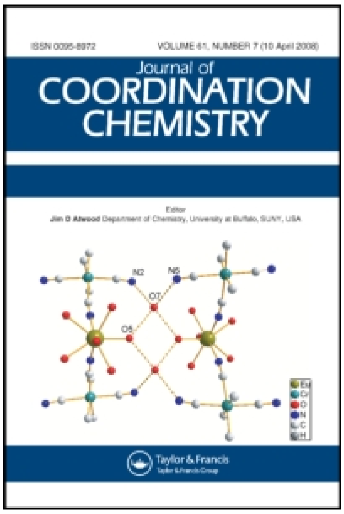

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Nickel(II) 1,10-Phenanthroline complexes: *cis*-[Aqua(Bromo)<i>bis</i>(1,10-Phenanthroline)Nickel(II)] Bromide Trihydrate and (<i>tris</i>(1,10-Phenanthroline)Nickel(II)] Bromide Octahydrate

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NICKEL(II) 1,10-PHENANTHROLINE COMPLEXES: *cis*-[AQUA(BROMO)*bis*(1,10-PHENANTHROLINE)-NICKEL(II)] BROMIDE TRIHYDRATE AND (*tris*(1,10-PHENANTHROLINE)NICKEL(II)] BROMIDE OCTAHYDRATE

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$[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ where phen is 1,10-phenanthroline, is a light-blue material which crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$, $a = 10.4300(4)$, $b = 25.310(2)$, $c = 9.7790(9)$ Å and $\beta = 102.932(6)°$. The structure was determined at ambient temperature from 5161 reflections with $R = 0.0643$ and $R_w = 0.1306$. The structure consists of a complex cation, a bromide anion and three waters of hydration. The Ni atom is *pseudo*-octahedral with a *cis* arrangement of Br and H_2O. This *cis* geometry persists in solution, as evidenced by ^1H NMR spectroscopy, although the Br may be replaced by another H_2O. $[Ni(phen)_3]Br_2 \cdot 8H_2O$ is a light-red material which crystallizes in the monoclinic space group $C2/m$ with $Z = 8$, $a = 23.6320(11)$, $b = 21.4880(13)$, $c = 15.5470(9)$ Å and $\beta = 107.927(3)°$. The structure was determined at 120 K from 6820 reflections with $R = 0.0733$ and $R_w = 0.1022$. The structure consists of a complex cation, two bromide anions and eight waters of hydration. The anions and waters are extensively disordered. The Ni atom is *pseudo*-octahedral.

Keywords: Crystal structure; Nickel(II) complexes; Phenanthroline; NMR of paramagnetic materials

INTRODUCTION

Recently we have become interested in dimeric octahedral nickel(II) compounds that contain the $\{NiX\}_2$ core, where X is either Cl or Br [1,2]. The Cl compounds have been studied for many years [3–8], and the coupling between the Ni centers is ferromagnetic. For the $[\{Ni(en)_2Cl\}_2]^{2+}$ series, where en is ethylenediamine, with Cl^-, ClO_4^- and BPh_4^- as the counter ions, the extent of ferromagnetic coupling increases as the Ni–Ni separation decreases and the sum of the Ni–Cl bonds also decreases [5,6,8]. In other words, in this series, the extent of coupling increases as the ferromagnetic superexchange pathlength decreases. How is the coupling affected by changing the bridging chlorides to bromides? So far, there is only one point of comparison where both the

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structures and the magnetic properties of the dimers are known [1,2]. In this case, for $[\{Ni(TPA)X\}_2](ClO_4)_2 \cdot 2HNEt_3ClO_4$ where TPA is *tris*(2-pyridylmethyl)amine and X is either Cl or Br, the effective ferromagnetic pathway (that is, the Ni–X–Ni pathlength adjusted for the difference in ionic radii between Cl and Br) is the same, yet the bromide analog is more strongly coupled ($J/k = 10.0(5)\,cm^{-1}$ for the bromo complex and the chloro complex has $J/k = 7.6(1)\,cm^{-1}$) [2]. However, only one other structure with the $\{NiBr\}_2$ core has been determined by single-crystal X-ray crystallography [9], and, since magnetic measurements have not been reported for this compound, we do not know if this increase in coupling upon changing from chloride to bromide in compounds that contain the $\{NiX\}_2$ core is general.

