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New stable colored complex of Al³⁺ with 1',3',3'trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (BIPS)

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Abstract

Ultraviolet-visible (UV-vis) absorption, flash photolysis, and ¹H and ¹³C NMR spectroscopy were used to investigate the mechanism of formation and structure of complexes in the 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (SP, also well known as BIPS) with Al³⁺ (inorganic salts) in ethanol (EtOH), methanol (MeOH), and in aqueous MeOH solutions. A labile (equilibrium constants \leq 5000 M⁻¹) complex of SP and Al³⁺ with broad absorption band in the UV-vis with $\lambda_{max} = 380$ nm appeared promptly in the presence of an excess of Al^{3+} . The slow formation of a stable complex (SC) between Al^{3+} and two merocyanine (MC) forms of SP with an intensive absorption band at λ_{max} = 430 nm is observed with a yield of 1.0 upon keeping the solutions of these two compounds at constant concentration ratio $[Al^{3+}] \ge [SP]/2$ in the dark. The rate constants of such SC formation were close to the corresponding rate constant of the transformation of SP into MC in the dark $(5.0 \times 10^{-5} - 1 \times 10^{-3} \text{ s}^{-1})$, depending upon the solvent). The photolysis of the SC with visible light ($\lambda >$ 400 nm) results in the total conversion of the SC into SP. The SC forms promptly after the addition of Al³⁺ at concentrations of the same order as those of MC. This method allows detection of $[Al^{3+}]$ to concentrations as low as 50 nM. The kinetics and thermodynamic parameters of the SP and MC reactions and of their complex formation with Al^{3+} are discussed.

KEYWORDS

BISP, complex, inorganic salts of Al, merocyanine, negative photochromism

1 | INTRODUCTION

Spirocompounds are well-known valuable photochromic systems (see for review Durr and Bouas-Laurent^[2]). Their photolysis leads to the highly colored merocyanine (MC) intermediates. A number of spirocompounds undergo efficient thermal opening of a spiro cycle with the formation of a corresponding MC as well. Scheme 1 presents transformation of a specific spirocompound, namely,

The sensitivity of the photochromic properties of spirocompounds towards solvent and different additives makes them valuable material for different applications, such as bio-imaging, sensors, logic gates, and molecular switches.^[3-8] Specifically, such compounds have been studied as dark or light-controlled chemosensors for metal ions^[8-11] and Al³⁺ in particular.^[8-15] There is always a demand for reliable and facile sensors for salts and compounds of Al.^[16-20]



SCHEME 1 . 1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'indoline] (SP, well known as BIPS), which was studied in the present communication.

The focus of our research was the kinetics and mechanism of complex formation of Al^{3+} with 1',3',3'trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (SP)/MC in ethanol (EtOH), methanol (MeOH), and MeOH/H₂O mixtures (up to 0.5 mole fraction). Previous studies of spirocompounds as chemosensors for Al^{3+} demonstrated the formation of relatively labile complexes (LCs) MC- $Al^{3+.[12-15]}$ The instability of these complexes limits the application of such systems. In the present work, the stable complex (SC) of Al^{3+} with two MC of SP is described.

Aluminum salts are known as Lewis acids. Al salts of strong acids undergo hydrolysis in the water-containing alcoholic solutions leading to acidic media. It is known that strong acids are able to protonate MC of SP and essentially stabilize it that way.^[21–23] Therefore, it is of interest to compare the reactivity of Al³⁺ and H⁺ towards SP/MC.

Despite its apparent simplicity, Al³⁺ produces multiple hydro and aqua complexes in the presence of water and polynuclear Al^{III} soluble compounds as well.^[24,25] These multiple species are in dynamic equilibrium, which depends on pH, the concentrations of salt, and other factors. The irreversible process of complex formation of the sensor with Al³⁺ is required for the quantitative measurements of the concentration of a dissolved salt of Al.

2 | EXPERIMENTAL

2.1 | SP

SP was prepared as previously described in.^[26] Purity (\geq 98%) was confirmed by high-performance liquid chromatography (HPLC). SP structure was verified by ¹H and ¹³C NMR (see Section 3.5).

