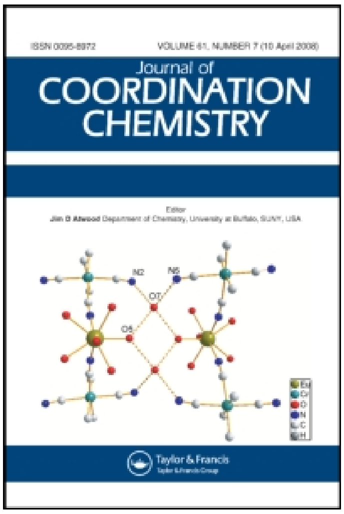

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ELECTRONIC STRUCTURE OF CYANO-BRIDGED DINUCLEAR IRON COMPLEXES

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A series of complexes of formula $[(NC)_5Fe^{II}—NC—Fe^{II}(CN)_4L]^{n-}$, with $L = H_2O$, pyridine, isonicotinamide and 4-cyanopyridine were prepared in aqueous solution by substitution of the corresponding $[Fe^{II}(CN)_5L]^{n-}$ ions into $[Fe^{II}(CN)_5H_2O]^{3-}$. The mixed valent (II, III) and fully oxidized (III, III) complexes were also obtained. The (II, II) complexes were moderately stable toward dissociation into the mononuclear species, but the mixed-valent ions were properly characterized by UV-vis-NIR spectroscopy and electrochemistry. Distinctive intervalence (IV) bands were assigned in the NIR region, with the energy being dependent on the binding properties of L; the IV band energy also correlated with the redox potential at the $[NC—Fe(CN)_4L]$ fragment. By application of the Hush model, a valence-trapped situation was found for the $[(NC)_5Fe^{III}—NC—Fe^{II}(CN)_4L]^{n-}$ ions. The class II behavior shows, however, a value of H_{ab}, the electronic coupling factor, of *ca.* $1600\,cm^{-1}$, indicating a moderate-to-strong communication between the metal centers.

Keywords: Cyanide complexes; Mixed-valence; Iron-cyanide complexes; Cyano-bridged complexes

INTRODUCTION

Cyano-bridged systems are currently used in studies of electronic communication between metal centers [1]. In dinuclear species like $[X_5M—CN—M'X'_5]^n$, we find large versatility for performing systematic

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studies on electron transfer, due to the ability to change the metals and/or coligands, either in symmetric or asymmetric arrangements [2]. A strong emphasis is put in systems containing metals with d^6-d^5 low spin configurations, particularly those of Group 8, Fe, Ru and Os [3].

The related dinuclear complexes with iron-pentacyanide fragments and different L-bridging ligands, $[(NC)_5Fe{-}L{-}Fe(CN)_5]^{n-}$ (L = pyrazine (pz) and other *N*-heterocyclic ligands) have been studied earlier [4]. A characterization of the different complexes with $Fe^{II}{-}Fe^{II}$, $Fe^{II}{-}Fe^{III}$ and $Fe^{III}{-}Fe^{III}$ structures has been made, showing that the mixed-valent species (only prepared in aqueous solution) are poorly stable toward disproportionation into the isovalent states. More recent studies with the pz-bridged "Creutz-Taube" pentacyanide-analogs showed [5–7] that the situation changes dramatically in organic aprotic media, leading to stabilization of the II,III species, approaching a delocalized structure, as found in the Creutz-Taube ion [8].

The above results led us to examine the cyano-bridged complexes, $[(NC)_5Fe{-}CN{-}Fe(CN)_5]^{n-}$, which were studied earlier [9]. Because of its unsaturated nature and small dimensions, cyanide behaves as a better bridge than pyrazine, in spite of its asymmetric character [3]. In the present work, we prepare a set of related complexes in aqueous solution, by introducing a slight asymmetry at one of the iron fragments, through the replacement of a cyanide ligand by another L (either H_2O or a substituted pyridine ligand). We present a spectral (UV-vis) and electrochemical characterization of the complexes in aqueous solution, describing their electronic structure and mechanism of formation, with emphasis on the mixed-valent species.

