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SYNTHESIS AND COMPLEXATION OF BIS(1-AZAAZULEN-2-YL)-AMINES AND BIS(1-AZAAZULEN-2-YL) SULFIDES

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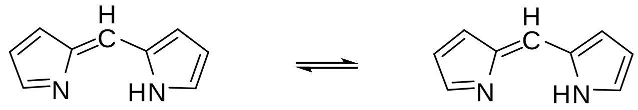
Abstract – Complexation of bis(3-phenyl-1-azaazulen-2-yl)amine with $Zn(OAc)_2$ and $Ni(OAc)_2$ was investigated, and four-coordinate bis-chelate complexes, M(II) bis[(3-phenyl-1-azaazule-2-yl)(3-phenyl-1-azaazulen-2-ylidene)aminate] (M = Zn, Ni), were obtained. Complexation of bis(1-azaazulen-2-yl) sulfide with $CoCl_2$ gave 2 : 1 ligand-metal complex as major product and complexation of bis(3-iodo-1-azaazulen-2-yl) sulfide with $CoCl_2$ gave 1 : 1 ligand-metal complex.

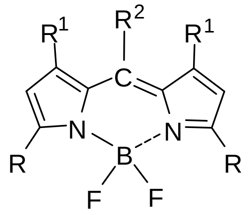
INTRODUCTION

Dipyrrins (**1**) (the molecule have been known by many names: dipyrromethene, dipyrrolemethene, diaza-*s*-indacene, etc.) are known because of their ability of the formation of charge-neutral chelated complexes with variety of metal cations.[1a] The chemistry of BODIPY (BF_2-chelated dipyrrin) was extensively investigated[1] as a new *El Dorado* for fluorescence tools.[1b] BODIPYs have found widespread applications from their property of highly fluorescent dyes and used as biolabels, light harvesters, sensitizers, for solar cells, fluorescent sensors, and energy-transfer reagent, etc.,[1] as well as laser dyes,[2] fluorescence probe for nitric oxide,[3] and for acidic pH.[4] For these utility, syntheses for many new type of BODIPY were investigated.[5-8]

Aza-dipyrrins (azadipyrromethenes) (**3**) are aza-analogues of dipyrrins (dipyrromethenes) and recently extensively investigated.[1d] Azadipyrromethene-BF_2 complexes (aza-BODIPY dyes) (**4**)[9-18] are modified BODIPY and showed fluorescent spectra at red to near-infrared (NIR) region, and used as phototherapeutic agents,[9] molecular sensors,[10-12] and NIR fluorescent probs.[13]



1 **1A**



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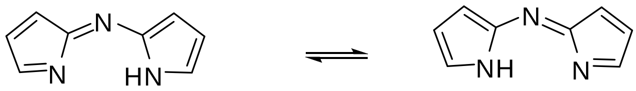
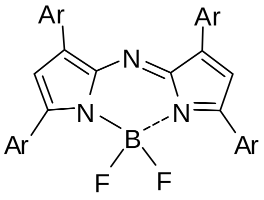


3 **3A**



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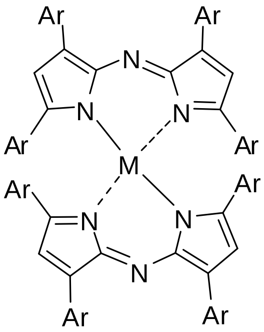
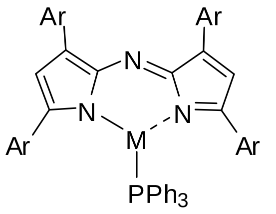
The complexes of azadipyrromethenes with metal cations other than BF_2 are investigated from the interest for future designed uses in catalysis, metal-organic frameworks, optical data storage, and electrochromic devices, but the reports were few. Recently, it is reported that azadipyrromethene with divalent metals [Co(II), Ni(II), Cu(II), Zn(II), and Hg(II)] consisted four-coordinate bis-chelate complexes (**5**)[19,20] and azadipyrromethene with monovalent metals [Cu(I), Ag(I), and Au(I)] formed tri-coordinate complexes (**6**).[21]



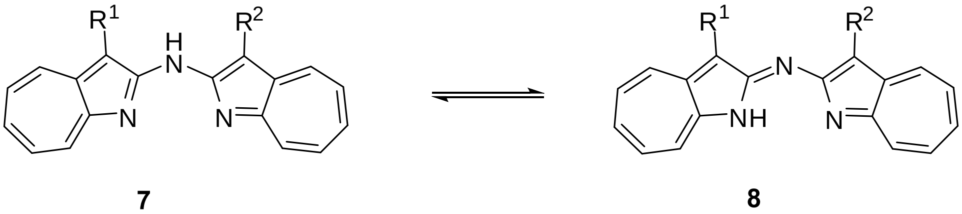
5 : M = Co(II), Ni(II), Cu(II), Zn(II), Hg(II)



6 : M = Cu(I), Ag(I), Au(I)

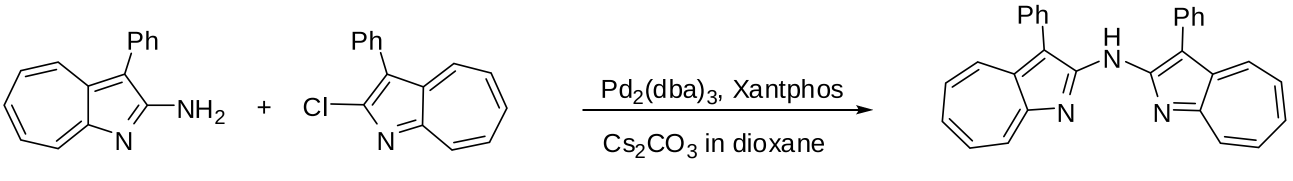
The chemistry of azaazulenes is attracted attention for their interest physical and chemical properties as well as physiological properties.[22] The chemistry of heteroaryl-substituted 1-azaazulenes as ligands is of interested and some reports about the complexation with metal ions were made.[23-25] It is reported that the complexes of 2-(2-pyridy)-1-azaazulene with metal cations[23] and [2-(2-pyridy)](1-azaazulen-2-yl)amine with metal cations caused interesting emissions,[24] where S_2-S_0 transition or S_1-S_0 transition occurred depend on the metal cation species. Recently, the investigation about synthesis and the emission spectra of 2-(2-hyddroxyphenyl)-1-azaazulene and its metal complexes was also reported.[26] It is considered that bis(1-azaazulen-2-yl)amines (**7**) could exist its tautomeric form (**8**) in the heteroaryl-substituted

1-azaazulenes, which are formally cyclohepta-annulated aza-dipyrrins (cyclohepta-annulated azadipyrromethenes), therefore their complexation with metal cations is of interest.



