Electrochemical data of Co(II) complexes containing phenanthroline functionalized ligands

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**A B S T R A C T**

The data presented in this paper are related to the research article entitled “Electrochemical properties of a series of Co(II) complexes, containing substituted phenanthrolines” (Ferreira et al., 2018) [1]. This paper presents detailed electrochemical data of eight octahedral Co(II) complexes containing functionalized phenanthrolines-ligands. The data illustrate the shift in the CoIII/II and CoII/I redox couples due to different substituents on the phenanthrolines. Polypyridine Co(II) and Co(III) complexes exhibit properties as potential mediators in dye-sensitized solar cells (DSSCs) (Gajardo and Loeb, 2011; Yu et al., 2011) [2,3]. The ability of a compound to act as a redox mediator to be used in DSSC, depends on the redox potential of the compound (Grätzel, 2005) [4]. Accurate data of the CoIII/II redox couple is presented here.

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**Specifications table**

| Subject area          | Chemistry                                      |
|-----------------------|------------------------------------------------|
| More specific subject area | Electrochemistry                                |
| Type of data          | Table, text file, graph, figure                |
| How data was acquired | BAS 100B/W electrochemical analyzer (Electrochemical studies). Raw and Analyzed. |

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Experimental factors

Samples was used as synthesized. The solvent-electrolyte solution in the electrochemical cell was degassed with Ar for 10 min, the sample was added, the sample-solvent-electrolyte solution was then degassed for another 2 min and the cell was kept under a blanket of purified argon during the electrochemical experiments.

Experimental features

All electrochemical experiments were done in a 2 ml electrochemical cell containing three-electrodes (a glassy carbon working electrode, a Pt auxiliary electrode and a Ag/Ag⁺ reference electrode), connected to a BAS 100B/W electrochemical analyzer. Data obtained were exported to excel for analysis and diagram preparation.

Data source location

Department of Chemistry, University of the Free State, Nelson Mandela street, Bloemfontein, South Africa.

Data accessibility

Data is with article.

Related research article

Hendrik Ferreira, Marrigje M. Conradie and Jeanet Conradie, Electrochemical properties of a series of Co(II) complexes, containing substituted phenanthrolines, Electrochimica Acta 292 (2018) 489–501. DOI:10.1016/j.electacta.2018.09.151.

Value of the data

- This data provide cyclic voltammograms and detailed electrochemical data for a comprehensive series of eight functionalized phenanthroline-Co(II) complexes, for scan rates over two orders of magnitude (0.05–5.0 V s⁻¹).
- This data illustrate the influence of differently functionalized phenanthroline ligands on the redox potential of the metal they are coordinated to.
- This data illustrate that up to three reversible redox couples can be obtained in acetonitrile as solvent for tris(1,10-phenanthroline)Cobalt(II) and differently functionalized phenanthroline-Co(II) complexes.

1. Data

The data presented in this paper are related to the research article entitled “Electrochemical properties of a series of Co(II) complexes, containing substituted phenanthrolines” [1]. This paper presents detailed electrochemical data of eight octahedral Co(II) complexes containing functionalized phenanthrolines-ligands. Polypyridine Co(II) and Co(III) complexes exhibit properties as potential mediators in dye-sensitized solar cells (DSSCs) [2,3]. The ability of a compound to act as a redox mediator to be used in DSSC, depends on the redox potential of the compound [4]. The data of the eight functionalized phenanthroline-Co(II) complexes, namely tris(5-nitro-1,10-phenanthroline)Cobalt(II) nitrate, [Co(5-NO₂-phen)₃][NO₃]₂ (1), tris(4,7-dichloro-1,10-phenanthroline)Cobalt(II) nitrate, [Co(4,7-di-Cl-phen)₃][NO₃]₂ (2), tris(5-chloro-1,10-phenanthroline)Cobalt(II) nitrate, [Co(5-Cl-phen)₃][NO₃]₂ (3), tris(1,10-phenanthroline)Cobalt(II) nitrate, [Co(phen)₃][NO₃]₂ (4), tris(5-methyl-1,10-phenanthroline)Cobalt(II) nitrate, [Co(5-Me-phen)₃][NO₃]₂ (5), tris(5,6-dimethyl-1,10-phenanthroline)Cobalt(II) nitrate, [Co(5,6-di-Me-phen)₃][NO₃]₂ (6), tris(1,10-phenanthroline-5-amine)Cobalt(II) nitrate, [Co(5-NH₂-phen)₃][NO₃]₂ (7) and tris(3,4,7,8-tetramethyl-1,10-phenanthroline)Cobalt(II) nitrate, [Co(3,4,7,8-Me-phen)₃][NO₃]₂ (8), is presented in this contribution, see Fig. 1 for the structures of 1–8.