EXPERIMENTAL

Analytical grade chemicals were used without further purification. The solutions were prepared with previous degassing under argon. $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ and $Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ were prepared according to literature procedures [10, 11]. The complexes $Na_3[Fe(CN)_5pyridine]\cdot 3H_2O$ [12], $Na_3[Fe(CN)_5isonicotinamide]\cdot 3H_2O$ [12] and $Na_3[Fe(CN)_54\text{-}cyanopyridine]\cdot 10H_2O$ [13] were obtained through the reaction of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ with an excess of the appropriate L ligand (hereafter: py, ison and 4-CNpy, respectively) in an aqueous-ethanol solution (90–10%); the mixtures were left for one hour and were precipitated with cold ethanol (or acetone for L = 4-CNpy). Recrystallization was achieved from H_2O-ethanol (L = py, ison) or H_2O-methanol (L = 4-CNpy) solutions. The solids were dried under vaccum over $CaCl_2$.

The stoichiometry of the fully-reduced species was studied by two complementary methods: for the molar-ratio experiments [14], a set of solutions of 1.1×10^{-3} M $Na_3[Fe(CN)_5py]\cdot 3H_2O$ was prepared, in the presence of ascorbic acid, containing variable amounts of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$, in the range 1:0.2 to 1:3. Successive UV-visible spectra were measured up to 40 min after mixing. For the continuous variation method [14], the above reagents were mixed in variable proportions, by fixing the total concentration, 5×10^{-2} M. The pH was 6.0 (ascorbic-ascorbate buffer). UV-visible spectra were obtained with a Hewlett-Packard 8452A instrument, using cells of 0.1 – 1 cm path lengths.

The oxidation of the fully reduced dimers was studied by UV-vis spectral measurements following successive additions of *ca.* 0.04 M H_2O_2 on equimolar solutions ($1-2 \times 10^{-3}$ M) of $[Fe(CN)_5NH_3]^{3-}$ and $[Fe(CN)_5py]^{3-}$ (pH 6.0, phosphate buffer).

The mixed-valence complexes were generated by the following procedures: (a) A 1.0×10^{-3} M solution of $[Fe(CN)_5py]^{2-}$ was prepared by reaction of $[Fe(CN)_5py]^{3-}$ with a stoichiometric amount of MnO_4^-, pH 6.0. To the mixture, the appropriate amount of $[Fe(CN)_5NH_3]^{3-}$ was added to obtain a 1.0×10^{-3} M solution. Successive UV-vis-NIR spectra were recorded up to 1.5 hours after mixing. The mixed-valent compound (see Results) was further treated with permanganate until formation of the fully oxidized dimer. (b) A 1.0×10^{-3} M solution of $[Fe(CN)_5NH_3]^{2-}$ was prepared at pH 6.0. Different amounts of solid $[Fe(CN)_5L]^{3-}$ compounds were added (L = py, ison, 4-CNpy, NH_3) and successive UV-vis-NIR spectra were recorded, up to 1 min – 1 hour after each addition. The NIR spectra were obtained with a Shimadzu 3101 PC instrument.

An adequate characterization of the different species present in the solution equilibria was achieved by using the SPECFIT software package [15]; this is a global least-squares fitting routine for equilibrium and kinetic studies which uses factor analysis decomposition methods [16].

The electrochemical experiments (square-wave voltammetry) [17] were performed with a PAR model 273 potentiostat, using KCl as supporting electrolyte. A vitreous carbon disc, a wire of Ag—AgCl (saturated KCl) and a platinum net were used as working, reference and counter electrodes, respectively.

RESULTS AND DISCUSSION

Formation of the II,II Complexes

The dinuclear complexes in the fully reduced state were obtained through direct mixing of the mononuclear reactants, as shown in Eq. (1) for the pyridine derivative (other L ligands behave similarly):

$$\begin{aligned}&[\mathrm{Fe^{II}(CN)_5NH_3}]^{3-} + [\mathrm{Fe^{II}(CN)_5py}]^{3-}\\ &\quad\Rightarrow [\mathrm{(NC)_5Fe^{II}{-}NC{-}Fe^{II}(CN)_4py}]^{6-} + \mathrm{NH_3}\end{aligned} \tag{1}$$

