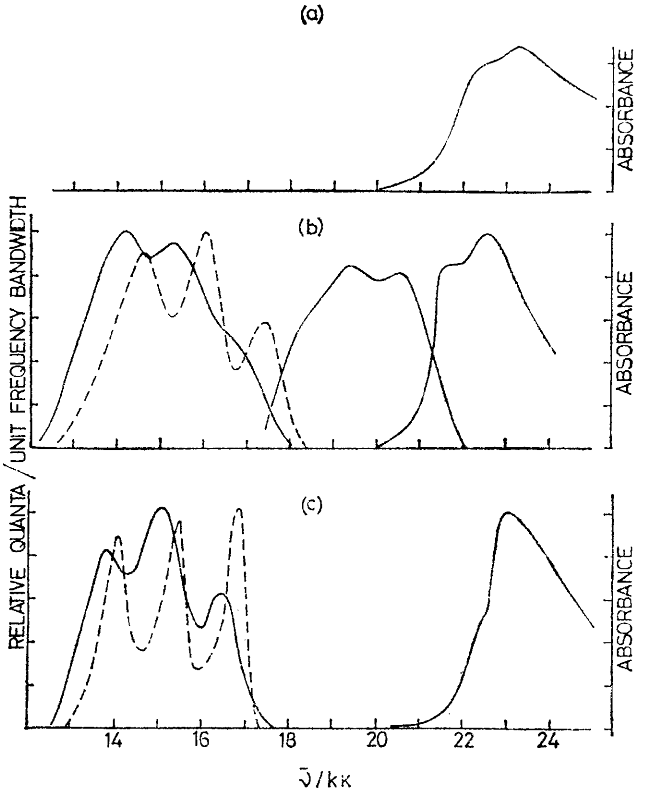


FIGURE 3 Absorption spectra of degassed solutions of 1,2,2,7,7,-12,12-heptamethyl-15-cyanocorrins of (a) nickel(II), (b) palladium(II), and (c) platinum(II) at room temperature (—) and 77 K (– – –) in MeOH–EtOH (2 : 1). The broad emission from palladium(II) corrin which overlaps the absorption spectrum could only be detected in aerated solution at room temperature

contrast, the palladium(II) and platinum(II) corrins display a readily detectable luminescence, but with interesting oxygen effects first pointed out to us by Professor G. Quinckert.[13] In degassed solutions palladium and platinum corrin have a structured luminescence both at room temperature and at 77 K. The platinum emission can also be detected in aerated solutions at both temperatures whereas that of palladium is unobservable in aerated solution. The structured emission is displaced 4000 and *ca.* 6000 cm^{-1} from the lowest energy absorption maximum of the palladium and platinum corrin, respectively. In the case of the palladium corrin, there is, in addition, a weak emission detectable only in aerated solution at room temperature. This emission forms a reasonably satisfactory mirror image of the lowest energy absorption band. All the reported luminescence spectra generate excitation spectra which agree with the absorption spectra.

The lifetimes of the structured emission of palladium and platinum corrin have been determined with the aid of two instruments, both made available to us by Dr. F. Wilkinson. One instrument excites the sample with a small repetitive flash and follows the decay at intervals after the flash, accumulating the signals in a multi-channel analyser. The second method involved laser flash excitation followed by measurement of the decay of the excited species *via* the absorption spectrum of the excited state. The results obtained with these techniques are summarised in Table 2.

TABLE 2

Measured lifetimes of long wavelength emission from heavy metal corrins

	$10^7\tau_M$ [a]/s	λ_M [b]/nm	$10^7\tau_M$ [c]/s	λ_M [b]/nm
Palladium(II) in MeOH/EtOH 2 : 1			22·3	510
Platinum(II) in MeOH/EtOH 2 : 1	4·62 [a] 39 [e]	615	3·76 [d]	523
Rhodium(III) dicyanide in MeOH	*ca.* 10—1 [e]	635	5·2 [d] 44 [e]	550

[a] Lifetime measured from decay of emission. [b] Wavelength at which decay was monitored. [c] Lifetime measured from decay of excited state absorption. [d] Aerated solution at room temperature. [e] Degassed solution at room temperature.

