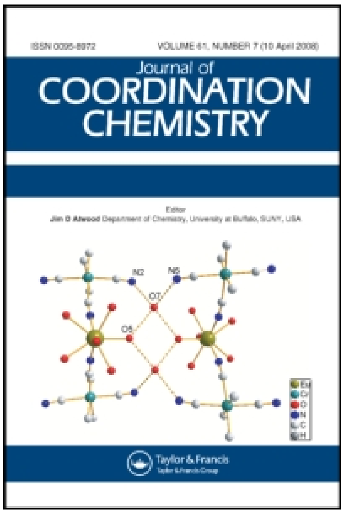

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Alberta E. Le Mire[a]; Misbah Ul-hasan[a]; Don Wiggins[a]; Ian M. Walker[a]; C. E. Holloway[a]
[a] Department of Chemistry, York University, Downsview, Ontario, Canada

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NON-AXIAL MAGNETIC BEHAVIOUR OF LANTHANIDES IN ION PAIRS:— CHARACTERIZATION OF ANIONIC $Ln(O_2CCF_3)_4$ AND $Ln(NCS)_6$ COMPLEXES IN SOLUTION

ALBERTA E. LE MIRE, MISBAH UL-HASAN, DON WIGGINS, IAN M. WALKER†, and C. E. HOLLOWAY

Department of Chemistry, York University, 4700 Keele Street, Downsview, Ontario, Canada, M3J 1P3.

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Paramagnetic anions which posess formal cubic symmetry behave, in an NMR sense, as though they are rhombic to an approaching cation in an ion-pair complex. The two series of complexes $Ln(O_2CCF_3)_4^-$ and $Ln(NCS)_6^{3-}$ have been prepared in order to examine the underlying theory of dipolar shifts in ion-paired systems. Both series show non-axial behaviour. The former anions might, on the basis of IR studies, be expected to be non-cubic in solution, in disagreement with the NMR spectra. The latter exhibit cubic symmetry, as expected.

KEY WORDS: NMR, lanthanides, Infrared spectroscopy, trifluoroacetate complexes, magnetic anisotropy, thiocyanate complexes.

INTRODUCTION

The study of ion-pair structure by NMR spectroscopy is feasible when one of the component ions exhibits magnetic anisotropy which is axially symmetric on a time average.[1,2] In many cases studied to date, the organic cation behaves as the "substrate" or probe of magnetic anisotropy, while the anion, usually paramagnetic, is the "shift reagent". Typical systems are[3] $[n\text{–}(C_4H_9)_4N^+]_2Ln(NO_3)_5$ or[4] $[\phi_3PC_4H_9]$ $[\phi_3PCoI_3]$ dissolved in low dielectric solvents such as chloroform or methylene chloride.

In our most recent article[1], we pointed out a curious fact: paramagnetic complex anions which formally posess cubic symmetry on the basis of the contents of the primary ligand field show obvious *rhombic* symmetry to associated cations in the second coordination sphere.

On the other hand, anions which posess either an axis of symmetry or rhombic symmetry as a result of the contents of the first coordination sphere show effective *axial* symmetry to attacking cations in the second coordination sphere.

In order to test the theories[5,6,7] as they apply to our case, we have prepared and examined NMR spectra of several new salts of organic cations containing paramagnetic lanthanides in anionic form with trifluoroacetate and thiocyanate ligands.

We had hoped to be able to report the preparation of a range of crystalline complexes containing $Ln(O_2CR)_4^-$ or $Ln(O_2CR)_5^{2-}$, since R can be made to vary considerably in size, hence in ability to prevent approach of the organic cation to the lanthanide centre. We were unable to isolate any complexes with R = CH_3 or C_6H_5 but a range of complexes is accessible with R = CF_3

Anionic trifluoroacetate complexes have not been studied extensively to date. The crystal structure of $[\phi_4As]$ $[Co(O_2CCF_3)_4]$ has been reported[8]; the trifluoroacetate ion is unidentate, unlike the analogous nitrate complex and the coordination about cobalt is tetrahedral, as expected. To our knowledge, anionic lanthanide complexes of this ligand have not been previously isolated, although $Ag_2Ge(O_2CCF_3)_6$ has been characterised in the solid state, along with the methylgermanium analogues[9], while the tetrahedral $B(O_2CCF_3)_4^-$ has been studied in anydrous trifluoroacetic acid[10]. Trifluoroacetate as a ligand has been the subject of a recent review[11].

