Inorg. Chem. **2002**, *41*, 1351–1353

Inorganic Chemistry
Communication

Modulating the Reduction Potential of Mononuclear Cobalt(II) Complexes via Selective Deprotonation of Tris[(2-benzimidazolyl)methyl]amine

Brian S. Hammes,*[,†] Matthew T. Kieber-Emmons,[†] Roger Sommer,[‡] and Arnold L. Rheingold[‡,§]

Department of Chemistry, Saint Joseph's University, Philadelphia, Pennsylvania 19131, and
Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received September 13, 2001

Remote site deprotonation of the coordinated tripodal ligand, tris((2-benzimidazolyl)methyl)amine, was examined using electronic spectroscopy and electrochemistry techniques. The solid-state structures $[CoH_3\mathbf{1}^{\mathbf{tba}}(NCS)]^+$ and $[CoH_2\mathbf{1}^{\mathbf{tba}}(NCS)]$ are reported. These complexes crystallized in the triclinic space group $P\bar{1}$ [$a = 13.3043(2)$ Å, $b = 13.8019(2)$ Å, $c = 14.1322(2)$ Å, $\alpha = 63.6670(10)°$, $\beta = 68.0590(10)°$, $\gamma = 81.8960°$; $Z = 2$] and the monoclinic space group $P2_1/n$ [$a = 15.3530(9)$ Å, $b = 11.0645(6)$ Å, $c = 19.1319(10)$ Å, $\beta = 105.6750(10)°$; $Z = 4$], respectively. Preliminary results suggest that selective and reversible deprotonation of coordinated benzimidazolyl ligands can tune the reduction potential of several isostructural cobalt(II) complexes.

The use of protonation/deprotonation of ancillary ligands coordinated to transition metal complexes has attracted increased attention recently because of their importance in biological, synthetic, and industrial processes.[1–3] For example, the relationship between proton coupled electron transfer and hydrogen atom transfer continues to gain increasing interest.[4,5] Recently, it has been reported by Williams and co-workers that the reduction potential of saturated iron complexes can be modulated between +0.920 and −0.460 V in an octahedral iron complex containing four imidazole/benzimidazole groups.[6] Although no attempt was made to deprotonate each imidazole selectively, it was believed that each deprotonation resulted in a redox potential shift of approximately 0.3 V per proton. This subtle and reversible method of modification potentially allows for a greater control of the stability and reactivity of transition metal complexes while avoiding the need for complicated synthetic manipulations. However, a major question, which has yet to be addressed, is whether the distal deprotonation of coordinated benzimidazolyl/imidazolyl ligands can be used to manipulate the chemistry of *unsaturated* metal complexes. To date, no literature reports have appeared describing the manipulation of electronic properties of unsaturated transition metal complexes via selective deprotonation of coordinated imidazole ligands. We have been investigating the coordination chemistry of tripodal ligands derived from imidazole. In particular, tris(2-benzimidazolylmethyl)amine[7] ($H_3\mathbf{1}^{\mathbf{tba}}$) which utilizes a tris(2-imidazolylmethyl)amine backbone will provide a useful first step in determining if tripodal ligands of this type can stabilize unsaturated metal complexes upon deprotonation. It should be noted that while the primary coordination around the metal ion(s) should remain constant, the selective deprotonatation will change the physical properties of the metal ion(s) coordinated within the tripodal framework.

Transition metal complexes containing tris(2-benzimidazolylmethyl)amine are not uncommon; however, they do provide a useful starting point to study selective deprotonation and the ability to control the electronic properties of a series of Co(II) complexes.[8,9] We report herein the reversible stepwise modulation of the electronic properties of several Co(II)−NCS complexes of tris(2-benzimidazolylmethyl)amine. These initial results demonstrate that sequential deprotonation of the coordinated benzimidazolyl arms result in the shift in the electrochemical potential of the Co(II) ion from +0.98 to +0.47 V or an average of 0.17 V per proton.

We are interested in the interdependence between the deprotonation of coordinated tripodal imidazolyl/benzimda-

---

* Author to whom correspondence should be addressed. Fax: 610-660-1783. Tel: 610-660-1794. E-mail: bhammes@sju.edu.

[†] Saint Joseph's University.

