

Synthesis and characterization of the cubic coordination cluster $[\text{Co}^{\text{III}}_6\text{Co}^{\text{II}}_2(\text{IBT})_{12}]^{14-}$ ($\text{H}_3\text{IBT} = 4,5\text{-bis}(\text{tetrazol-5-yl})\text{imidazole}$)

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ARTICLE INFO

Article history:

Received 17 January 2008

Received in revised form 24 March 2008

Accepted 24 March 2008

Available online 7 April 2008

This work is dedicated to the memory of Prof. F.A. Cotton

Keywords:

Coordination clusters

Cobalt

Tetrazoles

Mixed-valence

Cage compounds

ABSTRACT

A self-assembly reaction between the ditopic ligand 4,5-bis(tetrazol-5-yl)imidazole (H_3IBT) and cobalt(II) chloride in basic aqueous medium afforded the mixed-valence molecular species $(\text{NBu}_4)_{14}[\text{Co}^{\text{III}}_6\text{Co}^{\text{II}}_2(\text{IBT})_{12}] \cdot 22\text{H}_2\text{O}$ (**1**). X-ray analysis of **1** revealed a cubic arrangement of six trivalent and two divalent cobalt ions, with the latter situated on opposing vertices along the cube diagonal. The cubic coordination cluster was further characterized by cyclic voltammetry, mass spectrometry, and magnetic measurements.

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1. Introduction

Electronic interactions between metal centers within a coordination cluster can give rise to fascinating magnetic and spectroscopic signatures that are not observed in mononuclear species. Indeed, inorganic chemists have shown a long-standing interest in the synthesis of multinuclear metal-based coordination clusters, wherein metal ions are connected by multitopic organic bridging ligands [1]. One class of cluster molecules that has achieved recent prominence is that of the cage compounds. These are molecular species that contain internal cavities and thus present the possibility of accommodating guest molecules. Due to their unusual encapsulating abilities, cage-type molecules have found important applications in catalysis [2], while also providing an excellent basis for the study of unusual magnetic and electronic properties [3]. As expected, the ligand geometry and the coordination environment around the metal dictate the shape of a given cluster, and judicious choice of metal and ligand can, in principle, lead to a large number of pre-designed cluster geometries [4]. Constitutionally, however, there are surprisingly few types of ligands that have been employed so far in the synthesis of coordination cage compounds. Among these, polycarboxylates and polypyridyl ligands are more

frequent, although a significant number of such molecules have also been synthesized using cyanide and other bridging ligands [5].

We recently showed that multitopic tetrazolate ligands can successfully replace carboxylates in metal-organic frameworks, giving rise to structures with topologies identical to those formed by the latter [6]. Indeed, it had previously been shown that due to their high chemical stability and low pK_a values of 4–5, tetrazoles can be used as analogues of carboxylic acids in chemical biology and pharmacology [7]. It is thus conceivable that the utility of tetrazoles could be extended to discrete molecular species, such as molecular cage clusters. Herein, we report the synthesis of the first tetrazolate-based coordination cluster, exhibiting a cubic structure analogous to that of other transition metal clusters based on carboxylate linkers. X-ray crystallographic analysis suggests the existence of six Co^{3+} ions and two Co^{2+} ions that occupy the vertices of a distorted cube-shaped cage, and mass spectrometry and magnetic data confirm a $\text{Co}^{2+}/\text{Co}^{3+}$ mixed-valence state.

2. Experimental

2.1. Materials and apparatus

The compounds $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NaN_3 , 4,5-dicyanoimidazole, and $[\text{N}(\text{C}_4\text{H}_9)_4](\text{OH})$ (40 wt% aqueous solution) were obtained from commercial vendors and were used without further purification. Infrared

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spectra were collected on a Nicolet Avatar 360 FTIR spectrometer with an attenuated total reflectance accessory (ATR). Carbon, hydrogen, and nitrogen analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley. Cyclic voltammetry was performed in a 0.1 M acetonitrile solution of Bu₄NPF₆ using a Bioanalytical systems CV-50W voltammograph, a platinum disk working electrode, a platinum wire supporting electrode, and a silver wire reference electrode. Reported potentials are all referenced to the ferrocene/ferrocenium (Fc/Fc⁺) couple and were determined using ferrocene as an internal standard. Magnetic measurements were performed on a Quantum Design MPMSXL SQUID magnetometer at a field of 1000 Oe and 300 K. The sample was placed in a polycarbonate capsule. Data were corrected for diamagnetic contributions from the sample holder, as well as for the diamagnetism of the sample (estimated using Pascal's constants).

