Combining oximes with azides to create a novel 1-D [NaCo\textsuperscript{III}\textsubscript{2}] system: synthesis, structure and solid-state NMR†‡

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Received 2nd September 2009, Accepted 26th October 2009
First published as an Advance Article on the web 4th December 2009
DOI: 10.1039/b918082f

The synthesis and structure of a novel complex with the formula [NaCo\textsuperscript{III}\textsubscript{2}(dmo)\textsubscript{2}(\textmu-N\textsubscript{3})(N\textsubscript{3})\textsubscript{3}], \textit{I}, are reported. Complex \textit{I} was synthesized from the reaction of 1-(dimethylamino)propan-2-one oxime (Hdmo), CoCl\textsubscript{2}-6H\textsubscript{2}O, and NaN\textsubscript{3} in MeOH. It crystallizes in the monoclinic space group \textit{C2/c}. The molecular structure consists of one Na\textsuperscript{+} and two Co\textsuperscript{III} ions bridged by two oxime ligands, two end-to-end azide and three end-on azide anions. The units are linked, forming a 1-D chain. This complex was characterized by UV-Vis spectroscopy where the data confirm the presence of low-spin Co\textsuperscript{III} ions. Solid-state \textsuperscript{23}Na NMR experiments indicate the presence of one magnetically unique site in the repeating unit, that sample purity in the bulk powdered form is high, and that it possesses microcrystalline order. Solid-state \textsuperscript{59}Co NMR experiments at ultra-high field (\textit{B\textsubscript{0} = 21.1 T}) are in agreement with the structure obtained through X-ray crystallography where the Co\textsuperscript{III} ions are coordinated to five nitrogen atoms as well as an oxygen atom.

Introduction

Over the past decade, extensive research has been focused on cobalt coordination complexes due to their potential applications in catalysis, magnetic materials, and models of biological systems.\textsuperscript{1–4} Cobalt is a key element in the active centre of vitamin B12 (cobalamin), which plays an essential role in DNA synthesis, formation of red blood cells, and maintenance of the nervous system.\textsuperscript{4–6} In most cases of interest, cobalt exists in one of two oxidation states, II or III, where Co\textsuperscript{II} is actively pursued for its unique magnetic properties,\textsuperscript{7–12} and Co\textsuperscript{III} attracts much attention in the modeling of cobalamin. Co\textsuperscript{II} ions are commonly regarded as hard metal centers with high affinity for nitrogen or oxygen based ligands. In an attempt to mimic cobalamin, nitrogen or oxygen based ligands have been extensively used in the past.\textsuperscript{7–14}

Azide anions are versatile linkers often employed in supramolecular chemistry. They efficiently link metal ions \textit{via} end-on and/or end-to-end coordination modes to form extended systems.\textsuperscript{7–14,16–18} A variety of solvolytic synthetic methods based on Cu/Mn-azide chemistry have been developed to create extended magnetic systems;\textsuperscript{15} however, to our knowledge, Co\textsuperscript{II}/N\textsubscript{3} extended systems are rare. As part of our search for new preparative methods for extended systems, we have recently looked into oxime ligands in combination with azide anions. The tridentate 1-(dimethylamino)propan-2-one oxime (Hdmo) ligand was chosen not only for its ability to encapsulate metal ions, but also for its bridging capacity \textit{via} the -NO moiety. The latter attribute can also facilitate the formation of extended systems. Such oxime ligands can be prepared \textit{via} direct hydroamination of alkynes (eqn (1)).\textsuperscript{16}

\begin{equation}
\begin{array}{c}
\text{Me} \quad \equiv \\
\text{N} \\
\text{Me} \\
\end{array}
\xrightarrow{\text{aq. NH}_2\text{OH (1.5 equiv)}}
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Me} \\
\end{array}
\xrightarrow{i\text{-PrOH, 100 °C}}
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Me} \\
\end{array}
\xrightarrow{(dmp)}
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Me} \\
\end{array}
\xrightarrow{(Hdmo)}
\end{equation}

This synthetic approach is complementary to the typical condensation of carbonyl precursors with NH\textsubscript{2}OH, and is shown here to provide access to the tridentate ligand using a simple propargylic amine precursor under optimized reaction conditions. In addition, the complexation reactions of Hdmo and azide with cobalt ions have never been reported to our knowledge and this thus combines the fruitfulness of transition metal oxime chemistry with the effectiveness of azide anions to create extended systems.