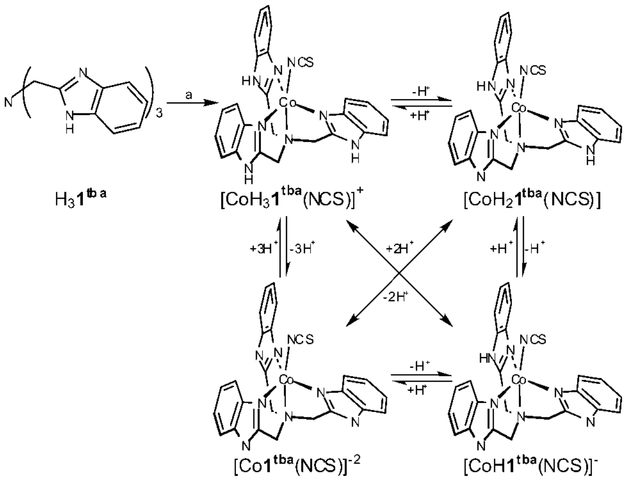
[‡] University of Delaware.

[§] Fax: 302-831-6335. Tel: 302-831-8720. E-mail: arnrhein@udel.edu.

(1) Stubbe J. A.; van der Donk W. A. *Chem. Rev.* **1998**, *98*, 705.
(2) Meunier, M., Ed. *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Imperial College Press: 2000.
(3) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.
(4) Roth, J. P.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 5486.
(5) Roth, J. P.; Mayer, J. M. *Inorg. Chem.* **1999**, *38*, 2760.
(6) Carina, R. F.; Verzegnassi, L.; Bernardinelli, G.; Williams, A. F. *Chem. Commun.* **1998**, 2681.
(7) Thompson, L. K.; Ramaswamy, B. S.; Seymour, E. A. *Can. J. Chem.* **1977**, *55*, 878.
(8) Addison, A. W.; Hendriks, H. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *20*, 103.
(9) Su, C.-Y.; Kang, B.-S.; Du, C.-X.; Yang, Q.-C.; Mak, T. C. W. *Inorg. Chem.* **2000**, *39*, 4843.

10.1021/ic0155885 CCC: $22.00

Scheme 1[a]



[a] Conditions: (a) $CoCl_2$, KSCN, CH_3OH.

zolyl ligands and the physical and chemical properties of a metal ion within the tripodal framework. Scheme 1 outlines the synthesis of the various Co(II) complexes. The Co(II) complex was readily prepared by the direct reaction of $H_3\mathbf{1}^{tba}$ with $CoCl_2{\cdot}6H_2O$ in methanol; addition of $NaBPh_4$ and KSCN gave the blue complex $[CoH_3\mathbf{1}^{tba}(NCS)]BPh_4$ in very good yield. The trigonal bipyramidal complex shows two d−d transitions at 576 nm ($\epsilon = 400\ M^{-1}\ cm^{-1}$) and 787 nm ($\epsilon = 40\ M^{-1}\ cm^{-1}$) in the visible region, which is consistent with trigonal bipyramidal geometry around the metal ion.[7,10] Upon treatment with 1 equiv of KH in DMF under an argon atmosphere, the solution became light purple. The electronic spectrum of this solution showed absorptions at 561 nm ($\epsilon = 340\ M^{-1}\ cm^{-1}$) and 893 nm ($\epsilon = 24\ M^{-1}\ cm^{-1}$) which corresponded to the monodeprotonated 5-coordinate complex $[CoH_2\mathbf{1}^{tba}(NCS)]$. Addition of two consecutive equivalents of KH to the light purple solution allowed isolation of the dideprotonated and the trideprotonated Co(II) complexes, $[CoH\mathbf{1}^{tba}(NCS)]^-$ and $[Co\mathbf{1}^{tba}(NCS)]^{2-}$,[11] respectively, with corresponding shifts in their absorption spectra (553 nm ($\epsilon = 340\ M^{-1}\ cm^{-1}$) and 770 nm ($\epsilon = 38\ M^{-1}\ cm^{-1}$) for $[CoH\mathbf{1}^{tba}(NCS)]^-$and 544 and 767 nm for $[Co\mathbf{1}^{tba}(NCS)]^{2-}$). The shifts in the d−d bands in the absorption spectra of the di- and trideprotonated complexes suggest that the trigonal bipyramidal coordination geometry of the Co(II) series remains unchanged throughout the series of Co(II) complexes. Initially, it was believed that the combination of absorption and infrared spectroscopy (with NCS^- as a ligand) would not only provide structural and electronic information but would also allow us to probe the electronic effect of deprotonation on the Co−NCS bond. However, the change in the overall charge on each complex resulted in no clear electronic trends in this series of complexes.