2.2. Synthesis of 4,5-bis(tetrazol-5-yl)imidazole (H₃IBT)

A mixture of 4,5-dicyanoimidazole (2.00 g, 17.0 mmol), NaN₃ (6.60 g, 102 mmol), and triethylamine hydrochloride (24.7 g, 102 mmol) in 80 mL of toluene and 20 mL of methanol was heated at reflux in a 250-mL round-bottom flask for 3 days. Upon cooling to room temperature, 100 mL of an aqueous solution of NaOH (1 M) was added, and the mixture was stirred for 30 min. The aqueous layer was treated with ca. 100 mL of dilute HCl (1 M) until no further white precipitate formed. The precipitate was then collected by filtration, dried in the air, and dissolved in aqueous NaOH (1 M). The resulting clear, colorless solution was titrated with ca. 75 mL of dilute HCl (1 M) until the pH of the solution was approximately 4. The ensuing white precipitate was washed copiously with distilled water (approx. 500 mL) and dried in air for 1 day to afford 3.39 g (93.5%) of product as a hemihydrate. H₃IBT is insoluble in water and most organic solvents with the exception of *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide (DEF), and dimethylsulfoxide (DMSO). Anal. Calcd for C₅H₄N₁₀·0.5H₂O: C, 28.31; H, 1.90; N, 66.02. Found: C, 28.54; H, 2.03; N, 66.04. IR (neat): 3163 (s, br), 2885 (m, br), 1637 (m), 1573 (vs), 1469 (m), 1407 (m), 1321 (w), 1245 (m), 1203 (w), 1163 (w), 1063 (s), 1048 (m), 1015 (w), 944 (m), 812 (m), 750 (m) cm⁻¹. ¹H NMR (DMSO-*d*⁶): δ 8.30 ppm (s, 1H). *Caution! Metal azides are water sensitive and can give rise to HN₃ gas; both azides and tetrazoles are potentially explosive and should be handled with care.*

2.3. Synthesis of [N(C₄H₉)₄]₁₄[Co₈(IBT)₁₂·22H₂O] (1)

Solid samples of CoCl₂·6H₂O (140 mg, 0.59 mmol) and H₃IBT (200 mg, 0.94 mmol) were added to 3 mL of deionized (MilliQ) water, and the resulting pink suspension was heated at reflux for 18 h. Dropwise addition of an aqueous solution of [N(C₄H₉)₄](OH) (1.7 mL, 40 wt%) to this mixture afforded a clear, dark red solution, which was heated at 90 °C for 30 min. The reaction mixture was allowed to cool to room temperature overnight, and a small quantity of black impurity was removed by filtration. The resulting deep red solution was then allowed to evaporate slowly at room temperature, producing 253 mg (51.4%) of large cube- and octahedron-shaped dark red crystals of product after 7–10 days. IR (neat): 3398 (vs, br), 2964 (s), 2941 (s), 2876 (s), 1649 (m, br), 1565 (m), 1484 (m), 1456 (m), 1382 (m), 1361 (w), 1194 (w), 1130 (m), 1089 (w), 976 (s), 882 (m), 739 (m), 665 (m) cm⁻¹. Anal. Calcd for C₂₈₄H₅₆₀Co₈N₁₃₄O₂₂: C, 51.09; H, 8.46; N, 28.11. Found: C, 50.76; H, 8.60; N, 28.84.

2.4. X-ray diffraction analysis of 1

A single crystal of **1** was coated with Paratone-N oil and mounted on a Kapton loop. The crystal was then quickly trans-

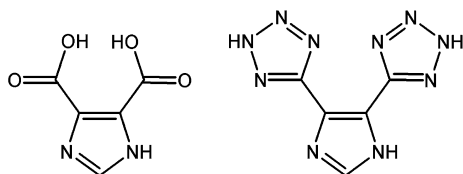
ferred to a Siemens SMART diffractometer, and cooled in a stream of nitrogen gas. Preliminary cell data were collected giving a unit cell consistent with the cubic Laue group. The unit cell parameters were later refined against all data, after a full hemisphere of data had been collected. The crystal did not show significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects using SAINT 7.07b and were corrected for absorption effects using SADABS 2.10. The space group assignment was based upon systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods and expanded through successive difference Fourier maps. It was refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached atom (1.5 times for methyl hydrogens). Extreme disorder of the electron density in the intercluster space prevented the modeling of 2 of the 14 tetrabutylammonium cations, which were inferred based on charge balance considerations and C, H, and N microanalysis. These cations, together with the guest water molecules were modeled as fully- and partially-occupied oxygen atoms.