We have begun a series of studies to investigate the structural and magnetic properties of dimeric octahedral nickel(II) compounds that contain the $\{NiX\}_2$ core, where X is either Cl or Br. During these studies, we attempted to prepare $[\{Ni(phen)_2Br\}_2]Br_2$ where phen is 1,10-phenanthroline, and obtained a mixture of light-blue crystals, light-red crystals and green solids. The light-blue crystals proved to be $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ and the light-red crystals proved to be $[Ni(phen)_3]Br_2 \cdot 8H_2O$. This paper reports the solid-state and solution structures of these materials.

EXPERIMENTAL

Synthesis

$NiBr_2 \cdot 6H_2O$ was prepared by dissolving $NiCl_2 \cdot 6H_2O$ (50.0 g, 0.238 mol) in 80 cm^3 aqueous HBr (48% by weight). The solution was heated and stirred. When the volume had decreased to about 15 cm^3, an additional 80 cm^3 aqueous HBr was added. This was repeated twice. The yellow-green hygroscopic solid was collected by filtration (41.05 g, 0.126 mol), washed with acetone and stored in a desiccator.

$[Ni(phen)_3]Br_2 \cdot 2H_2O$ was prepared following a published procedure [10].

$[Ni(phen)_3]Br_2 \cdot 2H_2O$ (2.97 g, 3.74 mmol) and $NiBr_2 \cdot 3H_2O$ (5.17 g, 19.0 mmol) were dissolved in a mixture of 5 cm^3 MeOH and 1 cm^3 H_2O. The resultant green-blue solution was refluxed for 10 min and then filtered. Green seed crystals were prepared by the slow addition of 1 cm^3 acetone to 1 cm^3 of this filtered solution. Subsequently, 10 cm^3 acetone was added dropwise to the remaining green-blue solution, followed by addition of the seed crystals and followed by another 10 cm^3 acetone. The mixture was stirred for 10 min, vacuum filtered, and washed with acetone twice. The green precipitate (7.83 g) was recrystallized from aqueous MeOH (1 : 10 H_2O : MeOH) giving a mixture of green solids, light-red and light-blue crystals. The light-blue crystals proved to be $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ (**1**) and the light-red crystals proved to be $[Ni(phen)_3]Br_2 \cdot 8H_2O$ (**2**) (*vide infra*).

Structure Determinations

Some details of the crystal and data collections are collected in Table I. X-ray diffraction data for both structures were collected at Louisiana State University. For **1**, data were collected at 296 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 1.54184$ Å). Two quadrants of data

TABLE I Crystallographic details for $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ (**1**) and $[Ni(phen)_3]Br_2 \cdot 8H_2O$ (**2**)

Formula	$NiBr_2C_{24}H_{24}N_4O_4$	$NiBr_2C_{36}H_{40}N_6O_8$
M	650.99	903.26
Crystal class	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$C2/m$ (#12)
Z	4	8
a (Å)	10.4300(4)	23.6320(11)
b (Å)	25.310(2)	21.4880(13)
c (Å)	9.7790(9)	15.5470(9)
β (°)	102.932(6)	107.927(3)
V (Å^3)	2516.0(3)	7511.5(7)
μ (mm^{-1})	5.161	2.710
ext. coef.	2.92×10^{-6}	
D_{calc} (g/cm^3)	1.718	1.597
$F(000)$	1304	3680
Radiation (λ, Å)	Cu Kα (1.5418)	Mo Kα (0.7107)
h, k, l collected	−13 to +12, 31, −12 to +11	28, −25, to +25, −18 to +17
Reflections measured	7852	12 600
Unique reflections	5162	6819
Observed (criterion)	4519 ($I > 3\sigma(I)$)	3630 ($I > 2\sigma(I)$)
Parameters	317	509
R	0.0643	0.0812
R_w	0.1306	0.1270
S (goodness of fit)	1.010	1.015

