# ANTIFERROMAGNETIC COMPLEXES WITH METAL—METAL BONDS

## VI *. TRANSFORMATION OF THE ANTIFERROMAGNETIC METALLACYCLE $(Cp_2Cr_2SCMe_3) \cdot (\mu^3\text{-}S)_2Co(CO)_2$ INTO THE DIAMAGNETIC METALLATETRAHEDRON $Cp_3Cr_3 \cdot (\mu^3\text{-}S)_4Co(CO)$

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## Summary

Heating the antiferromagnetic metallacycle $(CpCr(SCMe_3)CrCp) \cdot (\mu^3\text{-}S)_2Co(CO)_2$ (I) in toluene in the presence of diphenylacetylene yields the diamagnetic tetrahedral cluster $Cp_3Cr_3(\mu^3\text{-}S)_2 \cdot Co(CO)$ (II). Its X-ray analysis shows that the tetrahedron has a $Cp_3Cr_3$ triangle (mean Cr—Cr length is 2.818(4) Å) at the base and a Co(CO) group at the vertex (mean Co—Cr length is 2.658(4) Å). Each of the four S atoms is located on a tetrahedron face producing a pseudo-cubanic structure of Co and Cr atoms (Co—S mean length 2.163(6) Å and Cr—S mean length 2.244(6) Å).

## Introduction

In the course of our study of the reactions of an unusual antiferromagnetic complex with a metal—metal bond, $(CpCrSCMe_3)_2S$ [1] and metal carbonyls, LM(CO), we found when the coordination number of M is 5 (i.e. with $Fe(CO)_5$ and unbridged $Co_2(CO)_8$) the complex loses one tert-butyl group and produces a metallachain $(CpCr(\mu^2\text{-}SCMe_3)CrCp)(\mu^3\text{-}S)_2Fe(CO)_3$ [2] and a metallacycle $(CpCr(\mu^2\text{-}SCMe_3)CrCp)(\mu^3\text{-}S)_2Co(CO)_2$ (I) [3], respectively. Complex I is the first example of metallacycle having antiferromagnetic properties ($-2 J(Cr—Cr)$ 530 cm$^{-1}$) with direct exchange along the Cr—Cr bond (2.610 Å) and with an indirect exchange over two sulfide and one thiolate bridges as well as over the diamagnetic Co$^I$ atom.

In order to prepare new representatives of this interesting class of antiferromagnetic clusters we studied the reaction of complex I with diphenylacetylene $Ph_2C_2$ and tried to replace one or both carbonyl groups at Co with $Ph_2C_2$. Hübel et al. [4] have shown that such reactions afford acetylenic, cyclobutadienic and other ligands. On the other hand, Cotton et al. [5] have revealed an addition of hexafluorobut-2-yn at the Cr—Cr multiple bond in the antiferromagnetic $(CpCrOCMe_3)_2$ complex giving $(CpCrOCMe_3)_2 \cdot (CF_3)_2C_2$, which is also antiferromagnetic.

RESULTS AND DISCUSSION

Our study demonstrated that one of the products from the reaction of I with tolane in boiling toluene is a heteronuclear cluster $(Cp_3Cr_3)(\mu^3\text{-}S)_4Co(CO)$ (II) with a metallic $Cr_3Co$ skeleton:



(I)                    (II)
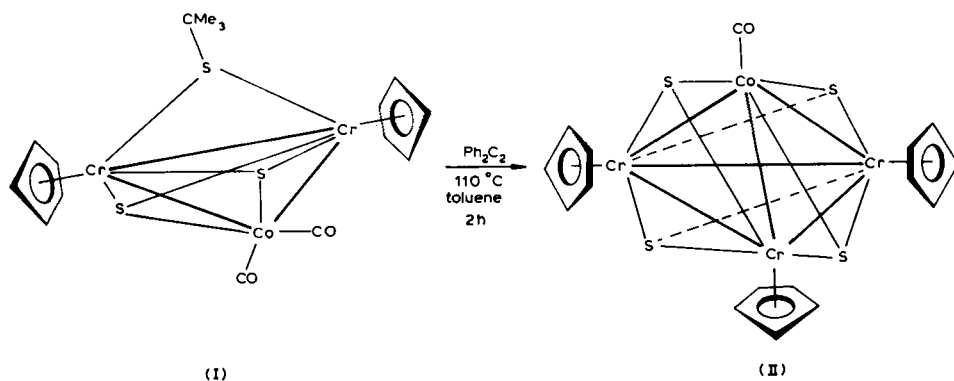
Precipitated from the reaction mixture in the form of brown-black crystals complex II is analytically pure. Its IR spectrum in KBr contains the $C_5H_5$ ligand bands (819, 1022, 1070, 1440 and 3120 cm$^{-1}$) along with a very strong stretching mode of the terminal carbonyl group (1940 cm$^{-1}$). Static magnetic susceptibility data show that the complex is diamagnetic.

