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Amidine/Amidinate Cobalt Complexes: One-Pot Synthesis, Mechanism, and Photocatalytic Application for Hydrogen Production

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ABSTRACT: A new synthetic route was carried out via a one-pot reaction to prepare a novel series of amidine/amidinate cobalt complexes 8-10 by mixing ligand 2 (6-pyridin-2-yl-[1,3,5]-triazine-2,4-diamine) with Co(II) in acetonitrile or benzonitrile. We observed that a change of solvent from methanol (used in complex 7, previously reported) to nitrile solvents (MeCN and PhCN) led to the *in situ* incorporation of the amidine group, ultimately forming 8-10. So far, this is a unique method reported to introduce amidine/amidinate groups into a pyridinyl-substituted diaminotriazine complex. Remarkably, the single crystal X-ray diffraction study (SCXRD) of these new compounds reveals



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associations involving Janus DATamidine and Janus DATamidinate. A mechanism is proposed to explain the formation of amidine/ amidinate groups by investigating the single crystal structures of the possible intermediates **11** and **12** where the cobalt ion acts as a template. These amidine/amidinate cobalt complexes were used as a model to assess the photocatalytic activity for the hydrogen evolution reaction (HER). Complexes **9** and **10** show a 74% and 86% enhancement, respectively, of the catalytic activity towards the HER compared to complex **7**. This highlights the structure–property relationship. By examining the novel cobalt complexes described here, we discovered the following: (i) a method to introduce an amidine group into a pyridine DAT-based complex, (ii) the efficiency of amidine complexes to form multiple hydrogen bonds to direct the molecular organization, (iii) the plausible mechanism of formation of amidines based on the SCXRD study, (iv) the modification of the final structure and hence the final properties by varying the reaction conditions, and (v) the utility of amidine complexes towards photocatalytic HER activity.

■ INTRODUCTION

The development and synthesis of novel ordered materials with well-controlled chemical compositions and tailored properties for their utility in diverse fields, such as catalysis, ion-exchange, batteries, nonlinear optics, medicine, photovoltaics, energy storage, gas absorption, magnetism, etc., is a predominant part of chemistry.¹ The continuously evolving and never-ending exploration of this prospect has led to the discovery of numerous innovative materials with sundry applications as well as an advancement of knowledge leading to a better understanding of the structure-property relationship. Crystal engineering plays a pivotal role in the synthesis of such ordered materials as it provides a platform to amalgamate different organic molecules that have requisite topologies with inorganic components (metal ions) to produce ordered materials with predictable structures.² This strategy also provides an opportunity to vary the metal ions, which allows the tuning of the properties of materials. It is well known that the properties of a complex depend upon its structure, which in turn depends on the reaction conditions, such as precursors, counterions, solvents, temperature, etc. Thus in crystal engineering, ligand, metal ion, and reaction conditions play a

crucial role in determining the final structure of the materials and hence their properties.

One of the ligands widely used in coordination chemistry, is 2,2'-bipyridine (2,2'-bipy), whose good chelating ability has led to its extensive utilization in conjunction with the metal ions to engineer crystalline complexes suitable for a wide range of applications.³ However, the lack of a straightforward and efficient synthetic route to functionalize 2,2'-bipy severely limits any prospect of its use to create versatile coordination complexes. Fortunately, the design of pyridinyl- and pyrazinyl-substituted diaminotriazine (DAT) derivatives 2-4 (Scheme 1), called tectoligands, has resulted in the elimination of most of the drawbacks in regard to 2,2'-bipy derivative synthesis.⁴ The DAT group is easy to prepare and can be incorporated in any organic fragment. Due to its presence, 2-4 have the ability

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Scheme 1. Molecular Structures of Amidine 1, Ligands 2-6, and Cobalt Complexes 7-12



Scheme 2. (a) In Situ Synthetic Route to Prepare Amidine/Amidinate Cobalt Complexes 8–10 and (b) Representation of the Molecular Structures of Janus DATamidine and Janus DATamidinate



to bind to metal ions with the same ligating mode as 2,2'-bipy and undergo self-assembly by multiple hydrogen bonds with reliable patterns.⁵ Complexes prepared with tectoligands are so-called metallotectons.⁶ So far, metallotectons have been mainly studied to advance knowledge in crystal engineering that is focusing on the organization of molecules via intermolecular interactions. To adapt these compounds for the various applications for which they have been designed, additional functional groups must be integrated.