were collected by $\omega - 2\theta$ scans, one $(+h, k, \pm l)$ to $\theta_{max} = 75°$ and the second $(-h, k, \pm l)$ to $\theta_{max} = 50°$. Data reduction included corrections for background, Lorentz, polarization, and absorption effects. Absorption corrections were based on ψ scans; decay was neglible. Equivalent data were combined ($R_{int} = 0.031$). For **2**, data were collected at 120 K to a maximum θ of 35° on a Nonius Kappa CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Data were corrected for Lorentz, polarization, and absorption effects. Equivalent data were combined ($R_{int} = 0.060$). Both structures were solved using direct methods [11], and expanded using Fourier techniques [12]. Full-matrix least-squares refinement with anisotropic thermal parameters for all of the non-hydrogen atoms converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0643$ for **1** (0.0733 for **2**) and $R_w[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.1306$ for **1** (0.1022 for **2**). The function minimized in refinement was $\Sigma w(F_o^2 - F_c^2)^2$ where $w = 1/[\sigma^2(F_o) + (p)^2 F_o^2/4]$, with $p = 0.12$ for **1** and 0.05 for **2**. Hydrogen atoms were placed in idealized positions (C–H 0.95 Å), with $U_{iso} = 1.2\,U_{eq}$ of the attached atom. Neutral atom scattering factors were taken from Cromer and Waber [13]. Anomalous dispersion effects were included in F_c [14], and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [15]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [16]. All calculations were performed using the teXsan for Windows [17] crystallographic software package. For **1**, two intense reflections (the 1,0,0 and 1,0,2) consistently gave F_c values much larger than their F_o values and were discarded. It is believed that these reflections were undercounted. The data were also corrected for secondary extinction. The atomic numbering scheme for **1** is shown in Fig. 1. Bond distances and angles of the coordination sphere are collected in Table II. During the refinement of the structure of **1**, various alternative scenarios were considered, modeled and rejected, for example disorder of the aqua and bromo ligands and disorder among the bromide counter ion and the waters of hydration. In these cases, refinement of the populations failed to

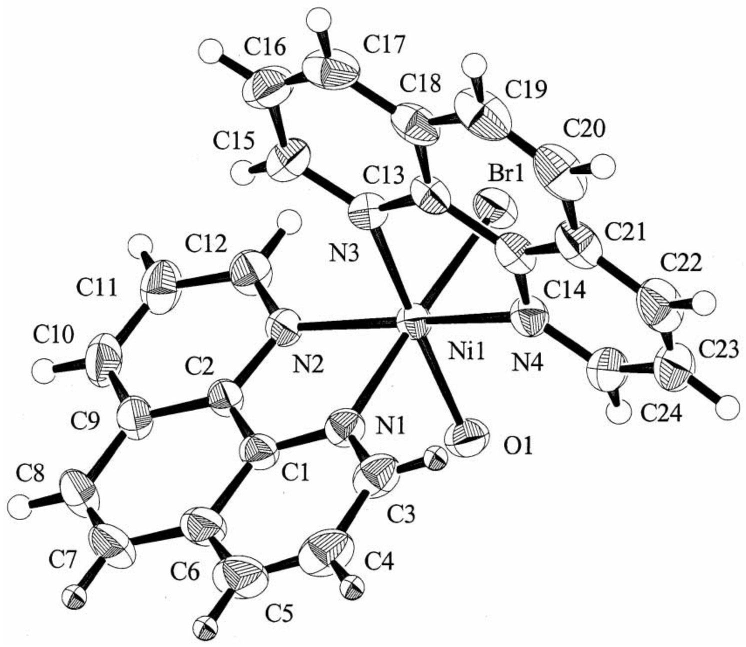

FIGURE 1 Perspective drawing of $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ (**1**) showing the atom numbering scheme. Ellipsoids are drawn at 50% probability.