2.5. Mass spectrometry analysis of 1

Mass spectra were acquired in the negative ion mode using a quadrupole time-of-flight (Q-ToF) mass spectrometer equipped with a Z-spray electrospray ionization (ESI) source (Q-ToF Premier™, Waters, Beverly, MA). Sample solutions were infused from a 250-μL Gastight® syringe (Hamilton, Reno, NV) into the ESI probe at a flow rate of 5 μL/min using a syringe pump. The electrospray was emitted from a stainless steel capillary with an inner diameter of 127 μm. The ion source parameters were as follows: ESI capillary voltage 2.4 kV, nebulizing gas (nitrogen) flow rate 800 L/h, sample cone, extraction cone and ion guide voltages 5 V, source block temperature 80 °C, and nebulizing gas temperature 200 °C. No cone gas was used. The pressures in the different stages of the instrument were as follows: first pumping stage 1.5 mbar, ion transfer stage 5 × 10⁻⁴ mbar, quadrupole analyzer 2 × 10⁻⁵ mbar, argon-filled cell 8 × 10⁻³ mbar, and Tof analyzer 9 × 10⁻⁷ mbar. The Tof analyzer was operated in “V” mode. Under these conditions, a mass resolving power [8] of 1.0 × 10⁴ was routinely achieved, which is sufficient to resolve the isotopic distributions of multiply charged ions. (In this study, ions with up to six negative charges were measured.) Thus, the mass and charge of an ion could be determined independently (i.e. the ion charge can be determined from the reciprocal of the spacing between adjacent isotope peaks in the *m/z* spectrum [8]). External mass calibration was performed immediately prior to measurements, using solutions of sodium formate. Mass spectra were processed using MassLynx software (version 4.1, Waters).

3. Results and discussion

Synthesis of a new tetrazolate-based coordination cluster was accomplished under conditions approximating those employed previously for the synthesis of similar clusters based on 4,5-imidazoledicarboxylic acid (H₃IDC) [9]. This dicarboxylate had previously been shown to promote the formation of coordination clusters with cubic geometry and, in trying to emulate its geometry, we synthesized the analogous ligand 4,5-bis(tetrazol-5-yl)imidazole (H₃IBT). The ligand H₃IBT, shown in Scheme 1, was prepared in 93.5% yield by an acid-catalyzed [3 + 2] cycloaddition reaction between 4,5-dicyanoimidazole and sodium azide in a mixture of toluene and methanol, and was purified by reprecipitation



Scheme 1. Molecular structures of the ligands 4,5-imidazolecarboxylic acid (H_3IDC) and 4,5-bis(tetrazol-5-yl)imidazole (H_3IBT).

from an aqueous solution of NaOH. Reaction of $H_3IBT \cdot 0.5H_2O$ with $CoCl_2 \cdot 6H_2O$ in a concentrated aqueous solution of $(NBu_4)OH$, followed by concentration of the mother liquor via slow evaporation at room temperature, afforded $[N(C_4H_9)_4]_{14}[Co_8(IBM)_{12}] \cdot 22H_2O$ (**1**) as dark red cube-shaped crystals.

X-ray analysis [10] of a single crystal of **1** revealed a cubic arrangement of eight cobalt ions bridged by triply deprotonated IBM^{3-} ligands that function as cube edges, as shown in Fig. 1. Each cobalt ion is octahedrally ligated by three facially-disposed nitrogen atoms from bridging imidazole rings, and another three nitrogen donors from tetrazole rings. Note that this structure is analogous to the structures of the coordination cubes $[Ni_8(HIDC)_{12}]^{8-}$ [9a], $[Ni_8(IDC)_{12}]^{20-}$ [9b], $[Co_8(IDC)_{12}]^{14-}$ [9c], and $[Co_8(IDC)_{12}]^{20-}$ [9c], and thus demonstrates that H_3IBT can indeed generate molecular clusters that are analogues of those formed by H_3IDC . Surprisingly, the crystallographic analysis of **1** revealed that six of the cobalt ions had average Co–N bond distances of 1.92(4) Å, while the other two ions, disposed at the ends of the cube diagonal, had average Co–N distances of 2.14(2) Å. The large difference between the average Co–N bond distances indicates a mixed-valence $Co^{III}_6Co^{II}_2$ redox state identical to that observed in $[Co_8(IDC)_{12}]^{14-}$ [9c]. A magnetic susceptibility measurement on a solid sample of **1** at 300 K gave $\mu_{eff} = 7.11\mu_B$, confirming the existence of two isolated high-spin Co^{2+} ions. As in $[Co_8(IDC)_{12}]^{14-}$, the mixed-valence state and the different Co–N distances lead to a distortion of the overall cubic geometry in **1**, with intermetallic distances of 6.125(2) and 6.300(2) Å for