Elucidating structural features of complex extended systems can be challenging. Single crystal X-ray crystallography has always been the tool of choice for resolving and obtaining structural information. It is also well-established that solid-state NMR is a powerful tool that offers a complementary perspective on molecular and electronic structure, and provides vital information regarding the structure and coordination environments at different metal centers.\textsuperscript{17} \textsuperscript{59}Co solid-state NMR, for example, has been commonly employed on mononuclear species;\textsuperscript{18} however, it can also be used to study heteronuclear as well as polynuclear complexes. Such studies are potentially useful for identifying polymorphs in the bulk phase, and for establishing relationships between local structure and the NMR observables.

Here, we report a detailed study of a unique 1-D chain [NaCo\textsuperscript{III}\textsubscript{2}(dmo)\textsubscript{2}(\textmu-N\textsubscript{3})(N\textsubscript{3})\textsubscript{3}], complex, using X-ray crystallography, UV-Vis spectroscopy, solid-state NMR spectroscopy and density functional theory (DFT).
Experimental section

General considerations

All chemical reagents and solvents were used as obtained commercially and without further purification. *Caution!* **Azide salts are potentially explosive. They should be used in small quantities and handled with care.**

Synthesis

Synthesis of 1-(dimethylamino)propan-2-one oxime (Hdmo).

An oven-dried sealed tube (75 mL), equipped with a magnetic stir bar, was purged with argon for 5 min. 3-(Dimethylamino)-1-propyne (dmp) (3.24 mL, 30.0 mmol), aqueous NH₂OH (2.76 mL, 45.1 mmol) and isopropanol (freshly distilled, 30 mL) were added to the reaction vessel under a constant flow of argon. The mixture was heated in a wax bath for 48 h at 100 °C. After cooling to room temperature, the mixture was concentrated under reduced pressure and recrystallized from hot hexanes. Oxime Hdmo was isolated as clear transparent crystals (2.47 g, 71% yield); ¹H NMR (300 MHz, DMSO-d₆) δ 9.39 (br, s, 1H), 2.95 (s, 2H), 2.22 (s, 6H), 1.93 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆) δ 156.4, 63.6, 45.3, 12.3; IR (KBr pellet, cm⁻¹): 2964 (s), 2877 (s), 2839 (s), 2724 (br), 1657 (w), 1470 (s), 1215 (s), 1181 (m), 1041 (s), 959 (s), 933 (s), 850 (s), 764 (m). HRMS (EI): Exact mass calcd 185 (w), 1657 (w), 1470 (s), 1279 (s), 1258 (s), 1181 (m), 1041 (s), 1039 (s), 1020 (s), 947 (s), 926 (s), 767 (w), 757 (s), 674 (m).

Solid-state sodium-23 (²³Na) and cobalt-59 (⁵⁹Co) nuclear magnetic resonance (NMR)

²³Na magic-angle spinning (MAS) and static (i.e., non-spinning) ⁵⁹Co NMR experiments were performed at $R_e = 11.75$ T; $(v(¹H) = 500$ MHz) using a Bruker AVANCE wide bore spectrometer.

- **Table 1** Summary of the crystal structure data collection and refinement for complex I

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{10}H_{22}Co_2N_{19}Na_2O_2$</td>
</tr>
<tr>
<td>$FW, g mol^{-1}$</td>
<td>581.32</td>
</tr>
<tr>
<td>Space group</td>
<td>$C2/c$</td>
</tr>
<tr>
<td>$a/Å$</td>
<td>201(2)</td>
</tr>
<tr>
<td>$b/Å$</td>
<td>201(2)</td>
</tr>
<tr>
<td>$c/Å$</td>
<td>201(2)</td>
</tr>
<tr>
<td>$β(°)$</td>
<td>90</td>
</tr>
<tr>
<td>$γ(°)$</td>
<td>90</td>
</tr>
<tr>
<td>$V/Å^3$</td>
<td>2291(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$ρ_g/g cm^{-3}$</td>
<td>1.685</td>
</tr>
<tr>
<td>$μ/mm^{1/2}$</td>
<td>2.980</td>
</tr>
<tr>
<td>$w_R_0[I &gt; 2σ(I)]^a$</td>
<td>0.0507, 0.1385</td>
</tr>
</tbody>
</table>