Cyclic voltammograms of the complexes 1–8, are presented in Figs. 2–9 and tabulated in Tables 1–8. The electrochemical data is obtained in CH₃CN for ca 0.002 mol dm⁻³ (or saturated) analyte solution. Complexes 3–8, all have three reversible peaks, namely the Co⁰³⁺ redox couple (peak 1), the Co²⁺ redox couple (peak 2) and the ligand reduction peak (peak 3). For complex 2 the ligand reduction peak (peak 3) is irreversible and for complex 1 the irreversible peak 2 is NO₂-ligand based. Data at scan rates 0.05–5.00 V s⁻¹ are provided. Data for the irreversible anionic nitrate oxidation peak at ca 1.63 V vs FcH/FcH⁺, is not included in the tables. The data obtained in this study,
compare good with available published data on some of the complexes, namely complex 2 [5],
complex 4 [6–9], complex 7 [9] and complex 8 [9], obtained under different experimental conditions
(different solvents, scan rates and supporting electrolytes).
Fig. 4. Cyclic voltammograms of complex 3 at scan rates of $0.05 \text{ V s}^{-1}$ (lowest peak current) – $5.00 \text{ V s}^{-1}$ (highest peak current). All scans initiated in the positive direction.

Fig. 5. Cyclic voltammograms of complex 4 at scan rates of $0.05 \text{ V s}^{-1}$ (lowest peak current) – $5.00 \text{ V s}^{-1}$ (highest peak current). All scans initiated in the positive direction.

Fig. 6. Cyclic voltammograms of complex 5 at scan rates of $0.05 \text{ V s}^{-1}$ (lowest peak current) – $5.00 \text{ V s}^{-1}$ (highest peak current). All scans initiated in the positive direction.
Fig. 7. Cyclic voltammograms of complex 6 at scan rates of 0.05 V s\(^{-1}\) (lowest peak current) – 5.00 V s\(^{-1}\) (highest peak current). All scans initiated in the positive direction.

Fig. 8. Cyclic voltammograms of complex 7 at scan rates of 0.05 V s\(^{-1}\) (lowest peak current) – 5.00 V s\(^{-1}\) (highest peak current). All scans initiated in the positive direction.

Fig. 9. Cyclic voltammograms of complex 8 at scan rates of 0.05 V s\(^{-1}\) (lowest peak current) – 5.00 V s\(^{-1}\) (highest peak current). All scans initiated in the positive direction.
Table 1
Electrochemical data (potential in V vs FcH/FcH\(^+\)) in CH\(_2\)CN for ca 0.002 mol dm\(^{-3}\) of complex 1 at indicated scan rates in V s\(^{-1}\). Peak 1 is the Co\(^{III/II}\) redox couple.

| Scan rate/V s\(^{-1}\) | \(E_{pa}\)/V vs FcH/FcH\(^+\) | \(E_{pc}\)/V vs FcH/FcH\(^+\) | \(E^{°}/\)/V vs FcH/FcH\(^+\) | \(\Delta E\)/V |
|------------------------|-------------------------------|-------------------------------|-----------------------------|--------------|
| Peak 1                 |                               |                               |                             |              |
| 0.05                   | 0.275                         | 0.110                         | 0.165                       | 0.193        |
| 0.10                   | 0.290                         | 0.115                         | 0.175                       | 0.203        |
| 0.20                   | 0.320                         | 0.120                         | 0.200                       | 0.220        |
| 0.30                   | 0.290                         | 0.110                         | 0.180                       | 0.200        |
| 0.40                   | 0.300                         | 0.110                         | 0.190                       | 0.205        |
| 0.50                   | 0.300                         | 0.105                         | 0.195                       | 0.203        |
| 1.00                   | 0.330                         | 0.095                         | 0.235                       | 0.213        |
| 2.00                   | 0.415                         | 0.050                         | 0.365                       | 0.233        |
| 5.00                   | 0.560                         | 0.005                         | 0.555                       | 0.283        |

Table 2
Electrochemical data (potential in V vs FcH/FcH\(^+\)) in CH\(_2\)CN for ca 0.002 mol dm\(^{-3}\) of complex 2 at indicated scan rates in V s\(^{-1}\). Peak 1 is the Co\(^{III/II}\) redox couple, peak 2 the Co\(^{II/I}\) redox couple.

