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

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ABSTRACT

Cobalt-diimine complexes have been used as structural and redox-active elements in a number of supramolecular assemblies. Frequently, it is necessary to functionalise the diimine ligand in order to incorporate it into a larger ensemble, and this can have a dramatic effect on the types of Co-diimine complexes that can form and their redox activity. Herein, we compare the solution-phase and redox chemistry of Co(II) complexes with 1,10-phenanthroline, 5,5′-dimethyl-2,2′-bipyridine and 2,9-dimethyl-1,10-phenanthroline (neocuproine), and show that in solutions containing Co(II) nitrate and neocuproine, the dominant species that forms is the mono-diimine complex $[Co(neocuproine)(NO_3)(CH_3CN)_2]^+$. The mono-neocuproine Co(II) complex is resistant to oxidation, either electrochemically or with iodine. We rationalise this behaviour by considering the steric constraints placed upon the metal centre by the bulky methyl substituents on the neocuproine ligand. Furthermore, from solutions of $[Co(neocuproine)(NO_3)(CH_3CN)_2]^+$, we isolate (and determine the structure of) crystals of formula $[Co(neocuproine)_2(NO_3)]^+\cdot[Co(neocuproine)(NO_3)_3]^-$ for the first time. We believe that this work will help to guide the development of Co-diimine supramolecular assemblies by highlighting the extent to which substituents close to the N-donor atoms can affect which species form in solution, and their likely redox activity.

KEYWORDS

Cobalt coordination chemistry, Co-diimine complexes, phenanthroline complexes, redox chemistry, crystallography

INTRODUCTION

Cobalt diimine complexes have been employed as templates and nodes in a range of supramolecular assemblies, including catenanes (*1-8*), rotaxanes (*7,9-13*), and more extended multi-nuclear species (*14-20*). Such cobalt complexes make ideal building blocks in supramolecular chemistry on account of their ability to direct the formation of well-defined structures (*21*) and because of the reversible Co(II)/Co(III) redox chemistry that often manifests in these complexes. Co(II) complexes are generally held to be significantly more substitutionally-labile than Co(III) complexes, with both tending to adopt octahedral coordination environments with N-donor ligands (*22,23*). Hence a particularly promising route to supramolecular assembly is the formation of a Co(II) complex with a desired ligand set and geometry by dynamic ligand exchange under thermodynamic control, followed by the "freezing" of this environment by oxidation to the much less labile Co(III) form (*24-30*).

In the course of our own studies into the various electronic and spectroscopic properties of cobalt coordination complexes containing diimine ligands (*31,32*), we became intrigued by the effect of bulky substituents close to the diimine N-donor atoms and how this might affect the assembly of the resulting structures and their redox properties. In particular, we were interested to know whether having methyl substituents adjacent to the N-donor would prevent the formation of *tris*- and/or *bis*-diimine complexes of Co(II) for steric reasons, and in probing whether the cobalt centres in any of these complexes (if they could form at all) would be amenable to oxidation to Co(III). Oxidation to Co(III) is expected to be highly dependent on the steric requirements of the ligands, as oxidation of Co(II) to Co(III) brings about a marked reduction in the ionic radius of the metal (*33*).

Herein, we compare the coordination and redox chemistry of Co(II) in the presence of 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (neocuproine). We show that the formation of $[Co(phen)_3]^{2+}$ is both rapid and quantitative upon mixing a suitable Co(II) salt and three equivalents of the ligand, and that $[Co(phen)_3]^{2+}$ can be readily and reversibly oxidised to $[Co(phen)_3]^{3+}$ both electrochemically and by using the mild oxidant iodine. In contrast, $[Co(neocuproine)_3]^{2+}$ cannot form at all in solution due to sterics. Using a battery of solution-phase techniques (^{1}H NMR, UV-vis, mass spectrometry, electrochemistry and electrical conductivity) we show that the dominant species formed in solution upon dissolution of Co(II) nitrate and three equivalents of neocuproine is the mono-diimine Co(II) complex $[Co(neocuproine)(NO_3)(CH_3CN)_2]^+$. We show that this complex cannot be oxidised to the Co(III) oxidation state either by treatment with iodine or by electrochemical methods. We rationalise this on the basis of the steric crowding that would result if the metal centre were oxidised to Co(III) and also assign the most likely structure of this mono-diimine complex. Meanwhile, upon standing, solutions of $[Co(neocuproine)(NO_3)(CH_3CN)_2]^+$ yield crystals of the previously unreported salt $[Co(neocuproine)_2(NO_3)](Co(neocuproine)(NO_3)_3)$, whose structure we determine using single crystal X-ray diffraction. These results have important implications for the design of supramolecular assemblies and molecular machines that incorporate cobalt centres and diimine ligands; if those ligands have bulky substituents adjacent to the N-donor, then the solution-phase species that form are likely to only contain one equivalent of the diimine ligand, and oxidation of the Co(II) centre may not be possible.

