Probing the effects of steric bulk on the solution-phase behaviour and redox chemistry of cobalt-diimine complexes

*Mark D. Symes\* and Claire Wilson*

WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ, United Kingdom. \*Email: [mark.symes@glasgow.ac.uk](mailto:mark.symes@glasgow.ac.uk)

**General Experimental Remarks:** 1,10-Phenanthroline (phen) (≥99%), 5,5′-dimethyl-2,2′-bipyridine (Me2bipy) (98%), 2,9-dimethyl-1,10-phenanthroline (neocuproine) (≥98%), Co(NO3)2·6H2O (98%), iodine (≥99.8%) and tetrabutylammonium hexafluorophosphate (TBA-PF6) (98%) were obtained from Sigma Aldrich.

All 1H spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 300 K. UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer using 1 cm pathlength cuvettes. CHN analyses were collected by the services facility at the School of Chemistry, University of Glasgow, as were LM-MS mass spectra (ESI, positive mode, Bruker micrOTOF-Q machine). IR spectra were collected in the solid state on a Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer. Experiments performed at “room temperature” were carried out at 20 °C. Electrochemical experiments were performed as below.

**Preparation of crystals of [Co(neocuproine)2(NO3)]+[Co(neocuproine)(NO3)3]−:** Co(NO3)2·6H2O (0.052 g, 0.178 mmol, 1 eq.) and neocuproine (0.111 g, 0.533 mmol, 3 eq.) were dissolved in acetonitrile (8 mL) with sonication and gentle heating (with a heat gun), yielding a pink solution. This solution was then stored in a sealed vial for a week, after which pink crystals suitable for X-ray diffraction were obtained. A total mass of 0.035 g of these crystals (38% based on cobalt) was obtained by decanting the supernatant solution, washing with acetonitrile and diethyl ether, and then drying overnight. The analysis of these crystals was then fitted with a molecule of diethyl ether (from the washing step) and a molecule of acetonitrile (observed in the crystal structure): Anal. calcd. for C48H49Co2N11O13: C 52.13, H 4.47, N 13.93. Found: C 52.49, H 4.13, N 13.95. IR (solid state, cm−1) ν = 3066 (w), 3016 (w), 1622 (w), 1593 (m), 1564 (w), 1479 (s), 1435 (vs), 1420 (vs), 1375 (m), 1364 (m), 1296 (vs), 1278 (sh), 1218 (m), 1157 (m), 1034 (s), 1026 (s), 993 (m), 856 (vs), 811 (s), 776 (m), 729 (s), 680 (m), 655 (m).

**Electrochemical Methods:** Electrochemical studies were performed in a single chamber cell in a three-electrode configuration using a Biologic SP-150 potentiostat. The supporting electrolyte was 1 M TBA-PF6 in acetonitrile. A boron-doped diamond electrode (area = 0.071 cm2, Windsor Scientific, UK) was used as the working electrode. A graphite rod was used as the counter electrode and an Ag/AgNO3 pseudo reference electrode was used. Potentials are reported relative to the ferrocenium/ferrocene couple, the position of which was judged by adding ferrocene to the samples analysed. Working electrodes were washed with acetone and deionised water prior to use. Cyclic voltammograms were collected at room temperature under air at a scan rate of 100 mV/s. Measurements were conducted without stirring and with *i*R compensation enabled.

Conductance measurements were made using a CH Instruments 700 series potentiostat in *i*R test mode. Two cylindrical graphite rods (0.5 cm diameter, 99.999%, Sigma Aldrich) were placed in the solutions to be tested at a depth of 1.5 cm and a fixed inter-rod distance of 0.6 cm. One rod was connected as the working electrode and the other connected as a combined reference and counter electrode. The resistance of the solution was then gauged by applying a step change (ΔV) of 0.05 V at a potential of 0 V as per the general method developed by He and Faulkner (*[[1]](#endnote-1)*). The *i*R test function on the potentiostat then extrapolates the signal-averaged currents at 54 and 72 ps after the voltage-step edge backwards to obtain a current at *t* = 0, where this current can also be expressed as ΔV/R. R in this case is the solution resistance that is sought. The final parameter that the user must select with this function is the acceptable stability limit of the system at the value of R measured (“% overshoot”): in our case a value of 2% was chosen (the default setting on the potentiostat). The resistance of a solution is the inverse of its conductance.

**Crystallography:** Crystallographic data were collected at the University of Glasgow on a Bruker APEX-II CCD diffractometer.A pink, block-shaped crystal of dimensions 0.17 × 0.13 × 0.12 mm was used for single crystal X-ray diffraction data collection. C14H12CoN5O9·C28H24CoN5O3·C2H3N crystallised in the monoclinic space group *P*21/*n*, with unit cell dimensions a = 14.5032 (13), b = 18.9956 (17), *c* = 16.0547 (13), β = 93.641 (3)°, and V = 4414.1 (7) Å3, T = 100 K. 55103 reflections were measured by ω scans, 10086 independent reflections with *R*int = 0.050, θmax = 27.5°, θmin = 2.2° using Mo *Kα* radiation, λ = 0.71073 Å. The structure was solved using SHELXS and refined using SHELXL (both within OLEX2) (*[[2]](#endnote-2)[[3]](#endnote-3)-[[4]](#endnote-4)*). OLEX2 was also used for molecular graphics and to prepare material for publication. CCDC 1556230 contains the supplementary crystallographic data for this paper. More details on the crystallographic data and its collection can be found in the Supporting Information.

REFERENCES

1. () He, P.; Faulkner, L. R. *Anal. Chem.* **1986**, *58*, 517-523. [↑](#endnote-ref-1)
2. () Sheldrick, G. M. *Acta Cryst.* *A*, **2015**, *71*, 3–8. [↑](#endnote-ref-2)
3. () Sheldrick, G. M. *Acta Cryst. C,* **2015**, *71*, 3–8. [↑](#endnote-ref-3)
4. () Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341. [↑](#endnote-ref-4)