| Scan rate/V s\(^{-1}\) | \(E_{pa}\)/V vs FcH/FcH\(^+\) | \(E_{pc}\)/V vs FcH/FcH\(^+\) | \(E^{°}/\)/V vs FcH/FcH\(^+\) | \(\Delta E\)/V |
|------------------------|-------------------------------|-------------------------------|-----------------------------|--------------|
| Peak 1                 |                               |                               |                             |              |
| 0.10                   | 0.200                         | 0.070                         | 0.130                       | 0.135        |
| 0.20                   | 0.260                         | 0.070                         | 0.190                       | 0.165        |
| 0.30                   | 0.250                         | 0.050                         | 0.200                       | 0.150        |
| 0.40                   | 0.270                         | 0.050                         | 0.220                       | 0.160        |
| 0.50                   | 0.260                         | 0.030                         | 0.230                       | 0.145        |
| 1.00                   | 0.300                         | 0.020                         | 0.280                       | 0.160        |
| 2.00                   | 0.380                         | 0.000                         | 0.380                       | 0.190        |
| 5.00                   | 0.400                         | –0.070                       | 0.470                       | 0.165        |
| Peak 2                 |                               |                               |                             |              |
| 0.10                   | –1.120                        | –1.200                        | 0.080                       | –1.160       |
| 0.20                   | –1.105                        | –1.195                        | 0.090                       | –1.150       |
| 0.30                   | –1.105                        | –1.200                        | 0.095                       | –1.153       |
| 0.40                   | –1.100                        | –1.210                        | 0.110                       | –1.155       |
| 0.50                   | –1.100                        | –1.225                        | 0.125                       | –1.163       |
| 1.00                   | –1.080                        | –1.250                        | 0.170                       | –1.165       |
| 2.00                   | –1.075                        | –1.260                        | 0.185                       | –1.168       |
| 5.00                   | –1.060                        | –1.310                        | 0.250                       | –1.185       |

For Co(5-NO\(_2\)-phen)\(_3\)\(^{2+}\) complex 1, see Fig. 2 and Table 1.
For Co(4,7-di-Cl-phen)\(_3\)\(^{2+}\) complex 2, see Fig. 3 and Table 2.
For Co(5-Cl-phen)\(_3\)\(^{2+}\) complex 3, see Fig. 4 and Table 3.
For Co(phen)\(_3\)\(^{2+}\) complex 4, see Fig. 5 and Table 4.
For Co(5-Me-phen)\(_3\)\(^{2+}\) complex 5, see Fig. 6 and Table 5.
For Co(5,6-Me-phen)\(_3\)\(^{2+}\) complex 6, see Fig. 7 and Table 6.
For Co(5-NH\(_2\)-phen)\(_3\)\(^{2+}\) complex 7, see Fig. 8 and Table 7.
For Co(3,4,7,8-Me-phen)\(_3\)\(^{2+}\) complex 8, see Fig. 9 and Table 8.

2. Experimental design, materials, and methods

Electrochemical studies by means of cyclic voltammetry (CV) were performed either on 0.002 mol dm\(^{-3}\) or on saturated compound solutions of the complexes in dry acetonitrile, containing 0.1 mol dm\(^{-3}\) tetra-n-butylammoniumhexafluorophosphate ([n(Bu\(_4\)N)][PF\(_6\)]) as supporting electrolyte, under a blanket of purified argon, at 25 °C, utilizing a BAS 100B/W electrochemical analyzer. A three-electrode cell was used, with a glassy carbon (surface area 7.07 × 10\(^{-6}\) m\(^2\)) working electrode, Pt auxiliary electrode and a Ag/Ag\(^+\) (0.010 mol dm\(^{-3}\) AgNO\(_3\) in CH\(_3\)CN) reference electrode [10].
**Table 3**
Electrochemical data (potential in V vs FeH/FeH⁺ and current in A) in CH₂CN for ca 0.002 mol dm⁻³ of complex 3 at indicated scan rates in V s⁻¹. Peak 1 is the CoII/III redox couple, peak 2 the CoII/III redox couple.