To establish unequivocally the structure of II we carried out a complete X-ray analysis of the complex (Fig. 1). The atomic coordinates and anisotropic temperature factors are listed in Table 1, and the bond lengths and angles are shown in Tables 2 and 3, respectively. The molecule of II contains a $Cr_3Co$ tetrahedron which is somewhat distorted by shorter Co—Cr (mean 2.658(4) Å) compared with Cr—Cr (mean 2.818(4) Å) bonds. The tridentate sulfide bridge (bond lengths: Co—S mean 2.163(6) Å, Cr—S(I) mean 2.235(5), Cr—S mean 2.247(6) Å) is situated above the $Cr_3Co$ tetrahedron face, the tetrahedron being part of a pseudo-cubanic structure $Cr_3CoS_4$ with almost planar faces (the dihedral angles between CrSCo and CrSCo as well as CrSCr and CrSCr are 179.2(1)° and 176.5(1)°, respectively). Moreover, each Cr atom is bound to the $\pi$-coordinated $C_5H_5$ ligand (Cr—C mean 2.22(2), C—C(Cp) 1.40(4) Å), while the Co atom is linked to with the linear terminal carbonyl group (Co—C 1.71(2), C—O 1.18(3) Å, < CoCO 179(2)°).

The diamagnetism of II correlates with the electronic saturation of each metal
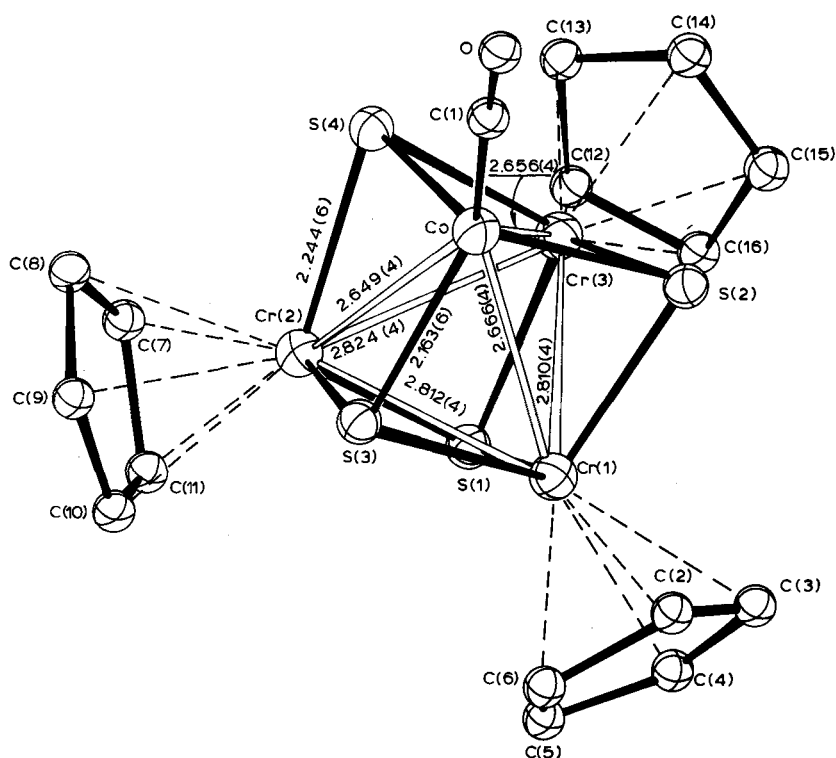
Fig. 1. Structure of complex II.