Additional ⁵⁹Co MAS and static NMR experiments were carried out at 21.1 T, $(v(¹H) = 900$ MHz) using a Bruker AVANCE II standard bore spectrometer. At 11.75 T, this corresponded to resonance frequencies of ca. 132.29 MHz and ca. 118.67 MHz for ²³Na and ⁵⁹Co, respectively, and ca. 215.69 MHz for ⁵⁹Co at 21.1 T. Prior to NMR experimentation, samples were powdered and packed into a 4 mm o.d. zirconia rotor for experiments at 11.75 T, while 2.5 mm o.d. and 1.3 mm o.d. rotors were used for the static and MAS ⁵⁹Co NMR experiments at 21.1 T, respectively. All experiments used Bruker MAS probes. Solid-state NMR signals were acquired using a solid echo experiment with appropriately scaled solid π/2 pulse lengths of 9 μs and 0.5–1 μs for sodium and cobalt, respectively (solid π/2 pulse length is scaled from the solution π/2 pulse length by a factor equal to $1/(1 + 0.5)$). The solid echo experiments take the form π/2–τ₁–π/2–τ₂–acq, where τ₁ and τ₂ represent interpulse delays. Data acquisition for the MAS experiments was rotor synchronized. A τ₁ of 71 μs was used for ²³Na while values of 30–40 μs and 16.1 μs were used for static and MAS ⁵⁹Co NMR experiments, respectively. At 11.75 T, 800 and 64k time-domain signals were acquired, averaged and processed using standard techniques to generate the final ²³Na and ⁵⁹Co NMR spectra, respectively, while at 21.1 T, 9008 and 45500 scans were collected for the static and MAS ⁵⁹Co NMR experiments, respectively. Recycle delays of 0.5 s and 0.5–1.0 s were used for ²³Na and ⁵⁹Co NMR experiments, respectively. High-power ¹H decoupling $(v(¹H) = 50$ kHz) was used for the collection of the ²³Na NMR signal. The rf powers and chemical shift reference for ²³Na were established using 0.1 M NaCl in D₂O $(δ(²³Na) = 0.0$ ppm), while similar parameters for ⁵⁹Co were set using 0.56 $m_{K_i}[Co(CN)_6]_i$ in D₂O $(δ(⁵⁹Co) = 0.0$ ppm). Both references were chosen based upon recent IUPAC recommendations.¹⁶ NMR lineshape analysis was carried out using WSolids¹⁷ and SIMPSON.²²

IR and UV-Vis Spectroscopy

Infrared spectroscopy was performed on a Magna-IR 550 spectrometer in the 4000–700 cm⁻¹ region. UV-Vis spectroscopic...
measurements were carried out in a methanol solution on a Spectra Max M5 spectrophotometer in the 45000–10000 cm⁻¹ region.

Density functional theory (DFT) calculations

DFT calculations were performed using Gaussian 03 and the B3LYP exchange–correlation functional. The TZVP basis set and tight SCF convergence criteria were used for calculations. Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the ground state. Excitation energies and oscillator strengths of the first 70 spin singlet–singlet electronic transitions were calculated using time-dependent DFT at the same level as the electronic structure analysis. Calculated excitation energies and oscillator strengths were converted into absorption spectra using the pseudo-Voigt functions (50% Gaussian and 50% Lorentzian) and the 3000 cm⁻¹ half-bandwidths as previously described.

The analysis of molecular orbitals (MOs) in terms of atomic orbital contributions and the calculation of two-center Mayer bond orders were carried out using the AOMix program and the Mulliken population analysis. Atomic charges were calculated by natural population analysis (NPA) as implemented in Gaussian 03.