RESULTS AND DISCUSSION

We began our investigations into the effect of bulky substituents close to the diimine N-donors by examining the electrochemistry of a series of allied cobalt complexes. The unsubstituted complex $[Co(phen)_3]^{2+}$ was prepared by mixing one equivalent of cobalt(II) nitrate and three equivalents of phenanthroline in acetonitrile under air, giving a yellow solution. Cyclic voltammetry on this complex (black line in Figure 1A) revealed a reversible one-electron redox process centred around −0.2 V (*vs.* ferrocenium/ferrocene), as expected for the $[Co(phen)_3]^{3+/2+}$ couple in acetonitrile (*34*). In contrast, when one equivalent of cobalt(II) nitrate was mixed with three equivalents of neocuproine in acetonitrile, a pink solution was formed which did not show any redox waves over the potential range +0.2 to −0.8 V (Figure 1A, red line). Comparison was also made with the complex formed by the addition of three equivalents of 5,5′-dimethyl-2,2′-bipyridine (Me_2bipy) to one equivalent of cobalt nitrate in acetonitrile. In this complex, the methyl substituents are remote from the N-donor atoms and so do not impose any steric constraints on the formation of the *tris*-diimine complex. This complex has previously been reported to have a reversible one-electron redox wave ascribed to the $[Co(Me_2bipy)_3]^{3+/2+}$ redox couple (*35*), as evident by the wave at around −0.3 V in Figure 1B (black line). However, even over the wider potential window used in Figure 1B, the cobalt-neocuproine solution evinces no reversible redox chemistry that can be assigned to a

Co(III)/Co(II) redox couple. Likewise, a cyclic voltammogram of one equivalent of cobalt(II) nitrate and three equivalents of neocuproine in a dimethylformamide electrolyte also shows no redox waves over this potential range (see Figure S1).

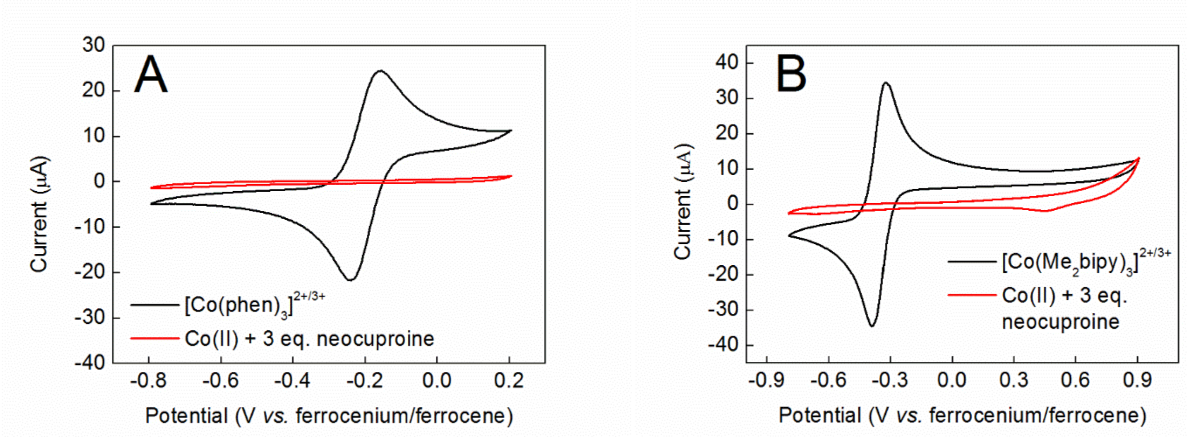

Figure 1. A: Cyclic voltammograms in acetonitrile / 1 M TBA-PF_6 run according to the procedure given in the Experimental Section of a 6 mM solution of $[Co(phen)_3]^{2+}$ (black line) and a 6 mM solution of Co(II) nitrate in the presence of 3 equivalents of neocuproine (red line). **B**: Cyclic voltammograms in acetonitrile / 1 M TBA-PF_6 run according to the procedure given in the Experimental Section of a 6 mM solution of $[Co(Me_2bipy)_3]^{2+}$ (black line) and a 6 mM solution of Co(II) nitrate in the presence of 3 equivalents of neocuproine (red line).