Through a literature survey, we found that the amidine functional group is facile to prepare and has several applications. Amidine groups can be formed by the reaction of a nitrile (RCN) with an amine (R'NH₂) in the presence of Lewis acids. They are a class of organic compounds that have a $-C(=NH)NH_2$ group homologous to a carboxamide in which the oxygen atom of the oxo has been replaced by the N-H group. They are present in numerous complexes that find applications in medicinal chemistry, pharmacology,

catalyst design, material science, etc.⁷ Besides, substituted amidines have a significant role in several biological activities; due to which, their synthesis has been of interest for many research groups. In principle, it should be viable to incorporate an amidine functionality into DAT substitution-based complexes. However, no report has been presented so far on the synthesis of amidine compounds using the $-NH_2$ of the DAT group.

Herein, combining the self-assembly provided by DAT groups with the versatile properties associated with amidines, we have developed a new facile synthetic route to prepare amidine cobalt complexes 8-10 via a one-pot reaction by reacting 2 with Co(II) salt in either acetonitrile (MeCN) or benzonitrile (PhCN) under reflux (Scheme 2a). This work is the unique report on the synthesis of an amidine using the $-NH_2$ of the DAT group. In our previous work, we showed the synthesis of complex 7 by mixing 2^8 with Co(II) salt in MeOH under reflux (Scheme 1).^{4c} We observed that a change

Scheme 3. Reactions Performed to Elucidate the Mechanism of Amidine/Amidinate F

Reaction A:	2	MeCN or PhCN, reflux	No amidine was isolated
Reaction B:	2	$\frac{\text{Co(ClO}_4)_2.6\text{H}_2\text{O}}{\clubsuit}$ MeCN, rt to ~75°C	11
Reaction C:	11	MeCN, reflux	8
Reaction D:	4	$\frac{\text{Co(ClO}_4)_2.6\text{H}_2\text{O}}{\clubsuit}$ MeCN, reflux	12

of solvent from MeOH to either MeCN or PhCN led to the formation of 8–10. Interestingly, by analyzing diverse reaction conditions (Scheme 3) and the crystallographic structure of complexes 8-12, a plausible mechanism for amidine/ amidinate formation was proposed. Based on the principles of organic and inorganic chemistry, 11 could be the reactive intermediate to form 8. We also showed that 9 and 10 are catalytically efficient toward the light-driven hydrogen evolution reaction (HER) and show a significantly improved activity compared to that of complex 7 (prepared under different reaction conditions). The HER is one of the best possible solutions to control the currently deteriorating situation of our environment due to increased global warming and the greenhouse effect.9 During the past decade, cobalt complexes have been widely used as catalysts for H₂ generation that are photochemically driven. In particular, cobalt complexes based on polypyridine have attracted considerable attention for photocatalytic proton reduction.¹⁰ In this regard, the design of functionalized polypyridyl complexes still represents one of the most important challenges in the field of catalysis. The results obtained in the present work demonstrated an enhanced HER activity with the presence of amidine/amidinate groups in 9 and 10 as compared to that of 7.¹¹ Hence, a modification in the preparatory strategy led to novel complexes with different structures and improved hydrogen evolution, emphasizing the relationship between a compound's structure and its properties.

RESULTS AND DISCUSSION

In a previous study, we described the design, synthesis, and characterization of 7 and investigated its catalytic activity for the light-driven hydrogen evolution reaction (HER).^{4c,11} To develop a new method to functionalize complexes with amidine/amidinate functional groups and potentially improve the catalytic activities for the HER, we prepared 8–10 (Scheme 2a). Our method to synthesize amidine/amidinate cobalt complexes is advantageous because the coordination and the formation of 5, 5', 6, and 6' are *in situ* and no further purification step is required (Scheme 1). Compounds 5, 5', 6, and 6' were never isolated but simply were the initial intermediates that led to the formation of ultimate intermediates (11 and 12), which were followed by the final complexes (8-10). A similar kind of analogous *in situ* reaction

was observed in the hydration of the nitrile group into carboxamide with a ferrous center as the Lewis acid reaction site.¹² We also examined the effect of counterions using $Co(ClO_4)_2$ and $Co(BF_4)_2$ salts. Our results showed that the change of the counterion did not prevent the formation of the amidine/amidinate group. In addition, we found that the incorporation of the amidine/amidinate group and a change of the counterion results in the greater stability of 9 and 10 in HBF₄ compared to that of 7. In this work, we have laid an emphasis on studying the mechanism of amidine/amidinate formation. Furthermore, because 9 and 10 have shown a good stability in acid conditions, we tested their catalytic activity for the HER.

