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THE ELECTROCHROMIC BEHAVIOUR OF LANTHANIDE BISPHTHALOCYANINES: THE ANOMALOUS NATURE OF THE GREEN LUTETIUM SPECIES

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THE ELECTROCHROMIC BEHAVIOUR OF LANTHANIDE BISPHTHALOCYANINES: THE ANOMALOUS NATURE OF THE GREEN LUTETIUM SPECIES

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Double integration of the electron paramagnetic resonance signal associated with the green form of lutetium bisphthalocyanine in dimethylformamide solution indicates it is a minor species. Magnetic circular dichroism spectroscopy strongly suggests the chromophore is not a radical. These findings are in keeping with the recently resurrected hypothesis [Daniels *et al.*, *J. Coord. Chem.* (1993) **28**, 23–31] that the “electrochromic” color changes observed in lanthanide bisphthalocyanine chemistry are acid-base in nature and not due to oxidation-reduction processes involving the phthalocyanine rings.

KEYWORDS: Bisphthalocyanine, electrochromism, EPR, MCD

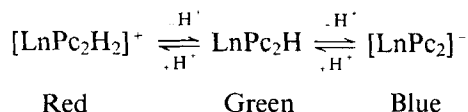
INTRODUCTION

Lanthanide bisphthalocyanines (LnPc_2H) represent an interesting type of “electrochromic” material, *i.e.* when prepared as solid films and subjected to an applied electrical potential, they reversibly change color. The noteworthy feature of these materials is that they exist in at least three stable forms (red, green and blue) and also, if the electrical potential is removed, then the last stable form to have been produced persists indefinitely.

It has recently been reported¹ that in acetonitrile solution and in the absence of an applied potential, the color changes blue \rightarrow green \rightarrow red can be effected by the addition of acid and then quantitatively reversed by the addition of base, leading

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to the following suggested mechanism for the observed color changes:



In the case of the blue to green interconversion, this kind of acid-base mechanism was originally proposed by Moskalev and Kirin² and later supported by MacKay *et al.*³ However, alternate mechanisms involving oxidation-reduction chemistry of the phthalocyanine rings are much more widespread in the literature. These stem directly from a report by Corker *et al.*⁴ who observed a radical EPR signal associated with the green form of lutetium bisphthalocyanine, which disappeared upon its "reduction" to the blue form.

In this paper, we show that the EPR signal associated with the green form of the lutetium complex represents a minor species existing in solutions of LuPc₂H. The absence of any oxidation-reduction chemistry associated with the phthalocyanine rings in the conversion of the blue form of the lutetium complex to the green form is confirmed by magnetic circular dichroism (MCD) spectroscopy at cryogenic temperatures. The implications that these results have regarding the electrochromic behaviour of lanthanide bisphthalocyanine films is briefly considered and the remaining questions concerning the mechanism of the color changes observed are discussed.

METHODS

Lanthanide bisphthalocyanine complexes were prepared from the appropriate acetates and purified chromatographically as previously described.¹ The products were stored as concentrated dimethylformamide (DMF) solutions prior to use.

Electronic absorption spectra were recorded using Varian DMS 100 and Cary 14 spectrophotometers. EPR spectra were recorded on a Bruker ESR 300 spectrometer fitted with an Oxford Instruments ESR 900 flow cryostat. Liquid secondary ion mass spectra (LSIMS) were obtained using a VG AutoSpec high resolution instrument. MCD spectra were recorded with an Aviv Associates 41DS circular dichroism spectrometer in conjunction with a Cryomagnetics Incorporated cryomagnat.

RESULTS AND DISCUSSION

The x-band EPR spectrum of the green form of lutetium bisphthalocyanine from 10 K to 80 K consists of a single isotropic signal exhibiting no hyperfine structure at *ca.* *g* = 2.00 (not shown). This is in keeping with it arising from a radical species, as previously observed by others in electrochemical experiments.⁴ Prior to its conversion to the green form by the addition of acetic acid, the blue form of lutetium bisphthalocyanine exhibits no EPR signals.