At pH 6, the time scale of reaction 1 is consistent with aquation of the ammine-complex ($k = 1.6 \times 10^{-2}\,\mathrm{s^{-1}}$, 25.0 C) [18] and further coordination of the pyridine-containing fragment into the $[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-}$ ion through a cyanide bridge. Both the Job plots and the continuous variation method point to a 1 : 1 stoichiometry. The absorption maximum at 366 nm, $\varepsilon = 4.0 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$, is close to the value for the $[\mathrm{Fe^{II}(CN)_5py}]^{3-}$ ion (362 nm, $\varepsilon = 3.7 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$) [12]; these small shifts do not warrant discussion, because significant percentages of the mononuclear species could still be present in the mixtures, according to the estimated formation constant for the dimer, *ca.* $10^3\,\mathrm{M^{-1}}$ [19].

Formation of the II,III Complexes

Oxidation of the products of Eq. (1) with increasing amounts of hydrogen peroxide gave first the mixed-valent complexes (as evidenced by a strong absorption in the NIR region) and then the fully oxidized dinuclear species (as shown by the progressive disappearence of the NIR band and the rise of a new band at *ca.* 560 nm). We also followed an alternative procedure, described by Eq. (2), starting from the Fe(III) ammine-complex:

$$\begin{aligned}&[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-} + [\mathrm{Fe^{II}(CN)_5L}]^{3-}\\ &\quad\Rightarrow [\mathrm{(NC)_5Fe^{III}{-}NC{-}Fe^{II}(CN)_4L}]^{5-} + \mathrm{NH_3}\\ &\quad(\mathrm{L} = \mathrm{py,\ ison,\ 4\text{-}CNpy,\ H_2O})\end{aligned} \tag{2}$$

All complexes show intense bands in the NIR region ($\varepsilon = 3.0-4.0 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$, see below), with wavelength maxima depending on the ligand L. The bands are assigned to intervalence charge transfer (IVCT) processes; they are supressed by the addition of 1 equivalent of potassium permanganate, while new bands develop around 560 nm, corresponding to the (III,III) species [20]. Both the (II,III) and (II,II) species can then be regenerated by adding appropriate amounts of ascorbic acid. For the four studied compounds, reaction 2 developed slowly, with rates depending on the relative concentrations of the reactants and on the nature of L. In the Job experiments, the increase in absorbance of the IVCT band, for both the pyridine- and isonicotinamide derivatives did not reach saturation unless a 5 – 10 fold excess of the Fe(II) complex was added, preventing the determination of the molar absorbances. However, addition of a cationic polyelectrolyte allowed saturation for a 1.5 fold excess.

A factor analysis study showed that the species present in the equilibria were in agreement with Eq. (2), *i.e.*, only one product is in equilibrium with the mononuclear reactants, without the interference of polynuclear species. The equilibrium constants for all the complexes are in the range $1-2 \times 10^3\,M^{-1}$ (Eq. (2)). Moreover, this procedure allowed us to calculate the molar absorbances; the values agree with those obtained from the experiments containing polyelectrolyte.

As shown in Figure 1, intense bands appear also in the UV-visible region, in addition to the IVCT transition, at close energies to those found in the