Synthesis and Structural Characterization. Complexes 8-12 were characterized by electrospray ionization mass spectrometry (ESI-MS), infrared (IR) spectroscopy, elemental analysis (EA), and single crystal X-ray diffraction (SCXRD). Their thermal stabilities were investigated by thermogravimetric analysis (TGA) (Figure S1). Compounds 8-11 are thermally stable up to ~ 270 °C, and 12 is thermally stable up to ~200 °C. Analyses by ESI-MS measurements confirm the presence of the metal ions for all complexes (Experimental Section). The IR spectra of 8-12 indicate the presence of typical broad bands characteristic of symmetric and asymmetric N-H stretching in the range from 3100 to 3500 cm⁻¹ (Figure S2). In the case of 8-10, the presence of the C=N bond of the C(=NH)NH group is mainly diagnosed by the bands at ~ 1522 cm⁻¹. The bands at ~ 2270 cm⁻¹ in the spectra of 11 and 12 could be attributed to the $-C \equiv N$ bond of coordinated acetonitrile molecules. For 8, 9, 11, and 12, the bands corresponding to perchlorate (ClO₄⁻) are observed between 1000 and 1100 cm⁻¹. For **10**, the band at 1020 cm⁻¹ is ascribed to tetrafluoroborate (BF₄⁻). SCXRD was performed to confirm the obtention of 8-12 and to study the selfassembly by hydrogen bonds involving Janus DATamidine and Janus DATamidinate (Scheme 2b). Figure 1 shows the structures of these compounds. The general formulas of 8-12 determined by EA (Experimental Section) are in good agreement with their crystallographic data (Tables S1 and S5).

The structure of 8 is shown in Figures 1a, S3, and S4. In the structure, the Co(III) ion is bound by ligands 5 and 5' oriented perpendicular to each other (dihedral angle δ = 87.98° between triazinyl rings) with each molecule coordi-

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Figure 1. (a-e) View of the main hydrogen bonding interactions in the structures of 8-12, respectively. Hydrogen bonds are represented by dashed lines. Carbon atoms are shown in gray, hydrogen atoms are shown in white, oxygen atoms are shown in red, nitrogen atoms are shown in blue, chlorine atoms are shown in green, boron atoms are shown in orange, fluorine atoms are shown in cyan, and cobalt atoms are shown in pink. Hydrogen atoms attached to a carbon atom were omitted for clarity.

nated via the (NNN) set using triazine, pyridine, and amidine/ amidinate nitrogen atoms to form a distorted octahedral dication complex $[Co(5)(5')]^{2+}$. The charge of the complex is balanced by an amidinate ligand 5' and two disordered perchlorate ions. In the structure, complexes with λ and Δ configurations are alternately linked by N–H…N hydrogen bonds according to motif I to form chains (Chart 1a). Chains are further joined by N–H…O hydrogen bonds involving bridging of the perchlorate to generate a 2D sheet (Figure 1a). It is noted that the change of oxidation state from Co(II) to Co(III) due to the experimental condition is also described in several other reports.¹³ Selected hydrogen bonds and angles are given in Table S2. To evaluate the effect of the R substituent, several nitrile compounds (RCN) with electron donating (R = $-CH_3$ and -Phenyl) and withdrawing groups (R = $-PhNO_2$ and $-PhCF_3$) were utilized to prepare amidine/amidinate cobalt complexes. The synthesis with 4-trifluoromethyl-benzonitrile and 4-nitro-benzonitrile in MeOH or DMF (as solvents), respectively, did not deliver amidine/amidinate compounds. However, with benzonitrile, **9** was successfully obtained in a good yield. Complex **9** is structurally analogous to **8** with the unique mononuclear $[Co(6)(6')]^{2+}$ in the crystal lattice (Figures 1b, S5, and S6). These two compounds differ only in the substituent present on the amidine/amidinate moiety (a methyl in ligands **5** and **5**' vs a phenyl ring in ligands **6** and **6**'). Chart 1. Hydrogen Bonding Motifs (a) I–III of Amidine/Amidinate and (b) IV–VI of the Diamino-1,3,5-triazinyl Group (DAT)



Complex 9 is connected by N-H…N hydrogen bonds according to motif II (Chart 1a) to form chains, which are then joined by bridging involving ClO_4^- to generate a 2D sheet (Figure 1b). It is noteworthy that 9 is solvated with ethyl acetate and benzonitrile molecules. Details of hydrogen bonds and angles are provided in Table S3.

To determine if the counterion plays a key role in the formation of the amidine/amidinate, we also synthesized **10** using **2** and $Co(BF_4)_2 \cdot 6H_2O$. Cationic complex **10** with a chemical formula of $[Co(6')_2]^+$ has an identical coordination geometry around the Co(III) ion as those of **8** and **9** (Figures 1c and S7). In the structure, two amidinate ligands 6' and one BF_4^- balance the charge of the Co(III). Adjacent complexes (λ and Δ) self assemble by N–H···N hydrogen bonds according to motif III (Chart 1a) to form 1D chains running along the *c*-axis. These chains are packed together to produce the final structure (Figure S8). The crystal of **10** is a solvate incorporating one diethyl ether and four benzonitrile molecules. A summary of hydrogen bonds and angles is given in Table S4.