2.2 | Other reagents

Chemicals Al $(NO_3)_3 x 9 H_2O$, AlCl₃x 6 H₂O, hydrochloric acid (HCl) 37 wt.%, and solvents MeOH and EtOH were sourced from Sigma-Aldrich. They were used as received. Solvents were of a spectral grade. Water-bidistillate was

used. The solvent used for NMR (CD_3OD) had 99.8 atom % D and 0.2 vol. % H₂O. Its composition was confirmed by NMR.

2.3 | NMR

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III-500 spectrometer with the working frequency of 500 and 126 MHz, respectively. Chemical shifts are given relative to tetramethylsilane. CD₃OD was also used as an internal standard (δ 3.35 and 49.3 ppm, for methyl groups in ¹H and ¹³C measurements, respectively). We used COSY spectroscopy for attribution of NMR signals (a COSY spectrum is not presented). The concentration of SP in CD₃OD in all NMR measurements was 6.0 × 10⁻² M; the concentration of Al salts varied from 1.0 × 10⁻² M to 0.3 M.

2.4 | Chromatography

Preparative adsorption column chromatography was performed on Kieselgel 60 (0.040-0.063 mm, Merck) or on HPLC-chromatograph Smart Line 1000 (Knauer).

2.5 | UV-vis absorption and fluorescence spectroscopies

Ultraviolet-visible (UV-Vis) absorption spectra were measured in quartz cells with optical paths length l=10 mm on a Shimadzu UV-2140PC spectrophotometer. The kinetics of the photocoloration and photodecoloration processes were taken on a fiber-optic set spectrophotometer HR-2000 and spectrofluorimeter USB4000-FL (Ocean Optics, USA) in a quartz cells (l=10 mm). The irradiation was performed with the UV ($270 \le \lambda \le 370$ nm) or vis ($\lambda \ge 400$ nm) light of an LC8 lamp (Hamamatsu, Japan, irradiance 180 mW/cm²). An appropriate light filters were used. The samples were stirred during irradiation.

The fluorescence measurements were performed on a Fluorat-02 Panorama spectrofluorimeter (Lumex, Russia).

2.6 | Flash photolysis

A conventional flash photolysis setup with UV-vis absorption registration was used.^[27] The transient absorption spectra and the kinetics of formation and decay of intermediates were measured in the time range $t \ge 10 \ \mu s$ in the spectral region $400 \le \lambda \le 800 \ nm$. The photoexcitation of the SP solutions $(5.0 \times 10^{-5} \ M)$ was performed through the appropriate light filter $(270 \le \lambda$ \leq 370 nm). The quartz cuvette with optical paths l= 20 cm was used in these experiments.

All measurements were performed at room temperature.

3 | RESULTS AND DISCUSSION

3.1 | Photochromism and thermochromism of SP

Absorption spectra and photochromic properties of SP/MC in alcohol solutions have been reported.^[21,22,26,28,29] The long-wavelength band in the absorption spectrum of SP has $\lambda_{max} = 295$ nm with extinction coefficient $\epsilon_{295} = 6.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (see Figure 1a). Additionally,

the MC absorption band with $\lambda_{max} = 550$ nm (Figure 2) is barely seen in nonpolar

solvents but can be observed in relatively concentrated alcoholic solutions in the dark.^[21,22] It is formed in the reaction ((1)). The extinction coefficient of MC absorption band with $\lambda_{max} =$

$$SP \rightleftharpoons_{k_{-1}}^{k_1} MC$$
 (1)

550 nm was estimated as a six-fold of that of SP $\varepsilon_{295.}^{[28]}$ Based on this value the equilibrium constants, $K_1 = k_1/k_{-1}$ were calculated (see Table 1):

It is worthwhile mentioning that a relatively small shoulder was found at λ =430 nm in UV-vis spectra of SP in MeOH as well as in H₂O/MeOH mixtures and it was assigned to a small amount of protonated MC



FIGURE 1 Ultraviolet-visible absorption spectrum of SP (0.1 mM) in MeOH (*a*). Absorption spectra of the same solution were measured promptly after addition of different concentrations of Al $(NO_3)_3 \times 9H_2O$ (in mM): 0.2 (b), 0.4 (c), 0.9 (d),1.9 (e), 3.8 (f), and 7.3 (g). OD here and below stands for optical density. The role of Al³⁺ is discussed in Section 3.2 below



FIGURE 2 Long-wavelength part of ultraviolet-visible absorption spectrum of 1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (0.01 M) in MeOH/H₂O mixtures with mole fraction of water: (a) 0, (b) 0.022, (c) 0.0435, (d) 0.083, (e) 0.12, (f) 0.15, (g) 0.189, (h) 0.25, (i) 0.31, (j) 0.409, and (k) 0.47

(MCH⁺) (Figure 2).^[21,22] The intensity of this band is negligible in ethanol (EtOH).

