Co^{II} Complexes of Triazine-Based Tridentate Ligands with Positive and Attractive $Co^{II/III}$ Redox Couples

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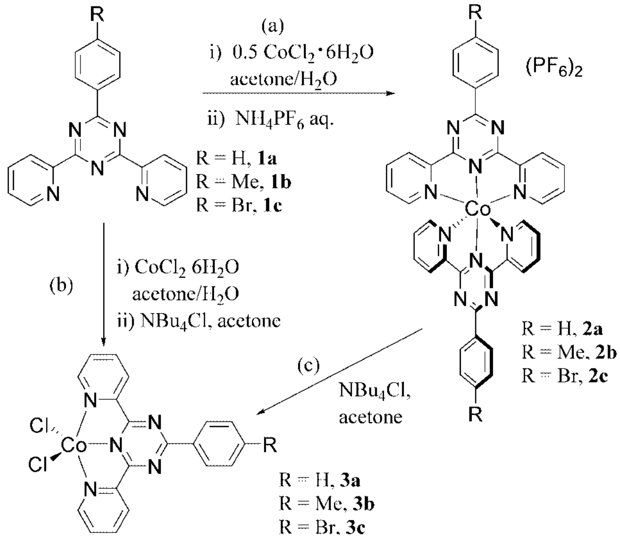
Co^{II} complexes based on the triazine ligand 2,4-di(2′-pyridyl)-6-(p-R-C_6H_4)-1,3,5-triazine have been synthesized and characterized. Cyclic voltammetry shows that the $Co^{II/III}$ redox couple is more positive than previously described Co complexes of tridentate ligands. The $Co^{II/III}$ redox couple may be varied depending on the nature of the substituent on the phenyl ring of the triazine ligand.

Introduction

Dye-sensitized solar cells (DSSCs) have been intensely studied in the last fifteen years since Grätzel published his landmark work.[1,2] In order to advance the field, many groups have focused their efforts on improving the excited-state properties of the polypyridine Ru^{II} complexes that act as the photosensitizers in the Grätzel cell.[3] Much less attention has been paid to the redox mediator, even though it contributes directly to the maximum photocurrent attainable by the DSSC.[2,3] Whereas the classic redox mediator in such systems is the volatile and corrosive I^-/I_3^- couple, its redox potential is fixed and, therefore, cannot be varied to improve the efficiency of the DSSC.[4] Recently, Co^{II} complexes of heterocyclic ligands have been shown to be effective redox mediators in DSSCs, as they are non-corrosive, non-volatile and modifiable.[5–7] Herein we report on a new family of Co^{II} complexes based on tridentate triazine ligands that are easily synthesized and modified. Their considerably more positive $Co^{II/III}$ redox couples than previously reported Co^{II} complexes of polypyridine ligands favors their use in DSSCs.[5,6]

Results and Discussion

The synthesis of triazines ligands **1a**[8] and **1b**[9] has previously been reported. Ligand **1c** was synthesized by the addition of p-bromobenzonitrile to a solution of $LiNMe_2$ in anhydrous diethyl ether.[9,10] The amidinate intermediate that forms reacts with two equivalents of 2-cyanopyridine to afford ligand **1c** after loss of dimethylamide. A series of homoleptic Co^{II} complexes of ligands **1a**–**c** were synthesized by allowing the ligands to react with $CoCl_2{\cdot}6H_2O$ followed by precipitation of complexes **2a**–**c** from the reaction mixture by the addition of NH_4PF_6 [see (a) in Scheme 1].[11] Heteroleptic complexes **3a**–**c** may be obtained directly by treating ligands **1a**–**c** with one equivalent of $CoCl_2{\cdot}6H_2O$ in the presence of tetrabutylammonium chloride (Bu_4NCl) [see (b) in Scheme 1] or indirectly when Bu_4NCl is introduced into an acetone solution of complexes **2a**–**c** [see (c) in Scheme 1].[12] It has previously been established that an equilibrium exists between the homo- and heteroleptic state of Co^{II} complexes of 2,4,6-tripyridyl-s-triazine in acidic solution.[13] In this case, heteroleptic Co^{II} complexes **3a**–**c** could be obtained by the addition of Bu_4NCl to complexes **2a**–**c**.



Scheme 1. Synthesis of Co^{II} homo- and heteroleptic complexes.