Mechanism. Our study demonstrates that the concomitant addition of Co(II) salts $(Co(ClO_4)_2 \cdot 6H_2O)$ or $Co-(BF_4)_2 \cdot 6H_2O)$ and 2 in RCN solvent (R = methyl or phenyl)) under reflux offers a novel one-pot synthesis of 8–10. To determine the sequence of steps involved in the mechanism of amidine/amidinate formation, we performed reactions A–D (Scheme 3).

Usually, when nitrile (RCN) and amino $(R'NH_2)$ compounds are mixed in an acidic solution, the amidine product 1 can be obtained. However, reaction A of free ligand 2 with MeCN or PhCN at reflux in acidic or basic conditions, respectively, did not result in 5. This shows that in our case the $-NH_2$ groups of DAT groups are not "normal" amino groups. We believe that the lone pair of the nitrogen atom of $-NH_2$ group is in resonance with the triazinyl ring, which is no longer available for nucleophilic attack. Besides, it also indicates that the metal ion governs the reaction between RCN and 2 by providing the necessary coordination sites for binding to allow the formation of the amidine. Reaction B was also performed

to assess the importance of temperature. In all reactions below the temperature of the boiling point of MeCN, only 11 was isolated. The molecular structure of 11 shows a Co(II) ion surrounded by two ligands 2 and two MeCN in the cis position, forming a distorted octahedral complex (Figures 1d and S9). Ligands 2 are dispositioned in two different planes, as is apparent from the dihedral angle ($\delta = 71.54^{\circ}$) between triazine rings. Neighboring complexes (λ and Δ) are associated by N-H…N hydrogen bonding in accordance with motifs IV and VI (Chart 1b) to produce a three dimensional network (Figures 1d and S10). The complex is further strengthened by hydrogen bonding interactions involving the hydrogen atom of the free $-NH_2$ group and the nitrogen atom of the coordinated MeCN. N-H…O hydrogen bonds involving bridging ClO₄⁻ also reinforce the network (Figure S10). A summary of hydrogen bonds and angles is given in Table S6.

From a structural point of view, compound 11 could be the reactive intermediate to generate 8. Indeed, in the crystal structure shorter distance of \sim 3 Å between the inner $-NH_2$ of the DAT group and the carbon atom of the coordinated MeCN is thought to enable the formation of 8. To validate our hypothesis, we conducted reaction C by refluxing compound 11 in MeCN. Unsurprisingly, we managed to isolate 8. From the crystallographic study of 8-11, we believe that only the -NH₂ near the coordinated MeCN can contribute to the formation of amidine/amidinate functional groups. Moreover, we also think that this reaction happens intramolecularly since the outer -NH₂ of the DAT group did not generate the amidine/amidinate unit, as can be seen from molecular structures of 8-10. To verify these assumptions, we performed reaction D by mixing 4 with the $Co(ClO_4)_2 \cdot 6H_2O$ salt in MeCN under reflux and obtained 12. SCXRD analysis shows that the Co(II) ion is bound by two ligands of 4, two H_2O_1 , and two MeCN molecules in the trans positions to generate an octahedral coordination geometry (Figures 1e and S11). Adjacent complexes are linked by N-H…N hydrogen bonds following motif V (Chart 1b) to form a 2D sheet (Figure 1e). Sheets are interlinked by the bridging of ClO_4^- to generate a



Scheme 4. Proposed Mechanism for the Formation of Amidine Cobalt Complexes 8-10

Figure 2. (a) TONs and (b) TOFs of the hydrogen evolution reactions of 9 and 10 in blue light (complex concentration of 1 mM).

3D hydrogen-bonded network (Figure S12). A summary of hydrogen bonds and angles is given in Table S7.

The molecular structure of 12 shows that although MeCN is coordinated to a cobalt ion, the formation of the amidine/ amidinate does not occur because the $-NH_2$ and -CN groups are too far from each other. It also demonstrates that an intermolecular nucleophilic attack from the $-NH_2$ of one complex to the other does not happen. After isolation of 12 by filtration, the filtrate was also analyzed by ESI-MS to exclude the presence of an amidine/amidinate cobalt complex in solution. The unique recognizable peak detected corresponds to the free ligand 4.