| Scan rate/V s⁻¹ | Eₚa/V vs FeH/FeH⁺ | Eₚc/V vs FeH/FeH⁺ | E°/V vs FeH/FeH⁺ | ΔE/V | 10⁶Iₚ/A | Iₚ/Iₚa |
|-----------------|------------------|------------------|-------------------|------|--------|--------|
| Peak 1          |                  |                  |                   |      |        |        |
| 0.05            | 0.018            | 0.034            | 0.071             | 0.074| 17.5   | 1.0    |
| 0.10            | 0.022            | 0.032            | 0.077             | 0.090| 26.0   | 1.0    |
| 0.20            | 0.022            | 0.034            | 0.078             | 0.088| 39.5   | 1.0    |
| 0.30            | 0.026            | 0.022            | 0.079             | 0.114| 44.2   | 1.0    |
| 0.40            | 0.016            | 0.016            | 0.079             | 0.126| 51.4   | 1.1    |
| 0.50            | 0.010            | 0.010            | 0.077             | 0.134| 63.0   | 1.1    |
| 1.00            | 0.004            | 0.004            | 0.078             | 0.148| 87.5   | 1.1    |
| 2.00            | −0.024           | 0.076            | 0.200             | 117.0| 1.1    |        |
| 5.00            | −0.070           | 0.066            | 0.272             | 200.0| 1.0    |        |
| Peak 2          |                  |                  |                   |      |        |        |
| 0.05            | −1.220           | −1.292           | −1.265            | 0.072| 17.0   | 0.9    |
| 0.10            | −1.216           | −1.296           | −1.256            | 0.080| 25.0   | 1.0    |
| 0.20            | −1.218           | −1.292           | −1.255            | 0.074| 37.0   | 1.0    |
| 0.30            | −1.210           | −1.300           | −1.255            | 0.090| 42.3   | 1.1    |
| 0.40            | −1.210           | −1.314           | −1.262            | 0.104| 53.0   | 1.0    |
| 0.50            | −1.208           | −1.314           | −1.261            | 0.106| 64.8   | 1.0    |
| 1.00            | −1.206           | −1.318           | −1.262            | 0.112| 98.0   | 1.0    |
| 2.00            | −1.192           | −1.346           | −1.269            | 0.154| 135.0  | 1.0    |
| 5.00            | −1.180           | −1.398           | −1.289            | 0.218| 192.0  | 1.2    |

**Table 4**
Electrochemical data (potential in V vs FeH/FeH⁺ and current in A) in CH₂CN for ca 0.002 mol dm⁻³ of complex 4 at indicated scan rates in V s⁻¹. Peak 1 is the CoIII/II redox couple, peak 2 the CoIII/II redox couple and peak 3 the ligand reduction peak.

| Scan rate/V s⁻¹ | Eₚa/V vs FeH/FeH⁺ | Eₚc/V vs FeH/FeH⁺ | E°/V vs FeH/FeH⁺ | ΔE/V | 10⁶Iₚ/A | Iₚ/Iₚa |
|-----------------|------------------|------------------|-----------------|------|--------|--------|
| Peak 1          |                  |                  |                 |      |        |        |
| 0.05            | 0.012            | −0.076           | −0.032          | 0.088| 17.8   | 1.12   |
| 0.10            | 0.010            | −0.082           | −0.036          | 0.092| 29.5   | 1.08   |
| 0.20            | 0.026            | −0.082           | −0.028          | 0.108| 34.5   | 1.10   |
| 0.30            | 0.032            | −0.086           | −0.027          | 0.118| 44.0   | 1.07   |
| 0.40            | 0.038            | −0.092           | −0.027          | 0.130| 51.0   | 1.14   |
| 0.50            | 0.040            | −0.094           | −0.027          | 0.134| 62.0   | 1.13   |
| 1.00            | 0.060            | −0.096           | −0.018          | 0.156| 59.0   | 1.20   |
| 2.00            | 0.074            | −0.116           | −0.021          | 0.190| 82.0   | 1.20   |
| 5.00            | 0.130            | −0.180           | −0.025          | 0.310| 136.0  | 1.07   |
| Peak 2          |                  |                  |                 |      |        |        |
| 0.05            | −1.326           | −1.398           | −1.362          | 0.072| 22.8   | 0.99   |
| 0.10            | −1.328           | −1.404           | −1.366          | 0.076| 32.3   | 1.04   |
| 0.20            | −1.322           | −1.404           | −1.363          | 0.082| 41.3   | 0.99   |
| 0.30            | −1.318           | −1.410           | −1.364          | 0.092| 54.0   | 0.98   |
| 0.40            | −1.316           | −1.414           | −1.365          | 0.098| 60.0   | 1.08   |
| 0.50            | −1.314           | −1.416           | −1.365          | 0.102| 76.0   | 1.01   |
| 1.00            | −1.304           | −1.424           | −1.364          | 0.120| 81.0   | 0.98   |
| 2.00            | −1.292           | −1.446           | −1.369          | 0.154| 99.0   | 1.19   |
| 5.00            | −1.256           | −1.516           | −1.386          | 0.260| 150.0  | 1.20   |
| Peak 3          |                  |                  |                 |      |        |        |
| 0.05            | −2.026           | −2.104           | −2.065          | 0.078| 21.0   | 1.93   |
| 0.10            | −2.026           | −2.114           | −2.070          | 0.088| 45.0   | 1.51   |
| 0.20            | −2.018           | −2.130           | −2.074          | 0.112| 56.0   | 1.47   |
| 0.30            | −2.016           | −2.140           | −2.078          | 0.124| 75.0   | 1.41   |
| 0.40            | −2.010           | −2.144           | −2.077          | 0.134| 91.0   | 1.43   |
| 0.50            | −2.008           | −2.152           | −2.080          | 0.144| 114.0  | 1.37   |
| 1.00            | −1.998           | −2.172           | −2.085          | 0.174| 108.0  | 1.41   |
| 2.00            | −1.984           | −2.206           | −2.095          | 0.222| 148.0  | 1.44   |
| 5.00            | −1.964           | −2.316           | −2.140          | 0.352| 200.7  | 1.5    |
Table 5
Electrochemical data (potential in V vs FcH/FcH⁺ and current in A) in CH₃CN for ca 0.002 mol dm⁻³ of complex 5 at indicated scan rates in V s⁻¹. Peak 1 is the Co⁰/⁺ redox couple, peak 2 the Co⁺/⁰ redox couple and peak 3 the ligand reduction peak.