atom; the 18 electron shell arising by formation of ordinary Cr—Cr and Cr—Co bonds. The Cr—Cr lengths in II are significantly shorter compared with the ordinary Cr—Cr bonds in the $Cr_2(CO)_{10}^{2-}$ dianion (2.97(1) Å), with eclipsed conformation of the equatorial CO groups [6] and in the neutral dimer $[CpCr(CO)_3]_2$ (3.28 Å) [7]. It should be pointed out that repulsion of CO group at different Cr atoms (most pronounced in the latter complex) elongates the Cr—Cr bond. Thus the Cr—Cr distance (2.818(4) Å) in the sterically less hindered complex II may correspond best of all to the "normal" length of an ordinary Cr—Cr bond.

The covalent radius of Cr (1.41 Å) found from the Cr—Cr distance in II is comparable to the value of 1.37 Å obtained by subtracting the covalent radius of Co (1.29 Å) [8] from the Co—Cr length (2.658(4) Å, mean). Although the "theoretical" estimates of the normal Cr—Cr bond length are rather approximate it is interesting to compare them with the Cr—Cr bond lengths in $(CpCrSCMe_3)_2S$ (2.689 Å) [1] and in $(CpCrOCMe_3)_2$ (2.65 Å) [5]. Because of the steric hindrance in these molecules arising from the short $S\cdots C(Cp)$ contacts (3.2 Å) [1] the Cr—Cr distances are longer than the bond lengths determined solely by electronic characteristics. Thus the Cr—Cr bonds in the binuclear complexes are by 0.13 and 0.17 Å shorter than the normal Cr—Cr bonds in II. This could be evidence for multiple character of the Cr—Cr bonds in $(CpCrSCM_3)_2S$ and $(CpCrOCMe_3)_2$ (formally triple and quadruple bonds, respectively), which is in

TABLE 1

ATOMIC COORDINATES ($\times 10^4$)(FOR Co, Cr AND S $\times 10^5$) AND ANISOTROPIC TEMPERATURE FACTORS [a]

| Atom | X | Y | Z | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 17 743(32) | 25 938(15) | 23 185(14) | 3.0(1) | 2.9(1) | 2.5(1) | -0.3(1) | 0.74(9) | -0.3(1) |
| Cr(1) | 41 921(37) | 37 026(19) | 20 347(18) | 3.2(2) | 3.2(2) | 3.1(1) | -0.6(1) | 1.2(1) | -0.3(1) |
| Cr(2) | 22 830(35) | 38 324(18) | 35 043(18) | 2.7(1) | 2.2(1) | 2.6(1) | 0.3(1) | 0.7(1) | 0(1) |
| Cr(3) | 45 951(36) | 24 858(20) | 34 037(18) | 2.6(1) | 3.7(2) | 2.8(2) | 0.6(1) | 0.4(1) | -0.2(1) |
| S(1) | 50 781(59) | 38 845(33) | 34 746(31) | 2.9(3) | 3.8(2) | 3.6(2) | -0.3(2) | 0.8(2) | -0.5(2) |
| S(2) | 42 302(63) | 22 852(30) | 19 121(31) | 3.4(2) | 3.4(2) | 3.1(2) | 0(2) | 1.1(2) | -1.1(2) |
| S(3) | 14 157(59) | 39 381(33) | 20 425(29) | 3.2(3) | 3.3(2) | 2.6(2) | 0.2(2) | 0.3(2) | 0.2(2) |
| S(4) | 19 131(59) | 24 418(31) | 37 454(27) | 3.2(2) | 2.5(2) | 2.9(2) | 0(2) | 0.9(2) | 0.1(2) |
| O | -945(23) | 1 560(13) | 1 506(11) | 7(1) | 11(1) | 5.8(9) | -1(1) | 1.6(8) | -0.7(9) |
| C(1) | 158(30) | 1 980(13) | 1 841(14) | 5(1) | 3.2(9) | 4(1) | -1.2(9) | 3.0(9) | -1.1(8) |
| C(2) | 4 734(56) | 4 927(19) | 1 424(26) | 11(3) | 7(2) | 8(2) | -3(2) | 7(2) | 0(2) |
| C(3) | 4 120(37) | 4 384(24) | 728(18) | 6(2) | 10(2) | 4(1) | -3(2) | 1(1) | 2(1) |
| C(4) | 5 291(55) | 3 738(20) | 738(20) | 10(2) | 7(2) | 6(2) | -2(2) | 6(2) | 0(1) |
| C(5) | 6 572(36) | 3 914(19) | 1 349(24) | 5(1) | 10(2) | 10(2) | -1(1) | 5(2) | -1(1) |
| C(6) | 6 226(42) | 4 635(23) | 1 779(17) | 5(2) | 8(2) | 5(2) | -2(2) | 0(1) | 2(1) |
| C(7) | 728(35) | 5 010(14) | 3 651(13) | 6(1) | 3(1) | 3(1) | 2(1) | -1(1) | 0.2(9) |
| C(8) | 41(27) | 4 295(16) | 4 051(19) | 3(1) | 5(1) | 8(2) | 0(1) | 2(1) | -5(1) |
| C(9) | 1 121(37) | 4 058(13) | 4 780(16) | 7(1) | 3(1) | 5(1) | -1(1) | 4(1) | -0.8(9) |
| C(10) | 2 539(30) | 4 536(14) | 4 788(13) | 5(1) | 5(1) | 2.8(9) | 3(1) | 0.2(8) | -1.4(9) |
| C(11) | 2 217(31) | 5 120(13) | 4 080(16) | 5(1) | 3(1) | 6(1) | 0(1) | 4(1) | -2(1) |
| C(12) | 5 244(33) | 1 743(19) | 4 620(16) | 5(1) | 8(1) | 5(1) | 3(1) | 0(1) | 1(1) |
| C(13) | 6 569(35) | 2 335(15) | 4 586(16) | 6(1) | 5(1) | 6(1) | 3(1) | -1(1) | -1(1) |
| C(14) | 7 286(29) | 2 200(18) | 3 776(18) | 4(1) | 6(2) | 8(2) | 0(1) | 2(1) | 0(1) |
| C(15) | 6 606(29) | 1 487(15) | 3 413(16) | 4(1) | 4(1) | 7(1) | 1(1) | 1(1) | 1(1) |
| C(16) | 5 341(31) | 1 199(14) | 3 862(18) | 6(1) | 3(1) | 9(2) | 3(1) | 0(1) | 3(1) |