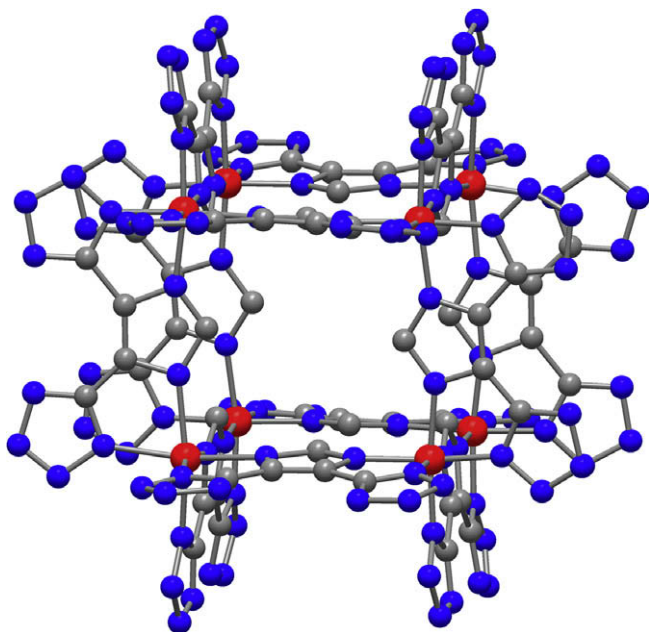


Fig. 1. Crystal structure of the cubic coordination cluster $[Co_8(IBM)_{12}]^{14-}$, as observed in **1**. Red, blue, and grey spheres represent cobalt, nitrogen, and carbon atoms, respectively. Hydrogen atoms were omitted for clarity. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

$Co^{3+} \cdots Co^{3+}$ and $Co^{2+} \cdots Co^{3+}$, respectively. The negative charge of the $[Co_8(IBM)_{12}]^{14-}$ anion is balanced by 14 tetrabutylammonium cations, 12 of which surround the cube snugly. While the solubility

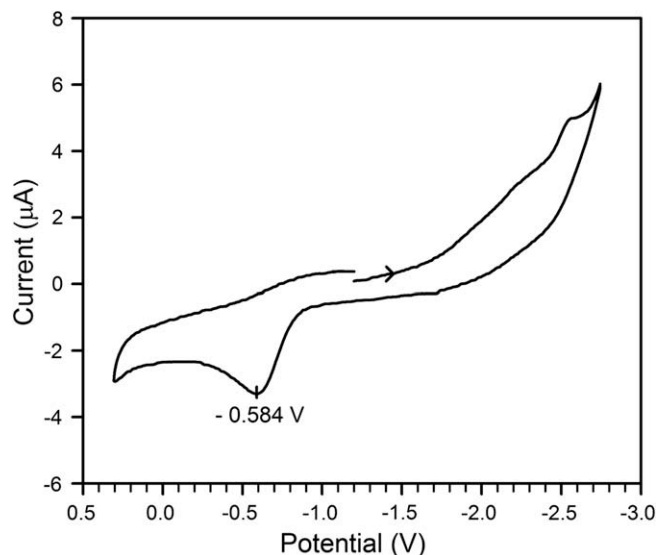


Fig. 2. Cyclic voltammogram of **1** in acetonitrile. The measurement was performed on a platinum electrode at a scan rate of 100 mV/s, with 0.1 M Bu_4NPF_6 as the supporting electrolyte. Potentials are referenced to the Fc/Fc^+ couple.