TABLE II Chemical bond distances (Å) and angles (°) for the coordination sphere of $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ (**1**)

Br(1)–Ni(1)	2.5722(5)
Ni(1)–O(1)	2.096(2)
Ni(1)–N(1)	2.114(2)
Ni(1)–N(2)	2.066(2)
Ni(1)–N(3)	2.086(2)
Ni(1)–N(4)	2.082(2)
Br(1)–Ni(1)–O(1)	88.77(6)
Br(1)–Ni(1)–N(1)	172.16(6)
Br(1)–Ni(1)–N(2)	96.50(6)
Br(1)–Ni(1)–N(3)	94.23(6)
Br(1)–Ni(1)–N(4)	92.20(7)
O(1)–Ni(1)–N(1)	84.38(8)
O(1)–Ni(1)–N(2)	91.94(8)
O(1)–Ni(1)–N(3)	174.15(8)
O(1)–Ni(1)–N(4)	94.58(9)
N(1)–Ni(1)–N(2)	79.96(9)
N(1)–Ni(1)–N(3)	92.94(9)
N(1)–Ni(1)–N(4)	92.15(9)
N(2)–Ni(1)–N(3)	92.71(9)
N(2)–Ni(1)–N(4)	169.23(9)
N(3)–Ni(1)–N(4)	80.29(9)

suggest any improvements over the final model. The hydrogen atoms of the solvent molecules were not located, and were not included explicitly in the refinement. Their presence was included in the molecular formula, the formula mass and the density determinations.

TABLE III Chemical bond distances (Å) and angles (°) for the coordination sphere of $[Ni(phen)_3]Br_2 \cdot 8H_2O$ (**2**)

Ni(1)–N(1)	2.093(6)
Ni(1)–N(2)	2.098(6)
Ni(1)–N(3)	2.079(6)
Ni(1)–N(4)	2.081(6)
Ni(1)–N(5)	2.082(6)
Ni(1)–N(6)	2.081(6)
N(1)–Ni(1)–N(2)	79.8(2)
N(1)–Ni(1)–N(3)	92.1(2)
N(1)–Ni(1)–N(4)	168.8(2)
N(1)–Ni(1)–N(5)	91.7(2)
N(1)–Ni(1)–N(6)	92.5(2)
N(2)–Ni(1)–N(3)	93.6(2)
N(2)–Ni(1)–N(4)	92.7(2)
N(2)–Ni(1)–N(5)	168.2(2)
N(2)–Ni(1)–N(6)	92.4(2)
N(3)–Ni(1)–N(4)	80.1(2)
N(3)–Ni(1)–N(5)	94.8(2)
N(3)–Ni(1)–N(6)	173.0(2)
N(4)–Ni(1)–N(5)	96.9(2)
N(4)–Ni(1)–N(6)	96.0(2)
N(5)–Ni(1)–N(6)	79.8(2)

For **2**, the cation is well ordered, but the bromide anions and water molecules are extensively disordered. Various models of this disorder were considered. The final model utilizes seventeen positions with fixed partial occupancy for bromide ions and two positions with partial occupancy for water molecules. Cell-volume and electrical-charge considerations led to the formulation of the compound as containing a total of two bromide ions and eight water molecules. The water positions are disordered among the bromide positions. Attempts to model this disorder with models that summed the bromide occupancies to two per nickel and summed the oxygen occupancies to eight per nickel were unsuccessful. Bond distances and angles of the coordination sphere are collected in Table III. The cation is shown in Fig. 2, and Fig. 3 shows a cell packing diagram.

^{1}H NMR Spectroscopy

^{1}H NMR spectra were recorded at ambient temperature on a JEOL EX/400 spectrometer at 400 MHz. Chemical shifts were referenced to the proton signal of residual CD_2HOD in the CD_3OD. The acquisition conditions were 5.0 µsec pulses, 8192 data points, 161 kHz scan width, 50.8 msec acquisition time and 1000 scans.