Results and discussion

Synthesis

The majority of previously reported oxime-based chelating ligands were synthesized using Schiff base reactions. The use of such ligands has been fruitful for the synthesis of transition metal complexes. Recently, we have developed a new synthetic approach to oxime ligands involving direct hydroamination of alkenes. The latter approach enables the synthesis of tunable chelates that are rarely explored in transition metal chemistry, and builds on the availability of propargylic alcohol and amine precursors. Using propargylic alcohols, the hydroamination approach provides access to tridentate hydroxy oxime ligands. Extension of this strategy to propargylic amines was sought since the parent amino oxime ligands could have increased affinity for other transition metal ions. While initially Hdmo could not be formed efficiently from amine dmp under similar reaction conditions, the use of lower reaction temperatures and reducing the amount of NH₂OH provided gram-scale access to the desired amino oxime ligand, Hdmo, from the commercially available dmp precursor.

Reaction of CoCl₂·6H₂O with Hdmo resulted in a linear 1-D chain, I, which consists of a dinuclear CoIII unit linked via azide anions to bridging NaI ions. The cobalt metal centers in I are in the III oxidation state which is favored by the nitrogen based Hdmo ligand and azide anions. The oxidation state of the cobalt was confirmed by UV-Vis spectroscopy as well as charge considerations and solid-state ⁵⁷Co NMR (vide infra). When sodium azide was omitted from the reaction, the resulting solution did not crystallize. As a base and linking molecule was confirmed when other reagents, such as triethylamine, sodium hydroxide, sodium cyanide, and potassium thiocyanate were added but complex I did not crystallize. Only a handful of azido bridged 1-D cobalt chains have been reported where cobalt ions are all in the II oxidation state and the azide anions only exhibit one coordination mode. In complex I, the cobalt ions are in the III oxidation state and the azide linkers exhibit both coordination modes; end-on (EO) and end-to-end (EE), linking the dinuclear cobalt units as well as sodium ions.

Structural analysis

Complex I crystallizes in the monoclinic space group C2/c and consists of two ligands as well as five azide molecules coordinated to two CoIII and one NaI ions, with Co1···Co1a distances of 3.09 Å (Fig. 1). The CoIII ions have pseudo-octahedral geometry and are linked through an EO μ–N₃ with an angle of 106.0° as well as two oxime bridges with torsion angles of 25.6°. Selected bond distances and angles are presented in Table 2. The μ₂-oxygen (O1) of the oxime (–NO) moiety is key in bringing the dinuclear cobalt unit to the mononuclear sodium atom thus forming the 1-D linear [NaICOIII₂] chain. In addition, the NaI ions also exhibit pseudo-octahedral geometry by coordinating to two EE and two EO azide anions as well as two oxygen atoms from oxime groups.

![Fig. 1 Molecular structure of a disodium dicobalt unit of I. Hydrogen atoms are omitted for clarity. Dotted lines indicate the planes in the molecule. Color code: Purple (Na), Light Blue (Co), Red (O), Blue (N).](image)

The latter atoms connect the alternately inverted dinuclear complexes producing distinct chains (Fig. 2) along the c-axis, which run parallel to the crystallographic c-axis, with a separation of 4.28 Å between the closest nitrogen atoms of two chains (Fig. 3). The dinuclear cobalt plane is set at an angle of 67° to the plane of the sodium ions (Fig. 1).

The IR spectrum of I shows characteristic peaks for the oxime group of the ligand at 1631 cm⁻¹ (C=N), and 1103 cm⁻¹ (N–O). The N–O peak is slightly shifted due to the coordination of O

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Selected bond distances (Å) and angles (°) for I</th>
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<tbody>
<tr>
<td>Bond distances/Å</td>
<td>Co1–N(1)</td>
</tr>
<tr>
<td>Co1a–O(1)</td>
<td>1.936(3)</td>
</tr>
<tr>
<td>Co1–N(6)</td>
<td>1.937(3)</td>
</tr>
<tr>
<td>Co1–N(9)</td>
<td>1.966(4)</td>
</tr>
<tr>
<td>Co1–N(3)</td>
<td>1.957(4)</td>
</tr>
<tr>
<td>Co1–N(2)</td>
<td>2.001(4)</td>
</tr>
<tr>
<td>Co1–N(6)–Co1a</td>
<td>106.02</td>
</tr>
<tr>
<td>Co1a–O(1)–N(1)–Co(1)</td>
<td>25.65</td>
</tr>
<tr>
<td>Co1–N(5)–N(5)–Na(1)</td>
<td>23.47</td>
</tr>
</tbody>
</table>