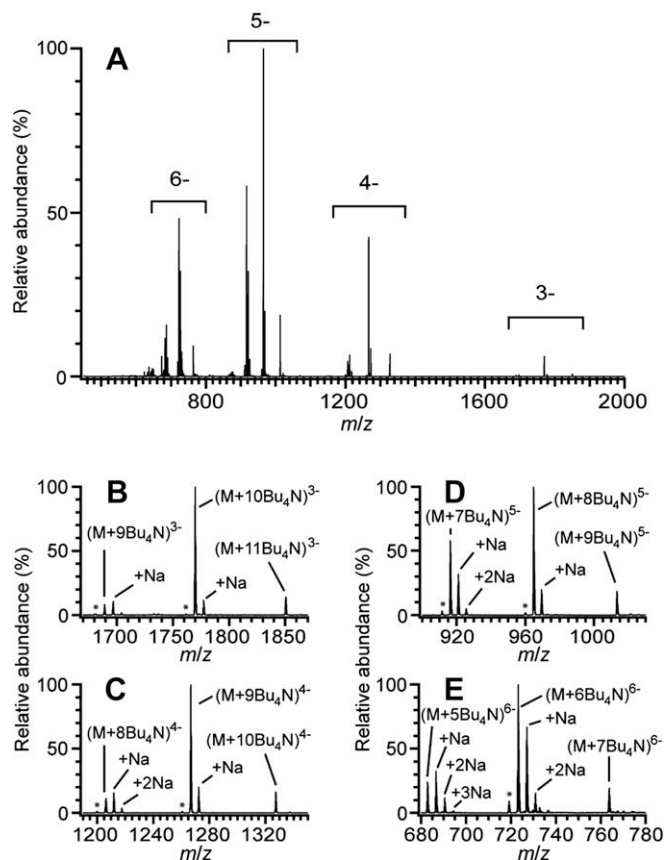


Fig. 3. (A) Full range ESI mass spectrum, and detail for the (B) 3-, (C) 4-, (D) 5-, and (E) 6-charge state groups. “M” denotes the intact cluster, $[Co_8(IBM)_{12}]^{n-}$, where $n = 11-14$. The asterisks denote ions that are lower in mass by 24 Da.