RESULTS AND DISCUSSION

Solid-state Structures

The structure of blue $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ (**1**), which is shown in Fig. 1, consists of three waters of hydration, a bromide ion and a complex cation. The complex cation has an octahedral nickel(II) center coordinated by two 1,10-phenanthrolines, a water and a bromide. The water and bromide are *cis*. This structure is very similar

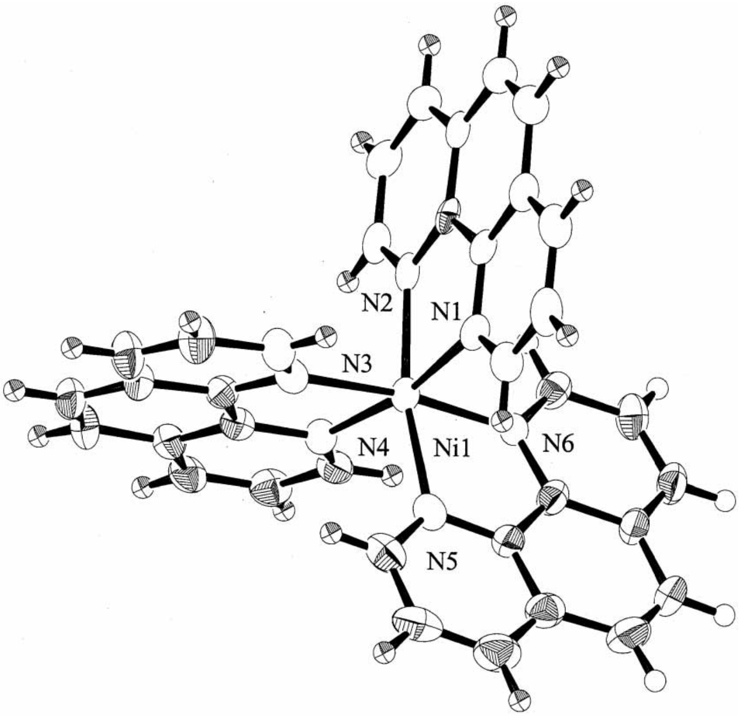

FIGURE 2 Perspective drawing of the cation of $[Ni(phen)_3]Br_2 \cdot 8H_2O$ (**2**) showing the atom numbering scheme. Ellipsoids are drawn at 50% probability.

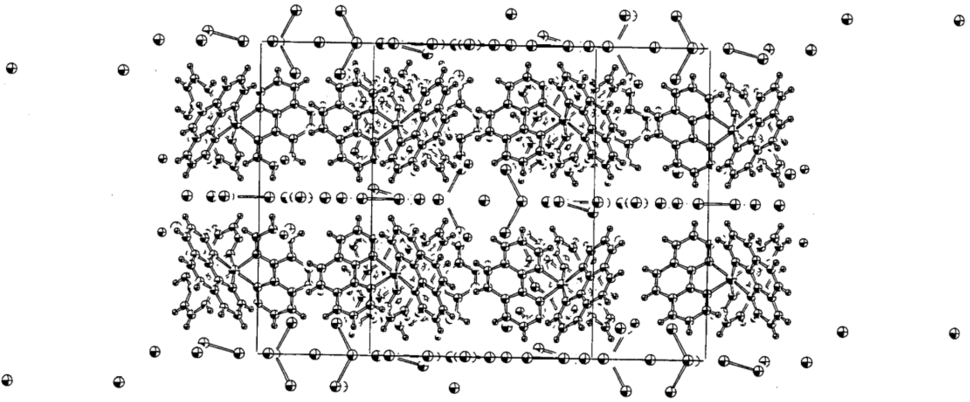

FIGURE 3 Cell packing diagram for $[Ni(phen)_3]Br_2 \cdot 8H_2O$ (**2**) emphasizing the co-planar nature of the disordered anions and solvent.