| Scan rate/V s⁻¹ | E⁺⁺/V vs FcH/FcH⁺ | E⁺/V vs FcH/FcH⁺ | E⁺⁺/V vs FcH/FcH⁺ | ΔE/V | 10⁵I⁺⁺/A | I⁺⁺/I⁺⁺ |
|-----------------|------------------|-----------------|------------------|------|----------|---------|
| Peak 1          |                  |                 |                  |      |          |         |
| 0.05            | −0.046           | −0.118          | −0.082           | 0.072| 22.0     | 1.0     |
| 0.10            | −0.042           | −0.116          | −0.079           | 0.074| 25.0     | 1.1     |
| 0.20            | −0.036           | −0.122          | −0.079           | 0.086| 37.5     | 1.0     |
| 0.30            | −0.028           | −0.126          | −0.077           | 0.098| 45.0     | 1.1     |
| 0.40            | −0.026           | −0.130          | −0.078           | 0.104| 54.5     | 1.1     |
| 0.50            | −0.018           | −0.134          | −0.076           | 0.116| 62.0     | 1.3     |
| 1.00            | 0.002            | −0.144          | −0.071           | 0.146| 84.0     | 1.1     |
| 2.00            | 0.014            | −0.166          | −0.076           | 0.180| 120.0    | 1.1     |
| 5.00            | 0.070            | −0.222          | −0.076           | 0.292| 188.0    | 1.1     |
| Peak 2          |                  |                 |                  |      |          |         |
| 0.05            | −1.350           | −1.418          | −1.384           | 0.068| 22.5     | 0.9     |
| 0.10            | −1.348           | −1.414          | −1.381           | 0.066| 25.0     | 1.0     |
| 0.20            | −1.342           | −1.422          | −1.382           | 0.080| 39.5     | 1.0     |
| 0.30            | −1.338           | −1.428          | −1.383           | 0.090| 48.0     | 1.0     |
| 0.40            | −1.332           | −1.430          | −1.381           | 0.098| 56.0     | 1.1     |
| 0.50            | −1.332           | −1.436          | −1.384           | 0.104| 69.0     | 1.0     |
| 1.00            | −1.322           | −1.448          | −1.385           | 0.126| 104.0    | 1.0     |
| 2.00            | −1.312           | −1.470          | −1.391           | 0.158| 144.0    | 1.0     |
| 5.00            | −1.274           | −1.528          | −1.401           | 0.254| 230.0    | 1.0     |
| Peak 3          |                  |                 |                  |      |          |         |
| 0.05            | −2.046           | −2.128          | −2.087           | 0.082| 37.1     | 1.3     |
| 0.10            | −2.050           | −2.138          | −2.094           | 0.088| 45.8     | 1.3     |
| 0.20            | −2.046           | −2.156          | −2.101           | 0.110| 61.0     | 1.4     |
| 0.30            | −2.034           | −2.160          | −2.097           | 0.126| 84.0     | 1.3     |
| 0.40            | −2.030           | −2.168          | −2.099           | 0.138| 105.0    | 1.3     |
| 0.50            | −2.026           | −2.174          | −2.100           | 0.148| 124.0    | 1.2     |
| 1.00            | −2.012           | −2.204          | −2.108           | 0.192| 172.0    | 1.3     |
| 2.00            | −2.002           | −2.228          | −2.115           | 0.226| 214.0    | 1.3     |
| 5.00            | −1.974           | −2.332          | −2.153           | 0.358| 250.0    | 1.6     |
**Table 6**

