



Metal complexes of dual-pendant sulfonate bis(indolenine)squaraines



Daniel E. Lynch ^{a,*}, Martin Cox ^b

^a Exilica Limited, The Technocentre, Puma Way, Coventry CV1 2TT, UK

^b Faculty of Health and Life Sciences, Coventry University, Coventry CV1 5FB, UK

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ABSTRACT

Eight metal complexes of dual-pendant sulfonate bis(indolenine)squaraines (four *d*-transition metals and four *f*-transition metals) have been prepared and examined as fluorescent probes for solution protein determination. Of the eight, the cobalt-squaraine complex exhibited the highest fluorescence response in the presence of protein (in aqueous solution) and the partial determination of its crystal structure meant that it could be examined further and compared against the previously determined bis-piperidinium and bis-morpholinium squaraine species. Comparative examination of these three variants in water, 10 mM phosphate buffer (pH = 7.0), and 10 mM Tris/HCl buffer (pH = 7.0) led to the conclusion that the use of Tris/HCl buffer resulted in less reduction of fluorescence intensity (over that of water alone) than the more widely used phosphate buffer.

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1. Introduction

Bis(indolenine)squaraines have, for more than twenty years, been studied in varying forms as solution based protein sensitive fluorescent probes [1–4]. In a recent study it was discovered that metal complexes of dual-pendant sulfonate bis(indolenine)squaraines could be prepared through the exchange of the organic cation (present from the squaraine synthesis) with a metal ion [5]. However, it was concurrently found that any metal-squaraine complex, other than those with lithium, sodium or potassium, was mostly insoluble in water, leading to a cessation in application as a stain for gel electrophoresis (the subject of that particular study). A number of *d* and *f* transition salts were prepared to affirm insolubility in water and one metal-squaraine salt, the copper salt, was found to be sparingly soluble enough in ethanol that the slow evaporation of such a solution of the squaraine complex gave crystals from which an almost complete X-ray crystal structure was determined, although not to a suitable resolution for full publication. The X-ray structure of the copper-squaraine complex yielded an independent squaraine bis-anion molecule whose charge was balanced by a $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ cation. Furthermore the squaraine anions and the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ cations were separately arranged in layers with the

$\text{Cu}(\text{H}_2\text{O})_6^{2+}$ layers sandwiched between two squaraine layers (Fig. 1). Since that study the authors have re-examined the water solubility of the complexes that were initially prepared and it was found that although the complexes certainly do not have enough solubility for examination as stains for gel electrophoresis (as did the Li, Na and K complexes), they do have enough solubility for examination as fluorescent probes for solution protein determination. With respect to this application area, the performance of a number of dual-pendant sulfonate squaraine variants in the presence of increasing concentrations of bovine serum albumin (5–50 nM) have been previously studied, but only in water because initial experiments showed a significant reduction in fluorescence yield in the presence of phosphate buffer [6]. However, following a number of screening studies to determine the optimum performing dual-pendant sulfonate bis(indolenine)squaraines, it has been the intention of the authors to re-address the use of buffers in these experiments. Reported here is the examination of eight metal-squaraine complexes (four *d*-transition metals and four *f*-transition metals) as fluorescent probes for solution protein determination as well as examination of the effect of two types of buffer solutions on the fluorescent performance of the optimum metal-squaraine complex compared to the two optimum cationic squaraine complexes (bis-morpholinium and bis-piperidinium) determined from previous studies [6,7]. Further reported are the low resolution partial X-ray crystal structures of the cobalt-squaraine complex and the iron-squaraine complex (Fig. 2).

* Corresponding author. Tel.: +44 (0)24 7765 8505.

E-mail address: d.lynych@exilica.co.uk (D.E. Lynch).