RESULTS AND DISCUSSION

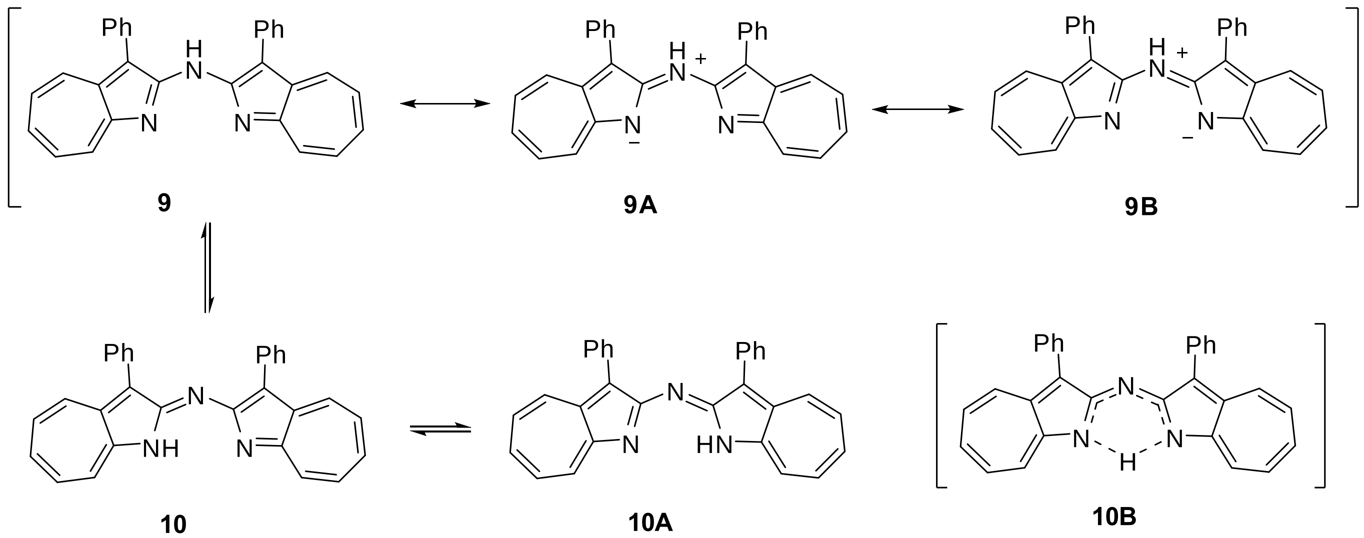
We previously reported the synthesis of bis(1-azaazulen-2-yl)amines (**7**) by Buchwald-Hartwig coupling, but their details about the structure were not discussed in the report.[27] So, we investigated some properties of **7** in this paper. At first we examined the synthesis of bis(3-phenyl-1-azaazulen-2-yl)amine (**9**) from bis(3-iodo-1-azaazulen-2-yl)amine, but an iodinatation of bis(1-azaazulen-2-yl)amine with *N*-iodosuccinimide (NIS) or a coupling reaction of 2-amino-3-iodo-1-azaazulene and 2-chloro-3-iodo-1-azaazulene in the presence of $Pd_2(dba)_3$, Xantphos, and Cs_2CO_3 were failed. Finally, **9** was synthesized by the reaction of 2-amino-3-phenyl-1-azaazulene and 2-chloro-3-phenyl-1-azaazulene in the presence of $Pd_2(dba)_3$, Xantphos, and Cs_2CO_3 in 43% yield.



9

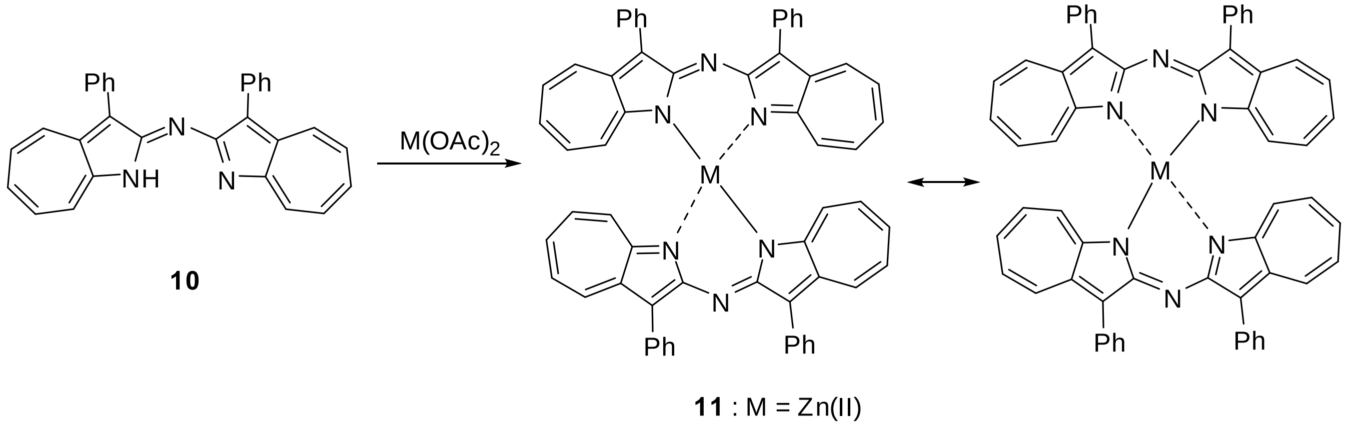
The ^{1}H and ^{13}C NMR spectra of bis(3-phenyl-1-azaazulen-2-yl)amine showed highly symmetrical feature. In the ^{1}H NMR spectrum, an amine proton was appeared at rather lower field (δ 13.57). The UV-Vis spectrum of **9** shows strong and wide range absorptions at λ_{max} 289 nm (log ε 4.64), 369 (4.29), 404 (4.08, sh), 468 (4.09, sh), 498 (4.19), 568 (4.40), 603 (4.41), and 650 (4.06, sh), and its feature was rather different from the ordinal 1-azaazulene form (Figure 1). Therefore, it is considered that bis(3-phenyl-1-azaazulen-2-yl)amine takes the tautomeric form **10** and **10A**; **10B** would be a more adequate form.