To investigate the species present in these solutions in more detail, we conducted ^1H NMR studies both before and after attempted oxidation with the mild oxidant iodine. Figure 2 shows stacked NMR plots for the complex $[Co(phen)_3]^{2+}$ before and after oxidation with iodine, whilst Figure S2 shows a comparison between the high field portion of the oxidised spectrum and a spectrum of the free ligand. Hence it is apparent (despite the paramagnetic shift and broadening of the phenanthroline peaks) that $[Co(phen)_3]^{2+}$ exists in solution as a highly symmetrical complex (with only four aromatic signals at 107.7, 50.2, 33.4 and 17.3 ppm, as shown previously by Constable and co-workers (*36*)), and that treatment with excess iodine leads to the generation of diamagnetic $[Co(phen)_3]^{3+}$, whose peak pattern is distinct from the free ligand. Similar stack plots for $[Co(Me_2bipy)_3]^{2+}$ are shown in the Supporting Information (Figures S3 and S4), and show that this complex too may be oxidised with iodine to yield $[Co(Me_2bipy)_3]^{3+}$. Meanwhile, the ^1H NMR spectrum of a solution containing four equivalents of phenanthroline and one equivalent of Co(II) shows the expected four paramagnetically-shifted peaks for $[Co(phen)_3]^{2+}$ in addition to four peaks below 10 ppm corresponding to free ligand (Figure S5). This shows that exactly three equivalents of phenanthroline are bound to the metal centre at any time; when additional equivalents of ligand are present, these appear as free, non-coordinated phenanthroline.

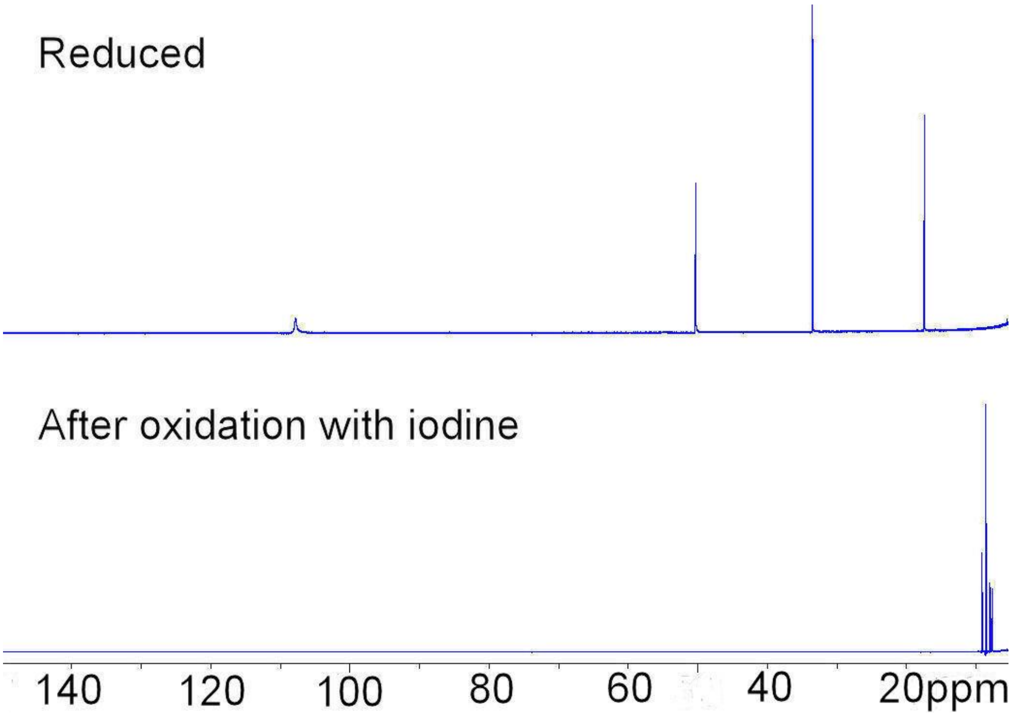

Figure 2. Stacked ^1H NMR spectra (400 MHz, 298 K, 10%/90% CD_3CN/CH_3CN) of 20 mM $[Co(phen)_3](NO_3)_2$ (top) and the same sample 4 hours after the addition of 10 equivalents of solid iodine (lower spectrum).

