

Supporting Information for:

High Seebeck coefficient thermogalvanic cells *via* the solvent-sensitive charge additivity of cobalt 1,8- diaminosarcophagine

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Table S1 – Table of data for thermogalvanic properties.

Synthetic experimental details

[Co(en)₃]Cl₃

CoCl₂·6H₂O (11.99 g, 50.39 mmol) was dissolved in water (35 mL) to give a clear purple solution. Separately, ethylenediamine (10.5 mL, 9.45 g, 157.24 mmol) was added to water (30 mL), cooled on ice, and acidified with HCl (10 mL, 6 M). The two solutions were combined with stirring and H₂O₂ (10 mL, 30 %) was added resulting in effervescence and the formation of a dark orange-brown solution. Once effervescence had ceased, the solution was warmed gently to reduce the total volume to 60 mL. Then concentrated HCl (60 mL) was added along with ethanol (120 mL). The resulting mixture was cooled on ice for 1 hour. An orange precipitate formed which was filtered and washed with ethanol (2 x 30 mL) and ether (2 x 30 mL) to yield the product as an orange solid. [Co(en)₃]Cl₃: 14.14 g, 40.92 mmol, 79 %. ¹H NMR (400 MHz, D₂O) δ 5.12 (s, 6H), 4.82 (s, 6H), 2.94 (s, 6H), 2.84 (s, 6H).

[Co(NO₂)₂sar]Cl₃

NaOH (4.66 g, 116.50 mmol) was dissolved in water (30 mL) and cooled on ice. Separately, [Co(en)₃]Cl₃ (10.00 g, 29.06 mmol), nitromethane (6.2 mL, 115.50 mol), and formaldehyde (37%, 22.0 mL) were dissolved in water (20 mL) to give an orange solution which was cooled on ice. The first solution was then added rapidly to the second whilst cooling on ice with vigorous stirring for 15 minutes. The solution changed colour from orange to violet. Concentrated HCl (34 mL) was then added and the solution was cooled on ice for 3 hours forming an orange precipitate. This mixture was then filtered and the orange product was dried in air. [Co(NO₂)₂sar]Cl₃: 9.477 g, 175.67 mmol, 94.2%. ¹H NMR (400 MHz, D₂O) δ

3.91 (d, $J = 13.4$ Hz, 6H), 3.58 (d, $J = 9.2$ Hz, 6H), 3.38 (d, $J = 13.8$ Hz, 6H), 2.95 (d, $J = 9.3$ Hz, 6H).

[Co(NH₃)₂sar]Cl₅

[Co(NO₂)₂sar]Cl₃ (3.70 g, 6.85 mmol) was dissolved in water (200 mL) and degassed with N₂ for 20 minutes. Under a blanket of N₂, Zn dust (7.51 g, 114.81 mmol) was added with stirring, followed by the addition of concentrated HCl (18.5 mL) to give a green solution. The progress of the reaction was monitored periodically by taking a few drops of reaction mixture and mixing with a few drops of H₂O₂ (30%), a colour change was observed from green to orange solution. A few drops of this mixture were then added to a microcolumn of Sephadex C-25 and eluted with sodium citrate solution (0.1 M). When only one band was visible after approximately 2 hours, H₂O₂ (30 %, 8 mL) was added to the reaction vessel, inducing a colour change from green to orange solution. This mixture was then adsorbed onto a Dowex 50WX2 column (5 cm x 4 cm), and washed with water (300 mL), HCl (1 M, 500 mL) and then eluted with HCl (5M, 250 mL). The orange eluate was then evaporated until small crystals had formed on the walls of the flask. Ethanol was then added to the point of turbidity and the mixture was cooled in an ice/ethanol bath for 15 minutes to form small orange crystals of product which were then filtered through a glass frit and dried in air. [Co(NH₃)₂sar]Cl₅: 2.96 g, 6.18 mmol, 90.2 %. ¹H NMR (400 MHz, D₂O) δ 3.54 (m, 12H), 2.94 (m, 12H). ¹³C NMR (101 MHz, D₂O) δ 56.21, 54.76, 51.32.