Consideration of the structure of **10b** suggested that **10** could form complexes with metal cations. Therefore we examined the complexation of **10** with BF_3 at first. When **10** was treated with $BF_3 \cdot OEt_2$ in the presence of Et$_3$N, a fluorescent product was observed by TLC, but the product was changed to blue powders by the separation with column chromatography on silica gel and could not be isolated. So we could not assign the structure of fluorescent product. Next, we treated **10** with Zn(OAc)$_2$·2H$_2$O in THF, and obtained 2 : 1 ligand-metal complex (**11**) as reddish brown powders in 62% yield. The ^{1}H and ^{13}C NMR spectra of **11** showed highly symmetrical feature. Its Uv-Vis spectrum was somewhat resembled to that of **10**, but the absorption of longest wavelength of **11** was rather strong [λ_{max} 634 nm (log ε 4.90)] than that of **10** (Figure 1). From these results as well as elemental analysis, we assigned the structure as Zn(II) bis[(3-phenyl-1-azaazule-2-yl)(3-phenyl-1-azaazulen-2-ylidene)amine], which has the four-coordinate structure. Because we could not obtain favorable crystals for X-ray crystallographic analysis unfortunately, we could not define the exact structure. But the presented structure would be reasonable from the consideration of the structure of **5**.[20] Similar treatment of **10** with Ni(OAc)$_2$·4H$_2$O in THF gave **12** in 24% yield. The UV-Vis spectrum of **12** was resembled to that of **11**. Although the



9 **9A** **9B**

10 **10A** **10B**

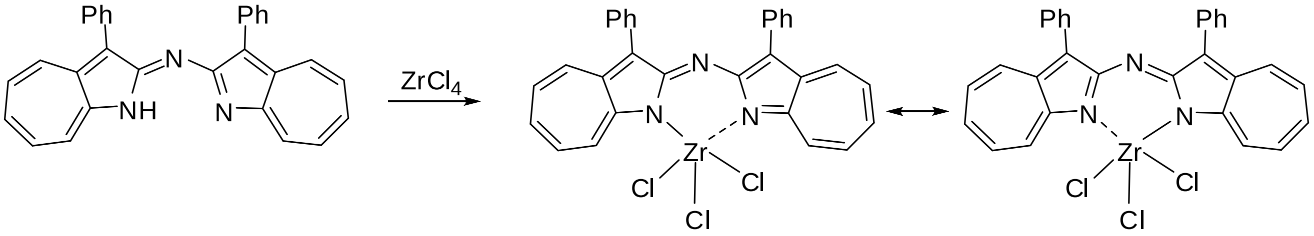


10

11 : M = Zn(II)
12 : M = Ni(II)

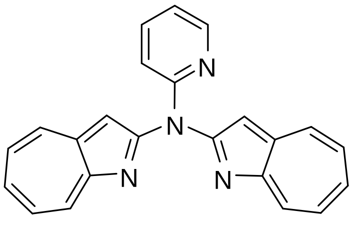
intensity of the absorption of **12** was weak than that of **11** [λ_{max} 627 nm (log ε 4.71)] (Figure 1), it was about twice of that of **10**. The results suggested that two bis(3-phenyl-1-azaazulen-2-yl)amine moieties exist. The Ni(II) complex (**12**) would be paramagnetic and its ^{1}H NMR spectrum was appeared at wide range and showed broadening signals: δ -2.55 (4H, br, H-4), 2.16 (8H, br, H-*o*-Ph), 4.95 (4H, br, H-*p*-Ph), 5.55 (8H, br, H-*m*-Ph), 9.43 (4H, br, H-5), 14.78 (8H, br, H-6 and 7), and 22.16 (4H, br, H-8).

Unlike the cases of Zn(II) and Ni(II) complexes of **10**, the complexation of **10** with Zr(IV) showed a different feature. The reaction of **10** with 0.44 equivalent of $ZrCl_4 \cdot 2THF$ gave 1 : 1 ligand-metal complex (**13**), which was determined by elemental analysis. Its ^{1}H NMR spectrum showed symmetrical feature, and some bond alternation was observed from the consideration of coupling constants of the seven-membered ring protons (*J* 9.2~11.4), which would be owing to contribution of heptafulvene form. The UV-Vis spectrum of **13** was resembled to those of **11** and **12**, but the absorption of longest wavelength was rather weak compared to those of **11** and **12** and is suitable as possessing one bis(3-phenyl-1-azaazulen-2-yl)amine moiety [λ_{max} 635 nm (log ε 4.32)] (Figure 1). So we assigned the structure to formally penta-coordinate chelate complex (**13**). The resemblance of the UV-Vis spectra of **11**, **12**, and **13** suggested that the influences to the electronic state of (1-azaazule-2-yl)(1-azaazulen-2-ylidene)amine nuclei by coordination of metal cations would be basically similar.



10 **13**

Recently, Oda et al. reported about the synthesis of **14** and its UV-Vis spectrum and emission spectrum in the presence of $Zn(ClO_4)_2$.[24] Although they did not discuss about the structure of **14**-Zn(II) complex, the fact that the UV-Vis spectrum of **14** in the presence of metal cation was resembled to **11** is of interest for comparison with above mentioned results.