a In the form $T = \exp[-\frac{1}{4}(B_{11}h^2 a^{*2} + ... + 2B_{12}hka^*b^* + ...)]$.

TABLE 2

BOND LENGTHS

| Bond | $d(\text{Å})$ | Bond | $d(\text{Å})$ | Bond | $d(\text{Å})$ |
|---|---|---|---|---|---|
| Co—Cr(1) | 2.666(4) | Cr(2)—Cr(3) | 2.824(4) | O—C(1) | 1.18(3) |
| Co—Cr(2) | 2.649(4) | Cr(2)—S(1) | 2.235(6) | C(2)—C(3) | 1.40(5) |
| Co—Cr(3) | 2.656(4) | Cr(2)—S(3) | 2.249(5) | C(2)—C(6) | 1.34(5) |
| Co—S(2) | 2.163(6) | Cr(2)—S(4) | 2.244(6) | C(3)—C(4) | 1.38(5) |
| Co—S(3) | 2.171(6) | Cr(2)—C(7) | 2.25(2) | C(4)—C(5) | 1.34(5) |
| Co—S(4) | 2.154(5) | Cr(2)—C(8) | 2.17(2) | C(5)—C(6) | 1.35(5) |
| Co—C(1) | 1.71(2) | Cr(2)—C(9) | 2.24(3) | C(7)—C(8) | .141(3) |
| Cr(1)—Cr(2) | 2.812(4) | Cr(2)—C(10) | 2.22(2) | C(7)—C(11) | 1.31(4) |
| Cr(1)—Cr(3) | 2.810(4) | Cr(2)—C(11) | 2.21(2) | C(8)—C(9) | 1.38(4) |
| Cr(1)—S(1) | 2.233(5) | Cr(3)—S(1) | 2.237(6) | C(9)—C(10) | 1.36(4) |
| Cr(1)—S(2) | 2.240(6) | Cr(3)—S(2) | 2.259(5) | C(10)—C(11) | 1.41(3) |
| Cr(1)—S(3) | 2.246(6) | Cr(3)—S(4) | 2.249(6) | C(12)—C(13) | 1.41(4) |
| Cr(1)—C(2) | 2.20(3) | Cr(3)—C(12) | 2.19(3) | C(12)—C(16) | 1.43(4) |
| Cr(1)—C(3) | 2.24(3) | Cr(3)—C(13) | 2.27(3) | C(13)—C(14) | 1.41(4) |
| Cr(1)—C(4) | 2.22(3) | Cr(3)—C(14) | 2.21(2) | C(14)—C(15) | 1.34(4) |
| Cr(1)—C(5) | 2.27(3) | Cr(3)—C(15) | 2.25(2) | C(15)—C(16) | 1.35(3) |
| Cr(1)—C(6) | 2.25(3) | Cr(3)—C(16) | 2.20(2) | | |