Both techniques were used to determine the lifetime of emission from platinum corrin in degassed solution at room temperature. The difference between the values obtained, 4·62 and 3·76 × 10^{-7} s, indicates the uncertainty in our measurements. It is clear from Table 2 that there is a significant quenching effect of oxygen on the emission process. It is possible to calculate a quenching constant, k_Q, by taking values of 4·62 × 10^{-7} and 3·9 × 10^{-6} s for the lifetimes of platinum corrin in aerated and degassed solutions and by assuming a value for the dissolved oxygen concentration of 10^{-3}M.[14] The value of k_Q obtained thus is 1·9 × 10^9 l mol^{-1} s^{-1} which agrees well with typical diffusion controlled rate constants for ethanolic solutions saturated with air at 25 °C.[14]

TABLE 3

Energies and vibrational spacings of low energy emission from open shell corrins

	Energy of 0–0 band/cm^{-1}	Vibrational interval/cm^{-1}
Palladium(II) corrin	17 400	1350 ± 50
Platinum(II) corrin	16 850	1375 ± 25
Dicyanorhodium(III) corrin	16 070	1360 ± 50

The quantum efficiency of the structured emission of platinum corrin is 0·7.

Table 3 records the energies of the 0–0 bands of the structured emissions and the frequency of the vibrational progression. The frequency is characteristic of one of the quasi-aromatic stretching frequencies of the corrin ring. They have been seen especially clearly in the emission spectra of Toohey's red corrin,[5] and in the resonance enhanced Raman spectrum of vitamin B_{12} derivatives.[15]

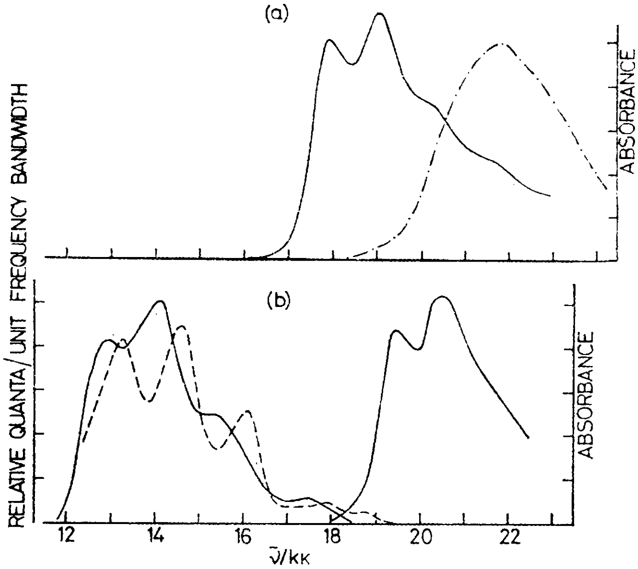


FIGURE 4 (a) Absorption spectra of dicyanocobalt(III) 1,2,2,7,7,12,12-heptamethyl-15-cyanocorrin (—) and the same corrin of copper(II) (– · – ·) at room temperature in MeOH–EtOH; (b) absorption and emission spectra of dicyanorhodium(III) 1,2,2,7,7,12,12-heptamethyl-15-cyanocorrin at room temperature (—) and 77 K (– – –) in MeOH–EtOH (2 : 1)

d^6 *Metal ions.* Dicyanorhodium(III) corrin shows an emission in degassed solution at room temperature and 77 K, Figure 4. On the other hand, dicyanocobalt(III) corrin does not give a readily detectable emission even in degassed solution at low temperature. It was possible to detect an emission at room temperature only. This spectrum mirrors the lowest energy absorption band. However, it was not possible to obtain an excitation spectrum in good agreement with the absorption spectrum. The emission could only be detected when the spectrometer slits were opened wide and the gain of the apparatus set to the maximum. We were unable to record the emission at 77 K possibly because the presence of a Dewar vessel around the sample tube lowers the optical speed of the apparatus since the distance between sample and slits is now increased. Unfortunately, we are not able to claim the unambiguous detection of emission from cobalt(III) corrin. This is dis-

---

[13] G. Quinckert, personal communication.

[14] C. A. Parker, 'Photoluminescence of Solutions,' Elsevier, 1968.

[15] W. J. Wozniak and T. G. Spiro, *J. Amer. Chem. Soc.*, 1973, **95**, 3402.

appointing in view of the key role occupied by cobalt in the chemistry and, as will be discussed later, in the photochemistry of both open- and closed-ring corrins.