The ^1H NMR chemical shifts of the homoleptic complexes are typical of paramagnetic Co^{II} complexes that are low spin, with chemical shifts ranging over approximately

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110 ppm (Table 1).[14] The signals are broadened considerably, and therefore no coupling constants could be obtained from the spectra. The greatest shifts are observed for the protons *ortho* to the pyridine nitrogen atoms and, therefore, closest to the paramagnetic Co^{II} center. The protons farthest from the paramagnetic center, those on the phenyl ring, have the smallest shift as compared to the free ligands.[9]

Table 1. ^{1}H NMR chemical shifts of homoleptic complexes **2a**, **2b** and **2c** in CD_3CN.

	δ [ppm]						
	Pyridyl				Phenyl		CH_3
1c	8.99	8.87	8.74	7.60	8.74	7.73	
2a	115.08	80.09	37.54	22.87	13.51	6.17	
2b	113.39	78.56	37.13	21.99	13.27	6.13	5.83
2c	111.88	79.38	36.28	22.96	13.36	6.66	

The X-ray crystal structure of **2c** is shown in Figure 1.[15] The Co^{II} ion is bound by two orthogonal ligands **1c** in a pseudo-octahedral coordination environment as the peripheral pyridines in each ligand pinch in to form N–Co–N angles of 151.79°. The Co–N bond length to the central triazine (1.986 Å) is shorter than the Co–N bond length in homoleptic terpyridine complex (2.022 Å) and the homoleptic triazine complex of 2,4,6-tris(2′-pyridyl)-1,3,5-triazine ligand (2.058 Å).[16,17] The Co–N bond lengths to the peripheral pyridine rings range from 2.134 Å to 2.158 Å, similar to those found in terpyridine complexes of Co^{II}.

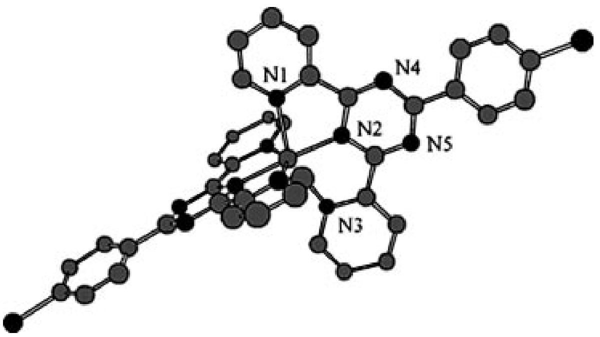

Figure 1. Ball-and-stick representation of the X-ray crystal structure of **2c**. The counteranions and solvent of crystallization have been omitted for clarity.

The phenyl ring is twisted by 13.3° relative to the central triazine ring (Figure 1). This near planar arrangement is due to favorable N-to-CH hydrogen bonding interactions between the N lone pairs and the hydrogen atoms *ortho* to the interannular bond. The slight twist in the interannular bond is a result of edge-to-face packing between the phenyl rings in different molecules of **2c**, which are separated by 3.514 Å (Figure 2). A planar arrangement should easily be adopted in solution which would permit greater electron delocalization between the triazine and the phenyl ring. The two PF_6 counterions are found above and below the planes of the triazine rings and do not interfere with the phenyl packing arrangement, consistent with other extended packing arrangements in the solid state.[18] There is also a short Br1···Br2′ distance of 3.395 Å between adjacent molecules which is indicative of favorable van der Waals interactions which give rise to a linear one-dimensional tape in the solid state (Figure 2).

In the electronic spectra of complexes **2a**–**c**, a very weak metal-centered transition is found at approximately 470 nm (Figure 3). The $\lambda_{max.}$ for these d–d transitions are difficult to identify due to the low energy tail from the ligand-based transitions but the extinction coefficients are in the order of 500 $M^{-1}\,cm^{-1}$ for all three complexes. For applications in DSSC, a low extinction coefficient is desirable so as to minimise the competition between the redox mediator and sensitiser for absorption in the visible region.[5–7] Intense ligand-based $\pi \rightarrow \pi^*$ transitions are observed in the UV region. Lower energy $\pi \rightarrow \pi^*$ transitions are observed for the Me- and Br-substituted complexes as compared to the complex with R = H. In **2b**, the electron donating methyl groups destabilise the ligand π orbitals to a greater extent than the ligand π^* orbitals. Conversely, in **2c** the ligand π^* orbitals