Employing the 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) in solvent DMF as the EPR integration standard and using $\epsilon_{\text{max}} = 2.0 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ as the extinction coefficient for the green form of lutetium bisphthalocyanine,⁵ it is

possible to compare the concentration of chromophore and radical in samples. These data are presented for several lutetium bisphthalocyanine preparations in Table 1, where the ratio of spins/chromophore concentration is evidently variable. We have been unable to establish a quantitative relationship between spin concentration and *any* experimental parameter, such as amount of acid added. Nevertheless, the radical species (*i.e.* spin concentration) is consistently found to be present at substoichiometric amounts relative to the chromophore concentration. These data strongly suggest that the radical and the chromophore are associated with different molecular species. Moreover, other lanthanide bisphthalocyanines in their green forms do not exhibit radical EPR spectra. While it can be argued that this might be due to magnetic coupling effects, MacKay *et al.*³ found that the EPR spectra of *both* blue and green forms of gadolinium bisphthalocyanine contained only signals attributable to half-odd-integer (*i.e.* $S = 7/2$) spin systems.

The majority of the studies reported in the literature concerning lanthanide bisphthalocyanines and electrochromism have involved the lutetium species. This is unfortunate, because in addition to the radical EPR signal associated with the green form there is a further line of evidence suggesting the behaviour of the lutetium compound(s) to be anomalous compared to the other lanthanide bisphthalocyanines. Consider the mass spectrum of Figure 1. The base peak is at m/z 1201, corresponding to $[\text{LuPc}_2\text{H} + \text{H}]^+$, as expected.¹ In addition, another weaker cluster of peaks is centered at m/z 1346, which has the same isotope distribution pattern as that observed around the base peak and corresponds to $[\text{LuPc}_2 + 2 \text{DMF}]^+$. In our hands at least, other bisphthalocyanines, from the lanthanum to the thulium complex, exhibit only the $[\text{LnPc}_2\text{H} + \text{H}]^+$ ion by LSIMS and not the higher molecular mass species. There is no way of knowing if the m/z 1326 moiety is associated with the radical species detected by EPR, since the mass spectral data cannot be quantified.

The electronic absorption spectra of green forms of lutetium bisphthalocyanine in DMF solution (Figure 2B, —) and prepared as a solid film (Figure 2B, ----) are very similar indeed, barring some broadening in the spectrum of the solid. The MCD spectrum of the green form in DMF/*N*-methylformamide (NMF) solution between 4.2K and 25K (Figure 2A) is temperature independent and exhibits a derivative-shaped feature at the same wavelength as the maximum in the absorption spectrum. This is a Faraday A-term type of spectrum indicative of a non-degenerate ground state and a degenerate excited state of the chromophore.⁶ It is quite unlike the reported MCD spectra of well characterized phthalocyanine radicals.⁷ In particular, the spectra of Figure 2 lack the band at *ca.* 510 nm which is a "fingerprint" for the formation of the monoanion radical (Pc^-)⁸ and moreover,

Table 1 Comparison of Chromophore and Spin Concentrations in DMF Solutions of the Green Form of Lutetium Bisphthalocyanine.

$[\text{LuPc}_2\text{H}](\text{mM})^{\text{a}}$	Spin concentration (mM) ^b	Ratio spins/ $[\text{LuPc}_2\text{H}]$	Acid present ^c
0.33	0.25	0.76	trifluoromethanesulfonic acid
0.34	6.2×10^{-2}	0.18	trifluoromethanesulfonic acid
8.5×10^{-2}	1×10^{-3}	0.01	acetic acid
2.4×10^{-2}	7×10^{-3}	0.29	acetic acid
2.5×10^{-2}	8×10^{-3}	0.32	acetic acid

^a Calculated using $\epsilon_{\text{max}} = 2.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ (Ref. 5) ^b Determined by double integration of the EPR signal as described in the text. ^c Necessary to effect the blue to green conversion.