EXPERIMENTAL SECTION

Reagents

Hydrated Lanthanide trifluoroacetates and silver trifluoroacetate were prepared by dissolving the oxides in 50% HO_2CCF_3. Excess water was removed by gentle evaporation in air, and the resulting crystalline solids converted to the anhydrous salts by careful heating in excess trifluoroacetic anhydride.

N-butyl-4-phenylpyridinium (bu-py-ϕ) iodide was prepared as previously outlined.[2] This particular

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†To whom correspondence should be addressed.

cation was chosen for the NMR studies because the resulting complexes are exceptionally well crystallised.

Preparation of Complexes

Complexes of the formula (bu-py-ϕ) $Ln(O_2CCF_3)_4$ are prepared by reacting 2 moles (bu-py-ϕ) I with 2 moles AgO_2CCF_3 in acetonitrile. The silver iodide was removed by filtration and 1 mole of $Ln(O_2CCF_3)_3$ was added. After dissolution had taken place, the solvent was removed and the resulting oil was set aside until partial crystallization took place. Crystallization was completed by addition of H_2CCl_2. The complexes were filtered off and recrystallized from acetone solution by slow addition of ether.

Complexes of the formula Cs $Ln(O_2CCF_3)_4$ can be similarly prepared from 2 moles Cs Cl, 2 moles AgO_2CCF_3 and 1 mole $Ln(O_2CCF_3)_3$ in acetonitrile. The silver salts of formula $AgLn(O_2CCF_3)_4 \cdot 4CH_3CN$ are prepared by direct reaction of the component trifluoroacetates in acetonitrile.

The dibutylammonium salts may be prepared by reaction of dibutylamine, trifluoroacetic acid and $Ln(O_2CCF_3)_3$ in acetone.

The complexes were analyzed for Ln^{+3} by titration with standard EDTA. The data for all complexes may be found in Table I.

TABLE I
Analytical data

Complex	% Ln	
	Calc.	Obs'd
[bu-py-ϕ] La $(O_2CCF_3)_4$	17.29	17.43
[bu-py-ϕ] Nd $(O_2CCF_3)_4$	17.84	18.27
[bu-py-ϕ] Eu $(O_2CCF_3)_4$	18.61	18.48
[bu-py-ϕ] Ho $(O_2CCF_3)_4$	19.89	19.66
[bu-py-ϕ] Tm $(O_2CCF_3)_4$	20.30	20.74
[bu-py-ϕ] Yb $(O_2CCF_3)_4$	20.66	21.64
$[bu_2NH_2]$ Nd $(O_2CCF_3)_4$	19.85	19.49
$[bu_2NH_2]$ Eu $(O_2CCF_3)_4$	20.70	20.75
Cs Nd $(O_2CCF_3)_4$	19.78	19.65
Ag La $(O_2CCF_3)_4 \cdot 4CH_3CN$	16.10	16.40
Ag La $(O_2CCF_3)_4 \cdot 2CH_3CN$	17.78	17.54
Ag Pr $(O_2CCF_3)_4 \cdot CH_3CN$	18.99	18.54
Ag Nd $(O_2CCF_3)_4 \cdot 4CH_3CN$	16.61	16.65
Ag Er $(O_2CCF_3)_4 \cdot 4CH_3CN$	18.76	18.80
	% SCN	
$[(C_6H_5)_3PC_4H_9]_3$ Tb$(NCS)_6$	23.8	23.4
$[(C_6H_5)_3PC_4H_9]_3$ Dy$(NCS)_6$	23.7	23.3
$[(C_6H_5)_3PC_4H_9]_3$ Tm$(NCS)_6$	23.6	23.3
$[(C_6H_5)_3PC_4H_9]_3$ Yb$(NCS)_6$	23.6	23.8

Complexes of the formula $[(C_6H_5)_3PC_4H_9]_3$ $Ln(SCN)_6$ were prepared according to the method of Burmeister, et al.[12] and were recrystallized from dichloromethane by slow addition of ethyl acetate. Thiocyanate was determined by the Volhard method in these laboratories; the data may be found in Table I.