[Co(NH₃)₂sar](CF₃SO₃)₅

[Co(NH₃)₂sar]Cl₅ (0.44 g, 0.92 mmol) was dissolved in triflic acid (5.00 g, 33.32 mmol) with stirring to give an orange solution. This solution was degassed for 30 minutes with N₂

before diethyl ether (10 mL) was added to precipitate the product as a waxy orange solid. This product was then filtered through a glass frit. The waxy orange solid was then suspended in diethyl ether (30 mL) and filtered through a glass frit once more to give the product as an orange powder which was then further dried *in vacuo* to give an orange powder. [Co(NH₃)₂sar)](OTf)₅: 0.60 g, 0.53 mmol, 57.0 %.

Synthesis of Zn amalgam

HgCl₂ (0.1 g, 0.37 mmol) dissolved in H₂O (10 mL) acidified using concentrated HCl (0.5 mL). Zinc (dust, 1.0 g) was added to the solution and stirred (< 1000 rpm) at room temperature overnight. The ZnHg forms as grey/silver spheres, which were filtered and then washed multiple times with 0.1 M HCl before use.

Synthesis of Co(ii) Sarcophagine

Co(III)Sarcophagine (50 mM) was dissolved in the required solvent (either water, DMSO or [Emim][NTf₂]), and then acidified using concentrated HCl (aqueous) or H(OTf)₃ (DMSO, [Emim][NTf₂]) to achieve a final concentration of 0.1 M. The solution was thoroughly degassed using Ar, and ZnHg (5-8 spheres) added to the solution. Ar gas was continually bubbled through the solution for 30 mins, upon which a colour change from orange to yellow can be seen, indicating the reduction is complete. The solution was then removed by syringe and added to solid of the Co(III) equivalent such that a 50:50 ratio of oxidised to reduced species were present for subsequent thermoelectrochemical analysis.

Unfortunately the ZnHg method did not work efficiently in ionic liquid, so an alternative method was trialled, using nitrosyl tetrafluoroborate. The $[\text{Co}(\text{Sar})]^{2+/3+}$ was dissolved in ionic liquid to make a 25 mM solution, and the solution thoroughly degassed with Ar and kept under an Ar atmosphere. Then excess nitrosyl tetrafluoroborate was added as a solid, and degassing continued. This was also unsuccessful, possibly due to the presence of water in the solution and reduced solubility in ionic liquid.

Electrochemical analysis

Cyclic voltammetric experiments were carried out using a PGSTAT204 potentiostat with NOVA software (Metrohm, UK). The electrochemical setup was a 1.6 mm diameter Au disc working electrode. The counter electrode was a 1.6 mm diameter Pt disc electrode, using an Ag/AgCl (3 M NaCl) reference electrode (all BASi, USA). All scans were recorded at a scan rate of 100 mV s^{-1} , unless specified otherwise. The cyclic voltammetry was performed *ex-situ* of the thermoelectrochemical setup, at ambient temperature (*ca.* 22 °C).

Thermoelectrochemical analysis

All thermoelectrochemical measurements were performed using a tailormade poly(methyl methacrylate) (PMMA) thermocell, which was made in-house, as described in detailed elsewhere.^{1,2} The thermocell was machined from a single block of PMMA (30 mm (width) × 20 mm (height) × 8.4 mm (depth)).^{1,2} The cell was a 6.7 mm diameter cylinder cut through the 8.4 mm width of the block. The electrodes were 10 mm diameter solid gold discs, which were inserted into 0.5 mm deep lips machined around the chambers in the thermocell (1 mm thick discs with 10 mm diameter, from Surepure Chemetals, USA). Because of these lips the and two electrodes had an inter-electrode spacing of 7.4 mm and a geometric electrode

surface area of 35 mm² (for each electrode). Once assembled the cell was completely sealed except for 2 small holes drilled through the PMMA body, to allow the introduction of a syringe needle (to inject the sample); the sample was injected through one hole until excess liquid came out through the other hole, and the clear cell allowed confirmation that there were no trapped air bubbles.