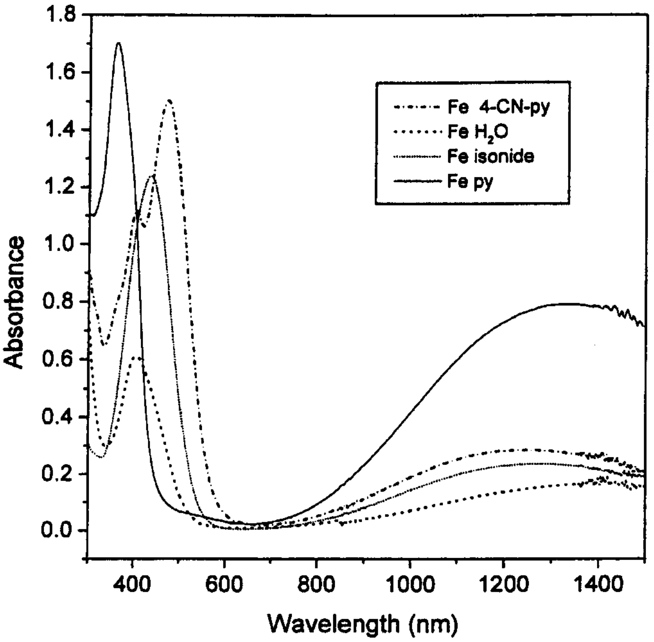

FIGURE 1 Electronic absorption spectra of the mixed-valent $[(NC)_5Fe^{III}—NC—Fe^{II}(CN)_4L]^{5-}$ species for $L = H_2O$, py, isonicotinamide and 4-CNpy.

corresponding mononuclear complexes (except for L = H_2O). We assign them to MLCT transitions from Fe^{II} to the vacant LUMO at the heterocyclic ligand [12]. Thus, we can conclusively assign the Fe^{II} fragment as the one containing the *N*-heterocyclic ligand, while the other fragment corresponds to $[Fe^{III}(CN)_5]^{2-}$ binding to the N-end of bridging cyanide.

A confirmation of the electronic structure is given by the electrochemical experiments, as described in Figure 2 for the pyridine compound. At short times after the mixing of the reactants (Eq. (2)), only one (broad) peak centered at *ca.* 0.47 V is found; this corresponds to an overlap of the peaks associated to the redox potentials of both reactants, which are very similar for L = NH_3 and py [22]. As the reaction proceeds, the height of the initial peak decreases and two new peaks develop at greater (0.59 V) and lower (0.30 V) potentials. This is consistent with the onset of reaction 2. The lower potential corresponds to redox activity at the iron pentacyanide-fragment (bound to the N-end of bridging cyanide), describing the oxidation of the II,II species to the III,II one. The value is significantly smaller than for other $[Fe^{III,II}(CN)_5L]^{2,3-}$ redox couples, which usually cover the range 0.4 – 0.7 V, depending on L [22], and can be traced to the back-bonding ability of the vicinal $[Fe^{II}(CN)_5py]^{n-}$ fragment, which makes the relevant

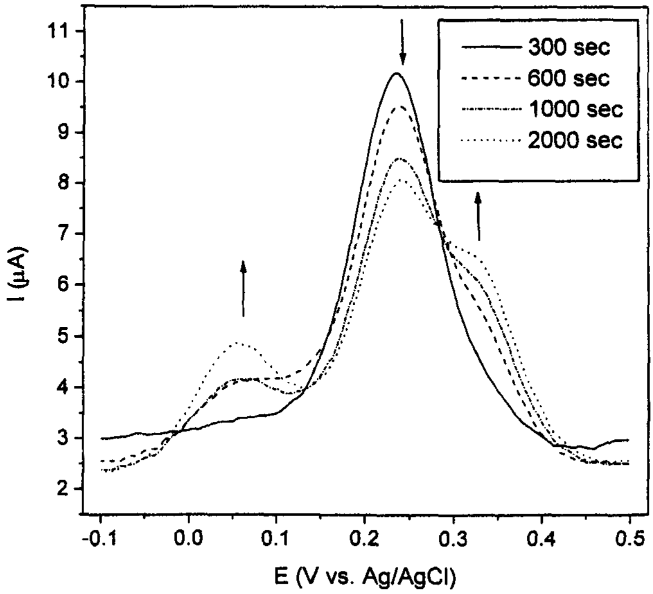

FIGURE 2 Square-wave voltammograms during the reaction between $[Fe^{II}(CN)_5py]^{3-}$ and $[Fe^{III}(CN)_5NH_3]^{2-}$.