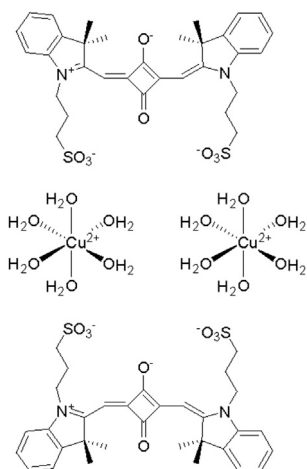


Fig. 1. Chemical schematic illustrating the layered solid-state packing arrangement in the copper-squaraine complex from Ref. [5].

2. Materials and methods

2.1. Synthesis

All chemicals were purchased from Sigma–Aldrich and were used as received without further purification. The water used in this study was purified using reverse osmosis techniques. Infrared spectra were recorded as KBr discs using a Nicolet 205 FT-IR spectrometer. Samples of the bis-quinolinium (**1**), bis-piperidinium (**2**), bis-morpholinium (**3**), and copper(II) hexahydrate (**7**) variants of 2,4-bis-(3,3-dimethyl-(1-propan-3-sulphonate)-2-indolylidene)methyl)cyclobutene-1,3-diolate, prepared for previous studies, were used [5–7].

2.1.1. Metal(II) 2,4-bis-(3,3-dimethyl-(1-propan-3-sulphonate)-2-indolylidene)methyl)cyclobutene-1,3-diolate complexes

Iron (**4**), cobalt (**5**), nickel (**6**) complexes were prepared by the separate warming (50 °C) of mixed solutions of **2** (1.53 g, 1.9 mmol) in water (50 cm³) and for **4**, iron(II) sulphate heptahydrate (530 mg, 1.9 mmol); for **5**, cobaltous acetate tetrahydrate (476 mg, 1.9 mmol); for **6**, nickel(II) chloride (320 mg, 1.9 mmol) in water (10 cm³), for 20 min. For **4**, a metallic brown powder; for **5** and **7**, metallic green powders; and for **6**, a metallic blue powder were each collected *in vacuo*, washed with petroleum ether (60/40), and were used

without further purification. Yield: for **4**, 0.77 g (53%); for **5**, 1.10 g (69%); and for **6**, 1.36 g.

2.1.2. Metal(III) 2,4-bis-(3,3-dimethyl-(1-propan-3-sulphonate)-2-indolylidene)methyl)cyclobutene-1,3-diolate complexes

Lanthanum (**8**), praseodymium (**9**), neodymium (**10**), erbium (**11**) complexes were prepared by the separate warming (50 °C) of mixed solutions of (a three molar equivalent of) **1** (150 mg, 167 μmol) in water (100 cm³) and (a two molar equivalent of) for **8**, lanthanum(III) chloride heptahydrate (41 mg, 111 μmol); for **9**, praseodymium(III) chloride hexahydrate (41 mg, 111 μmol); for **10**, neodymium(III) acetate hydrate (36 mg, 111 μmol); for **11**, erbium(III) acetate hydrate (38 mg, 111 μmol) in water (10 cm³), for 20 min. Metallic green powders were each collected *in vacuo*, washed with petroleum ether (60/40), and were used without further purification. Yield: for **8**, 140 mg; for **9**, 135 mg; for **10**, 140 mg; and for **11**, 140 mg.