Spectra

^{1}HNMR spectra were recorded in acetone at ambient temperature for the $Ln(O_2CCF_3)_4^-$ complexes at 100 MHz on the Varian HA100 NMR spectrometer. ^{1}H and ^{13}C NMR spectra for the $Ln(NCS)_6^{3-}$ complexes were recorded on the Varian CFT-20 NMR spectrometer operating at 79.54 and 20.0 MHz respectively. The solvent for the ^{13}C studies was H_2CCl_2 containing 10% d^6 acetone for the purpose of maintaining deuterium lock. IR spectra were obtained on nujol and hexachlorabutadiene mulls using the Beckman IR-12 spectrometer.

Results

Characterization of Lanthanide Trifluoroacetate Complexes

All crystalline species which we have identified in this study have the composition (cation) $Ln(O_2CCF_3)_4$. Attempts to prepare compounds of the composition (cation)$_2$ $Ln(O_2CCF_3)_5$ either by increasing the amount of univalent trifluoroacetate in the system, or by employing large divalent cations such as Sr^{2+} have met with failure.

Nonetheless, preparations which employ (cation) (O_2CCF_3) and $Ln(O_2CCF_3)_3$ in 1:1 mole ratio generally result in products which are deficient in cation indicating that an excess of (cation) (O_2CCF_3) is essential to success.

The silver salt is unusual in that it crystallizes as large needles with four moles of coordinated acetonitrile from acetonitrile solutions containing ~10% H_2O; on the other hand, the product from anhydrous acetonitrile is granular.

Infrared spectra give no evidence of coordinated water in these systems; however, the presence of acetonitrile is confirmed by the sharp doublet (CN stretch) at 2280, and 2311 cm^{-1}.

On standing in air, the crystals lose acetonitrile. It is possible to remove a considerable amount of the acetonitrile under vacuum; samples evacuated for 6 hr or more had the composition Ag $Ln(TFA)_4 \cdot$ 1-2CH_3CN (Table I). At the higher temperatures needed to remove the acetonitrile quantitatively, the complexes decompose, presumably *via* decarboxylation.

None of the other salts gave any indication of coordinated acetonitrile. This leads us to suspect that the silver ion in these crystals is present as a tetrahedral solvate, as has been demonstrated for $AgClO_4 \cdot 2NC(CH_2)_4CN$ by Barnhart, et al.[13] An X-Ray investigation of the La complex is in progress.

IR Spectra

The carboxylate C–O stretch region is usually the most sensitive indication of coordination in these complexes. The freshly prepared $Ag\,Ln(O_2CCF_3)_4 \cdot 4CH_3CN$ complexes show the symmetric stretch as a sharp band at 1460 ± 5 cm^{-1}, and the anti symmetric stretch as a broad envelope at 1670 ± 10 cm^{-1}. On successive removal of the coordinated acetonitriles, a band at 1750 cm^{-1} grows in, becoming of comparable intensity to the 1670 band in some cases. The band positions are not dependent on the lanthanide ion.

All other $Ln(O_2CCF_3)_4^-$ complexes show *both* bands in the antisymmetric stretch region. In the $(C_4H_9)_2NH_2^+$ salts, there are three bands in this region at 1640, 1660 and 1760 cm^{-1}.

In the nonsolvated complexes, the symmetric stretch at 1460 cm^{-1} is frequently found as a doublet while in the silver derivative it is a singlet.

The above evidence suggests to us that the trifluoroacetate may be attached to the lanthanide in more than one way in the complex anion. In any event, the removal of coordinated acetonitrile results, in the silver salt, in a change in the coordination about the lanthanide. Unfortunately, the collective experience of other workers[11] indicates that one cannot unambiguously associate IR frequency shifts with specific modes of coordination, such as unidentate, bidentate bridging, etc., so that speculation concerning the attachment of the O_2CCF_3 groups is pointless in this case.

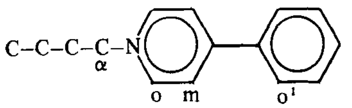
It should be pointed out that the band at 1670 cm^{-1} corresponds closely to that of "ionic" trifluoroacetate in $NH_4O_2CCF_3$ ($\nu_{sym} = 1465\ cm^{-1}$, $\nu_{antisym} = 1667\ cm^{-1}$).[11] This may indicate that the metal-ligand interaction is quite weak in these complexes.