Electrochemical data (potential in V vs FcH/FcH\(^+\) and current in A) in CH\(_3\)CN for ca. 0.002 mol dm\(^{-3}\) of complex 6 at indicated scan rates in V s\(^{-1}\). Peak 1 is the Co\(^{III/II}\) redox couple, peak 2 the Co\(^{II/I}\) redox couple and peak 3 the ligand reduction peak.

| Scan rate/V s\(^{-1}\) | \(E_{pa}/V\) vs FcH/FcH\(^+\) | \(E_{pc}/V\) vs FcH/FcH\(^+\) | \(E^*/V\) vs FcH/FcH\(^+\) | \(\Delta E/V\) | \(10^6I_{pa}/A\) | \(I_{pc}/I_{pa}\) |
|------------------------|-------------------------------|-------------------------------|-----------------------------|----------------|--------------------|--------------------|
| Peak 1                 |                               |                               |                             |                |                    |                    |
| 0.05                   | 0.118                         | 0.180                         | 0.149                       | 0.062          | 11.0               | 0.9                |
| 0.10                   | 0.114                         | 0.188                         | 0.151                       | 0.074          | 23.0               | 1.0                |
| 0.20                   | 0.108                         | 0.188                         | 0.148                       | 0.080          | 33.0               | 1.0                |
| 0.30                   | 0.104                         | 0.192                         | 0.148                       | 0.088          | 42.0               | 1.0                |
| 0.40                   | 0.096                         | 0.198                         | 0.147                       | 0.102          | 49.0               | 1.0                |
| 0.50                   | 0.094                         | 0.198                         | 0.146                       | 0.104          | 57.0               | 1.0                |
| 1.00                   | 0.086                         | 0.210                         | 0.148                       | 0.124          | 80.0               | 1.0                |
| 2.00                   | 0.068                         | 0.228                         | 0.148                       | 0.160          | 112.0              | 1.0                |
| 5.00                   | 0.026                         | 0.288                         | 0.157                       | 0.262          | 173.0              | 1.0                |
| Peak 2                 |                               |                               |                             |                |                    |                    |
| 0.05                   | 1.366                         | 1.428                         | 1.397                       | 0.062          | 13.4               | 0.9                |
| 0.10                   | 1.360                         | 1.430                         | 1.395                       | 0.070          | 25.7               | 0.9                |
| 0.20                   | 1.352                         | 1.432                         | 1.392                       | 0.080          | 43.5               | 0.8                |
| 0.30                   | 1.352                         | 1.436                         | 1.394                       | 0.084          | 48.0               | 0.9                |
| 0.40                   | 1.344                         | 1.444                         | 1.394                       | 0.100          | 56.0               | 1.0                |
| 0.50                   | 1.346                         | 1.444                         | 1.395                       | 0.098          | 63.0               | 1.0                |
| 1.00                   | 1.340                         | 1.454                         | 1.397                       | 0.114          | 93.0               | 1.0                |
| 2.00                   | 1.326                         | 1.476                         | 1.401                       | 0.150          | 127.0              | 0.9                |
| 5.00                   | 1.292                         | 1.532                         | 1.412                       | 0.240          | 204.0              | 1.0                |
| Peak 3                 |                               |                               |                             |                |                    |                    |
| 0.05                   | 2.064                         | 2.146                         | 2.105                       | 0.082          | 29.5               | 1.3                |
| 0.10                   | 2.068                         | 2.152                         | 2.110                       | 0.084          | 41.2               | 1.3                |
| 0.20                   | 2.058                         | 2.162                         | 2.110                       | 0.104          | 60.5               | 1.3                |
| 0.30                   | 2.054                         | 2.172                         | 2.113                       | 0.118          | 72.5               | 1.3                |
| 0.40                   | 2.046                         | 2.190                         | 2.118                       | 0.144          | 87.0               | 1.3                |
| 0.50                   | 2.046                         | 2.184                         | 2.115                       | 0.138          | 103.0              | 1.3                |
| 1.00                   | 2.034                         | 2.206                         | 2.120                       | 0.172          | 144.0              | 1.3                |
| 2.00                   | 2.022                         | 2.246                         | 2.134                       | 0.224          | 188.0              | 1.3                |
| 5.00                   | 1.994                         | 2.342                         | 2.168                       | 0.348          | 238.0              | 1.5                |
Table 7
Electrochemical data (potential in V vs FcH/FcH⁺ and current in A) in CH3CN for ca 0.002 mol dm⁻³ of complex 7 at indicated scan rates in V s⁻¹. Peak 1 is the CoIII/II redox couple, peak 2 the CoII/I redox couple and peak 3 the ligand reduction peak.