The flash photoexcitation of SP results in the formation of an additional amount of MC followed by its thermal relaxation to the equilibrium concentration (Equation (1)). The study of decay kinetics of this MC leads to the values of k_{-1} , which allows, in turn, the determination of $k_1 = K_1 \times k_{-1}$ (Table 1). The obtained values of these constants are similar to those reported in other polar solvents to within 1 order of magnitude.^[28,29]

An increase of the polarity of alcohol under transition from EtOH (dielectric constant $\varepsilon = 24$) to MeOH ($\varepsilon = 33$) leads to a shift of equilibrium ((1)) to the right mostly due to the increase of k_1 (Table 1).

The increase of water content in the MeOH/H₂O mixture results in the increase of the relative intensity of MC absorption at $\lambda_{max} = 550$ nm as well as MCH⁺ at $\lambda = 430$ nm demonstrating the shift of the equilibrium ((1)) to the right side (Figure 2). Figure 3 presents plots of k_{-1} and k_1 vs. water content.

An increase of concentration of highly polar water leads to the increase of the dielectric constant of MeOH/H₂O mixture that stabilizes zwitterion MC and leads to the pronounced increase in the rate of MC formation (see k_1 in Table 1 and Figure 3). On the other hand, the simultaneous decrease of k_{-1} is relatively insignificant.

The dependence of dielectric constant ε of a mixture MeOH/H₂O on H₂O mole fraction is linear.^[30] At the same time, similar plots of the constants, K_1 , k_1 , and k_{-1} upon H₂O mole fraction, essentially deviate from the linear dependence and nicely fit to exponentials. That fact

TABLE 1 Rate constants k_1 , k_{-1} , k_{SC} , k_{MCH}^+ , and the equilibrium constant K_1 , K_2 , K_3 , and K_5

LEVIN ET AL.

| Solvent | $K_1 	imes 10^{4a}$ | k_{-1}, s^{-1a} | $k_1 \times 10^4$, s ^{-1 b} | $k_{\rm SC} 	imes 10^4$, s ^{-1a} | $k_{\mathrm{MCH}}^{+} \times 10^{4},$ s ^{-1a} | $K_2 \times 10^{-2}$, M ^{-1a} | $K_3 \times 10^{-2}$, M ^{-1 a} | $K_5 \times 10^{-5}$, M ^{-1a} |
|---|---------------------|-------------------|---------------------------------------|--|---|---|--|---|
| EtOH | 1.1 | 0.48 | 0.53 | 0.66 | - | 7.1 | - | - |
| МеОН | 5.1 | 0.45 | 2.3 | 2.5 | 1.4 | 49 | 21 | 1.8 |
| MeOH/H ₂ O (mole fractions 0.80:0.20) | 11 | 0.29 | 3.3 | 3.9 | 2.9 | 3.1 | 1.6 | 0.24 |
| MeOH/H ₂ O (mole fractions $0.58:0.42$) | 44 | 0.19 | 8.4 | 8.9 | 7.1 | 0.8 | 0.4 | 0.10 |

Note. The K_1 -value was obtained from the band intensities of MC at $\lambda_{max} = 550$ nm and the known concentration of SP assuming the corresponding extinction coefficient to be 3.6×10^4 M⁻¹ cm^{-1.[28]}

^aDetermination error 10%.

^bDetermination error 20%.



FIGURE 3 Plots of the rate constant k_{-1} and k_1 vs. mole fraction of water in MeOH. The solid lines are a fit to an exponential. All experiments were done at [SP] = 10 mM. The figure also presents rate constants k_{sc} (squares) and k_{MCH+} (triangles) vs. water content. The latter data were obtained under [SP] = 5.0×10^{-5} M and [Al (NO₃)₃ × 9H₂O] = 2.5×10^{-5} M or [HCl] = 1 mM. The triangles and squares correspond to the right ordinate axis. Section 3.3 below explains the meaning of k_{SC} and k_{MCH+}

implies the linear dependence of the corresponding equilibrium (1) free energy ΔG_1° and activation free energies $\Delta G_1^{\#}$, $\Delta G_{-1}^{\#}$ on the mole fraction of MeOH/H₂O mixture.