$Fe^{II}(CN)_5NC^{3-}$ moiety easier to oxidize. On the other hand, the peak at greater potential relates to oxidation of the III,II species to the III,III one at the $[NCFe^{II}(CN)_4py]^{3-}$ fragment. The shift to a greater value compared to the mononuclear $[Fe^{II}(CN)_5py]^{n-}$ species (0.47 V) [22] reflects the stabilization of the Fe^{II} state because of the inductive influence of the vicinal $[Fe^{III}(CN)_5NC]$ moiety. A similar behavior is found for the dinuclear complexes containing L = ison and 4-CNpy as coligands (Tab. I). Quite significant potential shifts were also found for the heterodinuclear $[(NH_3)_5Ru^{II,III}—NC—M^{II,III}(CN)_5]^n$ complexes (M = Fe, Ru, Os) compared to the redox potential values for the corresponding mononuclear fragments [3]. This is a manifestation of the good electronic communication between the metal centers facilitated by the cyanide bridge (see below).

Analysis of the Intervalence Transition

By using the experimental information from the IVCT band, the electronic structure of the mixed-valence dinuclear complexes can be investigated according to the Hush model [23]. For the py-derivative (Fig. 1, $\nu_{max} = 7.62$ kK; $\varepsilon = 4.3 \times 10^3\,M^{-1}cm^{-1}$), the experimental band-width, $\Delta\nu_{1/2}$, is 4.4 kK, in good agreement with the value predicted by the Hush treatment, 4.2 kK. The value of α^2, a measure of the delocalization in the ground state, is 4.4×10^{-2}, and is related to the electronic coupling factor between the metal centers, H_{ab}, $1.6 \times 10^3\,cm^{-1}$. Similar values are obtained for the other derivatives. The results are consistent with those previously found for related cyanide-bridged complexes [3,4] and show that cyanide is a very efficient coupling bridge, even better than pyrazine; thus, the H_{ab} value suggests a moderate degree of coupling, intermediate between those found for typical Class II complexes (*ca.* $5 \times 10^2\,cm^{-1}$) and Class III complexes

TABLE I Intervalence band properties and reduction potentials for $[(NC)_5Fe^{III}—NC—Fe^{II}(CN)_4L]^{n-}$ mixed-valent species

L	λ_{max} (*nm*)	ν ($10^{-3}cm^{-1}$)	E_1^o (*V vs. NHE*)	E_2^o	*References*
H_2O	1410	7.09	0.34	0.50	this work
py	1310	7.62	0.30	0.59	id.
CN^-	1280	7.81	0.36	0.57	21
ison	1280	7.82	0.30	0.61	this work
4-CNpy	1250	8.00	0.30	0.66	id.
$Mepz^+$	1100	9.09	–	–	4b

E_1^o and E_2^o correspond to redox activity at the $[(NC)_5Fe—NC]$ and $[(NC)_5Fe—L]$ centers, respectively. The estimated uncertainties in the λ_{max} values for the complexes with L = py and ison, were ± 20 nm (as obtained with Specfic calculations). The same can be proposed for L = H_2O and 4-CNpy.

(*ca.* $3.0 \times 10^3\,cm^{-1}$) [8]. Figure 3 shows that the energies of the intervalence bands are linearly correlated with the redox potentials of the $[NC\text{—}Fe^{II,III}(CN)_4L]$ fragments, reflecting the stabilization of oxidation state II when the π-acceptor ability of L is increased.

Mechanism of Formation of the II,III Complexes

It is well known that the $[Fe^{III}(CN)_5L]^{n-}$ complexes are inert toward substitution of the L ligand (rate dissociation constants were estimated as *ca.* $10^{-8}\,s^{-1}$ at 25°C) [24]. Therefore, a direct interchange pathway is unlikely in our reaction conditions for reaction 2. However, a redox-catalyzed mechanism could be operative [24]. We suggest the following scheme, Eqs. (3)–(6), for explaining the onset of reaction 2:

$$[Fe^{III}(CN)_5NH_3]^{2-} + [Fe^{II}(CN)_5L]^{3-} \Rightarrow [Fe^{II}(CN)_5NH_3]^{3-} + [Fe^{III}(CN)_5L]^{2-} \qquad (3)$$