However, the situation is very different when neocuproine is used as a ligand. Figure 3 shows that when 3 equivalents of neocuproine are mixed with one equivalent of Co(II) nitrate in acetonitrile, two distinct species are observed by ^{1}H NMR: a paramagnetic species with three signals (at 51.5, 36.9 and 13.7 ppm) and a diamagnetic species with three signals below 10 ppm. Figure S6 shows a zoom of this diamagnetic region and compares this portion of the spectrum with that for free neocuproine in the absence of any Co(II). Hence it is apparent that these signals in the diamagnetic region of the spectrum are due to free (uncomplexed) neocuproine. If the experiment is repeated with a ratio of neocuproine to Co(II) of 2:1, then a very similar spectrum is obtained (Figure 3, second spectrum from the top), only now the intensities of the signals corresponding to free neocuproine are approximately halved. These results suggested to us that the paramagnetic complex that formed in these solutions contained only one neocuproine per cobalt centre, and that any additional neocuproine added to the solution remained unbound. The spectrum of Co(II) nitrate in the presence of one equivalent of neocuproine seems to bear this out (Figure 3, third spectrum from the top); now there are no peaks visible that are attributable to free neocuproine, and only three (paramagnetically shifted) signals are observed. We note at this juncture that the solubility of these neocuproine complexes is significantly lower than that of $[Co(phen)_3]^{3+/2+}$ or $[Co(Me_2bipy)_3]^{3+/2+}$. Indeed, upon standing for a few hours at room temperature, pink/red crystals are observed to form in these solutions (which are suitable for single crystal X-ray diffraction, *vide infra*). This did not prevent ^{1}H NMR spectra of Co(II) in the presence of 2 and 3 equivalents of neocuproine being collected in acetonitrile as for $[Co(phen)_3]^{3+/2+}$, but it did prevent suitable spectra of Co(II) in the presence of 1 equivalent of neocuproine from being obtained in this solvent. This spectrum was therefore obtained from a mixed methanol/acetonitrile (10:90) solution. The slightly different solvent used may therefore account for some of the shifting in peaks observed in this case relative to those with 2 or 3 equivalents of neocuproine. However, it is also possible that the difference in shifts (and also the considerable sharpening of the peak at the lowest field) when only one equivalent of neocuproine is present may be evidence for a degree of ligand exchange in the cases where there is excess neocuproine. Hence in the upper two spectra, some of the peaks are possibly broadened due to exchange with free neocuproine. We shall return to this point again later on when discussing the possible mechanism of crystal formation from these solutions.

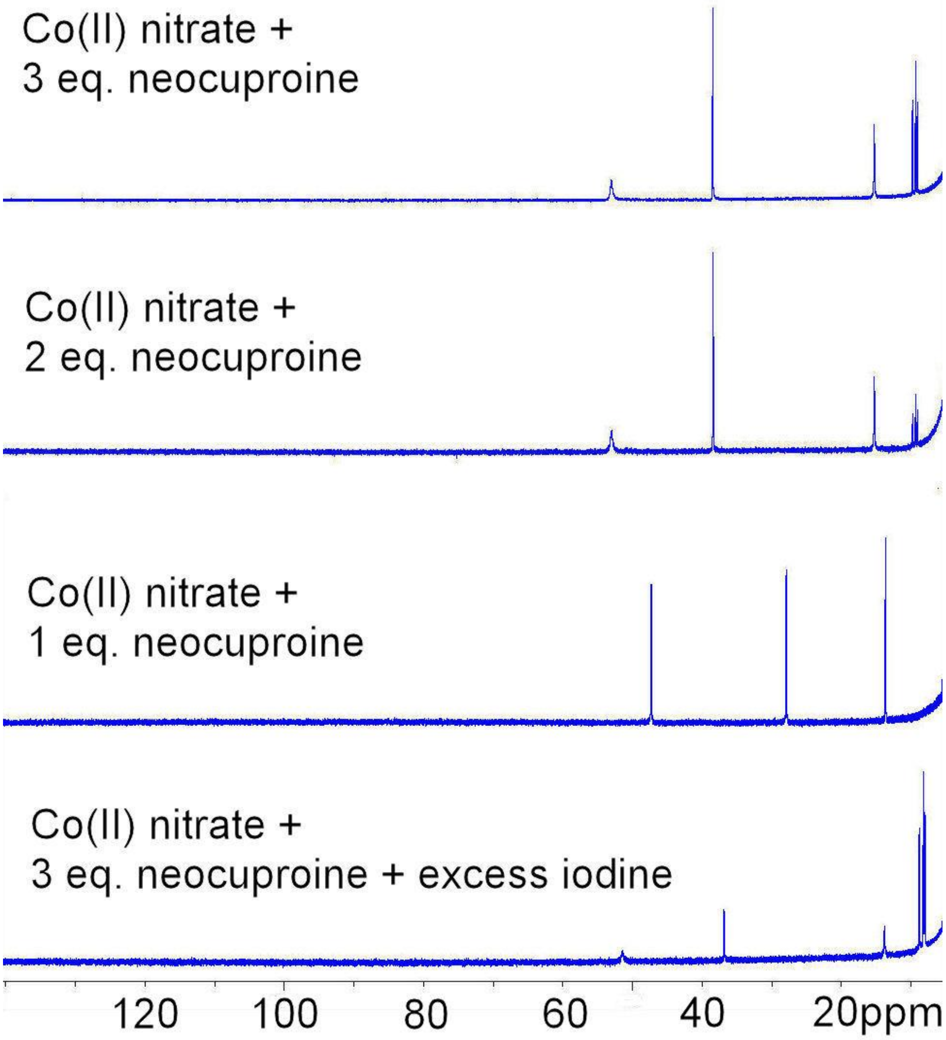

Figure 3. Stacked ^{1}H NMR spectra (400 MHz, 298 K, 10%/90% CD_3CN/CH_3CN) of a 20 mM Co(II) nitrate and 60 mM neocuproine solution (top), a 20 mM Co(II) nitrate and 40 mM neocuproine solution (second from top), a 20 mM Co(II) nitrate and 20 mM neocuproine solution (third from top, in 10%/10%/80% MeOD/CD_3CN/CH_3CN), and the 20 mM Co(II) nitrate and 60 mM neocuproine solution from the uppermost spectrum 4 h after the addition of

10 equivalents of solid iodine. An expansion of the region below 10 ppm is shown in the Supporting Information (Figure S6).