It was found that the spectral and kinetic properties of MC forms of some other spiro compounds are affected by solvent polarity, specific solvation ability (hydrogen bonding), and by other properties.^[31] However, in the case of SP/MC in MeOH/H₂O mixture, the linear experimental plots of the G_1° , $\Delta G_1^{\#}$, and $\Delta G_{-1}^{\#}$ on the mole fraction indicate the absence of essential preferential solvation effect by MeOH or H₂O (see Supporting Information S2 also).

In this work, we alternatively decided to look for correlations between K_1 and the known Dimroth-Reichard parameter E_T of a solvent.^[1,32,33] We got a dependence of log K_1 or ΔG_1° in MeOH/H₂O mixture, see Figure 4:

 $(G_1^{\circ} \text{ were calculated using van't Hoff equation.}^{[1]})$ One can see a systematic decrease of ΔG_1° (growth of K_1) with

the E_T increase. The dependence is not a straight line (Figure 4). A "forceful" fit into the linear law gives a slope of -1.0. We conclude that E_T quite satisfactory describes the observed dependence of K_1 upon solvent composition.

However, the longest wavelength of MC in solvents does not correlate with E_T despite the fact that both Dimroth-Reichard's betaine molecule and MC are both conjugated zwitterions. We observed the maximum hypsochromic shift in MC band as 5 nm, under transition from MeOH to MeOH/H₂O; mole fraction of H₂O is 0.5. Such change of the solvents is characterized by E_T change from 55.8 to 57.3 (kcal/mol), which is a noticeable difference. At the same time, such shift in MC band from 555 to 550 nm is a change in the light energy from 51.40 to 51.85 kcal/mol. The latter energy change is very small.

The longest wavelength of betaine is a charge-transfer (CT) transition.^[34] However, the longest waveband of MC seems to be of some other nature. In particular, MC has insufficient conjugation for CT transition compared with a conjugated system of betaine (see Scheme 1).



FIGURE 4 Dependence of Δ G₁° in MeOH/H₂O mixture upon E_T parameter of the mixture (see the text). E_T values are borrowed from Dawbler et al^[32]

3.2 | LC of SP and Al $^{3+}$

The formation of a LC of the closed form of SP and Al³⁺ was observed by UV-Vis absorption in alcoholic solutions as well as in MeOH/H₂O mixtures promptly after the mixing of solutions of Al³⁺ and SP. LC is characterized by the broad absorption band at $\lambda_{max} = 380$ nm (see Figure 1). The plots of UV-vis absorption at $\lambda_{max} = 380$ nm (OD₃₈₀) vs. [Al³⁺] (Figure 5) are characteristic for the equilibrium (2):

$$SP + AI^{3+} \rightleftharpoons^{K_2} SP \underset{LC}{-} AI^{3+}$$
 (2)

A kinetic treatment of Scheme 2 leads to Equation I where ε_{380} is the extinction coefficient

$$2[LC] = (2 \text{ OD}_{380}/\epsilon_{380}l) = [Al3^+]_0 + [SP]_0 + 1/K2 - \\ \times ([Al^{3+}]_0 + [SP]_0 + 1/K2)2 - 4[Al^{3+}]_0[SP]_0)^{0.5},$$
(I)



FIGURE 5 Plots of OD_{380} vs. [Al $(NO_3)_3x9H_2O$] in EtOH (a) and MeOH (b). (c) Plot of OD_{380} vs. [HCl] for equilibrium ((3)), see below. [SP]= 0.1 mM in all solutions. The solid lines are the fits to equation (I)

of LC at $\lambda_{\text{max}} = 380$ nm, *l*- optical path; $[\text{Al}^{3+}]_{\text{o}}$ and $[\text{SP}]_{\text{o}}$ are the initial molar concentrations. The values of K_2 obtained from the fits of plots of OD_{380} vs. [Al $(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$] using Equation I are presented in Table 1. The increase of organic solvent polarity stabilizes LC. The value of K_2 for MeOH is higher than that for EtOH (Table 1). However, K_2 essentially decreases upon the addition of water (see Table 1).