The luminescence from rhodium corrin is, however, intense and readily detected. The emission consists of two regions, one of which is of low intensity and overlaps the absorption band. The other part consists of a pronounced vibrational progression starting at 16 070 cm^{-1} and strikingly similar to that seen in the spectrum of palladium and platinum corrin. The vibrational interval is again the 1350 cm^{-1} frequency, Table 3. The lifetime of a transient species absorbing at 550 nm after laser flash excitation was measured under aerated and degassed conditions, Table 2. These values again reveal the effect of oxygen quenching, the effect being of the same order as that found in platinum corrin. It was not possible to make a measurement of the luminescence lifetime by direct observation of the decay since the emission falls in a region where the photomultiplier sensitivity (1P28) is low and signal/noise is a problem.

d^9 *Metal ion.* Copper(II) corrin has been examined in degassed solution at room temperature and at 77 K. No luminescence which can be ascribed to copper corrin has been detected. The absorption spectrum of the lowest transition is given in Figure 4 for comparison with the other corrins.

DISCUSSION

Corrins which contain a metal ion with an incomplete shell of *d*-electrons will possess excited states of two types. First, there will be states, both singlet and triplet arising from configurations of excited π electrons of the corrin ring. Secondly, the metal ion will give rise to states arising from excited *d*-electrons. We may consider these two types of state to be localised on the corrin ring and on the metal ion, respectively. Strictly covalency between the metal ion and the corrin ring will invalidate this classification. But it is possible to recognise the gross features of the spectrum of the corrin ring throughout the absorption spectra of all the compounds studied here. Hence this classification holds and accounts at least for the main features of the spectrum. For completeness we should consider a third class of excited state, one which may arise from a charge-transfer configuration. However, we may at the outset rule this out of consideration since there are no absorption bands unique to one corrin in the spectra of any of the corrins studied. There is a good one to one correspondence of absorption bands throughout the series. Therefore, in our assignment, we have to consider whether the observed luminescence originates from a corrin state or a metal *d*-state

On account of its similarity to the fluorescence of the closed-shell-metal corrins we assign the broad weak emission of palladium and rhodium corrin to the fluorescence of the lowest π state of the corrin ring. It is much weaker in the case of palladium and rhodium than for the other corrins. But this is to be expected if the heavy metals are enhancing the rate of crossing to a low-lying triplet by a spin–orbit coupling mechanism. The total absence of this emission in platinum corrin supports this argument.

The highly structured luminescence from palladium, platinum, and rhodium corrin is assigned to the phosphorescence of the corrin ring, that is, to the emission from a triplet state of a corrin localised transition. The following arguments led us to this conclusion.

First, the vibrational frequency in the band is characteristic of the corrin chromophore itself. The resonance enhanced Raman spectra of vitamin B_{12} show a number of vibrational frequencies of the corrin ring.[15] This technique picks out those vibrations of the corrin ring which are coupled to the π–π^* electronic transitions of the corrin ring. In some derivatives a set of strong Raman bands between 1395 and 1360 cm^{-1} are seen. This is in remarkably close agreement with the frequencies of the progression in the luminescence of palladium, platinum, and rhodium corrin (Table 3). Since no charge-transfer transitions are present in the spectra of any of these three metallocorrins, the luminescence must be occurring within a manifold of corrin levels. Secondly, the position of the structured emission is relatively invariant to the metal ion occupying the central hole of the corrin ring. If the emitting state were localised on the metal ion or indeed involved a metal orbital to any great extent the energies of the states are unlikely to be invariant to the metal. This argument applies with particular force to the comparison between palladium and platinum corrin. There is expected to be a shift to higher energy of between 3000 and 5000 cm^{-1} of the *d*-states of a d^8 ion on going from palladium to platinum (see later).

Therefore it can be concluded that the state from which the intense structured emission originates is predominantly corrin in character. Hence the only possible assignment is to the lowest triplet state of the corrin ring. However, there has nevertheless been considerable perturbation of the state by the metal ion. For example, the energy of the state has been shifted from 11 500 cm^{-1} in cadmium corrin to *ca.* 16 000 cm^{-1} in the transition metal corrins. The energies of the lowest singlet state, seen in absorption, have also been shifted so that the single–triplet separations are markedly smaller in the transition-metal corrins. Presumably this arises from the π-bonding with the corrin ring that will be most pronounced in the case of the transition-metal corrins. The short lifetimes, of the order of 10^{-6} s, also reflect the influence of the heavy metal ion on the character of the corrin state. The large spin–orbit coupling has reduced the radiative lifetime sufficiently that phosphoresence is now detectable in fluid solution, but pronounced oxygen quenching is observed since the lifetime is not shorter than the diffusion controlled rate constant. The lifetimes are sufficiently short that it should be possible to detect the singlet–triplet absorption readily in solution. No attempt has been made to locate these bands.