Addition of excess iodine to a solution containing 3 equivalents of neocuproine and one equivalent of Co(II) nitrate in acetonitrile does not appear to bring about oxidation of the sample (in agreement with the electrochemical data). This is shown by the bottom spectrum in Figure 3 (and also in the zoomed spectrum in Figure S6). Hence after standing in the presence of iodine for four hours (so as to compare with the data in Figure 2 for $[Co(phen)_3]^{2+}$ in the presence of iodine), the three signals for the free ligand are still evident, along with the three peaks characteristic of the unoxidised paramagnetic complex (the low intensity of these paramagnetically-shifted peaks is due to the gradual precipitation of material from solution after this length of time, see below). Hence the ^1H NMR data suggest that Co(II) coordinates to only one equivalent of neocuproine in solution, yielding a complex that cannot be oxidised either electrochemically or by treatment with iodine.

We note that a similar scenario unfolds if the cobalt salt is changed to $Co(BF_4)_2$, where the tetrafluoroborate anion is essentially non-coordinating. Hence Figure S7 shows the ^1H NMR spectrum that is obtained when two equivalents of neocuproine are mixed with one equivalent of $Co(BF_4)_2$ in acetonitrile. Two sets of peaks are obtained, and all these peaks are significantly broadened. The first set has three peaks at around 58, 42 and 12 ppm, and the second consists of a single broad peak covering the range 8.6 – 6.9 ppm. The position of these peaks matches well that for $Co(NO_3)_2$ in the presence of two equivalents of neocuproine (Figure 3), although the broadening perhaps suggests a more rapid exchange of the free and bound neocuproine ligands when the anion is tetrafluoroborate.

Solutions of neocuproine and Co(II) are pink, in contrast to solutions of $[Co(phen)_3]^{2+}$ and $[Co(Me_2bipy)_3]^{2+}$, which are yellow. The electronic spectrum in acetonitrile of a 3:1 mix of neocuproine and Co(II) nitrate is shown in Figure 4. The low colour intensity ($\varepsilon = 41$ M^{-1} cm^{-1} at $\lambda_{max} = 505$ nm) is typical of an octahedral species and is consistent with spectra previously reported for 1:1 mixtures of Co(II) salts and neocuproine (*37*,*38*). This result supports the NMR data in suggesting that only the mono-neocuproine complex forms in such solutions, and further suggests that the complex has an octahedral coordination geometry around the Co(II) centre.

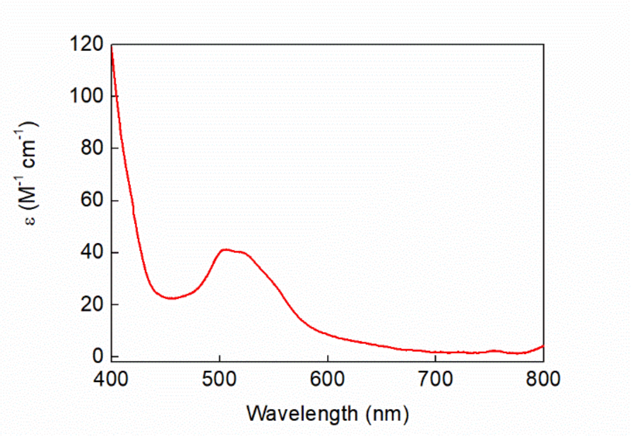

Figure 4. The electronic spectrum of a 3:1 mix of neocuproine and Co(II) nitrate in acetonitrile solution. The trace shown is an average of spectra run at three concentrations of Co(II) (4.4, 2.7 and 2.0 mM).