A similar absorption with $\lambda_{max} = 380$ nm appears upon addition of an excess of HCl to SP solutions (Figure 5c). When compared with the similar band observed in the presence of Al³⁺, only insignificant differences can be identified. These minor differences are the extinction coefficients and the form of a shoulder near $\lambda = 340$ nm. This band apparently belongs to a protonated SP (SPH⁺) formed in the acid-base equilibrium ((3)).^[21,22]

The K_3 values (Equation (3)) obtained in MeOH and in MeOH/H₂O mixtures are smaller than those

$$SP + H^+ \stackrel{K_3}{\rightleftharpoons} SP H^+ \tag{3}$$

of K_2 for Al³⁺ (see Table 1). This finding can be attributed to the three times larger positive charge on Al³⁺.

 Al^{3+} and H^+ can associate with the unshared pair of electrons of either O or N atoms of SP. Resonance Raman studies performed elsewhere^[22] led to the conclusion of protonation at the Natom of SP at relatively low concentration of HCl in MeOH. The water molecules form hydrogen bonds with N atom of SP, thus making this atom with unshared pairs of electrons screened off for Al^{3+} and H^+ .

The addition of concentrated HCl is accompanied by the addition of a minor amount of water in solution. However, at the highest used [HCl], the added amount of water is smaller than 0.02 mole fraction. Such low amounts do not affect the observed spectral and kinetic properties of the studied systems. The same holds true for Al salts, which contain coordinated water (crystallohydrates).



SCHEME 2 Chemical shifts (ppm) in NMR spectra of SP (top) and SC (bottom) in CD_3OD of ¹H NMR (two left structures) and ¹³C NMR (two right structures). Here n=1/2



FIGURE 6 Ultraviolet-visible absorption spectra of a solution SP $(3.0 \times 10^{-5} \text{ M})$ and Al $(NO_3)_3$ $(1.5 \times 10^{-5} \text{ M})$ in EtOH. The spectra were taken with every 10 min for the first hour after solution preparation, then every 30 min for the next 4 h, then every hour for the next 3 h. One final spectrum was taken at 24 h. One can see an isosbestic point testifying to quantitative conversion of SP into SC

3.3 | Slow formation of a SC of two MC with Al^{3+} and the protonated form of MC (MCH⁺)

The formation of a SC of two MC and Al³⁺ was observed by UV-vis absorption spectroscopy in alcohols and MeOH/H₂O mixture. In this section, the solutions with low [SP] = 1.0×10^{-5} - 1.0×10^{-4} M and with comparable to [SP] concentration of Al³⁺ will be considered. The absorption spectra of promptly prepared solutions change with time. The spectrum demonstrates growth of absorption at $\lambda_{max} = 430$ nm and the concurrent decrease of absorption at $\lambda_{max} = 295$ nm, see Figure 6:

The plots of the absorption at $\lambda_{max} = 430$ nm (OD₄₃₀) vs. time nicely fit with exponential function (Figure 7). The amount of SC formed and the rate of SC (OD₄₃₀) growth (k_{SC} in Table 1) are

independent of $[Al^{3+}]$ in the range $[Al^{3+}] \ge [SP]/2$. The final spectrum does not change during at least one week. The k_{sc} values are very close to the rate constant k_1 (Equation (1)) of the opening of SP into MC (see Table 1 and Figure 3). The limiting stage of SC production in the dark is the formation of MC. A similar conclusion was made in Minkovska et al^[12] on the formation of complexes of metal cations and of Al³⁺ in particular with other spirocompounds. A decrease of a ratio $[Al^{3+}]/[SP]$ to less than $\frac{1}{2}$ leads to a corresponding decrease of the amount of the formed [SC].