NMR Spectra

The effects of the $Ln(O_2CCF_3)_4^-$ anions on the 1-butyl-4-phenylpyridinum cation resonances may be found in Table II. Several features may be noted. First, the shifts are remarkably small compared to corresponding shifts in the $Ln(NO_3)_5^{2-}$ complexes of the same metals.[1,2] This could be due either to the larger expected size of the anion or to dissociation of the complex anion into diamagnetic $O_2CCF_3^-$ and neutral $Ln(O_2CCF_3)_3$.

Evidence for solvent induced changes in the first coordination sphere come from two sources. The role of the solvent is suggested by the fact that the acetone methyl resonance is shifted from its normal position by up to 0.3 ppm in one case. (Table II)

TABLE II
Cation proton shifts in complexes of $Ln(O_2CCF_3)_4^-$ with [bu-py-ϕ]



Ln	Pyridine o	m	Phenyl o'	Alkyl α-CH_2	Isotropic Shift Ratios o/m	o/α-CH_2	Acetone[c] Shift
La[a]	9.21	8.54	8.04	4.84			
Nd[b]	0.20	0.12	0.04	0.15	1.67	1.33	0.04
Eu[b]	−0.14	−0.07	−0.03	−0.11	2.00	1.27	−0.02
Tb[b]	1.49	0.63	d	1.07	2.37	1.39	0.32
Ho[b]	0.79	0.52	d	0.53	1.52	1.49	0.17
Tm[b]	0.83	0.56	0.50	0.67	1.48	1.24	−0.22
Yb[b]	0.34	0.49	0.70	1.09	0.69	0.31	−0.14

[a] Shift (δ, ppm) in acetone with respect to internal TMS.
[b] Shift of complex (ppm) in acetone with respect to the La salt. Positive sign indicates an upfield shift.
[c] Shift of acetone resonance with respect to diamagnetic value. Positive sign indicates an upfield shift.
[d] Shifts could not be determined due to poor resolution.

Such shifts are not observed in the case of $Ln(NO_3)_5^{2-}$, in which the anions are known not to dissociate in solution.

Solvent participation is further suggested by comparison of solution spectra (visible region) in acetone and acetonitrile with single crystal spectra of $Ag\,Nd(O_2CCF_3)_4\ 4CH_3CN$. Although the band maxima are in many cases the same, the band envelopes themselves are subtly different.

As a consequence of the small shifts the m- and p- phenyl protons were not well resolved in any of our spectra, unlike the $Ln(NO_3)_5^{2-}$ spectra, hence are not reported. The ratio of the isotropic shifts for the pyridine o- and alkyl α – protons, is roughly the same as it was for the $Ln(NO_3)_5^{2-}$ complexes, (Table II), but shows much greater variability down the lanthanide series. The $Yb(NO_3)_5^{2-}$ complex is distinctly anomalous, since the shifts *increase* with increasing distance from the pyridine nitrogen, as can be seen from the ratio of the o- and m- pyridine proton shifts, in Table II.

It is interesting to note that, unlike most lanthanide complexes showing effective axial symmetry in solution[5], there is no change in absolute sign of the shifts at the heavy end of the series, although the europium complex shows the normal behaviour in that it is in the opposite direction to the neodymium complex.

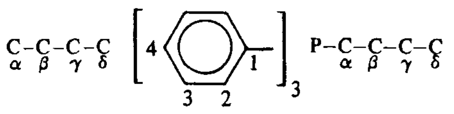
Taken together, the data require us to class the $Ln(O_2CCF_3)_4^-$ series with the cubic anions[1] as exhibiting rhombic symmetry in ion-pairs.

NMR Spectra of $Ln(NCS)_6^{3-}$ Complexes

Complexes of this type have been extensively characterized in H_2CCl_2 and other solvents by Burmeister, et al.[12] The evidence presented by these authors indicates that the complex anions are not appreciably dissociated under the conditions we used in obtaining the NMR spectra. The isotropic shifts may be found in Table III.