TABLE 3

BOND ANGLES

| Angle | $\omega(°)$ | Angle | $\omega(°)$ | Angle | $\omega(°)$ |
|---|---|---|---|---|---|
| Cr(1)CoCr(2) | 63.9(1) | Cr(3)Cr(1)S(3) | 98.7(2) | S(1)Cr(3)S(2) | 101.0(2) |
| Cr(1)CoCr(3) | 63.7(1) | S(1)Cr(1)S(2) | 101.7(2) | S(1)Cr(3)S(4) | 100.5(2) |
| Cr(1)CoS(2) | 54.1(2) | S(1)Cr(1)S(3) | 101.2(2) | S(2)Cr(3)S(4) | 100.9(2) |
| Cr(1)CoS(3) | 54.2(1) | S(2)Cr(1)S(3) | 100.7(2) | Cr(1)S(1)Cr(2) | 78.0(2) |
| Cr(1)CoS(4) | 105.3(2) | CoCr(2)Cr(1) | 58.36(9) | Cr(1)S(1)Cr(3) | 77.9(2) |
| Cr(1)CoC(1) | 146.0(7) | CoCr(2)Cr(3) | 57.95(9) | Cr(2)S(1)Cr(3) | 78.3(2) |
| Cr(2)CoCr(3) | 64.3(1) | CoCr(2)S(1) | 95.8(1) | CoS(2)Cr(1) | 74.5(2) |
| Cr(2)CoS(2) | 105.8(2) | CoCr(2)S(3) | 51.8(1) | CoS(2)Cr(3) | 73.8(2) |
| Cr(2)CoS(3) | 54.5(1) | CoCr(2)S(4) | 51.4(1) | Cr(1)S(2)Cr(3) | 77.3(2) |
| Cr(2)CoS(4) | 54.5(1) | Cr(1)Cr(2)Cr(3) | 59.8(1) | CoS(3)Cr(1) | 74.2(2) |
| Cr(2)CoC(1) | 139.3(7) | Cr(1)Cr(2)S(1) | 51.0(1) | CoS(3)Cr(2) | 73.6(2) |
| Cr(3)CoS(2) | 54.8(2) | Cr(1)Cr(2)S(3) | 51.2(1) | Cr(1)S(3)Cr(2) | 77.4(2) |
| Cr(3)CoS(3) | 105.6(2) | Cr(1)Cr(2)S(4) | 98.4(2) | CoS(4)Cr(2) | 74.0(2) |
| Cr(3)CoS(4) | 54.5(1) | Cr(3)Cr(2)S(1) | 50.9(1) | CoS(4)Cr(3) | 74.2(2) |
| Cr(3)CoC(1) | 141.4(7) | Cr(3)Cr(2)S(3) | 98.3(2) | Cr(2)S(4)Cr(3) | 77.9(2) |
| S(3)CoS(2) | 105.7(2) | Cr(3)Cr(2)S(4) | 51.1(1) | CoC(1)O | 179(2) |
| S(2)CoS(4) | 107.2(2) | S(1)Cr(2)S(3) | 101.0(2) | C(3)C(2)C(6) | 109(3) |
| S(2)CoC(1) | 114.8(7) | S(1)Cr(2)S(4) | 100.7(2) | C(2)C(3)C(4) | 105(3) |
| S(3)CoS(4) | 107.0(2) | S(3)Cr(2)S(4) | 101.4(2) | C(3)C(4)C(5) | 109(3) |
| S(3)CoC(1) | 112.9(7) | CoCr(3)Cr(1) | 58.31(9) | C(4)C(5)C(6) | 109(3) |
| S(4)CoC(1) | 108.7(7) | CoCr(3)Cr(2) | 57.73(9) | C(2)C(6)C(5) | 108(3) |
| CoCr(1)Cr(2) | 57.77(9) | CoCr(3)S(1) | 95.6(2) | C(8)C(7)C(11) | 105(2) |
| CoCr(1)Cr(3) | 57.95(9) | CoCr(3)S(2) | 51.4(1) | C(7)C(8)C(9) | 108(2) |
| CoCr(1)S(1) | 95.4(2) | CoCr(3)S(4) | 51.3(1) | C(8)C(9)C(10) | 108(2) |
| CoCr(1)S(2) | 51.4(1) | Cr(1)Cr(3)Cr(2) | 59.9(1) | C(9)C(10)C(11) | 105(2) |
| CoCr(1)S(3) | 51.6(1) | Cr(1)Cr(3)S(1) | 51.0(2) | C(7)C(11)C(10) | 112(2) |
| Cr(2)Cr(1)Cr(3) | 60.3(1) | Cr(1)Cr(3)S(2) | 51.0(2) | C(13)C(12)C(16) | 105(2) |
| Cr(2)Cr(1)S(1) | 51.0(1) | Cr(1)Cr(3)S(4) | 98.3(2) | C(12)C(13)C(14) | 107(2) |
| Cr(2)Cr(1)S(2) | 98.6(2) | Cr(2)Cr(3)S(1) | 50.8(1) | C(13)C(14)C(15) | 107(2) |
| Cr(2)Cr(1)S(3) | 51.3(1) | Cr(2)Cr(3)S(2) | 97.8(2) | C(14)C(15)C(16) | 112(2) |
| Cr(3)Cr(1)S(1) | 51.1(2) | Cr(2)Cr(3)S(4) | 51.0(1) | C(12)C(16)C(15) | 107(2) |
| Cr(3)Cr(1)S(2) | 51.7(1) | | | | |