Temperature control was achieved using copper heat exchangers connected to RS-TX150 thermostatic circulator baths (Grant Instruments Ltd, UK), as previously described.² The flat copper faces were applied at either end of the cell, in direct contact with the two gold electrode discs, and the entire assembly held together with plastic nuts and bolts. All measurements were recorded using the hot electrode set to 40°C and the cold electrode to 20°C, resulting in an applied temperature difference of 20 K. Since the Co(II) species was air sensitive, the Co(III) and Co(II) electrolytes were prepared separately, under Argon (Ar). They were then mixed in a 50:50 volumetric ratio under a blanket of Ar, and injected into the thermogalvanic cell. The two small entry holes to the cell were then sealed with blue tack, and a flow of Ar from a tube was directed at the cell for the duration of the thermogalvanic measurement (*ca.* 50 minutes).

All potential, current and power measurements were performed using a Keysight B2901A Source Measure Unit and Quick IV software (Keysight, UK), were carefully measured and allowed to reach steady-state, following precisely the ‘sequence of constant voltages’ method previously reported.¹ The two gold electrodes were in direct contact with the copper heat sources, and adhesive copper tape was used to complete the electrical connection to the Kelvin clips of the SMU. Briefly, the cells open circuit potential was recorded for 600 seconds, and the average from the final 300 seconds was recorded as the V_{ocp} . When divided by the applied temperature difference (20 K) this also gave the measured thermogalvanic Seebeck coefficient, S_e . Next, the current generated by the thermocell was

recorded for 600 s at three-quarters of the V_{ocp} (but only the average of the final 300 s was used). This was repeated at one-half and one-quarter of the V_{ocp} , and finally with the potential difference set to 0 (to yield the steady-state short circuit current density, j_{sc}). All data-points were characterised by a stable value from 301 to 600 s, indicating the cell had come to equilibrium and was at steady-state power generation. Plotting the 5 j - V data points gave the expected linear plot; multiplying j by V gave the power produced, and the P - V plot gave the expected parabolic power curve, with maximum power generated at half the V_{ocp} .