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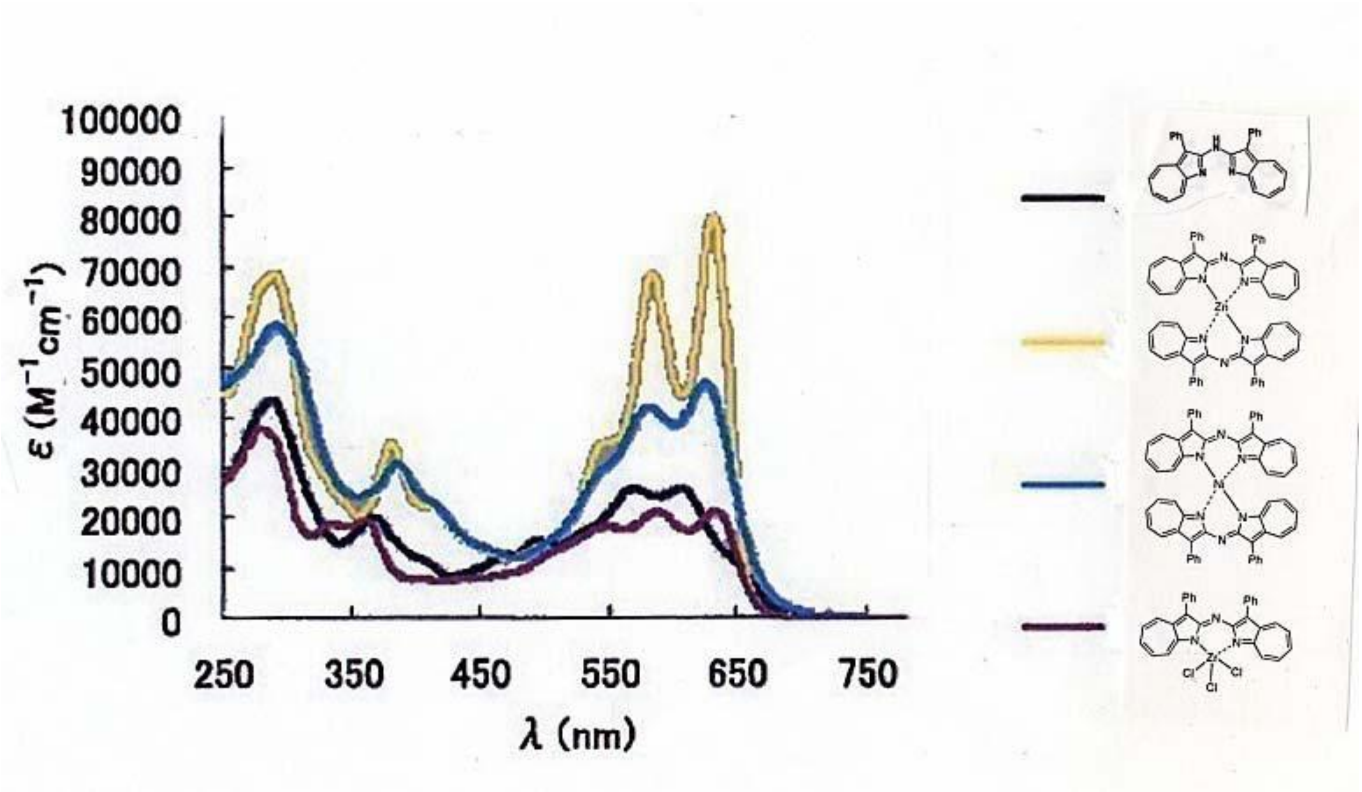


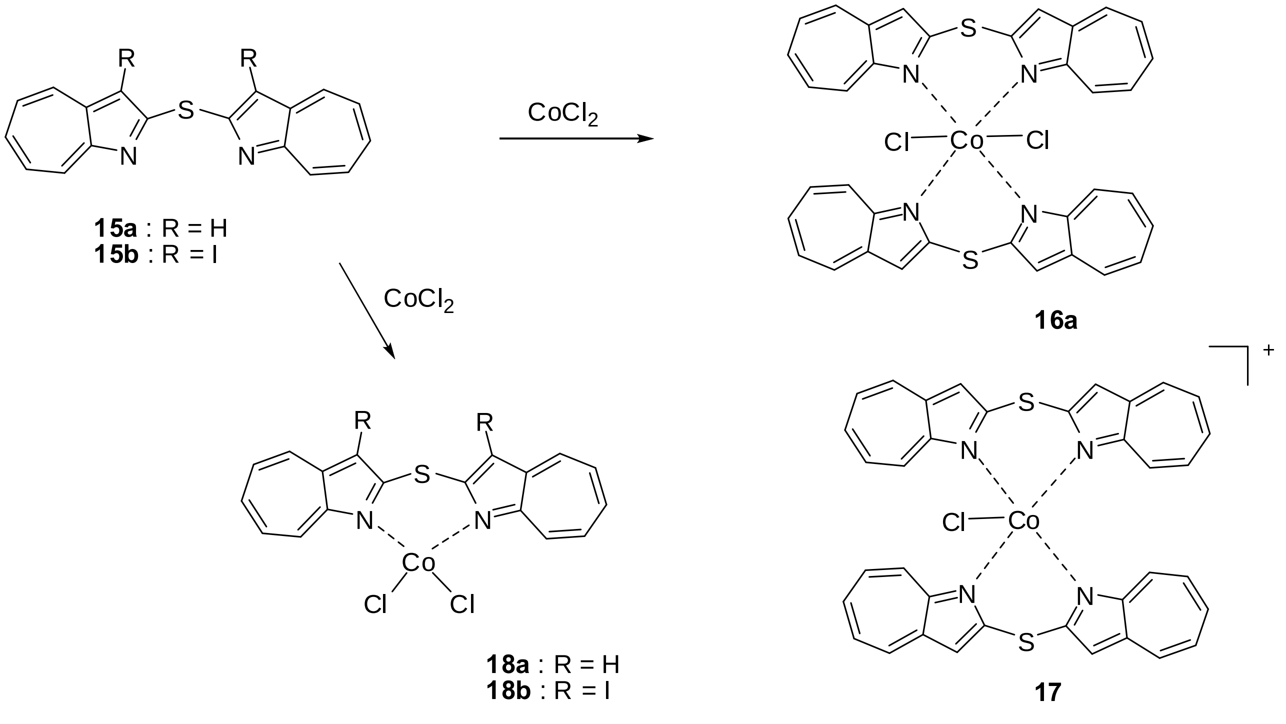
Figure 1. UV-Vis spectra of bis(3-phenyl-1-azaazulen-2-yl)amine and its complexes with metal ions

We next examined the complexation of bis(1-azaazulen-2-yl) sulfides. Bis(1-azaazulen-2-yl) sulfide (**15a**) was prepared by previously reported procedures.[26] Bis(3-iodo-1-azaazulen-2-yl) sulfide (**15b**) was prepared by iodinatation of **15a** with NIS in 56% yield. The UV-Vis spectrum of **15b** shows absorptions at $\lambda_{\max}$ (MeOH) 284 nm (log ε 4.48), 318 (4.27, sh), 397 (3.93), and 507 (3.52), and its feature was ordinal 1-azaazulene form (Fig. 2). Bis(3-phenyl-1-azaazulen-2-yl) sulfide was obtained only in trace yield by Suzuki coupling of **15b** with phenylboronic acid in the presence of Pd(dppf)$\cdot$$CH_2Cl_2$, BINAP, and Cs_2CO_3. Therefore we did not examine a complexation of this compound.