From reactions of Schemes 2 and 3, we concluded that the formation of amidine/amidinate only occurs under the following conditions: (i) both ligand 2 and nitrile compounds should be coordinated to the cobalt ion, (ii) only the $-NH_2$ group closer to the coordinated nitrile group can participate in the reaction, (iii) the reaction is intramolecular, and (iv) counterions do not affect the formation of amidine/amidinate. Using these results, we proposed a mechanism for the formation of 8-10 (Scheme 4). The mechanism involves four elementary steps I-IV. In step I, ligand 2 chelates the cobalt ion with the simultaneous coordination of two nitrile compounds to form an intermediate complex. In step II, the lone pair of the N atom from the inner -NH₂ group attacks the carbon atom of the nitrile group to form the chargeseparated ⁺N-C=N⁻ intermediate. Step III corresponds to a proton switch. The last elemental step IV is a single and double deprotonation to form 8, 9, and 10, respectively.

Hydrogen Evolution Reaction. The optical and electrochemical properties along with the photocatalytic activity for the H₂ evolution reaction (HER) were investigated for 9 and **10.** Figure S13 shows the UV-vis spectra for 2, 9, and 10 measured at room temperature in a DMF solution at a concentration of 8.8×10^{-6} M, while the inset shows the graphs corresponding to a concentration of 8.8×10^{-3} M. The absorption band at 265 nm observed for the free ligand 2 and a shoulder at ~260 nm in 9 correspond to a ligand-centered $\pi - \pi^*$ electronic transition. A sharp band at 330 nm for 9 and a shoulder at 310 nm for 10 are ascribed to an intraligand $n - \pi^*$ electronic transition. Characteristic weak d-d transition bands were observed for 9 and 10 at around 500 and 600 nm, respectively. Selected data (wavelengths (λ_{max}), absorbance (A), and molar absorptivity (ε)) are summarized in Table S8.

The electrochemical behavior of 9 and 10 was recorded using cyclic voltammetry in DMF solutions at a complex concentration of 1 mM with 1 M tetrabutylammonium hexafluorophosphate (TBA-PF₆) as the supporting electrolyte at a scan rate of 100 mV s⁻¹ (Figure S14). Cyclic voltammograms of 9 and 10 show quasi- and partially reversible oxidation and reduction peaks (Table S9), respectively, vs the saturated calomel electrode (SCE). The peaks in the range of -0.14 to -0.78 V correspond to the Co(III/II) redox couple, those in the range of -1.10 to -1.83V correspond to the Co(II/I) redox couple, and those in the range of -2.0 to -2.50 V correspond to a reduction of the ligand.¹⁴ The possibility of multiple redox states for these two

CONCLUSIONS

complexes indicates their potential application as catalysts, especially for the HER. Intrigued by the potential application of amidine/amidinate

complexes, we studied the catalytic activity of **9** and **10** for the HER. The HER experiment was conducted for 22 h in a DMF solution of **9** and **10** under blue light (452 nm) using triethanolamine (TEOA) as the sacrificial electron donor, $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ as the photosensitizer (PS), and aqueous HBF₄ as the proton source. TON and TOF curves of **9** and **10** are shown in Figure 2, and data are shown in Table 1. Complex

Table 1. Turnover Number and Turnover FrequencyMaxima for 9 and 10

sample	H_2 production (mmol h^{-1})	TON _{max}	TOF _{max}
7	0.11	16	307
9	0.43	50	786
10	0.78	179	878

 a The TON is reported in moles of hydrogen per mole of PS, and the TOF is reported in mmol of hydrogen per mole of PS per minute.

9 displays HER properties with a TON and TOF of 50 mol_{H2} mol_{PS}⁻¹ and 786 mmol_{H2} mol_{PS}⁻¹ min⁻¹, respectively. For **10**, a TON of 179 mol_{H2} mol_{PS}⁻¹ and a TOF of 878 mmol_{H2} mol_{PS}⁻¹ min⁻¹ were recorded. These values are much higher compared to those of 7 which exhibits a TON and TOF of 16 mol_{H2} mol_{PS}⁻¹ and 307 mmol_{H2} mol_{PS}⁻¹ min⁻¹, respectively. The hydrogen production rates of **9** and **10** are enhanced by 74% and 86%, respectively, compared to that of 7. Control experiments conducted using the metal salts illustrated that the metal ion has a negligible contribution towards the photocatalytic activity in comparison to the complexes (Figure S15). The control experiments conducted in the presence of PS/ TEOA alone with and without light showed no H₂ production.¹⁵