Solvent effect on Cyclic Voltammetry

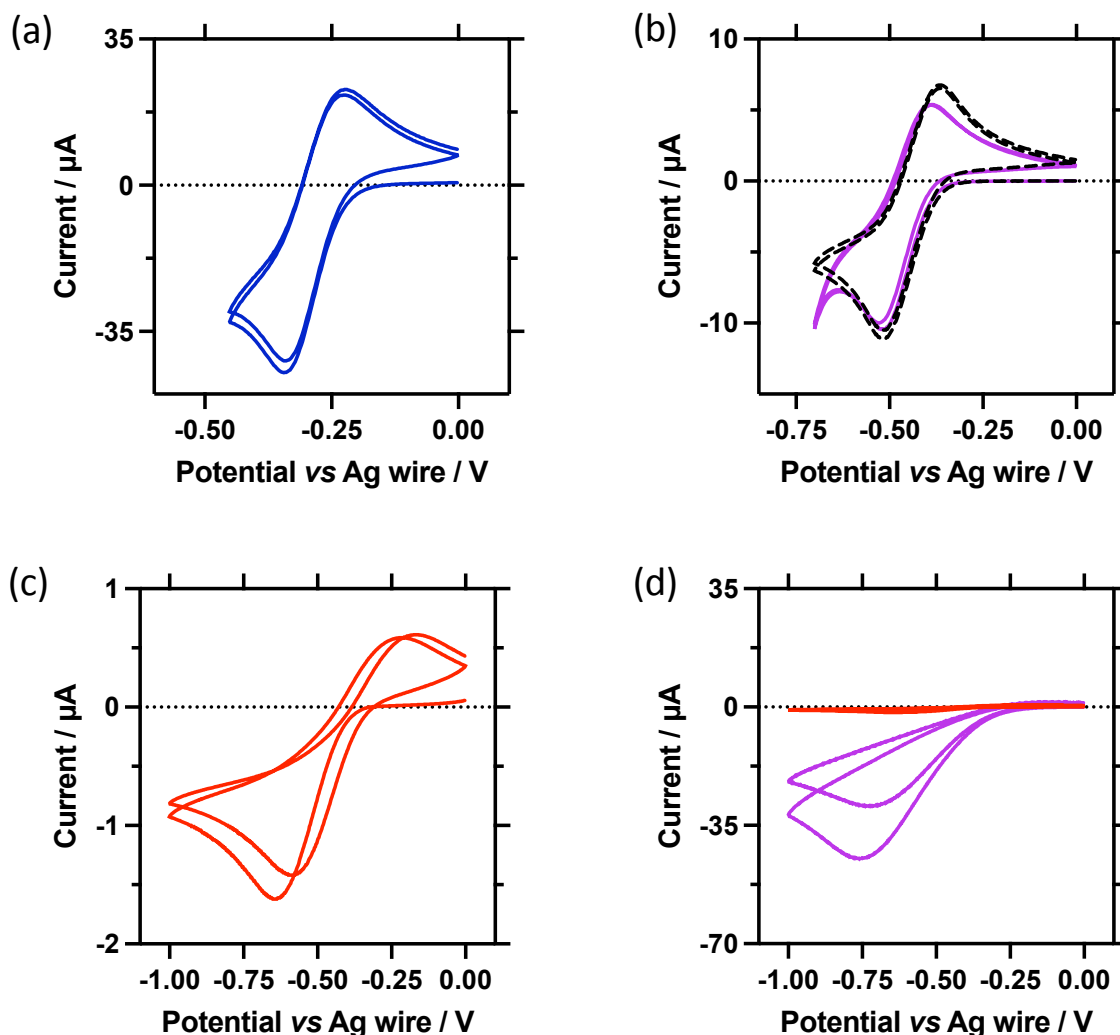


Figure S1 – A comparison of cyclic voltammograms in different solvents. All used 10 mM $[\text{Co}(\text{SARH}_2)]^+[\text{OTf}]_5^-$, a 1.6 mm gold working electrode and a silver wire as a *pseudo*-reference, and all show 2 consecutive 50 mV s^{-1} scans starting, from 0 V. Showing (a) the aqueous system, containing 0.1 M HCl, and (b) the DMSO system containing 0.1 M tetrabutylammonium hexafluorophosphate, and in the absence (black dashed line) and presence (purple solid line) of 0.1 M triflic acid. The latter shows some H_2 evolution starting at *ca.* -0.6 V. Both (c) and (d) show the ionic liquid system, $[\text{Emim}][\text{NTf}_2]$, with the red line in both in the absence of acid, and the purple line in (d) in the presence of 0.1 M triflic acid; in this case H_2 evolution occurred at the same potential as $[\text{Co}(\text{SARH}_2)]^{5+}$ reduction. While the presence of triflic acid interfered with the observation of the $[\text{Co}(\text{SARH}_2)]^{4+/5+}$ redox process, the Zn chemical reduction of $[\text{Co}(\text{SARH}_2)]^{5+}$ to $[\text{Co}(\text{SARH}_2)]^{4+}$ could not be achieved in the absence of the acid.

pH and buffer effect on Cyclic Voltammetry

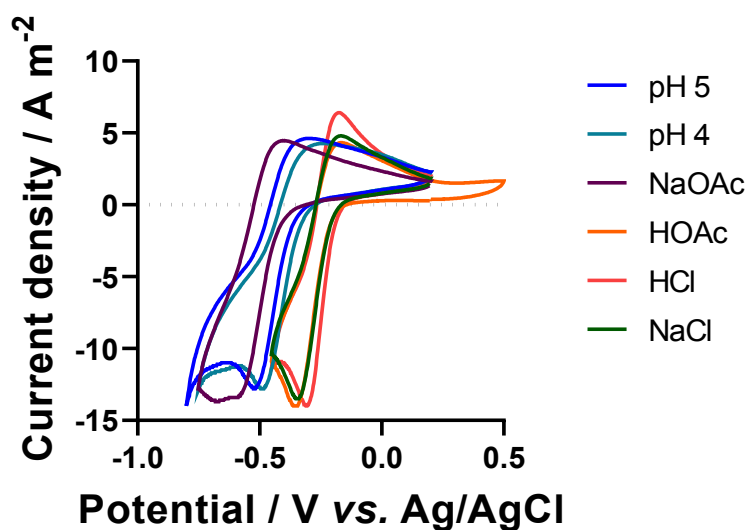


Figure S2 - Cyclic voltammetry of aqueous $[\text{Co}(\text{SAR})](\text{OTf})_5$ in acetic acid/sodium acetate buffer at various pH, compared to the cyclic voltammetry carried out in NaCl (0.1 M) and HCl (0.1 M) solutions.