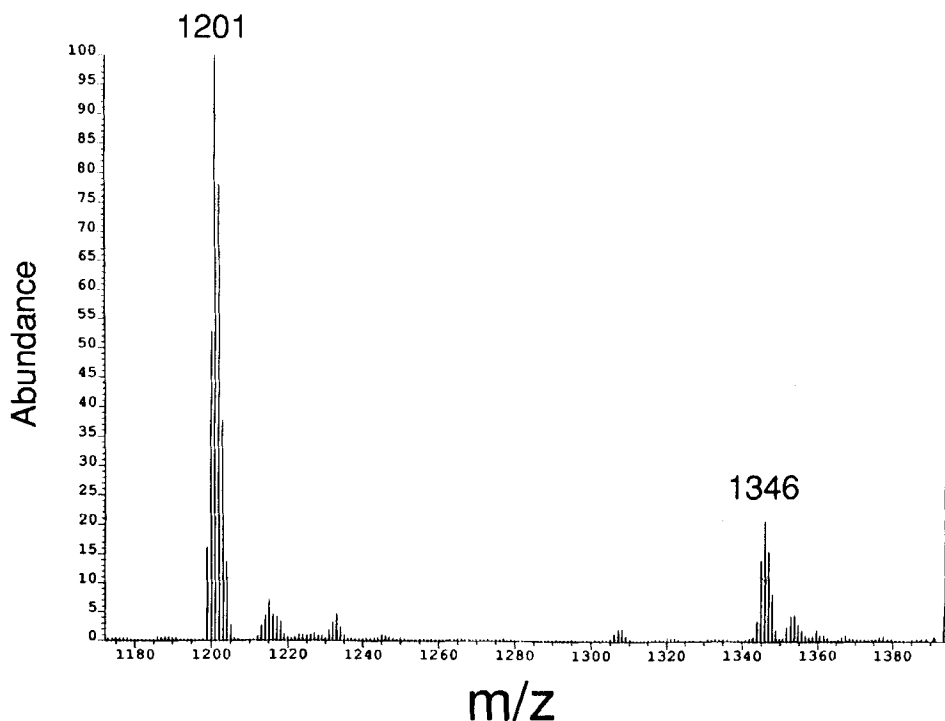


Figure 1 LSIMS of lutetium bisphthalocyanine. Sample prepared for introduction to the spectrometer by taking a DMF solution of the complex and diluting this in an equal volume of 15% (v/v) trifluoroacetic acid in glycerol.

appear very similar to those obtained for complexes of the dianion (Pc^{2-}) with various metal ions.⁶ This is an extremely important observation. Other groups have proposed mechanisms for the observed color changes in lanthanide bisphthalocyanines, involving oxidation-reduction of the phthalocyanine rings, which require the green form to contain one ring as the monoanion radical.^{4,5} Our findings clearly continue to argue strongly against this.

It has been reported that the green forms of lanthanide bisphthalocyanines exhibit a near-infrared absorption at *ca.* 910 nm assignable to a $1e_g(\pi) \rightarrow 1a_{1u}(\pi)$ transition arising from the hypothetical π -radical species.⁵ We have observed this band, which is not present in the spectra of either metal-free phthalocyanine (Figure 3A), or DMF solutions of, for example, thulium bisphthalocyanine (Figure 3C), but is present in the spectra of thulium bisphthalocyanine both in solid form (Figure 3B) and in methylene chloride solution (Figure 3D). The assignment of the transition in question to $1e_g(\pi) \rightarrow 1a_{1u}(\pi)$ was based on the *premise* that the green forms of lanthanide bisphthalocyanines contain monoanion radicals; but this does not follow directly from the electronic absorption data alone in any straightforward, reliable manner. The origins of both this band and the additional one to lower energy remain to be convincingly explained.