Reaction of **15a** with $ZrCl_4\cdot 2THF$ gave reddish orange powders, but we could not assign its molecular formula from MS-ESI$^+$, HRMS-ESI$^+$ and ^{1}H NMR spectrum. In its MS-ESI$^+$, peaks appeared at *m/z* 641 (rel intensity 3), 639 (6), 386 (2), 311 ([**15a** + Na]$^+$, 1), and 289 ([**15a** + H]$^+$, 100); where distinct assignable peaks due to **15a** – Zr(IV) complex were not observed. The ^{1}H NMR spectrum showed slightly dissymmetric feature [δ 7.93 (2H, s, H-3,3'), 8.26-8.12 (4H, m, H-6,7,6',7'), 8.35 (2H, dd, *J* 9.6 and 9.2, H-5,5'), 8.84 (1H, d, *J* 9.6, H-4), 8.86 (1H, d, *J* 9.6, H-4'), 8.93 (1H, d, *J* 8.8, H-8), and 8.94 (1H, d, *J* 8.8, H-8')]. Reaction of **15b** with $ZrCl_4\cdot 2THF$ gave unidentified red powders. Its ^{1}H NMR spectrum was deferent from that of **15b**. But its MS showed rather weak peak at *m/z* 585 (rel intensity 0.01) and a base peak at *m/z* 540 ([M + H]$^+$) owing to **15b**, and distinct assignable peaks were not found. These results suggested some kinds of complexation occurred, but we could not deduce the structures of the products.

Next, we examined the complexation of **15a** with Co(II). Treatment of **15a** with $CoCl_2 \cdot 6H_2O$ gave **16a** as red powders in 52% yield. Its HRMS-ESI$^+$ showed a peak at *m/z* 670.0466, owing to ${}^{12}C_{36}{}^{1}H_{24}{}^{14}N_{4}{}^{35}Cl^{59}Co^{32}S_{2}$, and which structure was assigned to **17** ([**16a** - Cl + Na]$^+$; rel intensity 22). In the MS, different from the case of Zr-complex, the peak owing to **15a** was not observed. In the MS of **16a**, a very weak peak (rel intensity 0.8) was found due to **18a** (*m/z* 439.9315([M + Na]$^+$, Calcd for ${}^{12}C_{18}{}^{1}H_{12}{}^{14}N_{2}{}^{35}Cl_{2}{}^{59}Co^{23}Na^{32}S$: 439.9328). This showed that the 1 : 1-complex (**18a**) is also produced in only trace amount, and it is considered that observed peak in MS was a contaminant in **16a**. The Co(II) complex (**16a**) would be paramagnetic and its ^1H NMR spectrum was broadening and appeared at wide range of magnetic field: we could not obtain distinct spectrum. In the UV-Vis spectrum of **16a**, a longest wavelength of absorption was slightly weak and the fact is suitable that **16a** possessed two bis(1-azaazulen-2-yl) sulfide moieties [λ_{max} 482 nm (log ε 3.78)] (Figure 2). So we assigned the structure. The Co-N bond in **16a** would be consisted with coordination bonding and not covalent bond.

On the contrary, the treatment of **15b** with excess $CoCl_2 \cdot 6H_2O$ gave 1 : 1-complex (**18b**) in 69% yield. Its HRMS-ESI$^+$ showed a peak at *m/z* 691.7263 due to ${}^{12}C_{18}{}^{1}H_{10}{}^{14}N_{2}{}^{35}Cl_{2}{}^{59}Co^{127}I_{2}{}^{23}Na^{32}S$ ([M + Na]$^+$). The UV-Vis spectrum of **18b** was resembled to that of **15b**, and a longest wavelength of absorption appeared at λ_{max} 526 nm (log ε 3.67) and it is suitable that **18b** possessed one bis(3-iodo-1-azaazulen-2-yl) sulfide moiety (Figure 2). So we assigned the structure. Limited changes in the UV-Vis spectra between **15b** and **18b** suggested that the coordination of $CoCl_2$ to **15b** is weak and the metal cation did not affect substantially to the electronic state of the azaazulene rings.