We turn now to the question of the striking difference between the emission properties of cobalt, nickel, and copper corrin and the heavier transition-metal corrins of rhodium, palladium, and platinum. In many respects the pattern observed for corrins is the same as that found for the luminescence properties of metal porphyrins and phthalocyanines. We consider the parallels in more detail in a later section.

The series of metallocorrins of nickel(II), palladium(II), and platinum(II) provide the key to understanding the total absence of emission from the nickel corrin. The electronic spectra of planar complexes of d^8 metal ions are relatively well understood. Planar palladium(II) and platinum(II) complexes are invariably diamagnetic and have a manifold of excited singlet and triplet states arising from excited configurations of *d*-electrons.[16] The energies of these states are highly dependent upon the nature of the ligands surrounding the metal ion. The data show that, in the case of platinum(II), the lowest energy *d*-state may lie between *ca.* 17 000 cm^{-1}, when four chloride ions surround the metal,[16] and *ca.* 23 000 cm^{-1} if cyanide ion is the ligand.[17] These two ligands generate respectively one of the lowest and highest ligand field strengths. Hence these examples provide us with a rough estimate of the energy range within which the lowest *d*-state of platinum(II) compounds will lie. The *d*-states of palladium lie *ca.* 2000 cm^{-1} below those of platinum for a given ligand.[16]

The n.m.r. spectrum of nickel(II) corrin confirms that it is diamagnetic.[18] However, the location of the lowest triplet *d*-state of planar nickel(II) complexes is not so clear cut mainly because there are rather few planar nickel compounds. However, there is evidence that the states must be low lying. Thus nickel(II) salicylaldimines can successfully quench the lowest triplet states of all organic triplet state donors down to an energy of 14 000 cm^{-1}, the position of the triplet state donor with the lowest available energy.[19] At the suggestion of this work these experiments were extended to the palladium(II) analogue which, it was shown, will only quench the triplet states of donors with energies greater than 17 000 cm^{-1}.[20]

Therefore we conclude that, for a given ligand, the energies of the *d*-states of planar d^8 ions fall in the following order $Pt > Pd \gg Ni$. Thus the difference between the luminescence properties of nickel corrin and palladium and platinum corrin has a clear explanation. In palladium and platinum corrin the lowest metal *d*-states are above the triplet state of the corrin ring and possibly above even the lowest corrin singlet since weak corrin ring fluorescence is detected from palladium corrin. But in nickel corrin the lowest *d*-state of the metal lies below the triplet state of the corrin ring and hence quenches corrin luminescence by promoting energy transfer from the corrin manifold to the metal *d*-levels. Presumably the nickel *d*-states emit in the inaccessible i.r. or, more likely, radiationless processes directly to the ground state become highly efficient.

A similar interpretation can be applied to the different luminescent properties of cobalt and rhodium corrins. For a given set of ligands the *d*-states of rhodium(III), again a set of singlet and triplet states, lie at much higher energy than those of cobalt(III). When a set of ligands generating a sufficiently strong field surround the metal ion the ligand localised luminescence is obtained. For example, the luminescence of $[Rh^{III}(o\text{-phenanthroline})_3]^{3+}$ at 22 300 cm^{-1} is said to originate from levels of the ligand on account of the pronounced aromatic stretching frequency seen in the spectrum.[21] On the other hand, the luminescence from $[Rh^{III}(pyridine)_2Cl_4]^{2-}$ at 15 150 cm^{-1} is broad and structureless [22] originating from the lowest metal *d*-state which has now dropped below the states of the ligand since chloride ion has a low ligand field strength. The luminescence from a crystal of $K_3Co(CN)_6$ found at 14 400 cm^{-1} and excited at 18 500 cm^{-1} indicates the highest energy possible for the lowest lying *d*-states of octahedral cobalt(III).[23] Thus, we can see that the *d*-states of cobalt(III) will lie considerably lower in energy than those of rhodium(III). We therefore conclude that the *d*-states of the rhodium ion are above the lowest triplet state of the corrin ring and also most likely above the lowest singlet state since fluorescence is seen from the ring.