In Figure 4B are shown the electronic absorption spectra of blue forms of

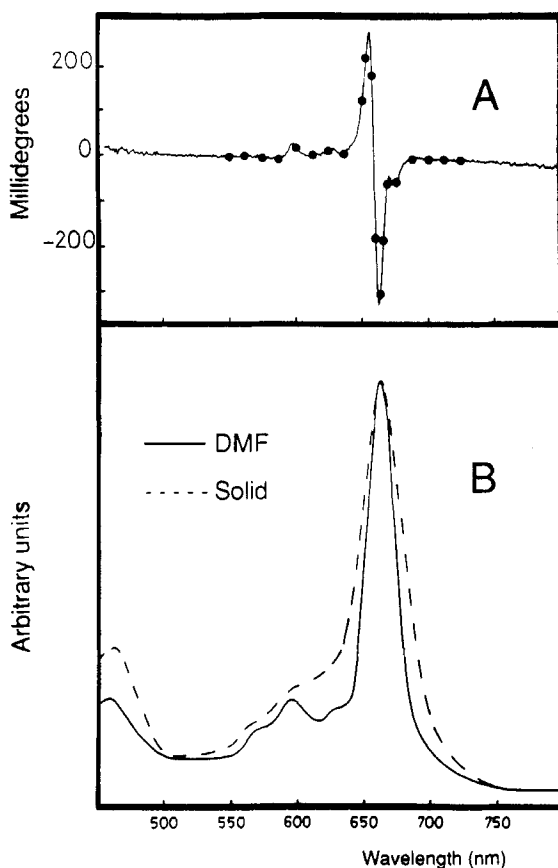


Figure 2 Electronic spectra of the green form of lutetium bisphthalocyanine. *A*: 5.0 T MCD spectrum at 25 K (---) and 4.2 K (•), 9.5 μM in *ca.* 50% (v/v) DMF/NMF, 0.5%(v/v) in trifluoromethanesulfonic acid, 1.0 mm pathlength; *B*: Absorption spectra in DMF solution following trifluoromethanesulfonic acid addition (—) and as prepared by sublimation onto tin oxide coated glass (---).

lutetium bisphthalocyanine in DMF solution (—) and prepared as a solid film (---). The difference between the wavelengths at which the maxima occur we ascribe to H_2O coordination in solution.¹ Otherwise, apart from some broadening in the spectrum of the solid film, leading to loss in resolution of the weaker features, these spectra are very similar. The small shoulder at *ca.* 675 nm on the longer wavelength maximum of the solution spectrum (Figure 4B, —) is an interesting feature, since we do not observe this in the absorption spectra of the blue forms of other lanthanide bisphthalocyanines. The MCD spectrum of the blue form in DMF/NMF solution is dominated by A-terms, being temperature independent and exhibiting derivative-shaped features at wavelengths corresponding to the maxima in the absorption spectrum (Figure 4A). The spectrum is unlike those of substantiated examples of phthalocyanine radicals.^{7,8}

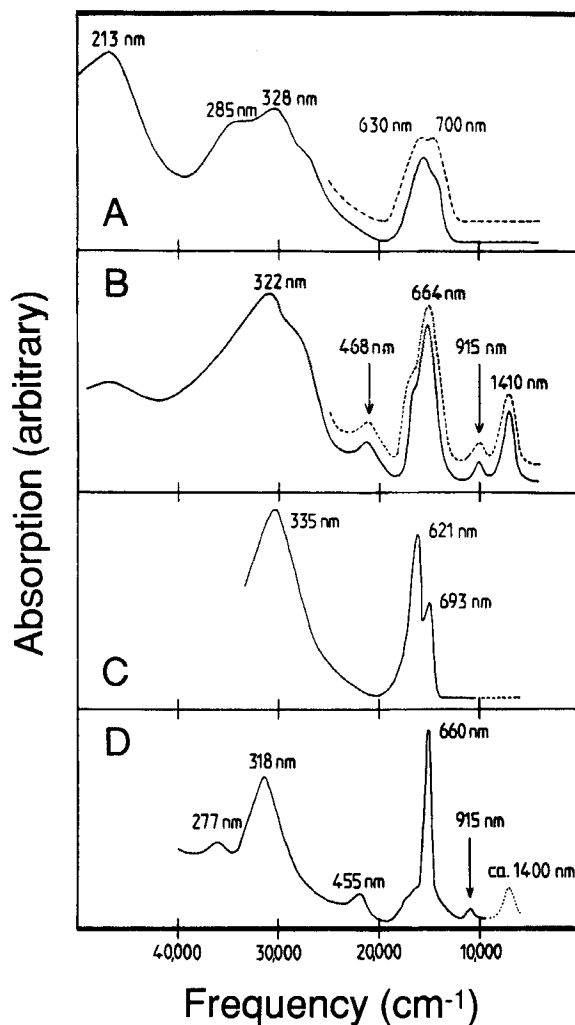


Figure 3 Electronic absorption spectra. *A*: Metal-free phthalocyanine, transmission spectrum of film sublimed onto quartz (—), reflectance spectrum of powder smeared onto filter paper (---); *B*: Solid thulium bisphthalocyanine obtained from purified preparation in DMF solution by drying at 150°C, transmission spectrum of film on quartz (—), reflectance spectrum of powder smeared onto filter paper (---); *C*: DMF solution of the partially redissolved solid thulium bisphthalocyanine; *D*: Methylene chloride solution of the partially redissolved solid thulium bisphthalocyanine.