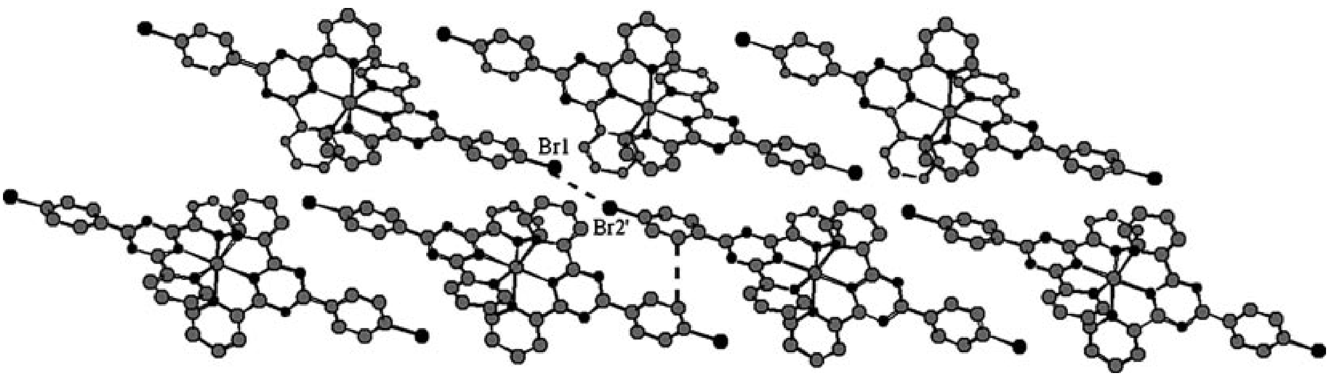

Figure 2. Intermolecular packing forces in the solid-state structure of **2c**. Phenyl-to-phenyl distance = 3.514 Å and the Br1···Br2′ distance = 3.395 Å. The PF_6 counteranions and solvent of crystallization have been removed for clarity.

are stabilized to a greater extent than ligand π orbitals due to the electron withdrawing nature of the bromine substituent.

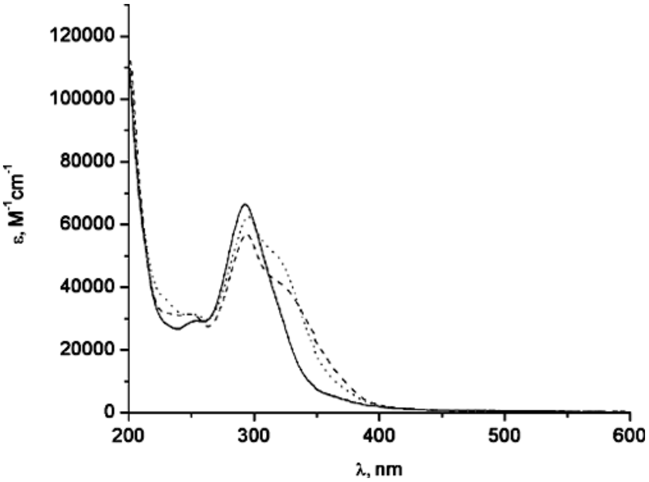

Figure 3. Electronic absorption spectra of complexes **2a** (solid line), **2b** (dashed line) and **2c** (dotted line).

The electrochemical parameters of complexes **2a**, **2b** and **2c** were measured in acetonitrile vs. tetrabutylammonium PF_6 using a Pt electrode and ferrocene as the internal standard. The data (reported vs. SCE) are gathered in Table 2. The $Co^{II/III}$ couples are centered at approximately +0.75 V, which is considerably more positive than previously reported Co^{II} of heterocyclic ligands.[5–7] In each case, oxidative processes are irreversible, which may be a result of limited solubility of the Co^{III} species. It had previously been noted that irreversibility of the $Co^{II/III}$ couple does not necessarily translate into inefficient redox mediators, but sometimes give rise to the most efficient redox mediators.[6] The more positive oxidation potential of **2a**–**c** as compared to terpyridine complexes of Co^{II} is favorable with respect to an increased photocurrent in DSSCs.[7] The $Co^{II/III}$ couple is only slightly affected by substituent on the phenyl ring, with complex **2c** being the most difficult to oxidise as a result of the electron withdrawing Br substituent and **2b** being the easiest as a result of the electron donating Me substituent. The $Co^{II/I}$ couple is also affected by the various substitutents, with **2b** being the hardest to reduce and **2c** the easiest to reduce. The greater variability in the $Co^{II/I}$ reduction potential is a reflection of the increased backbonding of the metal center to the ligand upon reduction. The two remaining reductions are independent triazine-based reductions and follow the electron-withdrawing effect of the substitutents.