FIGURE 7 Plots of OD_{430} vs. time for a solution SP/Al^{3+} in MeOH (a); MeOH/H₂O (0.2 mole fraction) (b); MeOH/H₂O (0.42 mole fraction) (c). We used [SP] = 5.0×10^{-5} , [Al³⁺] = 2.5×10^{-5} M. The solid lines are a fit to the exponential functions

Thus, SC is a stable compound with stoichiometry of two MC and one Al^{3+} , which is formed overall in reaction (4) (see Sections 3.4 and 3.5 below). In these experiments, the extinction

$$2MC + Al^{3+} \rightarrow SC \tag{4}$$

coefficient of MC, which is a constituent of the SC, was estimated as $\epsilon_{430} = 3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

NMR experiments confirm the structure of SC as $2MC:1Al^{3+}$ on the molar basis and demonstrate that

 Al^{3+} forms the SC by an attachment of Al^{3+} to the phenolate moiety of MC (see Section 3.5 below).

The addition of water accelerates both the formation of MC from SP and that of SC to the same extent (see values k_1 and k_{sc} in Table 1 and Figure 3) despite the fact that the equilibrium concentration of LC is significantly reduced by the presence of water (see Table 1 and Section 3.2). Apparently, LC is not necessarily involved as a precursor in the formation of the SC. Water has no effect on the final amount of SC formed even under molar ratio 2SP: $1AI^{3+}$. The latter fact means that reaction (4) is irreversible at concentrations of water up to 0.5 mole fraction.

The formation of similar absorption with $\lambda_{max} = 430$ nm is observed in solutions of SP containing HCl in the dark.^[21,22] However, in the case of H⁺, the equilibrium (5) is observed

$$MC + H^+ \rightleftharpoons MCH^+$$
 (5)

 $^{[21,22]}$ It is necessary to have an excess of HCl in order to reach the maximum possible OD_{430} and the complete conversion of SP into SPH⁺. The value of the extinction coefficient of MCH⁺ obtained for the samples with complete conversion of MC into MCH⁺ coincides with that of SC and with the value estimated from the spectrum of MCH⁺ presented in Yoda et al.^[21] The rate constants of MCH⁺ formation (k_{MCH+} in Table 1 and Figure 3) obtained from the curves similar to those presented in

Figure 6 are slightly smaller than k_1 and k_{SC} . The existence of equilibrium (5) results in an apparent decrease in the rate of MCH⁺ formation.

A gradual decrease of [HCl] leads to a decrease of the maximum obtainable OD_{430} . It is assumed that under such conditions [HCl] is still larger than [SP]. The value of K_5 obtained from the plots of limit OD_{430} values vs. [HCl] using equation similar to Equation I are presented in Table 1.

 K_5 strongly depends upon the amount of added water. K_5 decreases 10 times upon the addition of 0.2 mole fraction of water and 20 times upon the addition of 0.42 mole fraction of water (see Table 1). Apparently, H⁺ with its thrice lower charge than Al³⁺ forms a LC. Both complexes demonstrate similar absorption bands and close values of extinction coefficients due to the fact that they have the same chromophore MC. Small differences are observed only in the intensities of absorption shoulders at $\lambda = 360$ and $\lambda = 330$ nm due to the insignificant differences in the vibration structure.

Addition of water leads to the classic electrolytic dissociation of a salt-like MCH⁺. Therefore, H⁺ (H₃O⁺) is not able to compete with Al^{3+} in complex formation with MC. The studies of dynamics of MC of substituted BIPS in the presence of divalent and trivalent metal ions has demonstrated that the presence of water in the concentration more than 0.2 mole fraction prevents complex formation.^[35,36] One may expect that in the case of SP, the presence of water would prevent quantitative analysis of other metal ions except for Al³⁺.

Photoillumination of the colored MC stabilized with Al³⁺ or with H⁺ by visible light completely regenerates the starting SP, LC, or SPH+. Storage of the illuminated solutions in the dark leads to the regeneration of SP as well. This cycle can be repeated multiple times without noticeable consumption of reagents. SC is a stable compound with negative photochromism. Systems demonstrating negative photochromism are of interest for light-controlled devices, eg, molecular switches controlled by visible light.^[8]

3.4 | Fast formation of a SC of two MC with Al^{3+} and of protonated MC (MCH⁺)

In this section, the experiments were performed with solutions of the relatively large [SP] (1-10 mM) and small [Al³⁺] (0.05-50 μ M). Under such [SP], the registration of the MC absorption at $\lambda_{max} = 550$ nM (see Section 3.1) is already possible and the prompt formation of the SC absorption with $\lambda_{max} = 430$ nm is observed after the introduction of the small amounts of Al³⁺ to SP solutions. At the same time, the MC band with $\lambda_{max} = 550$ nm is preserved (see Figure 8):