The electronic spectra of the blue forms of lanthanide bisphthalocyanines have a pronounced split band structure (*e.g.* Figures 3C and 4B). This is the type of feature expected to arise from exciton transfer in aggregates of chromophores and which depends inversely upon the cube of the distance between the centers involved.⁹ Such features have previously been reported for metal free phthalocyanine in the solid form.¹⁰ Thus, it will be instructive to consider the blue forms of these

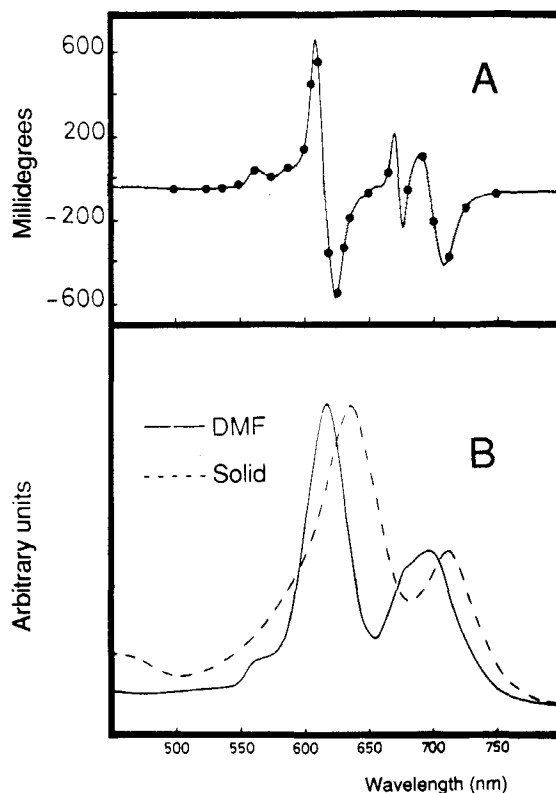


Figure 4 Electronic spectra of the blue form of lutetium bisphthalocyanine. *A*: 5.0 T MCD spectrum at 20 K (—) and 4.2 K (●), 52 μM in 50% (v/v) DMF/NMF at 1.0 mm pathlength; *B*: Absorption spectra as prepared in DMF solution (—) and as a thin film on tin oxide coated glass following electrochemical “reduction” (----).

compounds to behave like a pair of identical phthalocyanine rings, spectrally analogous to a dimer, in which the intervening distance between chromophores is determined by the diameter of the coordinated metal ion. Consequently, plotting the separation in energy units of the two absorption maxima for any given complex against the inverse cube of twice the relevant ionic radius, should give a linear relationship for the series. Using the tabulation of ionic radii given by Lide¹¹ this analysis is presented in Figure 5, where the straight line is a least squares fit to the data. Modern spectrophotometers typically have a wavelength reproducibility quoted as ± 0.3 nm. Consequently, rounding up to the nearest nanometer, the maximum error in the measured *difference* between the positions of two band maxima is ± 1 nm. The error bar on the dysprosium bisphthalocyanine point in Figure 5 indicates this maximum reasonable error. It should be noted that all the data presented in Figure 5 are derived from bisphthalocyanine preparations starting from lanthanide(III) acetates. If analogous results are obtained for preparations containing other potential ligands, such as those starting from chlorides, then the resulting data do not lie on the same straight line as those reported here.