to an analogous chloride structure $[Ni(phen)_2(H_2O)Cl]Cl \cdot 2MeOH$ [18]. The distances and angles within the phenanthrolines are unremarkable (see supplementary material). The Ni–N distances (average 2.087 Å) fall within the typical range of such distances [19–25]. One Ni–N distance is notably longer than the others, that *trans* to bromide. An elongated Ni–N distance is also observed for the analogous chloride structure (the N is *trans* to chloride). In **1**, the bite of the phenanthroline (80.12°) is also typical. The Ni–Br distance of 2.5722(5) Å is as expected. For example, in [{Ni(TPA)Br}$_2$](ClO$_4$)$_2$ · 2HNEt$_3$ClO$_4$ the distances [2] are 2.504(1) and 2.662(1) Å. The Ni–O(1) distance of 2.096(2) Å is somewhat longer than average (2.079 Å) [26]. In addition to aromatic ring stacking [the ring containing C(3)–C(5) shows a close approach to the central ring containing C(7)–C(9) – the shortest non-hydrogen interacting contact is 3.401 Å between C(5) and C(9)] there is extensive hydrogen bonding among the water molecules and the bromide ions in this structure, as expected. The contact distances are included in the supplementary data. Of particular note, O(1) (the oxygen atom bound to nickel) hydrogen bonds to a symmetry-related O(4) [the O–O separation is 2.735(3) Å], and O(4) hydrogen bonds to Br(2) (the O–Br separation is 3.318(3) Å) [27]. Further, O(2) hydrogen bonds to Br(1) [the Br–O separation is 3.476(3) Å] and also hydrogen bonds to a symmetry-related O(1) [the O–O separation is 2.836(3) Å]. While the metrical parameters of this complex are not unusual, the actual structure is novel. This compound was reported in 1967, when it was speculated to be [Ni(phen)$_2$(H$_2$O)Br]Br, based on the efflorescence and color change of a purported [Ni(phen)$_2$Br$_2$] species from green to blue [28]. One might expect this coordination geometry (*cis*-O(Br)N$_4$) to be typical; however, there is just one crystallographically characterized compound with this same coordination environment ([NiL(H$_2$O)Br]Br, where L is 1,7-dimethyl-1,4,7,10-tetraazacyclododecane) [29]. In this latter compound the Ni–Br distance is 2.610(2) Å and the Ni–O distance is 2.136(9) Å.

The structure of light-red [Ni(phen)$_3$]Br$_2$ · 8H$_2$O (**2**), which is shown in Fig. 2, consists of eight extensively disordered waters of hydration, two extensively disordered bromide ions and a complex cation. The Ni–N distances (average 2.086 Å) fall within the typical range of such distances [19–25]. As is typical, two of the Ni–N distances are notably longer than the other four. The bite of the phenanthroline (79.8°) is also typical. In addition to aromatic ring stacking, there is extensive hydrogen bonding. The disorder among the anions and water molecules precludes discussion of this hydrogen bonding; however, it is interesting to observe that most of these disordered atoms are coplanar (Fig. 3).

In this synthesis, light-red [Ni(phen)$_3$]Br$_2$ · 2H$_2$O was treated with excess yellow-green NiBr$_2$ · 6H$_2$O in aqueous methanol, producing a green precipitate which was recrystallized giving a mixture of green solids, light-red crystals (which proved to be [Ni(phen)$_3$]Br$_2$ · 8H$_2$O) and light-blue crystals (which proved to be [Ni(phen)$_2$(H$_2$O)Br]Br · 3H$_2$O). In a stoichiometric reaction one would expect four equivalents of [Ni(phen)$_3$]Br$_2$ to react with two equivalents of NiBr$_2$ to produce three equivalents of [{Ni(phen)$_2$Br}$_2$]Br$_2$; however, the results using this charging stoichiometry were unsatisfactory. We found that by increasing the relative amount of NiBr$_2$, crystalline products could be obtained. We think the green precipitate is likely solvated NiBr$_2$ which is reported [30] to be a green to yellow-brown solid depending upon the extent of solvation.