| Scan rate/V s⁻¹ | E_{pa}/V vs FcH/FcH⁺ | E_{pc}/V vs FcH/FcH⁺ | E°/V vs FcH/FcH⁺ | ΔE/V | 10⁹I_{pa}/A | I_{pa}/I_{pa} |
|-----------------|-----------------------|-----------------------|------------------|------|------------|---------------|
| Peak 1          |                       |                       |                  |      |            |               |
| 0.05            | 0.128                 | 0.216                 | -0.172           | 0.088| 12.5       | 1.0           |
| 0.10            | 0.127                 | 0.213                 | -0.170           | 0.086| 16.2       | 1.0           |
| 0.20            | 0.121                 | 0.218                 | -0.170           | 0.097| 23.3       | 1.0           |
| 0.30            | 0.116                 | 0.227                 | -0.172           | 0.111| 29.0       | 1.0           |
| 0.40            | 0.116                 | 0.230                 | -0.173           | 0.114| 35.0       | 0.9           |
| 0.50            | 0.109                 | 0.234                 | -0.172           | 0.125| 40.0       | 0.9           |
| 1.00            | 0.091                 | 0.244                 | -0.168           | 0.153| 55.5       | 0.9           |
| 2.00            | 0.080                 | 0.256                 | -0.168           | 0.176| 78.0       | 0.8           |
| 5.00            | 0.053                 | 0.272                 | -0.163           | 0.219| 130.5      | 0.8           |
| Peak 2          |                       |                       |                  |      |            |               |
| 0.05            | 1.401                 | 1.486                 | -1.444           | 0.085| 15.4       | 1.0           |
| 0.10            | 1.402                 | 1.473                 | -1.438           | 0.071| 20.5       | 0.9           |
| 0.20            | 1.398                 | 1.480                 | -1.439           | 0.082| 29.0       | 0.9           |
| 0.30            | 1.393                 | 1.482                 | -1.438           | 0.089| 32.5       | 1.1           |
| 0.40            | 1.391                 | 1.485                 | -1.438           | 0.094| 42.8       | 1.0           |
| 0.50            | 1.388                 | 1.491                 | -1.440           | 0.103| 51.0       | 0.9           |
| 1.00            | 1.376                 | 1.497                 | -1.437           | 0.121| 75.0       | 0.9           |
| 2.00            | 1.360                 | 1.515                 | -1.438           | 0.155| 109.0      | 0.9           |
| 5.00            | 1.340                 | 1.533                 | -1.437           | 0.193| 179.0      | 0.9           |
| Peak 3          |                       |                       |                  |      |            |               |
| 0.05            | -2.088                | -2.186                | -2.137           | 0.098| 28.2       | 1.1           |
| 0.10            | -2.086                | -2.174                | -2.130           | 0.088| 29.4       | 1.4           |
| 0.20            | -2.079                | -2.194                | -2.137           | 0.115| 38.2       | 1.5           |
| 0.30            | -2.071                | -2.195                | -2.133           | 0.124| 47.8       | 1.4           |
| 0.40            | -2.066                | -2.199                | -2.133           | 0.133| 52.0       | 1.6           |
| 0.50            | -2.063                | -2.215                | -2.139           | 0.152| 54.4       | 1.7           |
| 1.00            | -2.049                | -2.232                | -2.141           | 0.183| 69.4       | 1.8           |
| 2.00            | -2.037                | -2.263                | -2.150           | 0.226| 85.8       | 1.9           |
| 5.00            | -2.010                | -2.303                | -2.157           | 0.293| 133.4      | 2.0           |
Table 8
Electrochemical data (potential in V vs FcH/FcH"). CH3CN for ca 0.002 mol dm⁻³ of complex 8 at indicated scan rates in V s⁻¹. Peak 1 is the CoIII/II redox couple, peak 2 the CoII/I redox couple and peak 3 the ligand reduction peak.