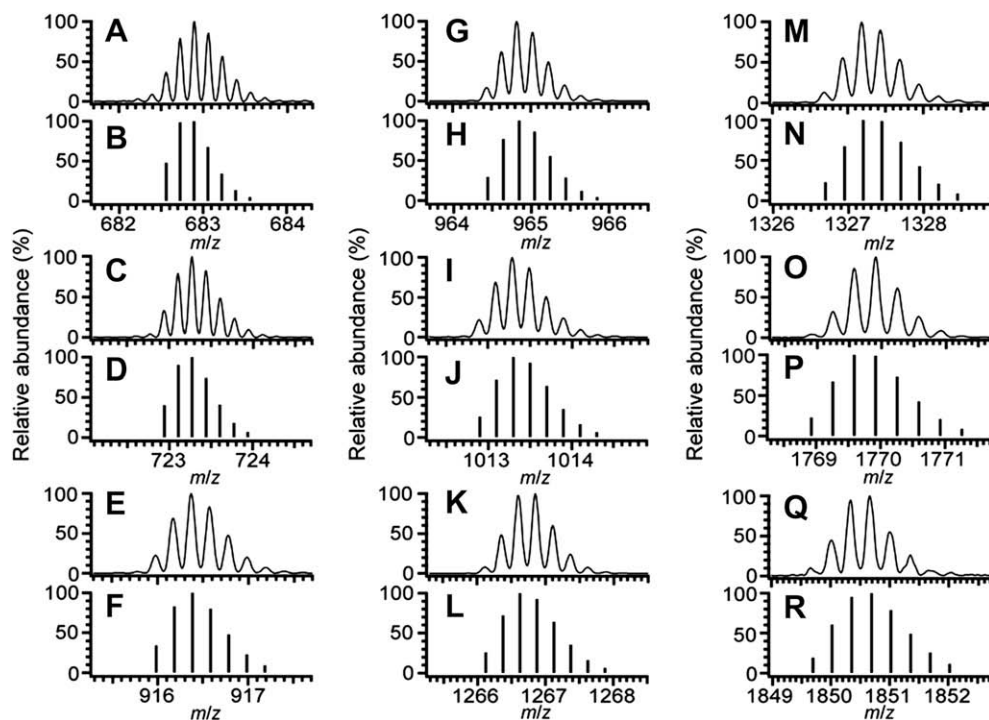


Fig. 4. Comparison of measured (A, C, E, G, I, K, M, O, Q) and calculated (B, D, F, H, J, L, N, P, R) isotopic distributions of the ions, $(M + 5\text{Bu}_4\text{N})^{6-}$ (A and B), $(M + 6\text{Bu}_4\text{N})^{6-}$ (C and D), $(M + 7\text{Bu}_4\text{N})^{5-}$ (E and F), $(M + 8\text{Bu}_4\text{N})^{5-}$ (G and H), $(M + 9\text{Bu}_4\text{N})^{5-}$ (I and J), $(M + 9\text{Bu}_4\text{N})^{4-}$ (K and L), $(M + 10\text{Bu}_4\text{N})^{4-}$ (M and N), $(M + 10\text{Bu}_4\text{N})^{3-}$ (O and P), and $(M + 11\text{Bu}_4\text{N})^{3-}$ (Q and R). The calculated distributions are based on the natural abundances of the isotopes.

of **1** in H_2O is not surprising given the highly-charged anion, the tight arrangement of Bu_4N^+ cations around the cluster likely contributes to the high solubility of **1** in organic solvents such as tetrahydrofuran and acetonitrile.

To probe the possibility of isolating oxidized or reduced versions of the coordination cube, a cyclic voltammogram for a solution of **1** was collected in acetonitrile. As shown in Fig. 2, the voltammogram displays a single redox event at -0.584 V versus the ferrocene/ferrocenium (Fc/Fc^+) couple. This irreversible process likely corresponds to the oxidation of one or both of the Co^{2+} ions, generating clusters of the form $[\text{Co}^{\text{III}}_7\text{Co}^{\text{II}}(\text{IBT})_{12}]^{13-}$ or $[\text{Co}^{\text{III}}_8(\text{IBT})_{12}]^{12-}$, respectively, or possibly to the formation of some other cluster decomposition product. Unfortunately, the irreversibility of the process precludes the quantitative determination of the number of electrons involved, and prevents us from drawing a definitive conclusion regarding the fate of the cluster upon oxidation.

Although the isolation and purification of the two oxidized versions of **1** were not possible in bulk, the existence of the mono- and di-oxidized clusters was confirmed by mass spectrometry. Indeed, the electrospray ionization (ESI) mass spectrum of a 10-mM solution of **1** in acetonitrile, shown in Fig. 3A, displays isotope distributions corresponding to the $\text{Co}_8(\text{IBT})_{12}$ cluster in charge states from -3 to -6 . The measured masses of the ions present are consistent with the predicted elemental composition ($\text{Co}_8\text{C}_{60}\text{H}_{12}\text{N}_{120}$) of the intact cluster, $[\text{Co}_8(\text{IBT})_{12}]^{n-}$ (where $n = 11-14$), adducted to different numbers of Bu_4N^+ and Na^+ cations (Fig. 3B–E). Among the isotope distributions present in the spectrum are those corresponding to a cluster of the form $[\text{Co}^{\text{III}}_6\text{Co}^{\text{II}}_2(\text{IBT})_{12}]^{14-}$, consistent with that observed in the crystal structure. In addition, singly- and doubly-oxidized clusters of the form $[\text{Co}^{\text{III}}_7\text{Co}^{\text{II}}(\text{IBT})_{12}]^{13-}$ and $[\text{Co}^{\text{III}}_8(\text{IBT})_{12}]^{12-}$, respectively, are observed. The oxidations, which likely occur during the ionization process within the mass spectrometer, are not surprising given the relatively low oxidation potential obtained for **1** through cyclic voltammetry. A mass peak corresponding to the ion $[\text{Co}_8(\text{IBT})_{12}]^{11-}$ was also observed, sug-

gesting that a further oxidative process takes place within the mass spectrometer, involving the abstraction of an electron either from one of the Co^{3+} cations, or from one of the IBT^{3-} ligands. All measured charge states (-3 to -6) were isotopically resolved, and the measured isotopic patterns were comparable to the theoretical isotopic patterns calculated based on the natural abundances of the isotopes (see Fig. 4). The measured masses of these ions agreed with theoretical values to within 20 ppm.

4. Conclusion

Synthesis of a new ditetrazolate ligand that mimics the geometry of 4,5-imidazolecarboxylic acid led to the isolation of a novel mixed-valence cobalt cluster that is isostructural with nickel- and cobalt-based carboxylate clusters. Future efforts will focus on the incorporation of other transition metals in similar tetrazolate-based architectures and on the use of such clusters as building units for extended metal-organic frameworks.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 674924. Copy of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1233 336033; <http://www.ccdc.cam.ac.uk>; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

This research was funded by NSF Grant No. CHE-0617063.

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