To gain further insight into the cobalt's coordination environment, and to determine if any nitrates are coordinated to the cobalt centre in solution, the electrical conductivity of various solutions was compared. An acetonitrile solution of Co(II) nitrate (1 mM) and neocuproine (3 mM) was found to have a molar conductivity of 133 Ω^{-1} mol^{-1} cm^2 when measured under the conditions detailed in the Experimental Section. This compares to a value of 252 Ω^{-1} mol^{-1} cm^2 for a 1 mM acetonitrile solution of $[Co(phen)_3](NO_3)_2$, in which the ions are present as free $[Co(phen)_3]^{2+}$ and NO_3^-. A conductivity reduction by a factor of two is consistent with a neocuproine complex that carries only half the charge of the phenanthroline salt (assuming that the ion mobilities of the two cobalt complex cations are roughly similar) (*39*), in turn suggesting that the neocuproine complex exists as a mono-cation/mono-anion salt. Moreover, these molar conductivity values are consistent with the ranges established by Geary for 1:1 and 2:1 electrolytes (120 – 160 and 220 – 300 Ω^{-1} mol^{-1} cm^{2} respectively) (*40*). Allied to the UV-vis data (which indicate an octahedral geometry at Co) and the ^{1}H NMR data (which suggest that only one neocuproine is bound per Co), this implies that the solution species contains one molecule of neocuproine, one molecule of nitrate and then two or three other (presumably acetonitrile) solvent molecules. There are, therefore, four possible compositions of the solution-phase complex, as shown in Figure 5.

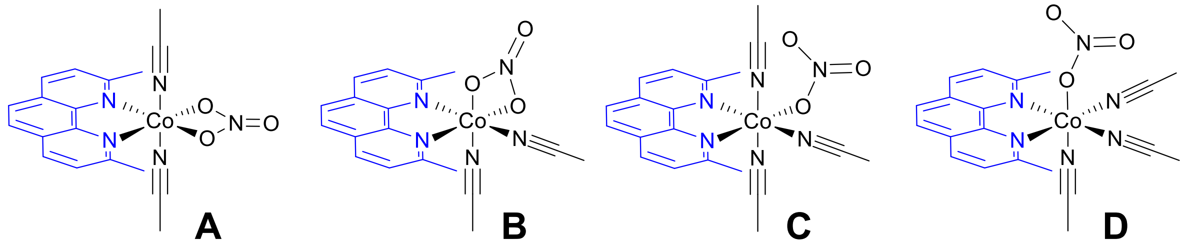

Figure 5. The possible structures of the mono-cationic cobalt complex formed in acetonitrile solutions containing neocuproine and Co(II) nitrate.

Co(II) complexes are known to undergo rapid ligand exchange in solution (*36*). Hence it is possible that all of the conformers shown in Figure 5 could be present and that the ^{1}H NMR spectra show only average conformations. However, within this caveat, steric considerations suggest that only one of the structures shown in Figure 5 (Structure A) is likely to be the dominant conformation in acetonitrile solution. Hence molecular modelling indicates that placing two acetonitrile molecules in the same plane as the neocuproine ligand (Structure D) incurs a severe steric penalty, which is lessened (but still significant) in the cases of Structures B and C (where only one acetonitrile molecule is in the same plane as the neocuproine ligand). In contrast, the small bite angle of bidentate nitrate (*ca.* 59°, see below) makes the conformer with the nitrate binding in a bidentate fashion in the same plane as the neocuproine ligand (Structure A) much less sterically encumbered. In this scenario, two acetonitrile molecules then occupy the much less sterically-demanding axial positions to complete the octahedral coordination geometry of the cobalt. The formula of the dominant solution-phase complex formed when Co(II) nitrate and neocuproine are dissolved in acetonitrile can then be considered as being $[Co(neocuproine)(NO_3)(CH_3CN)_2]^+$, with a further equivalent of free nitrate present as a non-coordinating counterion.

Upon standing for a few hours, pink/red crystals form in acetonitrile solutions containing both cobalt nitrate and neocuproine. When the ratio of cobalt to neocuproine is 1:3, the yield of these crystals (*ca.* 40% based on cobalt) indicates that these crystals correspond to a significant minority product. These crystals then proved suitable for single crystal X-ray diffraction, allowing the structure shown in Figure 6 to be determined. This shows that the crystals comprise cations of formula $[Co(neocuproine)_2(NO_3)]^+$ and anions of formula $[Co(neocuproine)(NO_3)_3]^-$.

Considering the cations first, all the Co−N distances between the central cobalt and the N-donor atoms on the neocuproine ligands are within the range 2.10 – 2.16 Å, which are typical of Co^{II}–N coordination bond lengths in cobalt-phenanthroline complexes (*41*). Meanwhile, the nitrate binds to the Co(II) centre in an asymmetric manner, with both a long (2.2326 (17) Å) and a short (2.1831 (16) Å) Co−O interaction, with the latter value being typical for bidentate nitrate bound to a Co(II) centre (*42*). Given the solution-phase behaviour of mixtures of Co(II) and neocuproine, it was initially surprising to us that such a species could form at all. At least part of the reason that we observe such complexes in the solid state must be because of the small bite angle of the bound nitrate ligand, where the O−Co−O angle is only 58.58 (6)°. This then allows more space for the bulky neocuproine ligands to fit around the cobalt centre, whose other internal angles show considerable deviation from the ideal of 90° for an octahedral geometry. For example, the O401−Co2−N10B, O402−Co2−N1A and N1B−Co2−N1A bond angles are 77.89 (6)°, 102.60 (6)° and 105.04 (7)° respectively. The crystal structures of allied $[Co(phen)_2(NO_3)]^+$ complexes have previously been reported (*43-45*), although in all these cases the diimine ligands are unsubstituted 1,10-phenanthroline. Meanwhile, a search of the Cambridge Structural Database (CSD) reveals that the nearest analogue containing neocuproine is a structure containing a cobalt centre coordinated to two neocuproine ligands and a chelating carboxylate group (*46*). The Co−N distances in our structure agree very closely with the distances reported in this latter work, which also displays a similar distorted octahedral geometry around the Co(II) centre.