Once again, the overall size of the shifts is smaller than in the corresponding $Ln(NO_3)_5^{2-}$ salts. In particular, this series is marked by a general lack of

TABLE III
Isoptropic shifts in salts
$[(C_6H_5)_3PC_4H_9]_3Ln(NCS)_6$



		Isotropic Shift^b					
Ln	Nucleus^a	1	2	3	4	α	δ
Nd	^{13}C	–0.24	–0.30	–0.22	–0.25		
Eu	^{13}C	0.10	0.00	–0.07	–0.10	0.1	–0.3
	^{1}H					0.2	0.0
Tb	^{13}C	0.40	0.35	0.75	0.86	0.2	1.3
	^{1}H					–0.1	0.7
Dy	^{13}C	1.05	0.93	0.74	0.57	2.7	0.6
	^{1}H					2.1	0.2
Ho	^{13}C	0.74	0.56	0.56	0.53	1.6	0.6
	^{1}H					0.8	0.2
Er	^{13}C	–0.60	–0.68	–0.62	–0.76	–0.7	–0.7
	^{1}H					–0.4	–0.1
Tm	^{13}C	–1.09	–1.18	–1.18	–1.46	–1.2	–0.6
	^{1}H					–0.5	–0.1
Yb	^{13}C	–0.80	–0.71	–0.44	–0.53	–1.1	–0.5
	^{1}H					–0.5	–0.1
$Ho(NO_3)_5^{2-}$	^{13}C	–1.84	–1.67	–0.98	–0.69		–0.1
	^{1}H					–5.9	–0.1

[a] All spectra obtained in H_2CCl_2 containing ~10% acetone d^6 on the Varian CFT-20 Spectrometer ^1H data were obtained at 79.54 MHz and ^{13}C at 20.0 MHz.

[b] In ppm with respect to corresponding resonance in $((C_6H_5)_3PC_4H_9)SCN$. A positive sign indicates an upfield shift.

attenuation of shift with increasing distance from the central phosphorus atom. This behaviour contrasts strongly with what was observed with the $Ln(NO_3)_5^{2-}$ salts with the same cation.

In the case of Tm, and even more markedly Tb, the shifts actually increase with increasing distance from the central P atom. Note also that the α- proton shift in this latter case is to low field, unlike the remaining protons. The reversal in the sign of the shifts at the end of the lanthanide series follows the normal order here. On the basis of the data, we must therefore classify the $Ln(SCN)_6^{3-}$ anions as effectively rhombic towards cations in ion pairs.

DISCUSSION AND CONCLUSIONS

In many complexes which possess symmetry less than axial, the NMR spectra can be nonetheless fitted to an axial model. The theory has been outlined in several recent articles.[5,6,7] The dipolar shift ($\Delta\nu/\nu_0$, ppm) is given by

$$\frac{\Delta\nu}{\nu_0} = K_3 \left[\frac{3\cos^2\theta - 1}{r^3}\right] \qquad (1)$$

where

$$K_3 = 1/2[K_1(3\cos^2\alpha - 1) + K_2 \sin^2\alpha \cos 2\beta] \qquad (2)$$

Here θ is the polar angle made by the proton metal vector with a reference (or symmetry) axis L located on the ligands while α and β are the polar and aximuthal angles which L makes with respect to the principal magnetic axes X_1, X_2, X_3 of the complex. K_1 and K_2 are functions of the magnetic susceptibilities of the metal ion.

It is now generally agreed that in order for nuclei to obey this equation, the ligand must either be relatively free to rotate about L, or to experience a large number of different magnetic environments.[7] In this latter case, K_3 is a time average geometric factor which will be different for each metal ion. Since, however, θ is a property of the ligand, $\Delta\nu/\nu_0$ should depend only on the position of the proton relative to L and effective axial symmetry results in the spectrum, giving the same shift pattern for all complexes in a given series of metals.

Cations show effective axial symmetry in the presence of anions such as $Ln(NO_3)_5^{2-}$ and $\phi_3PCoBr_3^-$ which possess a permanent non-cubic crystal field because vector L can assume a large number of different orientations with respect to the permanent magnetic axes on the anion.