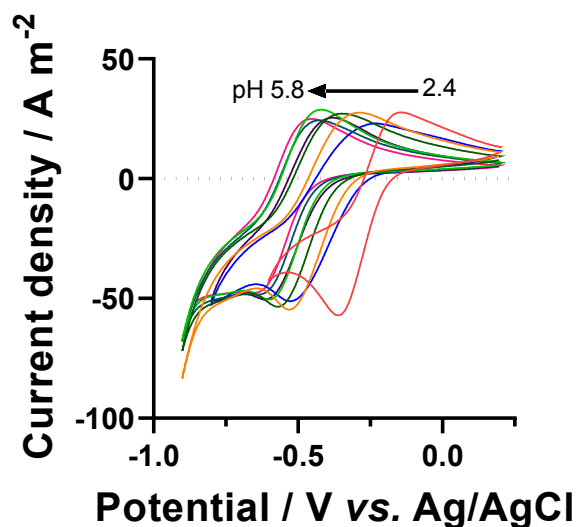


Figure S3 – Figure showing how the CV of the $[\text{Co}(\text{SAR})]$ (25 mM) in an aqueous solution changes with pH. The pH was altered using an acetic acid/sodium acetate buffer. At a pH of 2.4 the complex will be protonated yielding the $[\text{Co}(\text{SARH}_2)]^{5+}$, under these conditions the pH could not be lowered any further. Addition of AcONa was used to increase the pH as high as possible. This results in the complex $[\text{Co}(\text{SAR})]^{3+}$ being present in solution. It should be noted that the transition from the protonated and deprotonated species is less pronounced here in the weaker buffer compared to the HCl/KOH solutions shown in Figure 2 in the main text.

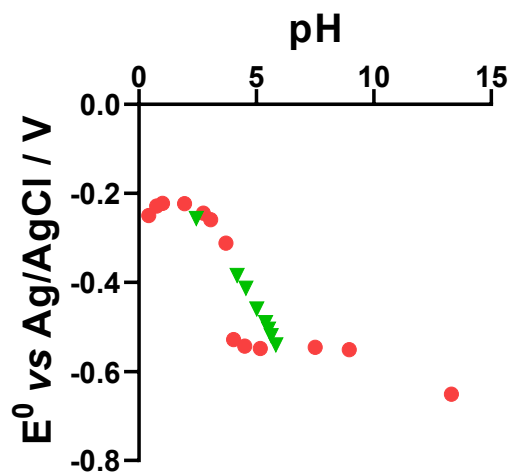


Figure S4 - Graph showing pH titration, E^0 vs pH, of $[\text{Co}(\text{SAR})](\text{OTf})_5$ in aqueous environments, from pH 1 to pH 15. $[\text{Co}(\text{SAR})](\text{OTf})_5$ in HCl/NaOH aqueous solutions (red dots) and $[\text{Co}(\text{SAR})](\text{OTf})_5$ in $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ solutions (green triangle).