Fig. 1 Molecular structure of a disodium dicobalt unit of I. Hydrogen atoms are omitted for clarity. Dotted lines indicate the planes in the molecule. Color code: Purple (Na), Light Blue (Co), Red (O), Blue (N).
Fig. 2  a. Na\textsuperscript{+} ions in 1 linking the dicobalt units forming a chain perpendicular to the \(a\)-axis of the unit cell. b. Space-filling model of 1 viewed perpendicular to the \(a\)-axis. Carbon spheres are transparent for clear visualization of different chains. Color code: Purple (Na), Light Blue (Co), Red (O), Blue (N).

Fig. 3  a. Packing arrangement of 1, along the \(c\)-axis. b. Space-filling model of 1 with transparent carbon spheres for clear visualization of the distance between different chains. Color code: Purple (Na), Light Blue (Co), Red (O), Blue (N).

Electronic structure and UV-Vis spectrum of 1

To study the electronic structure of 1, experimental UV/Vis and quantum chemical DFT calculations at the B3LYP\textsuperscript{23–25}/TZVP\textsuperscript{26} level were performed.\textsuperscript{48} The crystal structure of the complex was taken as an initial geometry and the H atomic positions were optimized. The valence description obtained for the transition metal ions (Co\textsuperscript{III}) matched the one derived experimentally and the calculated UV/Vis absorption spectrum of 1 is in good agreement with the experimental spectrum (Fig. 4).

Fig. 4 Experimental (black line) and calculated (red line) UV-Vis spectrum of 1 in a methanol solution at room temperature.

The complex clearly contains Co\textsuperscript{III} ions with the low-spin, closed-shell configuration. Metal–ligand bond orders are illustrated in Fig. 5 and indicate significant covalency for both Co–azide and Co–dmo bonds. The sum of Co–ligand bond orders (4.18) is in sharp contrast with the sum of Na–ligand bond orders (0.59). The resulting strong charge donation from the ligands to the Co\textsuperscript{III} ion. Strong peaks are seen at 2097 and 2040 cm\textsuperscript{-1} corresponding to EO and EE coordinated azide molecules, respectively.\textsuperscript{19}

Fig. 5 Metal–ligand bond orders (red) for complex 1. Color code: Light Blue (Co), Red (O), Blue (N).
the Co$^{III}$ ions can be further confirmed by the NPA-derived charge for the metal ions (+1.01 a.u.). Since $r(\text{Co} \cdots \text{Co})$ is fairly large (3.09 Å), there is very little orbital interaction between the Co ions (Co--Co bond order is 0.06).

Complex 1 exhibits a strong absorption band at 17500 cm$^{-1}$ with a molar absorption coefficient of 350 M$^{-1}$ cm$^{-1}$ (Fig. 4). Based on a comparison with other Co$^{III}$ six-coordinate complexes and TD-DFT calculations, this band can be assigned to a $^1A_g \rightarrow ^1E$ transition. Another $d$-$d$ based transition, $^1A_{1g} \rightarrow ^1A_1$, is calculated to be in the 22000--24000 cm$^{-1}$ region and corresponds to a shoulder/onset of the very intense, broad band at 33000 cm$^{-1}$. The latter band is a combination of several charge-transfer (CT) transitions from the $N_2^-$ ligands to the Co$^{III}$ ions.

**Solid-state NMR**

23Na solid-state NMR. The crystal structure of 1, established by single-crystal X-ray diffraction experiments, contains one unique sodium atom per unit cell (1 site symmetry). 23Na ($I = 3/2$) MAS NMR experiments were carried out to establish the electric-field gradient (EFG) tensor magnitude at the sodium nucleus and to measure $\delta(23Na)$. The utility of these measurements is that a direct relationship may be established between the structure about sodium and the NMR parameters which are characteristic of this structure. Solid-state 23Na NMR experiments may also be used to determine sample purity and the degree of sample crystallinity in the bulk state compared with the single crystal used to refine the structure. While powder XRD experiments are also sometimes useful in this regard, this is not always the case and SSNMR can offer more detailed information on the local structure of impurities or different polymorphs. The 23Na NMR spectrum in Fig. 6 was obtained under MAS conditions in order to remove the contributions of chemical shift anisotropy (CSA) from the sodium spectrum. The 23Na MAS NMR line shape is a characteristic second-order quadrupolar powder pattern, and from this we conclude that:

- (i) there is one magnetically unique sodium site;
- (ii) sample purity in the bulk-powdered form is high and
- (iii) the sample possesses microcrystalline order. There does not appear to be a significant amorphous or otherwise non-crystalline phase present, an effect which could be missed in powder or single-crystal XRD experiments but would still be readily observed by solid-state NMR. Line shape analysis reveals the following 23Na NMR parameters: $C_0(23Na) = 3.12(0.06)$ MHz; $\eta_0(23Na) = 0.67(0.05)$ and $\delta_0(23Na) = -1.5(0.8)$ ppm. The observed $\delta_0(23Na)$ is close to that of the reference solution, as well as simple sodium compounds such as NaBr, NaI and NaNO$_3$. This strongly suggests that the sodium is ionically bound and can be reasonably understood to act as an innocent counter ion. The measured $C_0(23Na)$ value is moderate, as compared to other inorganic and organometallic sodium complexes. The EFG about the sodium is non-axially symmetric (i.e., $\eta_0(23Na) \neq 0$), which is consistent with the sodium atom being at a site of low symmetry.

59Co solid-state NMR. The crystal structure of 1 possesses one crystallographically unique cobalt site; however, the two cobalt atoms having the smallest interatomic separation are not related by an inversion centre (or translational operation) and are thus magnetically inequivalent (vide infra). Solid-state 59Co ($I = 7/2$) NMR experiments were carried out to establish the 59Co NMR interaction tensor parameters and to relate these to the structure obtained by X-ray diffraction. It is also important to demonstrate that 59Co SSNMR may be used as an alternate tool to provide local structural and/or coordination information for polynuclear complexes when single-crystal XRD may not be feasible. In addition, the very large chemical shift range of cobalt (≈20 000 ppm) implies that the observed value of $\delta_0(59Co)$ for complex 1 should be diagnostic with regards to the immediate environment about the cobalt atom. The observed 59Co solid-state NMR line shape is over 2000 ppm in breadth and is dominated by CSA at both 11.75 T and 21.1 T (Fig. 7). The signal breadth due to second-order quadrupolar broadening prohibited the study of the 59Co nucleus in this compound by MAS NMR experiments at 11.75 T; however, static experiments were carried out with little difficulty. When analyzing the spectra of quadrupolar nuclei under static conditions, contributions from CSA should be considered.

**Fig. 6** Simulated (A) and experimental (B) MAS 23Na solid-state NMR spectra of complex 1. The experimental spectrum was acquired at an MAS frequency of 12.5 kHz. A trace amount of NaCl(s) is marked with a dagger (†).

**Fig. 7** Simulated (A) and experimental (B) static 59Co solid-state NMR spectra of complex 1 at $B_0 = 21.1$ T.
Under favorable conditions, the relative orientation of the EFG and magnetic shielding frames can also be quantified. This expands the number of potentially observable parameters from 3 (as was the case for the $^{23}$Na MAS NMR line shape) to 8. The greatest agreement between experimental and simulated line shapes, at 11.75 and 21.1 T simultaneously, is realized using the following parameters: $C_0(^{59}$Co) = 29.5(2.0) MHz; $\eta_0 = 0.84(0.06); \delta_{44} = 9\, 975(50)$ ppm; $\Omega = 2450(100)$ ppm; $\kappa = -0.82(0.05); \alpha = 55^o(8^o); \beta = 90^o(5^o); \gamma = 0^o(5^o)$.

It should be noted that due to the lack of symmetry at cobalt, there may be other sets of angles (i.e., $\alpha, \beta, \gamma$) which produce good fits to the experimental data; this is a general caveat which is not specific to the current study. The important point is that the isotropic chemical shift, CSA, and quadrupolar coupling magnitude are all well-defined as a result of the spectral fitting. The large positive isotropic chemical shift suggests that the oxidation state of the cobalt atom is III and that there are strong covalent bonding interactions with the ligands, also seen from the analysis of the electronic structure of 1.