| Scan rate/Vs⁻¹ | Epa/V vs FcH/FcH⁺ | Epc/V vs FcH/FcH⁺ | E°/V vs FcH/FcH⁺ | ΔE/V | 10⁶Ipå/A | Ipå/Ipa |
|----------------|--------------------|--------------------|-------------------|------|----------|---------|
| Peak 1         |                    |                    |                   |      |          |         |
| 0.05           | −0.216             | −0.314             | −0.265            | 0.098| 13.2     | 1.0     |
| 0.10           | −0.210             | −0.320             | −0.263            | 0.110| 19.5     | 1.1     |
| 0.20           | −0.210             | −0.314             | −0.262            | 0.104| 28.5     | 1.1     |
| 0.30           | −0.200             | −0.316             | −0.258            | 0.116| 34.5     | 1.2     |
| 0.40           | −0.192             | −0.318             | −0.255            | 0.126| 39.0     | 1.3     |
| 0.50           | −0.182             | −0.324             | −0.253            | 0.142| 43.0     | 1.4     |
| 1.00           | −0.166             | −0.326             | −0.246            | 0.160| 56.0     | 1.4     |
| 2.00           | −0.142             | −0.336             | −0.239            | 0.194| 86.0     | 1.3     |
| 5.00           | −0.136             | −0.348             | −0.242            | 0.212| 137.0    | 1.3     |
| Peak 2         |                    |                    |                   |      |          |         |
| 0.05           | −1.546             | −1.610             | −1.578            | 0.064| 14.0     | 1.0     |
| 0.10           | −1.560             | −1.615             | −1.581            | 0.055| 20.8     | 1.0     |
| 0.20           | −1.542             | −1.616             | −1.579            | 0.074| 31.5     | 1.0     |
| 0.30           | −1.540             | −1.616             | −1.578            | 0.076| 39.5     | 1.0     |
| 0.40           | −1.534             | −1.622             | −1.578            | 0.088| 45.0     | 1.0     |
| 0.50           | −1.532             | −1.628             | −1.580            | 0.096| 53.5     | 1.1     |
| 1.00           | −1.530             | −1.625             | −1.578            | 0.096| 81.0     | 1.0     |
| 2.00           | −1.526             | −1.634             | −1.580            | 0.108| 117.5    | 1.0     |
| 5.00           | −1.514             | −1.646             | −1.580            | 0.132| 190.0    | 1.1     |
| Peak 3         |                    |                    |                   |      |          |         |
| 0.05           | −2.196             | −2.382             | −2.289            | 0.186| 10.0     | 4.0     |
| 0.10           | −2.202             | −2.298             | −2.250            | 0.096| 8.0      | 6.1     |
| 0.20           | −2.204             | −2.392             | −2.298            | 0.188| 12.0     | 6.3     |
| 0.30           | −2.218             | −2.396             | −2.307            | 0.178| 19.0     | 4.4     |
| 0.40           | −2.218             | −2.402             | −2.310            | 0.184| 22.0     | 4.6     |
| 0.50           | −2.222             | −2.400             | −2.311            | 0.178| 20.0     | 5.6     |
| 1.00           | −2.222             | −2.428             | −2.325            | 0.206| 22.0     | 7.1     |
| 2.00           | −2.218             | −2.462             | −2.340            | 0.244| 22.0     | 10.3    |
| 5.00           | −2.204             | −2.532             | −2.368            | 0.328| 27.0     | 13.0    |
mounted on a Luggin capillary [11]. Scan rates for the CVs were 0.050–5.000 V s⁻¹. Successive experiments under the same experimental conditions showed that all oxidation and reduction potentials were reproducible within 0.010 V under our experimental conditions. Electrochemical data in Tables 1–8 is obtained from the cyclic voltammograms presented in Figs. 2–9. Potentials tabulated are referenced against the Fe(H/Fe(H⁺) couple, as suggested by IUPAC [12].

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Transparency document. Supplementary material

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