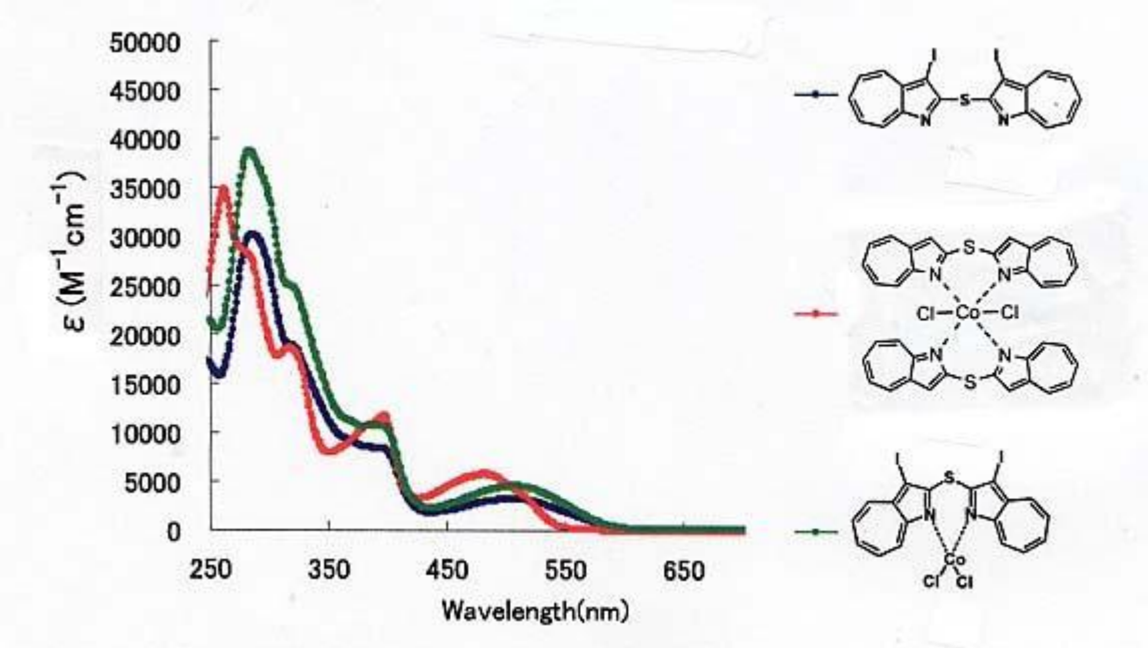


Figure 2. UV-Vis spectra of bis(3-iodo-1-azaazulen-2-yl) sulfide and the complexes with $CoCl_2$

CONCLUSION

We synthesized four-coordinate bis-chelate complexes (**11** and **12**) of bis(3-phenyl-1-azaazulen-2-yl)amine with divalent metal [Zn(II) and Ni(II)] and formally penta-coordinate chelate complex (**13**) with Zr(IV). We also synthesized bis-chelate complex (**16**) and mono-chelate complex (**18**) of bis(1-azaazulen-2-yl) sulfides with $CoCl_2$. The UV-Vis spectra of **11** and **12** showed longer wavelength of strong absorptions owing to (3-phenyl-1-azaazulen-2-yl)(3-phenyl-1-azaazulen-2-ylidene)amine nuclei. Whereas the UV-Vis spectra of **16** and **18** were scarcely changed from those of bis(1-azaazulen-2-yl) sulfides.

EXPERIMENTAL

Melting points were determined with a Yanagimoto micro-melting point MP JP-3 apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker Avance 400S (400MHz) using $CDCl_3$ as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* value are recorded in Hz. Uv-Vis spectra were recorded with JASCO V-570 spectrophotometer. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410. Mass Spectra (ESI$^+$-MS) were taken with JEOL JMS-T100CS. Elemental analyses were taken with a Perkin Elmer 2400II. Alumina Activated 300 (Nacarai Tesque) was used for column chromatography. Bis(3-phenyl-1-azaazulen-2-yl)amine (**10**) and bis(1-azaazulen-2-yl) sulfide (**15a**) were prepared by previously reported procedures.

Synthesis of bis(3-phenyl-1-azaazulen-2-yl)amine

Under argon atmosphere, a mixture of 2-amino-3-phenyl-1-azaazulene (0.209 g, 0.95 mmol), 2-chloro-3-phenyl-1-azaazulene (0.520 g, 2.17 mmol), Cs_2CO_3 (0.444 g, 1.86 mmol), Xantphos (0.038 g, 0.065 mmol), and $Pd_2(dba)_3$ (0.052 g, 0.057 mmol) in dry dioxane (12 mL) was refluxed for 24 h, then water (20 mL) was added. The mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. Chromatography of the residue with $CHCl_3$-AcOEt (1 : 1) gave bis(3-phenyl-1-azaazulen-2-yl)amine (**10**) (0.173 g, 43%).

10: Dark red powders (from $CHCl_3$-AcOEt), mp 255-256 ℃; ^{1}H NMR (DMSO-d_6) δ 7.29 (2H, like t, J 9.1, H-6 and 6'), 7.32 (2H, t, J 7.6, H-*p*-Ph), 7.34 (2H, like t, J 9.3, H-5 and 5'), 7.47 (4H, dd, J 7.6 and 7.3 H-*m*-Ph), 7.49 (2H, like t, J 10.0, H-7 and 7'), 7.78 (4H, d, J 7.3, H-*o*-Ph), 8.04 (2H, dm, J 10.0, H-8 and 8') and 8.05 (1H, dm, J 9.3, H-4 and 4') and 13.57 (1H, br, NH); ^{13}C NMR (DMSO-d_6) δ 120.33, 122.65, 126.80, 128.10, 128.60, 130.23, 131.12, 131.86, 131.92, 133.16, 140.05, 151.59, and 163.04; ν_{max} / cm^{-1} 3440 (NH); λ_{max} (CH_2Cl_2) nm (log ε) 289 (4.64), 369 (4.29), 404 (4.08, sh), 468 (4.09, sh), 498 (4.19), 568 (4.40), 603 (4.41), and 650 (4.06, sh). *Anal.* Calcd for $C_{30}H_{21}N_3$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.12; H, 5.13; N, 9.74.

Complexation of bis(3-phenyl-1-azaazulen-2-yl)amine with Zn(OAc)$_2$

A mixture of **10** (0.033 g, 0.078 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.008 g, 0.036 mmol) in THF (20 mL) was stirred for 17 h at rt. The precipitate was filtered through a celite pad and washed with CH_2Cl_2 and MeOH. Evaporation of the combined filtrate gave bis[bis(3-phenyl-1-azaazulen-2-yl)amine] – zinc complex (**11**) as black powders, which was recrystallized from THF to give reddish brown powders (0.020 g, 62%).

11: Reddish brown powders (from THF), mp >300 ℃; ^{1}H NMR δ 6.94 (4H, dd, J 10.5 and 8.8, H-7), 7.02 (4H, dd, J 10.5 and 9.6, H-6), 7.10 (4H, dd, J 10.7 and 9.6, H-5), 7.27 (4H, d, J 8.8, H-8), 7.38 (4H, dd, J 7.4 and 1.2, H-*p*-Ph), 7.52 (8H, dd, J 8.1 and 7.4, H-*m*-Ph), 7.96 (8H, dd, J 8.1 and 1.2, H-*o*-Ph), and 8.08 (4H, d, J 10.7, H-4); ^{13}C NMR δ 121.69, 123.69, 126.70, 128.64, 130.18, 130.43, 131.89, 133.49, 141.43, 155.92, and 165.27; λ_{max} (CH_2Cl_2) nm (log ε) 288 (4.87), 379 (4.54), 412 (4.36), 547 (4.54), 585 (4.83), and 634 (4.90). *Anal.* Calcd for $C_{60}H_{40}N_6Zn \cdot 2/3AcOEt$: C, 77.67; H, 4.71; N, 8.67. Found: C, 77.55; H, 4.51; N, 8.84.