The situation in dicyanocobalt(III) corrin is not clear from our results. The fluorescence from the corrin ring is undoubtedly exceedingly weak and there is no intense triplet state emission from the corrin ring. If the *d*-states of cobalt were above the corrin ring, it is difficult to understand why corrin fluorescence is so weak since spin–orbit coupling from the cobalt nucleus is unlikely to be strong enough to increase intersystem crossing markedly. The position of the states in $[Co(CN)_6]^{3-}$ indicates that the *d*-states in cobalt(III) corrin are almost certainly below the singlet state of the corrin ring. This would account for the very weak fluorescence of the ring. In cobalamins absorption bands of low intensity have been observed with axial ligands containing heavy atoms. For example, with I^- a band is seen at 740 nm, $NCSe^-$ 730 nm, and $S_2O_3^{2-}$ at 680 nm.[24] These bands are, however, most likely the spin-forbidden transitions of the corrin ring.

Comparisons with Metalloporphyrins and Phthalocyanines.—The long series of experiments on the emission properties of metalloporphyrins begun by Becker and his co-workers [25] and continued by Gouterman [26,27] reveal

---

[16] P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, 1965, **42**, 1973.

[17] A. M. Tkachuk and N. A. Tolstoi, *Opt. Spectrosk.*, 1966, **20**, 570.

[18] D. Bormann, A. Fischli, R. Keese, and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1967, **6**, 868.

[19] A. Adamczyk and F. Wilkinson, *J.C.S. Faraday II*, 1972, **68**, 2031.

[20] S. R. Allsop and F. Wilkinson, *Chem. Phys. Letters*, 1973, **19**, 535.

[21] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 1970, **70**, 199.

[22] G. A. Crosby and D. H. W. Carstons, ' Molecular luminescence,' ed. E. C. Lim, W. A. Benjamin, New York, 1969.

[23] M. Mingardi and G. B. Porter, *J. Chem. Phys.*, 1966, **44**, 4354.

[24] See ref. 2, p. 65.

[25] For a review see R. S. Becker, ' Theory and Interpretation of Fluorescence and Phosphorescence,' Wiley–Interscience, New York, 1969, p. 190.

[26] P. G. Seybold and M. Gouterman, *J. Mol. Spectroscopy*, 1969, **31**, 1.

[27] D. Eastwood and M. Gouterman, *J. Mol. Spectroscopy*, 1970, **35**, 359.

an interesting parallel with the luminescence properties of metallocorrins. Recently, studies of metallophthalocyanines [28] have shown that the similarity extends to these molecules as well. For both sets of molecules closed-shell-metal ions permit the fluorescence of the ring to be seen but the phosphorescence of the ring is readily detected only when heavy metal ions such as cadmium occupy the ring. In metal phthalocyanines it was possible to detect phosphorescence from magnesium, zinc, and cadmium phthalocyanines but the phosphorescence lifetime shortened markedly on replacing zinc by cadmium.

When transition-metal ions occupy the centre of the porphyrin or phthalocyanine ring a similar pattern to that seen here for corrin emerges. No emission has been detected from either nickel porphyrin [27] or phthalocyanine [28] whereas the palladium and platinum analogues show an intense phosphorescence. In the case of porphyrins both emit in degassed solutions at room temperature with lifetimes, at 77 K, of *ca.* 2000 and *ca.* 200 μs, for palladium and platinum respectively. On the other hand, although the phthalocyanines of palladium and platinum also show an intense phosphorescence in fluid solution they have lifetimes of 25 and 7 μs respectively. In palladium phthalocyanine a weak fluorescence of the ring was detected. Both sets of workers attribute the striking difference between the nickel and palladium, platinum compounds to the presence of *d*-states in the nickel compounds lying below the states of the ring.

There are no comparable studies on cobalt(III) or rhodium(III) porphyrins or phthalocyanines. There is an early report by Becker [29] of a weak luminescence from cobalt(III) mesoporphyrin in EPA at 77 K, but most studies have been concerned with cobalt(II) porphyrins and phthalocyanine neither of which give any detectable luminescence. Gouterman mentions briefly that rhodium etioporphyrin I gives a rapid fluorescence.[30]

The total absence of luminescence from copper(II) corrin places it in an anomalous position compared with copper(II) porphyrins and phthalocyanine.[31,28] Both the latter compounds emit in the near i.r. from states which have been described by Gouterman [32] as a mixture of the excited triplet state of the ligand and a doublet state of the copper ion. Thus, at ordinary temperatures, the emission is seen from both the resulting doublet and quartet states which have separations ranging between 50 and 500 cm^{-1} depending upon the compound. The mixing between the ligand and metal states is inversely proportional to their energy separation. Possibly the corrin ligand generates a lower ligand field strength than porphyrin and phthalocyanine so that the metal doublet state is much further below the corrin triplet in copper(II) corrin. If this were so, then the interaction between the corrin and metal states would be weaker and the lower lying state would have predominantly copper character leading to a quenching of all emission.