2.1.3. X-ray crystallographic analysis

Very small single crystals of the three metal-squaraine complexes **4–6** were obtained in each case by the slow evaporation of a dilute solution of each complex in ethanol. Crystallographic data for **4** was collected on a Rigaku Saturn724 + diffractometer using monochromatized Mo-K α X-ray radiation ($\lambda = 0.71075$ Å) equipped with an Oxford Cryosystem low temperature device, and for both **5** and **6** was collected at the Diamond Light Source beamline I19 ($\lambda = 0.68890$ Å) [8]. Partial structures of **4** and **5** were solved by direct methods SHELX97 [9], and attempted refinements were made using full-matrix least-squares calculations. Crystal data for **4**: C₇₄H₉₆FeN₆O₁₈S₄ [or ((Fe(H₂O)₂)(C₃₂H₃₄N₂O₈S₂)₂)²⁻·2(C₅H₁₂N)⁺]_n, Mw = 1541.66, monoclinic, I2/a, Z = 4, a = 27.897(2), b = 6.552(5), c = 40.880(3) Å, $\beta = 107.842(5)^\circ$, V = 7113(5) Å³, D_{calcd} = 1.440 g cm⁻³, T = 100(2) K, S = 1.580, 18409 reflections were collected, 8087 unique (R_{int} = 0.1682), 2468 observed (I > 2 σ (I)), R₁ = 0.1816, wR₂ = 0.3821. Crystal data for **5**: C₃₂H₅₀CoN₂O₁₆S₂ [or (Co(H₂O)₆)²⁺·C₃₂H₃₄N₂O₈S₂]₂·2H₂O], Mw = 841.79, monoclinic, C2, Z = 8, a = 44.57(5), b = 6.122(6), c = 29.79(3) Å, $\beta = 99.138(1)^\circ$, V = 8025(14) Å³, D_{calcd} = 1.393 g cm⁻³, T = 100(2) K, S = 1.370, 29836 reflections were collected, 7010 unique (R_{int} = 0.7257), 1138 observed (I > 2 σ (I)). Crystal data for **6**: Triclinic, P $\bar{1}$, Z = 2, a = 13.46(2), b = 19.58(2), c = 21.43(3) Å, $\alpha = 74.06(4)^\circ$, $\beta = 84.14(5)^\circ$, $\gamma = 86.07(7)^\circ$, V = 5403(12) Å³, T = 100(2) K, 10613 reflections were collected, 3658 unique (R_{int} = 0.2534), 1994 observed (I > 2 σ (I)).

For comparison, crystal data for **7**: C₁₂₈H₁₉₆Cu₄N₈O₆₂S₈ [or (Cu(H₂O)₆)₂²⁺·C₃₂H₃₄N₂O₈S₂]₄·6H₂O], Mw = 3349.57, triclinic, P1, Z = 1, a = 6.88(10), b = 22.4(3), c = 28.0(4) Å, $\alpha = 95.2(2)^\circ$, $\beta = 90.1(2)^\circ$, $\gamma = 98.2(3)^\circ$, V = 4253(10) Å³, D_{calcd} = 1.308 g cm⁻³,

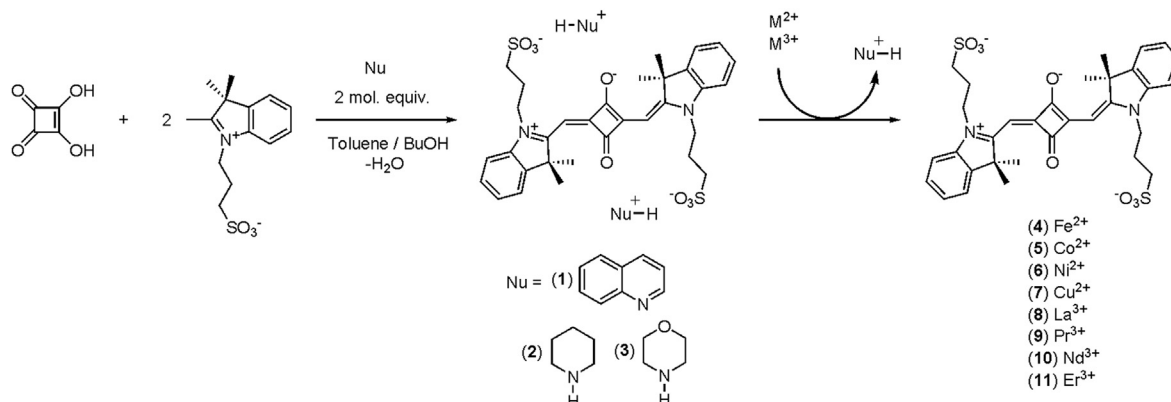


Fig. 2. Schematic showing the synthetic route developed from Ref. [5].

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