agreement with the ease of NO and hexafluorobut-2-yn addition to the latter complex [5].

The changes in Cr—Cr bond lengths on going from $(CpCrSCMe_3)_2S$ to I and II (2.689, 2.610, 2.818 Å, respectively) correlate with the CrSCr angle change (74.1°, 69.5° mean, 78.0° mean, respectively). The significantly shorter Co—Cr bond (2.658 Å mean) in II with respect to the Cr—Cr length corresponds to the smaller CoSCr (74° mean) angles with respect to CrSCr.

The mechanism of the formation of II from I is not yet clear and require the study of other reaction products.

## Experimental

All operations are carried out under pure argon atmosphere. Toluene was dehydrated by distilling over Na dispersion under argon.

*(CpCr(SCMe₃)CrCp)(μ³-S)₂Co(CO)₂.* I was prepared by a published method [3]. The IR spectrum was taken on a UR-20 instrument in KBr pellet. The X-ray analysis was performed on a Syntex P21 autodiffractometer ($\lambda$ Mo-$K_\alpha$, $2\theta \leqslant 50°$, $T = 20°C$). 1548 reflections with $F \geqslant 2$ were measured with full matrix iteration. The structure was decoded by direct method. The crystals are monoclinic, $a = 7.976(5)$, $b = 15.749(10)$, $c = 15.057(10)$ Å, $\beta$ 95.52(5)°, $V = 1882$ Å³, $Z = 4$, space group $P21/n$, $R = 0.081$, $R_w = 0.089$.

*Cp₃Cr₃(μ³-S)₄Co(CO).* 0.23 g (1.29 mmol) of $Ph_2C_2$ was added to 0.35 g (0.7 mmol) of I in toluene. The reaction mixture was refluxed for 2 h. The black-brown crystals precipitated were washed with toluene and dried under vacuo. Yield 20%. Found: C, 32.61; H, 3.15. $C_{16}H_{15}CoCr_3OS_4$ calcd.: C, 33.92; H, 2.65%. IR spectrum ($\nu$, cm⁻¹): 532w, 819s, 1022w, 1070w, 1440m, 1940vs, 3120w.

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