The direct measurements attest to the fast reaction of the complex formation between metal ions and MC forms of spirocompounds in solutions.^[35–37] The onset time of



FIGURE 8 Long-wavelength part of the ultraviolet-visible spectrum of SP in MeOH in the presence of Al $(NO_3)_3 \times 9H_2O$ in a small concentration; $[Al^{3+}]$, μ M: (a) 0.0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0, (f) 2.5, (g) 3.0, (h) 3.5, and (i) 4.0. [SP] =0.01 M in all solutions



FIGURE 9 Plots of OD_{430} vs. the concentration of Al $(NO_3)_3 \times 9$ H₂O (a) and of HCI (b) in MeOH solutions of SP (5 mM). The lines are the fits of experimental data to linear functions

the equilibrium ((1)) being equal to $1/(k_1 + k_{-1})$ is rather short (approximately ≤ 5 s). That means that all Al^{3+} is able to be consumed promptly (less than in 5 s) in the irreversible reaction (4) by the quickly appearing MC.

The intensity of the promptly formed band at $\lambda_{max} =$ 430 nm is directly proportional to [Al³⁺] (see Figures 8 and 9a). The slope of this plot (Figure 9a)

gives an apparent extinction coefficient of SC, which is 2 times larger than that obtained in Section 3.2 for one MC in the complex. This fact testifies to the structure of SC as consisting of two MC with one Al^{3+} .

In the case of H⁺, we observed equilibrium (5). An apparent extinction coefficient obtained by a similar manner like that for Al³⁺ from the slope of a linear plot for H⁺ (Figure 9b) was 2 times smaller than a similar value obtained in Section 3.3. The dependence of [MCH⁺] vs initial concentration of HCl ([HCl]_o) can be described by a simple equation (II) since the [MC] is practically constant in these experiments. The knowledge of genuine ε_{430} obtained in the

$$[\text{MCH}^+] = \text{OD}_{430} / (\varepsilon_{430} l) = [\text{HCl}]_0 / (1 + 1 / (K_5[\text{MC}]))$$
(II)

previous section allowed for calculation of K_5 -values, which turn out to be rather close to the values obtained in Section 3.3 (see Table 1).

The abrupt further increase of $[Al^{3+}]$ or [HCl] leads eventually to a prompt disappearance of the band at λ_{max} = 550 nm, and only the band at λ_{max} = 430 nm is observed. This means that the kinetics of the reaction becomes the same as described in Section 3.3 when the formation of MC according to equilibrium ((1)) is the *limiting stage* of the process.

At the end of this section, we will mention that we did not observe the fluorescence of a pure MC. SC demonstrates weak fluorescence at $\lambda = 550$ nm. Spectrophotometry is a convenient and reliable method of determination of Al^{3+} by using SP solutions. The detection limit as low as 50 nM can be estimated (see the Supporting Information). Similar results were obtained with $AlCl_3$.

3.5 | NMR study of SP, LC, and SC

¹H-,¹³C-, and COSY-NMR (Section 2.3) study was performed in order to figure out the binding sites of SP in LC and two MC with Al^{3+} in SC. Scheme 2 presents chemical shifts in ¹H and ¹³C NMR spectra of SP and SC in CD₃OD obtained. Our NMR data are consistent with

published data for SP in other solvents.^[38–40] Minor deviations observed are due to the specific solvation of SP by MeOH. ¹H NMR spectra of MC in SC are in accordance with the reported data for MCH^{+.[41]} ¹³C NMR spectra of MC as a component of SP are obtained for the first time.

NMR spectra of aliphatic and aromatic regions of SP obtained prior to addition and promptly after addition of an excess Al (NO₃)₃ × 9 H₂O (LC spectrum) are similar to each other. That means that the formed LC complex (see Section 3.2) is a complex of SP as was suggested, but not a complex of MC. We refer the reader to spectra a and b in Figure S1. The difference between spectra is due to essential broadening of lines in LC spectrum due to equilibrium (2), see above. We observed also a signal of H₂O (δ 4.85 ppm in ¹H NMR spectrum) and of a certain acidic proton (a broad line at δ ~10 ppm in ¹H NMR spectrum). The latter signal (0.04 M at the concentration of salt being equal to 0.2 M) is probably due to H⁺ of HNO₃ formed by hydrolysis of Al (NO₃)₃.