The cobalt chemical shift reported here is similar to $[\text{Co(NH}_3)_5\text{H}_2\text{O}]\text{ClO}_4$, $\delta_{44} = 9100$ ppm). This is unsurprising, as $[\text{Co(NH}_3)_5\text{H}_2\text{O}]\text{ClO}_4$, and complex 1 should possess identical cobalt first-coordination spheres. The measured $C_0(^{59}$Co) value is relatively small when one considers that the cobalt nucleus is not at a position which would require it to be zero by symmetry. Similar $C_0(^{59}$Co) values have been observed in systems of the form $[\text{Co(NH}_3)_5\text{X}]\text{Cl}$, (X = CN, Cl), while a $C_0(^{59}$Co) value in excess of 160 MHz has been observed for $[\text{Co(Ci}_3\text{H}_5)]\text{PF}_6$, by observing that both the quadrupolar and chemical shift tensors are non-axial, it is confirmed that the site symmetry at the cobalt is lower than $C_s$, in agreement with the structure obtained by single-crystal XRD. Although not surprising, the analysis again suggests that the bulk material is identical to the single crystal, and establishes useful relationships between structure and $C_0(^{59}$Co) which may be useful in future studies where single-crystal XRD may not be available. As mentioned earlier, the most spatially proximate cobalt nuclei are expected to be magnetically inequivalent. As a result, homonuclear cobalt dipolar coupling should be expected to contribute to the observed $^{59}$Co NMR spectra. The Co···Co distance determined by X-ray diffraction is 3.09 Å. This leads to an expected dipolar coupling constant of 225 Hz, which is not large enough to alter the observed $^{59}$Co NMR spectral simulations for a stationary sample at either 11.75 or 21.1 T. $^{59}$Co MAS NMR experiments at 21.1 T with a MAS rate of 60 kHz (see ESI, Figure S1) are consistent with the parameters derived from the fits of spectra of stationary samples, but are also not able to quantify this coupling, as the residual line shape broadening due to second-order quadrupolar effects is larger than the expected cobalt homonuclear dipolar splitting. Despite this, the second-order quadrupolar lineshape is somewhat featureless (see ESI), which could arise in part from small residual dipolar interactions. Due to the lack of a well-defined second-order quadrupolar line shape in this MAS NMR spectrum, we can only conclude that the $^{59}$Co MAS NMR spectrum is consistent with the presence of magnetically non-equivalent cobalt nuclei, but we cannot establish this independently of the crystal structure. In summary, the $^{59}$Co NMR experiments at 11.75 and 21.1 T clearly show the presence of a low symmetry Co$^{III}$ environment, and the parameters obtained from spectral simulations are consistent with local coordination by 5 nitrogen atoms and one oxygen atom.

**Conclusions**

An azido-, oximato-bridged 1-D [Co$^{III}$]$^2$ complex was successfully isolated and structurally characterized. Complex 1 is the first example of a 1-D Co$^{III}$ extended system obtained using the mixed bridging ligand/linker synthetic strategy. The structural analysis was confirmed by IR and UV-Vis spectroscopy, as well as DFT. Moreover, complex 1 was fully studied using $^{59}$Co and $^{23}$Na solid-state NMR; these studies showed that structure and composition of the bulk material are consistent with those obtained from single-crystal X-ray diffraction. The results also demonstrate the utility of solid-state NMR techniques in characterizing novel extended systems and providing vital information regarding the structure and coordination environments at different metal centers.

**Acknowledgements**

We thank the University of Ottawa, FFCR, the Canada Foundation for Innovation (CFI) and NSERC (Discovery and RTI grants) for their support of this work. C. M. W. thanks NSERC for an Alexander Graham Bell CGS D2 scholarship. C. M. W. and D. L. B. thank V. Terskikh for technical assistance. Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (Ottawa, Canada), a national research facility funded by the Canada Foundation for Innovation, the Ontario Innovation Trust, Recherche Québec, the National Research Council Canada, and Bruker Biospin and managed by the University of Ottawa (www.nmr900.ca). NSERC is acknowledged for a Major Resources Support grant.

**References**