Complexation of bis(3-phenyl-1-azaazulen-2-yl)amine with Ni(OAc)$_2$

A mixture of **10** (0.017 g, 0.040 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.005 g, 0.020 mmol) in THF (5 mL) was stirred for 18 h at rt. The precipitate was filtered through a celite pad and washed with CH_2Cl_2. Then the precipitate was washed with MeOH. Evaporation of the eluent of MeOH gave bis[bis(3-phenyl-1-azaazulen-2-yl)amine] – Ni(II) complex (**12**) as black powders, which was recrystallized from THF-pentane to give bronze needles (0.004 g, 24%).

12: Bronze needles (from THF-pentane), mp >300 ℃; ^{1}H NMR δ -2.55 (4H, br, H-4), 2.16 (8H, br, H-*o*-Ph), 4.95 (4H, br, H-*p*-Ph), 5.55 (8H, br, H-*m*-Ph), 9.43 (4H, br, H-5), 14.78 (8H, br, H-6 and 7), and 22.16 (4H, br, H-8); ^{13}C NMR δ 25.70, 67.97, 105.70, 125.97, 126.25, 137.59, and 204.24. λ_{max} (CH_2Cl_2) nm (log ε) 290 (4.63), 384 (4.48), 412 (4.36, sh), 550 (4.47, sh), 583 (4.61), and 627 (4.71). *Anal.* Calcd for $C_{60}H_{40}N_6Ni$: C, 79.74; H, 4.46; N, 9.30. Found: C, 80.02; H, 4.51; N, 9.13.

Complexation of bis(3-phenyl-1-azaazulen-2-yl)amine with $ZrCl_4$

Under argon atmosphere, a mixture of **10** (0.056 g, 0.132 mmol) and $ZrCl_4 \cdot 2THF$ (0.022 g, 0.058 mmol) in THF (5 mL) was stirred for 96 h at rt. The precipitate was filtered through a celite pad and washed with CH_2Cl_2. Then the precipitate was washed with MeOH. Filtrates of THF and CH_2Cl_2 were combined and evaporated. Chromatography of the residue (hexane : EtOAc = 5 : 1) gve recovered **10** (0.038 g, 68%). Evaporation of the filtrate of MeOH gave black powders, which was recrystallized from THF to give bis(3-phenyl-1-azaazulen-2-yl)amine – zirconium complex (**13**) (0.024 g, 67%, on the basis of $ZrCl_4 \cdot$ 2THF).

13: Black powders (from THF), mp 260 ℃ (decomp); ^{1}H NMR δ 7.27-7.42 (10H, m, H-*m*,*p*-Ph, 6, 6', 7, and 7'), 7.52-7.59 (6H, m, H-*o*-Ph, 5, and 5'), 8.11 (2H, d, *J* 11.4, H-4 and 4'), and 8.65 (2H, d, *J* 9.2, H-8 and 8'); δ (DMSO-d_6), 7.31 (2H, t, *J* 7.4, H-*p*-Ph), 7.44 (4H, dd, *J* 7.7 and 7.6, H-*m*-Ph), 7.57- 7.63 (8H, m, H-*o*-Ph, 6, 6', 7, and 7'), 7.68 (2H, dd, *J* 10.2 and 9.1, H-5 and 5'), 7.83 (2H, m, H-4 and 4'), and 8.11 (2H, d, *J* 10.1, H-8 and 8'); λ_{max} (CH_2Cl_2) nm (log ε) 278 (4.57), 332 (4.27), 361 (4.25), 402 (3.88), 547 (4.27), 589 (4.32), 635 (4.31), and 635 (4.32). *Anal.* Calcd for $C_{30}H_{20}N_3Cl_3Zr$: C, 58.11; H, 3.25; N, 6.78. Found: C, 58.02; H, 3.77; N, 6.89.

Synthesis of bis(1-azaazulen-2-yl) sulfide

A mixture of 2-mercapto-1-azaazulene (0.151 g, 0.936 mmol) and 60% NaH (0.047 g, 1.17 mmol) in dioxane (10 mL) was stirred for 30 min at rt. To the mixture was added 2-chloro-1-azaazulene (0.212 g, 1.23 mmol), and the mixture was refluxed for 4 h, then water (20 mL) was added. The mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. Chromatography on alumina of the residue with $CHCl_3$-AcOEt (1 : 1) gave bis(1-azaazulen-2-yl) sulfide (**15a**) (0.240 g, 88%).

15a: Red micro-needles (from CH_2Cl_2-hexane), mp 217-219 ℃; ^{1}H NMR δ 7.63 (2H, ddd, *J* 10.2, 9.9, and 1.3, H-7 and 7'), 7.76 (2H, ddd, *J* 10.2, 9.9 and 1.6, H-6 and 6'), 7.78 (2H, s, H-3 and 3'), 7.81 (2H, ddd, *J* 10.2, 9.9, and 1.0, H-5 and 5'), 8.41 (2H, d, *J* 9.9, H-4 and 4'), and 8.58 (2H, d, *J* 10.1 and 1.3, H-8 and 8'); ^{1}H NMR (DMSO-d_6) δ 7.77 (2H, dd, *J* 9.8 and 9.6, H-7 and 7'), 7.87 (2H, s, H-3 and 3'), 7.87 (2H, dd, *J* 10.0 and 9.8, H-6 and 6'), 7.96 (2H, dd, *J* 10.0 and 9.6, H-5 and 5'), 8.56 (2H, d, *J* 9.6, H-4 and 4'), and 8.60 (2H, d, *J* 9.6, H-8 and 8'); ^{13}C NMR δ 114.5, 129.4, 130.0, 133.4, 134.0, 136.6, 146.8, 157.8, and 164.4; ^{13}C NMR (DMSO-d_6) δ 114.2, 130.2, 130.5, 134.3, 134.40, 137.8, 146.5, 157.1, and 162.5.