Table 2. Electrochemical redox potentials for complexes **2a**–**c** in argon-purged acetonitrile solutions (vs. SCE).

	$E_{1/2}$ (V) [ΔE_p (mV)]			
Compound	$Co^{II/III}$	$Co^{II/I}$	Triazine reductions	
2a	0.76 [irr]	–0.42 [73]	–1.06 [72]	–1.47 [85]
2b	0.74 [irr]	–0.47 [64]	–1.11 [66]	–1.52 [64]
2c	0.77 [irr]	–0.40 [52]	–1.04 [56]	–1.46 [66]

Conclusions

Co^{II} complexes of tridentate triazine-based ligands, either heteroleptic or homoleptic, are readily synthesized and isolated. The electrochemical properties of the homoleptic complexes indicate that the $Co^{II/III}$ redox couples are more positive and more favorable for DSSC than those of Co^{II} terpyridine-based complexes. The $Co^{II/III}$ couple exhibits small shifts in oxidation potential upon modification of the phenyl ring substituents, whereas the $Co^{II/I}$ reduction potential is more readily modified. Further modifications to substitute electron withdrawing and donating groups directly on the triazine ring will be reported in due course.

Acknowledgments

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[10] Synthesis of 2,4-di(2′-pyridyl)-6-(*p*-bromophenyl)-1,3,5-triazine **1c:** *para*-bromobenzonitrile (0.68 g, 3.73 mmol) was added to a stirred mixture of $LiNMe_2$ (0.19 g, 3.73 mmol) in anhydrous diethyl ether. After 30 min, 2-cyanopyridine (0.77 g, 7.46 mmol) was added to the mixture. After an hour the reaction mixture was diluted with H_2O (250 mL) and the precipitate was collected. Recrystallization of the solid from ethanol afforded **1c** (0.90 g, 62%) as a white solid. ^1H NMR ($CDCl_3$): δ = 8.99 (d, J = 4.1 Hz, 2 H), 8.87 (d, J = 7.8 Hz, 2 H), 8.74 (d, J = 8.4 Hz, 2 H), 8.0 (t, J = 7.1 Hz, 2 H), 7.73 (d, J = 8.4 Hz, 2 H), 7.60 (t, 2 H, J = 5.0 Hz) ppm.
[11] General procedure for the synthesis of homoleptic Co^{II} complexes **2a**, **2b**, **2c**: The triazine ligand (0.42 mmol) was stirred in acetone (25 mL) and added to a solution of $CoCl_2{\cdot}6H_2O$ (0.38 mmol, 91 mg). After heating at reflux for 75 min and precipitation in aqueous NH_4PF_6, complexes **2a** (110 mg, 54%), **2b** (127 mg, 61%) and **2c** (103 mg, 43%) were collected.
[12] Synthesis of heteroleptic complexes **3a**, **3b** and **3c** followed the same procedure for complexes **2**. After heating for 75 min the acetone/water mix was removed under reduced pressure and the solution was dissolved in a small amount of acetone and precipitated by the addition of Bu_4NCl. Complexes **3a** (44%), **3b** (33%) and **3c** (23%) were collected. **3a**·$2H_2O$: calcd. C 47.82, H 3.59 N 14.68; found C 47.67, H 3.33, N 14.66. **3b**·H_2O: calcd. C 50.76, H 3.62, N 14.80; found C 51.38, H

3.46, N 15.09. **3c**·4 H_2O: calcd: C 38.54 H 3.40; N 11.83, found C 38.55, H 2.78, N 11.81.

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[15] Orange crystals of **2c** suitable for X-ray analysis could be grown by slow diffusion of isopropyl ether into a solution of the complex in acetonitrile. Crystal data for **2c**: $C_{38}H_{24}CoN_{10}\cdot 2(PF_6)$ was collected with a Bruker APEX at 100 K using Cu-K_α radiation (λ = 1.54178 Å). Full-matrix, least-squares refinements on F^2 using all data. 3198 reflections, M = 1129.36, monoclinic, space group $C2/c$, a = 14.7467(4), b = 20.8588(6), c = 16.6451(5) Å, α = 90°, β = 96.2640(10)°, γ = 90°, V = 5089.4(3) Å^3, Z = 4, $R1$ [$I > 2\sigma(I)$] = 4.28, $wR2$ = 8.36. CCDC-252138 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via otherwww.ccdc.cam.ac.uk/data_request/cif.

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