To the best of our knowledge, no amidine/amidinate complex has been previously utilized as a photocatalyst for the HER. However, we compared the photocatalytic efficiency with other cobalt-based photocatalysts reported in the literature whose HERs were carried out under similar conditions as ours. Brooker and co-workers screened 17 cobalt complexes, which were 11 dinuclear, three tetranuclear, and three mononuclear complexes, for photocatalytic hydrogen evolution in the presence of 0.1 mM $[Ru(bpy)_3]^{2+}$ as a photosensitizer (PS), 1 M triethanolamine as a sacrificial electron donor, and 0.1 M fluoroboric acid (HBF₄) as a proton source in DMF as a solvent. Among the 17 cobalt complexes, a dinuclear cobalt complex with the molecular formula $[Co^{II}(^{t-BuPh}Trz_{Me/Me})(\mu-BF_4)](BF_4)_3$ (where Trz = 1,2,4triazole was used as the central bridging moiety and ${}^{t\text{-BuPh}} Trz_{Me/Me}$ is an example of bis-tetradentate ligands) produced H₂ with the TON of 150 mol_{H_2} mol_{PS}^{-1} . In addition, the three mononuclear cobalt complexes $[Co^{II}(\mathbf{M}_{Et})]^+$, $[Co^{II}({}^{Br}M_{Et})]^+$ and $[Co^{II}(M_{pr})]^+$ (where M ligands are three different tetradentate diimine macrocycles featuring a diphenylamine head unit) produced H₂ with TONs of 130, 94, and 25 $mol_{H_2} mol_{PS}^{-1}$, respectively.¹⁵ Furthermore, the most widely reported standard reference cobaloxime catalyst $([Co^{III}(dmgH)_2(py)Cl])$ produces H₂ with a TON of 68 mol_{H_2} mole_{PS}^{-1.11} Comparatively, the hereby studied complex 10 produces a higher amount of H₂.

We have reported the synthesis of a new series of crystalline amidine/amidinate cobalt complexes 8-10 obtained by a onepot reaction of 2 with Co(II) in MeCN or PhCN under reflux. Their structures were confirmed, and the self assemblies were studied by SCXRD. In the solid state, Janus DATamidine and Janus DATamidinate groups were the main sticky sites by hydrogen bonds that dictated the supramolecular organization in the cases of 8-10. For 11 and 12, as expected, DAT groups form predictable hydrogen bond patterns to produce the 3D network. The mechanism of amidine/amidinate formation was elucidated by analyzing the crystal structures of 8–12. Mainly, four elemental steps were involved to form amidine/amidinate cobalt complexes. The HER performed on 9 and 10 demonstrated an improvement in the photocatalytic efficiency as compared to a previously reported cobalt complex 7 that differs in terms of amidine/amidinate groups and the counterion. Our work uncovered the following three principles of chemistry: (i) the effect of the variation of reactants and reaction conditions on the chemical reaction and hence the product formation, (ii) a reaction may occur if molecules are in proximity and in suitable conformations, and (iii) a small modification of the structure can drastically alter the properties of materials. This current study opens a door to prepare a large number of amidine/amidinate complexes with various metal ions and tectoligands that promise to be interesting candidates because of their potential applications.

EXPERIMENTAL SECTION

General Notes and Procedures for the Synthesis of 8–12. 6-(Pyridin-2-yl)-1,3,5-triazine-2,4-diamine 2 and 6-(pyridin-4-yl)-1,3,5-triazine-2,4-diamine 4 were synthesized according to the reported methods.¹¹ Complexes 8–12 were prepared following the method below. All the other chemicals were commercially available and were purchased and used without any additional purification.

General Procedure for Preparing 8–12. A stirred suspension of $Co(ClO_4)_2.6H_2O$ or $Co(BF_4)_2.6H_2O$ (1.0 equiv) and the ligand (2.0 equiv) were heated at reflux in a nitrile solvent (25 mL) for 16 h. In the case of 11, the reaction was conducted at room temperature. The resulting homogeneous mixture was cooled and subjected to crystallization.

Complex **8**. The reaction of **2** (0.05 g, 0.2656 mmol) with $Co(ClO_4)_2 \cdot 6H_2O$ (0.049 g, 0.1328 mmol) in MeCN according to the general procedure yielded **8** (83 mg, 0.1159 mmol, 87%). Orange-red crystals of composition $[Co(5)(5')](ClO_4)_2 \cdot 4(CH_3CN)$ were grown by allowing Et₂O to diffuse slowly into a solution in MeCN. FTIR (ATR): 3445, 3344, 3238, 2935, 2851, 1622, 1604, 1569, 1526, 1494, 1470, 1455, 1401, 1289, 1270, 1216, 1058, 1032, 1001, 956, 928, 843, 812, 782, 757, 700, 620 cm⁻¹. HRMS (ESI) Calcd for $[C_{20}H_{22}CoN_{14}]^+$ *m/e*: 517.1484. Found: 517.1433. Anal. Calcd for $C_{20}H_{21}Cl_2CoN_{14}O_8$: C, 33.58; H, 2.96. Found: C, 33.26; H, 2.90.