Further examination of ¹H NMR spectra of LC demonstrates additional signals of individual weakly acidic protons at δ 7.3 (1H), 7.6 (2H), and 7.75 (1H) ppm in the LC spectrum, which are absent in the spectrum of SP. One can suggest that these signals are due to H of water molecules in the coordination sphere of Al³⁺ in LC. These signals disappear in the spectrum of SC: compare spectra b and d (Figure S1).

The broadened signals of olefinic protons of LC at C3-C4-position are observed at δ 5.77 and 6.96 ppm with the coupling constant of *J*=9.5 Hz. The starting SP had coupling *J*=10.3 Hz. A decrease of *J* under formation of LC means a weakening of a double bond order in the complex.

NMR spectra of solutions of Al³⁺, SP, and LC undergo essential changes during their storage in the dark (see Figure S2). These changes reflect the conversion of SP into MC. The rates of the slow formation of SP in the dark measured by NMR were the same as those obtained in

UV-vis experiments. The most important transformations of NMR spectra are the following: (a) two non-equivalent methyl groups (3'; Scheme 2) in SP or LC (two distinct singlets at δ 1.18 and 1.31 ppm) became magnetically equivalent (the singlet for six equivalent H at δ 1.87 ppm) due to quasi-planar structure of MC in SC,^[34,41-43] (b) the signal of N-CH₃ observed for SP and LC at 2.73 ppm is downfield shifted to 4.16 ppm for SC due to the appearance of a positive charge on N-atom in MC,^[42] and (c) the two doublets of the olefinic protons at C3-C4-position of SP or LC (δ 5.77 and 6.96 ppm with the coupling constant of 10.2 and 9.5 Hz, respectively) were downfield shifted in SC (doublets at δ 8.72 and 7.77 ppm with the coupling constant of *J*=16.4 Hz) indicating the trans-MC form.^[34,41-43]

The essential unshielding of protons 5-8 (Scheme 2) can be attributed to the binding of phenolate anion with a metal ion. The same conclusion one can make considering chemical shifts in the ¹³C NMR spectrum (Scheme 2). The signal of atom C bound to O is essentially unshielded in MC compared with that in SP. ¹H-NMR spectra of SC obtained at different ratios of components demonstrate that SP has an established composition two MC and one Al³⁺. See the spectra in Figure S3.

Based on the NMR and other data presented above, we conclude that a new complex has the following structure (Scheme 3):

NMR spectra of SC, which had been kept for a long enough time in the dark, exhibited narrow signals. This observation testifies to the fact that the exchange processes disappear with time. SC is the stable individual chemical substance. LCs of MC obtained for other spirocompounds and metal ions and in particular Al³⁺ demonstrated broad NMR signals of MC fragment in a complex due to the exchange.^[14,34] The presence of electron-withdrawing nitro-group in widely studied nitro spirocompounds reduced the capability of the



corresponding nitro MC zwitterions for complexing with a metal ion.

In this work, we presented data related to aluminum nitrate. Experiments with $AlCl_3$ led to the same spectroscopic, kinetic and thermodynamic observations.

4 | CONCLUSIONS

The main achievement of this work is the discovery of a colored SC of Al^{3+} with two MC forms of the simple spirocompound BIPS. The alcoholic solutions of BIPS can be used as a sensitive chemosensor of Al^{3+} . It was demonstrated that $[Al^{3+}]$ can be measured by "simple" spectophotometry. The method has a high sensitivity due to the large extinction coefficient of the complex with *two* MC ligands, and the limit of a detectable Al^{3+} concentration was estimated as 50 nM (see Supporting Information S3 also). It was shown that strong acids cannot compete with Al^{3+} , and that SP collects all Al^{3+} from alcohols or from aqueous alcohols. The study of selectivity of a new chemosensor for Al^{3+} is in progress.

A new Al³⁺ complex is a stable reversible photoswitch with a negative photochromism, which may find an application as UV and visible light-activated light switch.

The comprehensive set of equilibria and rate constants of the studied processes was obtained. In addition, we found that the studied SC possesses negative photochromism.

AUTHORS AGREEMENT

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11 of 11 WILEY Journal of Physical Organic Chemistry

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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