Anal. Calcd for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.19; N, 9.71. Found: C, 74.75; H, 4.32; N, 9.84. MS: *m/z* (rel intensity) 289 ($[M + H]^+$; 100).

Synthesis of bis(3-iodo-1-azaazulen-2-yl) sulfide

A mixture of **15a** (0.259 g, 0.90 mmol), NIS (0.630 g, 2.80 mmol) and benzoyl peroxide (0.005 g, 0.05 mmol) in $CHCl_3$ (5 mL) was stirred for overnight. To the mixture was added water and extracted with $CHCl_3$. The extracted was dried over Na_2SO_4 and evaporated. The residue was chromatographed with $CHCl_3$ to give red powders, and recrystallization from CH_2Cl_2-hexane gave bis(3-iodo-1-azaazulen-2-yl) sulfide (**15b**) (0.271 g, 56%) as red powders.

15b: Red micro-needles (from CH_2Cl_2-hexane), mp 140-141 ℃; ^1H NMR δ 7.81 (2H, dd, *J* 10.4 and 9.6, H-5 and 5'), 7.82 (2H, dd, *J* 9.6 and 9.2, H-7 and 7'), 7.93 (2H, t, *J* 9.6, H-6 and 6'), 8.40 (2H, d, *J* 9.6, H-4 and 4'), and 8.66 (2H, d, *J* 9.6, H-8 and 8'); λ_{max} (MeOH) nm (log ε) 284 (4.48), 318 (4.27, sh), 397 (3.93), and 507 (3.52). *Anal*. Calcd for $C_{18}H_{10}N_2I_2S$: C, 40.02; H, 1.87; N, 5.19. Found: C, 40.38; H, 2.11; N, 5.33. MS: *m/z* (rel intensity) 541 ($[M + H]^+$; 100), 414 ($[M + H – I]^+$; 25), 287 ($[M + H – 2I]^+$; 6).

Reaction of bis(1-azaazulen-2-yl) sulfide with $ZrCl_4$

Under argon atmosphere, a mixture of **15a** (0.100 g, 0.27 mmol) and $ZrCl_4\cdot 2THF$ (0.085 g, 0.27 mmol) in THF (5 mL) was stirred for overnight at rt. The precipitate was collected by filtration and red powder (0.078 g) was obtained. Recrystallization from MeOH gave red orange powders, mp 280 ℃ (decomp); ^1H NMR δ (DMSO-d_6) 7.93 (2H, s, H-3,3'), 8.26-8.12 (4H, m, H-6,7,6',7'), 8.35 (2H, dd, *J* 9.6 and 9.2, H-5,5'), 8.84 (1H, d, *J* 9.6, H-4), 8.86 (1H, d, *J* 9.6, H-4'), 8.93 (1H, d, *J* 8.8, H-8), and 8.94 (1H, d, *J* 8.8, H-8'); MS: *m/z* (rel intensity) 641 (3), 639 (6), 386 (2), 311 ([**15a** + Na]$^+$, 1), and 289 ([**15a** + H]$^+$, 100).

Reaction of bis(3-iodo-1-azaazulen-2-yl) sulfide with $ZrCl_4$

Under argon atmosphere, a mixture of **15b** (0.050 g, 0.093 mmol) and $ZrCl_4\cdot 2THF$ (0.040 g, 0.106 mmol) in THF (5 mL) was stirred for overnight at rt. The precipitate was collected by filtration and red powder (0.039 g) was obtained. Recrystallization from MeOH gave red orange powders, mp 160 ℃ (decomp); ^1H NMR δ (DMSO-d_6) 8.09-8.17 (4H, m, H-6,7,6',7'), 8.27 (2H, dd, *J* 11.2 and 10.4, H-5,5'), and 8.59-8.69 (4H, m, H-4,4',8,8'). MS: *m/z* (rel intensity) 585 (0.01), 541 ([**15b** + H]$^+$; 100).

Complexation of bis(1-azaazulen-2-yl) sulfide with $CoCl_2$

A mixture of **15a** (0.100 g, 0.347 mmol) and $CoCl_2\cdot 6H_2O$ (0.066 g, 0.277 mmol) in THF (10 mL) was stirred for 24 h at rt. The precipitate was collected by filtration and bis[bis(1-azaazulene-2-yl) sulfide] – cobalt complex (**16a**) was obtained as red powders, which was recrystallized from MeOH to give red powders (0.090 g, 52% on the basis of **15a**).

16a: Red powders (from MeOH), mp >300 ℃; λ_{max} (MeOH) nm (log ε) 261 (4.54), 282 (4.45, sh), 318 (4.29), 399 (4.08), and 482 (3.78); MS: *m/z* (rel intensity) 672 ($[M - Cl]^+$; 10), 670 ($[M - Cl]^+$; 22), 529

(11), 394 (21), 312 (31), and 247 (100). HRMS: Calcd for $^{12}C_{36}{}^{1}H_{24}{}^{14}N_4{}^{35}Cl^{59}Co^{32}S_2$: 670.0463. Found: *m/z* 670.0466 ($[M - Cl]^+$).

Complexation of bis(3-iodo-1-azaazulen-2-yl) sulfide with $CoCl_2$

A mixture of **15b** (0.100 g, 0.185 mmol) and $CoCl_2 \cdot 6H_2O$ (0.024 g, 0.101 mmol) in THF (10 mL) was stirred for 24 h at rt. The precipitate was collected by filtration and bis(1-azaazulene-2-yl) sulfide – cobalt complex (**18b**) was obtained as red powders, which was recrystallized from MeOH to give reddish brown powders (0.048 g, 69% on the basis of $CoCl_2 \cdot 6H_2O$).

18b: Reddish brown powders (from MeOH), mp >300 ℃; λ_{max} (MeOH) nm (log ε) 283 (4.59), 320 (4.40, sh), 396 (4.03), and 526 (3.67); MS: *m/z* (rel intensity) 694 ($[M + Na]^+$; 13), 692 $[M + Na]^+$; 21), 668 (31), 666 (84), and 563 (100). HRMS: Calcd for $^{12}C_{18}{}^{1}H_{10}{}^{14}N_2{}^{35}Cl_2{}^{59}Co^{127}I_2{}^{23}Na^{32}S$: 691.7261. Found: *m/z* 691.7263 ($[M + Na]^+$).

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