Photochemistry of Metallocorrins.—The conclusions derived from the luminescence studies may now be applied to the interpretation of the photochemical properties of corrins. We consider first the photochemical properties of secocorrins, the open ring precursor of the corrins studied here. Professor Quinckert and his collaborators have been unable to detect luminescence from any of the secocorrins. Inspection of the absorption spectrum of a secocorrin shows a shift to the red by *ca.* 40 nm of the entire spectrum compared with the spectrum of the cyclised corrin. This is expected since there are two more electrons in the π-system of the secocorrin chromophore, and the chain length is two atoms greater. But also evident is the degraded nature of the lowest energy transition, the absorption maximum being far from the onset of absorption. We have alluded briefly to the shapes of the lowest energy absorption band of corrins earlier. The broadness undoubtedly arises from the severe non-planarity of the chromophore. This situation often leads to a large Stokes shift of emission and a low quantum efficiency of fluorescence. The polyenes related to vitamin A provide a good example of this effect.[33] In addition the additional flexibility of the coil may lead to efficient radiationless deactivation although it is difficult to believe that this effect is significant when a metal ion such as platinum(II) is occupying the centre of the coil. Apart then from the increased rates of radiationless deactivation of the secocorrin excited states the relative positions of the metal and corrin states are not expected to be very different in cyclised and secocorrins. Thus a striking parallel is now evident between these cyclised corrins which show corrin fluorescence and/or phosphorescence and these secocorrins which undergo photocyclisation (ref. 7, Figure 6). This constitutes strong evidence for the view that the same mechanism by which metal ions quench corrin luminescence also operates to quench photocyclisation. Since we have suggested that metal *d*-states lying below the corrin triplet states are necessary to quench corrin luminescence it is clear that low lying *d*-states are also responsible for preventing secocorrin photocyclisation reactions.

If the excitation energy from the corrin ring is rapidly transferred onto the metal ion in the centre of the ring one might then expect to see photochemistry typical of the central metal ion. Apparently in the case of many cobalt(III) compounds this is just what is observed. For example, photoaquation reactions of cobalamins occur with the displacement of an axial ligand of cobalt such as cyanide. Alternatively, homolytic cleavage of the cobalt–ligand bond takes place to generate a free radical and a cobalt(II) complex.[2] We have been able to show

---

[28] P. S. Vincett, E. M. Voigt, and K. E. Rieckhoff, *J. Chem. Phys.*, 1971, **55**, 4131.

[29] J. B. Allison and R. S. Becker, *J. Chem. Phys.*, 1960, **32**, 1410; R. S. Becker and J. B. Allison, *J. Phys. Chem.*, 1963, **67**, 2662, 2669.

[30] J. B. Callis, M. Gouterman, Y. M. Jones, and B. H. Henderson, *J. Mol. Spectroscopy*, 1971, **39**, 410.

[31] D. Eastwood and M. Gouterman, *J. Mol. Spectroscopy*, 1969, **30**, 437; M. Gouterman, R. A. Mathies, B. E. Smith, and W. S. Caughey, *J. Chem. Phys.*, 1970, **52**, 3795.

[32] R. L. Ake and M. Gouterman, *Theoret. Chim. Acta*, 1969, **15**, 20.

[33] A. J. Thomson, *J. Chem. Phys.*, 1969, **51**, 4106.

that the emission of dicyanocobalt(III) corrin is exceedingly weak. This fact taken together with the photochemical properties of the cobaltic ion strongly indicates that the excitation energy is rapidly lost to the cobalt ion.

We thank the S.R.C. for equipment and a studentship (to M. G.). We are indebted to Dr. Wilkinson for apparatus to measure emission lifetimes and to Professor G. Quinckert for sending us the results of his work prior to publication. Finally we acknowledge gratefully Professor A. Eschenmoser who has generously supplied beautiful samples of corrins almost to order and who has given us the benefit of his advice and encouragement throughout.

[3/2151 *Received, 22nd October,* 1973]