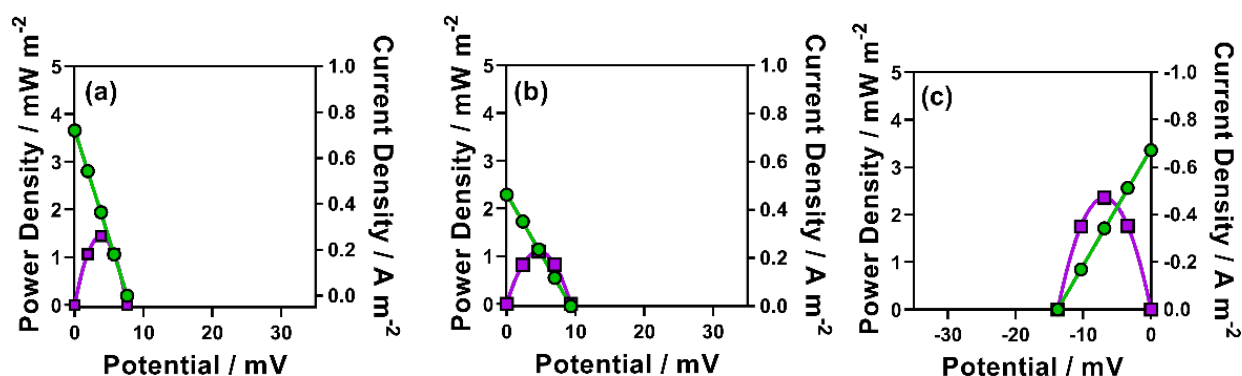


Figure S5 - Graphs displaying the current density and power density of $[\text{Co}(\text{SARH}_2)](\text{OTf})_{4/5}$ (25 mM of each Co(II/III)) thermocells in (a) 0.1 M HCl (pH 1.33), (b) 1 M HOAc (pH 2.02), and (c) 2.5 M NaOAc (pH 6.29). This shows how acidic solutions are broadly comparable, but moving to a more alkaline system results in an inversion of the Seebeck coefficient, resulting in an inverted entropic pathway.

This pH effect is somewhat unexpected, since it was expected that the aqueous systems responded to primarily to the $\text{Co}^{2/3+}$ metal centre, and so would be independent of the nature of the amino groups. However, the 1 M HOAc system (pH 2.02, $S_e = +0.48 \pm 0.04 \text{ mV K}^{-1}$) was significantly different to the 2.5 M NaOAc system (pH 6.29, $S_e = -0.77 \pm 0.02 \text{ mV K}^{-1}$). The inverted Seebeck coefficient indicates that the reduced Co^{2+} complex had a larger effective ionic effect upon the surrounding solvent molecules than the Co^{3+} complex. This is

hard to explain, unless additional chemistry is occurring which alters the overall situation environment.

Several pK_a values have been reported for $[\text{Co}^{\text{III}}(\text{SARH}_2)]^{5+}$ in the range of 2.7 - 3.4, but for $[\text{Co}^{\text{II}}(\text{SARH}_2)]^{4+}$ they fall in the range of 5.1 - 6.7.³ It is therefore tentatively speculated that in the 2.5 M NaOAc system (pH 6.29), the oxidised species is predominately the deprotonated $[\text{Co}^{\text{III}}(\text{SAR})]^{3+}$, while the reduced species could contain protonated $[\text{Co}^{\text{II}}(\text{SARH})]^{3+}$ and $[\text{Co}^{\text{II}}(\text{SARH}_2)]^{4+}$ alongside deprotonated $[\text{Co}^{\text{II}}(\text{SAR})]^{2+}$. Therefore the redox process will have an associated entropy upon the dissociation/association and solvation/desolvation of H^+ in solution.

The difference in S_e between the 1 M HOAc and 2.5 M NaOAc system is 1.25 mV K^{-1} .¹ Kobayashi *et al.*⁴ recently linked proton-coupled electron transfer with the high S_e observed for a partially protonated $[\text{Ru}(\text{imidazole})_6]^{2+/3+}$ complex. Three protons were speculated to be involved in the redox process, with a S_e of -3.7 mV K^{-1} (or 1.23 mV K^{-1} per H^+). The similarity between these values further supports the assumption that proton-coupled reactions are involved in the S_e inversion under alkaline conditions.

Table of data for thermogalvanic power

Table S1 – Tabulated values of [Co(SAR)](OTf)_{4/5} (50 mM total conc) thermo results in a variety of solvents. All values were repeated in triplicate and the error represents the standard deviation of the triplicate measurements, with the exception of the [Emim][NTf₂] sample, which failed to generate any stable power and was thus only measured once.

	pH	Power / mW m ⁻²	Seebeck mV K ⁻¹ /	<i>j</i> _{sc} / A m ⁻²	Δ <i>S</i> _{rc} / J K ⁻¹ mol ⁻¹
0.1 M HCl	1.33	1.46 ± 0.03	+0.43 ± 0.02	0.730 ± 0.013	+41.4
1 M HOAc	2.02	1.06 ± 0.06	+0.48 ± 0.04	0.460 ± 0.06	+46.7
2.5 M NaOAc	6.29	2.18 ± 0.26	-0.77 ± 0.02	-0.622 ± 0.071	-74.3
0.1 M HOTf (DMSO)	-	4.60 ± 0.54	+1.84 ± 0.02	0.526 ± 0.0572	+177.2
0.1 M HOTf ([Emim][NTf ₂])	-	-	<i>ca.</i> +2.0	-	-

References

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