Complex **9.** The reaction of **2** (0.05 g, 0.2656 mmol) with $Co(ClO_4)_2 \cdot 6H_2O$ (0.049 g, 0.1328 mmol) in PhCN according to the general procedure yielded **9** (95 mg, 0.1130 mmol, 84%). Orange-red crystals of composition $[Co(6)(6')](ClO_4)_2 \cdot 2(C_2H_3COOCH_3)$ -(PhCN) were grown by layering EtOAc over the solution in PhCN. FTIR (ATR): 3449, 3336, 3239, 3090, 1622, 1596, 1584, 1569, 1541, 1522, 1494, 1483, 1464, 1447, 1397, 1367, 1308, 1284, 1242, 1160, 1086, 1067, 1057, 1027, 1001, 990, 929, 875, 812, 781, 756, 727, 699, 671, 644, 619 cm⁻¹. HRMS (ESI) Calcd for $[C_{30}H_{26}CoN_{14}]^{2+}$ *m/e*: 320.5898. Found: 320.5901. Anal. Calcd for $C_{30}H_{25}Cl_2CoN_{14}O_8$: C, 42.92; H, 3.00. Found: C, 42.25; H, 2.96.

Complex 10. The reaction of 2 (0.05 g, 0.2656 mmol) with $Co(BF_4)_2 \cdot 6H_2O$ (0.045 g, 0.1328 mmol) in PhCN according to the general procedure yielded 10 (95 mg, 0.1165 mmol, 88%). Orange-red crystals of composition $[Co(6')_2](BF_4)_2 \cdot (C_2H_5OC_2H_5) \cdot 4(Ph-$

CN)₄ were grown by layering Et₂O over the solution in PhCN. FTIR (ATR): 3476, 3445, 3359, 3305, 3237, 3154, 3088, 1672, 1621, 1595, 1582, 1565, 1541, 1524, 1481, 1448, 1434, 1394, 1371, 1339, 1277, 1235, 1161, 1053, 1020, 984, 923, 876, 820, 785, 763, 699, 674, 659, 648, 631 cm⁻¹. HRMS (ESI) Calcd for $[C_{30}H_{26}CoN_{14}]^+$ *m/e*: 641.1797. Found 641.1734. Anal. Calcd for $C_{30}H_{24}BCoF_4N_{14}$: C, 49.61; H, 3.33. Found: C, 49.09; H, 3.15.

Complex **11.** The reaction of **2** (0.05 g, 0.2656 mmol) with $Co(ClO_4)_2 \cdot 6H_2O$ (0.049 g, 0.1328 mmol) in MeCN according to the general procedure yielded **11** (82 mg, 0.1144 mmol, 86%). Pink crystals of composition $[Co(2)_2(CH_3CN)_2](ClO_4)_2$ were grown by allowing Et₂O to diffuse slowly into a solution in MeCN. FTIR (ATR): 3481, 3460, 3349, 3230, 3119, 3084, 2930, 1678, 1620, 1584, 1563, 1515, 1488, 1463, 1448, 1400, 1367, 1300, 1283, 1269, 1197, 1159, 1091, 1057, 1022, 992, 930, 914, 824, 790, 756, 703, 684 cm⁻¹. HRMS (ESI) Calcd for $[C_{16}H_{16}CON_{12}]^{2+}$ *m/e*: 217.5476. Found: 217.5470. Anal. Calcd for $C_{20}H_{22}Cl_2CON_{14}O_8$: C, 33.53; H, 3.10. Found: C, 33.33; H, 3.23.

Complex 12. The reaction of 4 (0.05 g, 0.2656 mmol) with $Co(ClO_4)_2 \cdot 6H_2O$ (0.049 g, 0.1328 mmol) in MeCN according to the general procedure yielded 12 (91 mg, 0.1184 mmol, 89%). Pink crystals of composition $[Co(4)_2(H_2O)_2(CH_3CN)_2](ClO_4)_2 \cdot 2 \cdot (CH_3CN)$ were grown by allowing Et₂O to diffuse slowly into a solution in MeCN. FT-IR (ATR): 3445, 3363, 3338, 3207, 3152, 2934, 1643, 1622, 1579, 1533, 1448, 1414, 1399, 1322, 1260, 1218, 1080, 1059, 985, 930, 857, 809, 792, 748, 697, 621 cm⁻¹. HRMS (ESI) Calcd for $[C_{16}H_{16}CoN_{12}]^{2+}$ m/e: 217.5476. Found: 217.5444. Anal. Calcd for $C_{20}H_{26}Cl_2CoN_{14}O_{10}$: C, 31.93; H, 3.86. Found: C, 31.53; H, 3.63.