The anion in the crystal structure ($[Co(neocuproine)(NO_3)_3]^-$) also contains an octahedral cobalt centre, but in this case the coordination environment contains only one neocuproine ligand and three bound nitrates. The Co−N distances between the cobalt and the diimine ligand are 2.0869 (18) and 2.1113 (18) Å. Meanwhile, one nitrate binds in a bidentate fashion with a degree of asymmetry, manifesting in a short (Co1−O201 = 2.1523 (16) Å) and a long (Co1−O202 = 2.1865 (17) Å) Co−O bond. The other two nitrate ligands each bind in a monodentate manner. The first of these exhibits a Co−O bond length of 2.1068 (16) Å, whilst the other shows some isomerism in the nature of the nitrate binding, giving rise to two partially-occupied forms (with relative occupancy 0.83:0.17) displaying Co1−O301 = 2.051 (2) Å and Co1−O311 = 2.130 (12) Å respectively. The octahedral geometry of the Co(II) centre is again somewhat distorted from the ideal, with N1−Co1−N10 = 80.43 (7)°, N1−Co1−O311 = 80.1 (4)°, N10−Co1−O311 = 99.4 (3)° and O101−Co1−O201 = 92.20 (7)°. The chelating nitrate again displays a fairly acute bite angle (O201−Co1−O202 = 59.80 (6)°), as also observed in the cation. Through a search of the CSD, we were able to identify only two structures containing both a neocuproine ligand and a bidentate nitrate ligand around a cobalt centre (*47,48*). Both of these display similar chelating nitrate and diimine bond angles about cobalt, with Co−N and Co−O bond lengths in broad agreement with those we report here (including an asymmetry in the Co−O distances).

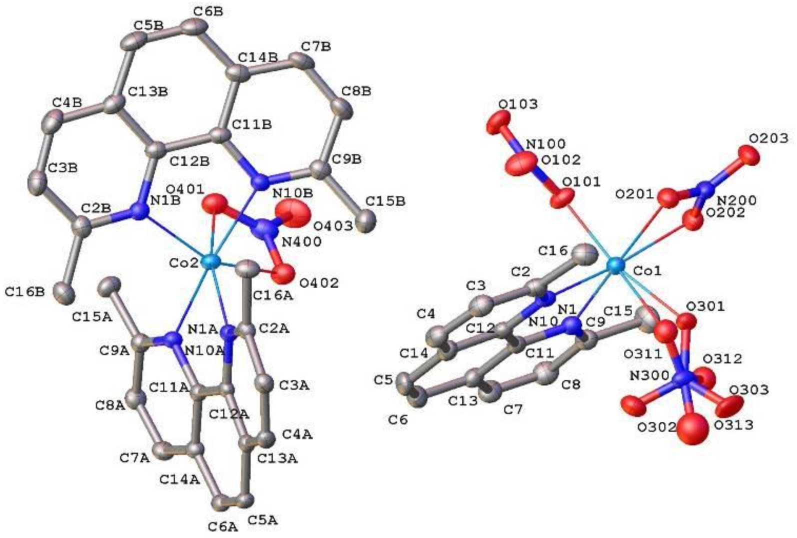

Figure 6. The crystal structure of [Co(neocuproine)$_2$(NO$_3$)]$^+$[Co(neocuproine)(NO$_3$)$_3$]$^-$. Crystallographic details can be found in the Supporting Information. Colour scheme: C = grey, N = dark blue, O = red, Co = pale blue. H atoms have been omitted, displacement ellipsoids are drawn at 50% probability level.