Evidence for axial behaviour comes from studies by Donato & Martin[14] on the $(CH_3)_4N^+$ ion in the presence of $Ln(2,6\text{-dipicolinate})_3^{3-}$ anions. The symmetry of the anion is expected to be axial (D_3) in solution. Recent studies[15] on cations in the presence of $Ln(edta)^-$ also point to axial behaviour, although data are available for only Pr and Eu.

The planar bis (benzene-1,6-dithiolato) cobaltate anion possesses a large susceptibility anisotropy, and as expected, appears to show axial behaviour in the NMR spectrum of associated tetrobutylammonium.[16]

Equation (1) breaks down for ion-pairs containing "cubic" anions because the cations do not experience a sufficiently large number of magnetic environments over the lifetime of the NMR experiment when they distort the crystal field of the anion. This has been related to the absence of a permanent principal magnetic axis on the anion.[1]

While effective cubic symmetry and hence rhombic shifts in the NMR is expected in the $Ln(NCS)_6^{3-}$ complexes, since they are analogous to the $LnCl_6^{3-}$ complexes,[1] it is hard to explain in the $Ln(O_2CCF_3)_4^-$ case. These anions might be expected to possess a permanent low symmetry field on the basis of the number of different modes of bonding seen in the infrared.

TABLE IV
Proton NMR shift ratios in bolaform cations
$[C_5H_5NC_nH_{2n}NC_5H_5]\ Ln\ (NO_3)_5$[a]

	Shift Ratio				
Proton	b	c	d	e	f
py-o	1.57	1.33	1.38	1.5	1.57
py-m	0.87	0.80	0.87	0.77	1.02
py-p	0.53	0.49	0.62	0.51	–
α-CH_2	1.00	1.00	1.00	1.00	1.00
β-CH_2	0.52	0.60	0.36	0.53	0.51
γ-CH_2	0.24	0.11	0.24	0.24	0.27
δ-CH_2	0.06	0.11	–0.14	0.07	0.10
ϵ-CH_2	–0.06	–0.03	–0.22	–0.09	0.02
ζ-CH_2	–	–	–	–0.15	–0.04

[a] All spectra obtained at 0.05 M concentration in d^6 acetone at 100 MHz. The data in columns 1–5 represent isotropic shift ratios referred to the α-methylene carbons of the alkyl chain, i.e. $\Delta\nu_i/\Delta\nu_{\alpha\text{-}CH_2}$.

[b] Ln = Tm, n = 10.

[c] Ln = Yb, n = 10.

[d] Ln = Er, n = 10.

[e] Ln = Tb, n = 12.

[f] Data taken from Reference 18 for $[C_8H_{17}NC_5H_4C_6H_5]_2$-$Tb(NO_3)_5$.

A possible explanation is that the $Ln(O_2CCF_3)_4^-$ complexes are arranged much as in the case of $Co(O_2CCF_3)_4^-$, the principle ligand field being tetrahedral, any non cubic component being averaged to zero on the nmr time scale by a process such as restricted rotation around the Ln–O bonds.

Cases in which non axiality in the NMR occurs due to restricted motion of the cations are unknown at present for singly charged cations. This may not, however, be true for bolaform electrolytes.

Data for the system $[C_5H_5NC_nH_{2n}NC_5H_5]$ $Ln(NO_3)_5$ may be found in columns b, c, d and e of Table IV, while in column f, data for the singly charged 1-n-octyl-4-phenylpyridinium (oct-py-ϕ) cation may be found.[18] The shifts at the pyridine protons in the bolaform cations follow closely those for the (oct-py-ϕ) cations in ion pairs. The chief difference between the two systems lies in the behaviour of the central alkyl chain protons. It can be seen that, in the bolaform systems, the position on the chain at which reversal in the sign of the shift occurs is metal ion dependent. Thus the central chain protons do not appear to sense effective axial symmetry, unlike the pyridine rings. The former protons lie in a region of space close to the nodes of the geometric factors; the shifts are thus expected to be exceptionally sensitive to variations in the metal ion susceptibility tensors.

The shift ratios in the central alkyl chain region are expected to be different from those for the singly charged cation since in the case of the bolaform cation, the chain must wrap around the anion in order to coordinate both "head groups" (pyridiniums). The chain in the singly charged cation extends out into the solvent where it experiences considerable motional freedom as can be shown from calculations.

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