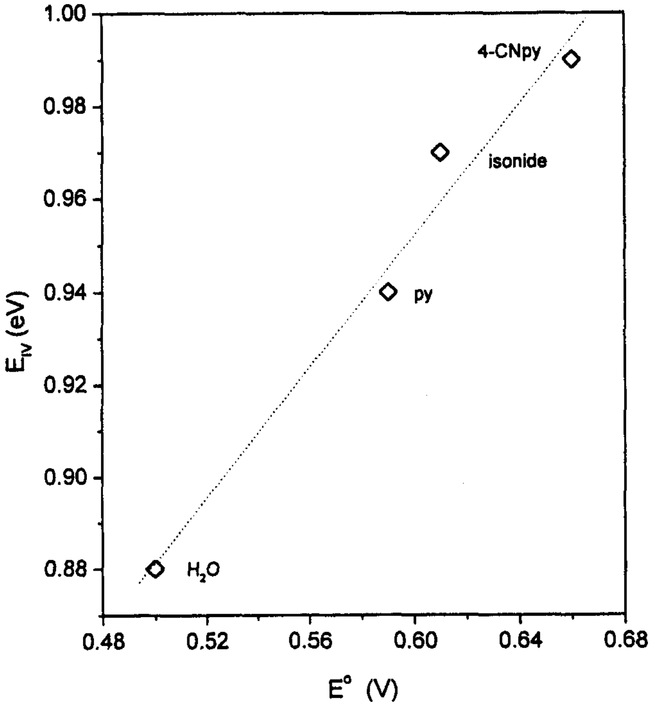

FIGURE 3 Plot of the IVCT band energy, E_{IV}(eV), against the redox potential of the $[NCFe^{II,III}(CN)_4L]$ fragment in the mixed-valent complex, E_2^o(V).

$$[Fe^{II}(CN)_5NH_3]^{3-} + H_3O^+ \Rightarrow [Fe^{II}(CN)_5H_2O]^{3-} + NH_4^+ \qquad (4)$$

$$[Fe^{II}(CN)_5H_2O]^{3-} + [Fe^{III}(CN)_5L]^{2-} \Rightarrow [(NC)_5Fe^{II}{-}NC{-}Fe^{III}(CN)_4L]^{5-} + H_2O \qquad (5)$$

$$[(NC)_5Fe^{II}{-}NC{-}Fe^{III}(CN)_4L]^{5-} \Rightarrow [(NC)_5Fe^{III}{-}NC{-}Fe^{II}(CN)_4L]^{5-} \qquad (6)$$

Reaction 3 is a fast outer-sphere redox equilibration process, which is followed by the slower substitution reactions 4–5 ($k_4 = 1.6 \times 10^{-2}\,s^{-1}$ and $k_5 =$ *ca.* $1\,M^{-1}s^{-1}$) [18, 25]. The product in reaction 5 is the unstable electronic isomer, which evolves to the more stable one (reaction 6) through a fast intramolecular electron transfer process [26]. Although the equilibrium constant for reaction 3 should be increasingly lower for the π-acceptor ligands L, the increase in concentration of the $[Fe^{II}(CN)_5L]^{3-}$ reactant was useful for enhancing the completion of reaction. The polyelectrolyte effect is known to influence significantly the rate of the formation reactions when the reactants are of like charge, as in Eq. (5); however, no significant influence is expected on the rate of dissociative reactions, as in Eq. (4) [27]. The feasability of this kind of catalytic mechanism has been proposed for the coordination of other potentially reductant ligands such as azide on the $[Fe^{III}(CN)_5H_2O]^{2-}$ ion [24].

Conclusions and Outlook

A series of asymmetric dinuclear mixed-valence complexes has been described, $[(NC)_5Fe^{III}{-}NC{-}Fe^{II}(CN)_4L]^{5-}$. Significant changes on the electronic absorption features and redox potentials are found upon dinuclear complex formation, tunable through the selection of L, and showing a moderate-to-strong electronic coupling between the metals (intermediate between Class II and III in terms of the Hush model). The series appears as promising for developing further studies focusing on the changes in the electronic structure and reactivity of L, induced by: (i) specific interactions with acceptor solvents, (ii) coordination of selected fragments with redox activity to the exposed cyanide (*e.g.* $[Ru^{II,III}(NH_3)_5]$), (iii) use of isocyanide instead of cyanide as the communicating bridge. A special effort will be directed to complexes containing $L = NO^+$, looking for significant changes in chemical reactivity upon manipulation of the above mentioned factors.

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