A possible route of formation for these crystals is by ligand exchange in solution (see Figure 3 and associated discussion), which may lead to small amounts of the *bis*-neocuproine cation forming. Although we do not observe any *bis*-neocuproine species at sufficient levels to be evident explicitly in the ^{1}H NMR spectra, mass spectrometry suggests that such species can indeed form. Hence the mass spectrum of a 6 mM solution of Co(II) in acetonitrile containing 3 equivalents of neocuproine shows peaks at 329.0134 (corresponding to [Co(neocuproine)(NO$_3$)]$^+$, for which the calculated *m/z* is 329.0211) and 537.1097 (corresponding to [Co(neocuproine)$_2$(NO$_3$)]$^+$, for which the calculated *m/z* is 537.1211) in addition to a peak for free, uncomplexed neocuproine at around *m/z* = 209. Thus, formation of small amounts of $[Co(neocuproine)_2(NO_3)]^+$ in solution (suggested also by the broadening of some of the peaks in the ^1H NMR spectra when more than one equivalent of neocuproine is present) may then lead to ion pairing with anionic $[Co(neocuproine)(NO_3)_3]^-$ moieties and subsequent precipitation of the resulting salt. Over time, this could lead to the formation of insoluble crystalline material to a considerably greater degree than might be expected on the basis of the amount of *bis*-neocuproine cation present in solution at any given time. Hence it seems that the dominant solid-state and solution-phase species are distinct from other another, with the former being a salt of composition $[Co(neocuproine)_2(NO_3)]^+\cdot[Co(neocuproine)(NO_3)_3]^-$ and the latter a mono-diimine species akin to $[Co(neocuproine)(NO_3)(CH_3CN)_2](NO_3)$.

CONCLUSIONS

In summary, we have shown that in solutions containing Co(II) nitrate and neocuproine, the dominant species that forms is the mono-diimine complex $[Co(neocuproine)(NO_3)(CH_3CN)_2]^+$. This is the case even when excess neocuproine is present, and there is no evidence for the formation of significant quantities of *bis*- or *tris*-neocuproine complexes analogous to $[Co(phen)_3]^{2+}$. The mono-neocuproine Co(II) complex is resistant to oxidation, either electrochemically or with iodine. The underlying cause of this lack of redox activity is likely to be the same as that which prevents the *bis*- and *tris*-neocuproine complexes from forming; namely, the steric requirements of the methyl groups on the neocuproine ligands. These methyl groups make it very difficult for the contraction of the metal centre that is required for oxidation of Co(II) to Co(III) to take place within the ligand set of the Co(II) centre. Hence the Co(II) centre is extremely hard to oxidise in comparison with the ease and reversibility of the $[Co(phen)_3]^{3+/2+}$ redox couple. Despite the steric bulk of the ligands, however, small amounts of the *bis*-neocuproine complex can form in solution, and this leads to the precipitation of crystals of formula $[Co(neocuproine)_2(NO_3)]^+ \cdot [Co(neocuproine)(NO_3)_3]^-$ in reasonable yield. These findings have implications for the development of supramolecular assemblies and molecular machines that use Co-diimine units as structural or redox-active elements, by highlighting the extent to which substituents close to the N-donor atoms can affect which species are likely to form in solution and what their redox activity may (or may not) be.

EXPERIMENTAL SECTION

General Experimental Remarks: 1,10-Phenanthroline (phen) (≥99%), 5,5′-dimethyl-2,2′-bipyridine (Me_2bipy) (98%), 2,9-dimethyl-1,10-phenanthroline (neocuproine) (≥98%), $Co(NO_3)_2 \cdot 6H_2O$ (98%), $Co(BF_4)_2 \cdot 6H_2O$ (99%), iodine (≥99.8%) and tetrabutylammonium hexafluorophosphate (TBA-PF_6) (98%) were obtained from Sigma Aldrich.

All ^{1}H 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 $[Co(neocuproine)_2(NO_3)]^+[Co(neocuproine)(NO_3)_3]^-$: $Co(NO_3)_2 \cdot 6H_2O$ (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 $C_{48}H_{49}Co_2N_{11}O_{13}$: 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-PF_6 in acetonitrile, unless otherwise stated. A boron-doped diamond electrode (area = 0.071 cm^2, Windsor Scientific, UK) was used as the working electrode. A graphite rod was used as the counter electrode and an Ag/$AgNO_3$ 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 0.7 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 (*49*). 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. $C_{14}H_{12}CoN_5O_9{\cdot}C_{28}H_{24}CoN_5O_3{\cdot}C_2H_3N$ crystallised in the monoclinic space group $P2_1/n$, with unit cell dimensions $a = 14.5032$ (13), $b = 18.9956$ (17), $c = 16.0547$ (13), $\beta = 93.641$ (3)°, and $V = 4414.1$ (7) Å^3, T = 100 K. 55103 reflections were measured by ω scans, 10086 independent reflections with $R_{\mathrm{int}} = 0.050$, $\theta_{\mathrm{max}} = 27.5°$, $\theta_{\mathrm{min}} = 2.2°$ using Mo *Kα* radiation, $\lambda = 0.71073$ Å. The structure was solved using SHELXS and refined using SHELXL (both within OLEX2) (*50-52*). 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.

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SUPPORTING INFORMATION

Additional ^{1}H NMR spectra and crystallographic data for

$C_{14}H_{12}CoN_5O_9 \cdot C_{28}H_{24}CoN_5O_3 \cdot C_2H_3N$.

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