Characterization Studies of 8-12. Crystallographic data were collected at 100 K using a Bruker Microstar diffractometer with Cu K α radiation (λ = 1.54178 Å) for compounds 9–11 and at 150 K using a Bruker Venture Metaljet diffractometer with Ga K α radiation $(\lambda = 1.34139 \text{ Å})$ for compounds 8 and 12. The structures were solved by intrinsic phasing using either SHELXT or direct methods using SHELXS, and non-hydrogen atoms were refined anisotropically with SHELXL-2018 for compounds 8 and 12.¹⁶ Hydrogen atoms attached to carbon atoms were treated by first locating them from difference Fourier maps, recalculating their positions using standard values for distances and angles, and then refining them as riding atoms. Hydrogen atoms attached to nitrogen or oxygen atoms were found by Fourier difference maps and fully refined. UV-vis spectra were recorded on a Cary 5000 instrument. The ATR-FTIR spectra were recorded with a Nicolet iS 10 Smart FT-IR spectrometer within 600-4000 cm⁻¹. The thermogravimetric analysis was performed using a PerkinElmer TGA instrument. The samples were heated from 25 to 800 °C with a rate of 10 °C min⁻¹.

Electrochemical measurements were achieved in pure dimethylformamide purged with argon at room temperature with a BAS SP-50 potentiostat. The counter electrode was a Pt wire, a glassy carbon electrode was used as a working electrode, and silver wire was the pseudo-reference electrode. The reference of electrochemical potential was set using 1 mM ferrocene as an internal standard, and the values of potentials were reported vs the SCE.¹⁷ The concentration of the samples was 1 mM. Tetrabutylammonium hexafluorophosphate (TBA-PF₆) (0.1 M) was used as the supporting electrolyte. Cyclic voltammograms were performed at a scan rate of 100 mV s⁻¹ and a current amplitude of 100 μ A.

A PerkinElmer Clarus-480 gas chromatograph (GC) was used to measure the hydrogen gas evolved from the reaction. The assembly of the chromatograph consists of a thermal conductivity detector, a 7 in. HayeSep N 60/80 precolumn, a 9 in. molecular sieve 13X 45/60 column, a 2 mL injection loop, and argon gas as a carrier and eluent. DMF was used as the solvent in our experiments. Three separate solutions of a photosensitizer $[Ru(bpy)_3]$ (PF₆)₂, a sacrificial donor and proton source, and a catalyst were prepared to obtain 5 mL of sample solutions in standard 20 mL headspace vials. In DMF, the resulting molar concentration of the photocatalytic components were as follows: 0.1 M HBF₄, 0.56 M water, 1 M triethanolamine (TEOA), 0.1 mM photosensitizer $[Ru(bpy)_3]$ (PF₆)₂, and 1 mM catalyst (9 and

10) (pH \sim 8 to 9). The resulting mixture was placed on a panel of blue LED 10 W center at 445 nm in a thermostatic bath set at 20 °C, which was sealed with a rubber septum and pierced by two stainless steel tubes. Argon was carried in the first tube at a flow rate of 10 mL min⁻¹ (the flow rate was adjusted with a manual flow controller (Porter, 1000) and referenced with a digital flowmeter (PerkinElmer Flow Mark)). The second stainless steel tube carried the flow to the GC sample loop, passing through a 2 mL overflow protection vial and an 8-port stream select valve (VICCI). Timed injections were done by a microprocessor (Arduino Uno) coupled with a custom PC interface. Corresponding to a specific argon flow, the H₂ production rate was calibrated. For the calibration of the H₂ production rate at a specific argon flow, a syringe pump (New Era Pump) equipped with a gastight syringe (SGE) and a 26s-gauge needle (Hamilton) was used to bubble different rates of pure hydrogen gas into the sample to a minimum of 0.5 μ L min⁻¹. This gave a linear fit for peak area for H₂ vs the flow rates of H₂. For calibration testing, stock cylinders of a known concentration of H_2 in argon replaced the argon flow (inserted at the prebubbler to keep the same vapor matrix). The measured results independent of the flow rate (under same pressure) can be easily converted into the rate of hydrogen using eq 1. The errors associated to the TON and TOF are estimated to be 10%.¹⁸

Rate of production of H₂ (μ L in⁻¹)

=
$$[H_2 \text{ standard}] (ppm) \times \text{Ar flow rate } (L \text{ in}^{-1})$$
 (1)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01495.

Additional crystallographic details (including thermal atomic displacement ellipsoid plots), FT-IR and TGA data of 8-12, and HER curves of cobalt salts (PDF)

Accession Codes

CCDC 1996216–1996220 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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