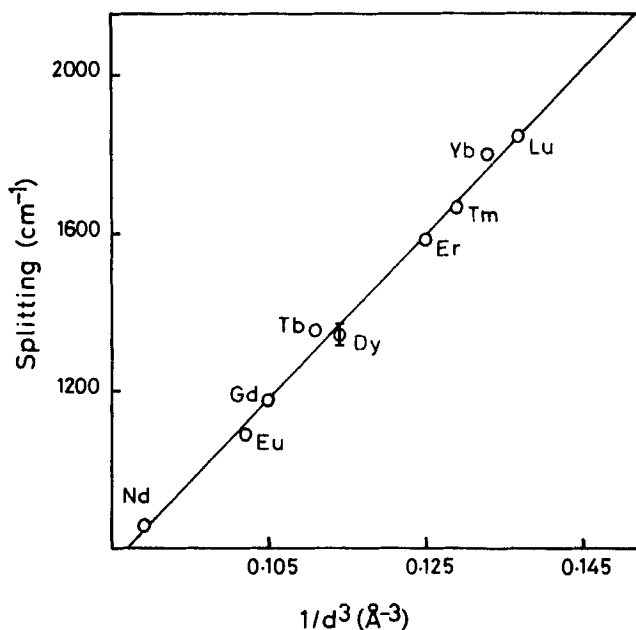


Figure 5 Near-infrared electronic transitions of the blue forms of lanthanide bisphthalocyanines in DMF solution (as purified). Magnitude of band splitting (cm^{-1}) versus inverse cube of the lanthanide ion diameter (\AA^{-3}) where d is twice the ionic radius as given by Reference 11.

CONCLUSION

Apart from the presence of a small amount of contaminant, evident from the *ca.* 675 nm shoulder in the absorption spectrum of the lutetium complex (Figure 4B), the blue forms of lanthanide bisphthalocyanines appear essentially analogous in DMF solution, exhibiting a trend in their spectral characteristics that can readily be understood in terms of the well-known lanthanide contraction (Figure 5). These findings are in keeping with the notion that the blue forms contain two identical dianionic phthalocyanine rings (Pc^{2-}) per complex and would seem to be uncontroversial.

In the case of the green forms, the oxidation levels of the phthalocyanine rings in the complex and hence the overall stoichiometry, are controversial. Both the previous¹ and current LSIMS data (Figure 1) indicate the green species in solution to contain 1 lanthanide ion (Ln^{3+}), 2 dianionic phthalocyanine rings (Pc^{2-}), plus 1 proton. These results seem to be quite unambiguous.

The MCD data of Figure 2A argue strongly that the radical species observed in the EPR of the lutetium compound is not part of the green chromophore *per se*. In particular, the Q band [$1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$] at 660 nm is indicative of the dianion. This transition is expected to be red shifted somewhat in the case of the monoanion radical, but not beyond about 800 nm.^{8,12} Further to the point, the absorption spectra of Figures 2B, 3B and 3D show no evidence for the band at approximately 510 nm characteristic of monoanion radical species.⁸

We cannot categorically exclude the possibility that the EPR detectable radical might be associated with the bisphthalocyanine complex, as an additional ligand perhaps, but the data of Table 1 indicate that this could only be a minority species. Based on the presently available information, the scheme given in the Introduction involving acid-base chemistry, remains a very tenable hypothesis for explaining the observed color changes in these compounds. Furthermore, the previous findings of Walton *et al.*,¹³ who reported that the radical EPR signal associated with the green form of lutetium bisphthalocyanine did not disappear upon "electrochemical oxidation," are in agreement with this suggestion.

The question of the mechanism of the observed electrochromism in lanthanide bisphthalocyanine films remains open. *Some* electrochemical process clearly does take place and furthermore, a number of independent groups have claimed this to be entirely reversible for many cycles following the first oxidation-reduction sweep. In light of the present results, it now appears reasonable to stipulate that the electrochemical process probably involves anodic oxidation coupled to production of protons and cathodic reduction coupled to consumption of protons. The notion that this could simply be something like the electrolysis of coordinated water is difficult to accept given the reversibility of the process. Moreover, despite the variability in the reported experimental determinations, most authors are of the opinion that these processes are one electron transfers.¹⁴ It seems inescapable that a key piece of information regarding the mechanism of the observed electrochromism is still missing, or there is at least one significant error in the literature, since much of the data reported from different laboratories cannot easily be reconciled. We are currently engaged in further work aimed at resolving this issue.

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