Structure in Solution

The solution structure for [Ni(phen)$_2$(H$_2$O)Br]Br · 3H$_2$O was investigated using ^{1}H NMR spectroscopy. In CD$_3$OD, six resonances are observed downfield at 51, 47, 25, 23, 18 and 17 ppm, as three pairs of resonances. The most shifted resonances are the broadest, while the least shifted are the sharpest, as expected for paramagnetically shifted resonances. All of the resonances have comparable intensity. To assign these resonances, we first reviewed the situation observed for the TPA structures [2]. In those systems, the $\{NiX\}_2$ core remained intact in solution, and the electronic structure suggested that the complexes were *pseudo*-octahedral in solution. The ^1H NMR spectrum showed a highly symmetric spectrum (with singlets assignable to each proton of a single picolyl arm of TPA – all arms were equivalent). This equivalence was offered as evidence that the e_g electronic level remained degenerate in solution since a significant splitting of this level would be expected to lead to different picolyl environments [2]. For comparison, we also measured the ^1H NMR spectrum of $[Ni(phen)_3]Br_2$ in CD_3OD, which exhibited just three resonances of equal intensity at 50, 25 and 18 ppm. This small number of resonances attests to a highly symmetric, *pseudo*-octahedral solution structure for this species. All ligands are symmetrically equivalent, and the two "ends" of the ligand are related by a two-fold axis. *Tris* phenanthroline- and methyl-substituted phenanthroline complexes of nickel(II) have been reported previously [31,32], and based on those studies, we assigned the feature at 18 ppm (the narrowest and least shifted resonance) to the protons in the 4 and 7 positions (using the standard numbering scheme for 1,10-phenanthroline), the resonance at 25 ppm to the protons at the 5 and 6 positions, and the resonance at 50 ppm to the protons in the 3 and 8 positions. No resonance assignable to the protons in the 2 and 9 positions was observed. Presumably they were broadened beyond detection in a 9.4 T field owing to their close proximity to the nickel(II) center.

For $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$, the observation of six resonances rather than three suggests some inequivalence of the phenanthrolines. If the two phenanthroline ring systems were truly inequivalent (in NMR terms), one would expect a different signal for each observable proton, for a total of 12 signals (six for each phenanthroline arising from the 3, 4, 5, 6, 7 and 8 positions). This is clearly not the case. If the two phenanthrolines are equivalent, but the two ends are different (thus lacking the two-fold axis observed for $[Ni(phen)_3]Br_2$), one would expect six signals, as is observed. The solid-state structure shows that for each phenanthroline ring, one end is *trans* to the other phenanthroline ring, while the other end is *trans* to either Br or H_2O. If the e_g level is no longer degenerate for this system, the splitting of the d_{z^2} and $d_{x^2-y^2}$ orbitals provides different magnetic environments for the two ends of the phenanthrolines. If the axis that contains the mutually *trans* nitrogen atoms is the z axis, then this end of the two phenanthrolines would be in the same magnetic environment (affected most strongly by the d_{z^2} orbital) and the other end would also be in the same environment (affected most strongly by the $d_{x^2-y^2}$ orbital). Any other assignment of magnetic axes would lead to complete inequivalence of the phenanthrolines. The resonances at 17 and 18 ppm are assigned to the protons in the 4 and 7 positions, the resonances at 23 and 25 ppm to the protons in the 5 and 6 positions, and the resonances at 47 and 50 ppm to the protons in the 3 and 8 positions. No attempt has been made to determine if the 3 and 4 positions are located in the end of the phenanthroline rings which are mutually *trans* to one another [that is, bound to C(10), C(11), C(22) and C(23)], or in the other end [*trans* to either Br or H_2O – that is, bound to C(4), C(5), C(16) and C(17)]. Note that this analysis does not depend upon the nature of the *cis* ligands (the Br and H_2O), merely that they remain *cis*. Consequently the species in solution may be either the $[Ni(phen)_2(H_2O)Br]^+$ species, or the $[Ni(phen)_2(H_2O)_2]^{2+}$ species, with the second water provided by the lattice water. NMR is expected to be insensitive to this change.

CONCLUSIONS

The solid-state structure of $[Ni(phen)_2(H_2O)Br]Br \cdot 3H_2O$ has been determined and consists of a complex cation, a bromide anion and three waters of hydration. The Ni atom has *pseudo*-octahedral geometry with a *cis* arrangement of Br and H_2O. This *cis* geometry persists in solution although the Br may be replaced by another H_2O. The solid-state structure of $[Ni(phen)_3]Br_2 \cdot 8H_2O$ has been determined and consists of an ordered complex cation, and extensively disordered bromide anions and eight waters of hydration.

Acknowledgments

We are grateful to Frank Fronczek of Louisiana State University for collecting the X-ray data and to the Louisiana Board of Regents Support Fund for financial support.

Supplementary Data

CCDC 227315 and CCDC 227316 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.

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