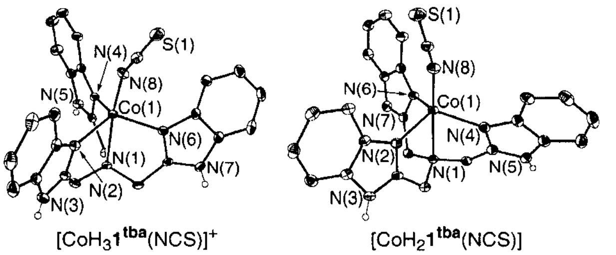


Figure 1. Thermal ellipsoid diagram of $[CoH_3\mathbf{1}^{tba}(NCS)]^+$ (left) and $[CoH_2\mathbf{1}^{tba}(NCS)]$ (right). The ellipsoids are drawn at the 40% probability level, and only the benzimidazolyl hydrogen atoms are shown. Selected bond lengths (Å) and angles (deg) for $[CoH_2\mathbf{1}^{tba}(NCS)]$ {$[CoH_3\mathbf{1}^{tba}(NCS)]^+$}: Co(1)−N(1), 2.3547(19) {2.4078(18)}; Co(1)−N(2), 2.031(2) {2.0312(19)}; Co(1)−N(4), 2.061(2) {2.0078(18)}; Co(1)−N(6), 2.0046(19) {2.0308(19)}; Co(1)−N(8), 2.019(2) {2.0409(19)}; N(1)−Co(1)−N(2), 76.20(7) {75.72(7)}; N(1)−Co(1)−N(4), 75.69(7) {76.45(7)}; N(1)−Co(1)−N(6), 76.42(7) {75.30(7)}; N(1)−Co(1)−N(8), 177.93(8) {172.20(7)}; N(2)−Co(1)−N(4), 115.65(8) {112.27(7)}; N(2)−Co(1)−N(6), 108.00(8) {123.34(7)}; N(2)−Co(1)−N(8), 102.80(9) {102.61(8)}; N(4)−Co(1)−N(6), 119.48(8) {106.66(8)}; N(4)−Co(1)−N(8), 103.27(8) {111.02(7)}; N(6)−Co(1)−N(8), 105.64(8) {99.85(8)}.

The molecular structures of $[CoH_3\mathbf{1}^{tba}(NCS)]^+$ and $[CoH_2\mathbf{1}^{tba}(NCS)]$ were determined by X-ray diffraction methods. The overall structures of both complexes are very similar (shown in Figure 1), with both complexes having a trigonal bipyramidal coordination geometry around their cobalt centers.[12] In $[CoH_2\mathbf{1}^{tba}(NCS)]$, two benzimidazolyl nitrogens and one benzimidazolylate nitrogen define the trigonal plane with an average $Co(1)-N_{benz}$ bond length of 2.0233(11) Å while the $Co(1)-N_{benzimidazolylate}$ bond length is considerably shorter at 2.0046(19) Å. This was expected for a monoanionic benzimidazolyl ligand coordinated to a cobalt ion.[13] In $[CoH_3\mathbf{1}^{tba}(NCS)]^+$, the three benzimidazolyl nitrogens made up the trigonal plane with an average $Co(1)-N_{benz}$ bond distance of 2.0232(11) Å, which is consistent with those reported for other benzimdazolyl complexes.[14−17] The metal ion in each complex lies slightly out the trigonal plane formed by the benzimidazolyl/benzimidazolylate nitrogen atoms N(2), N(4), and N(6) toward the isothiocyanato ligand (0.215 Å for $[CoH_3\mathbf{1}^{tba}(NCS)]^+$ and 0.212 Å for $[CoH_2\mathbf{1}^{tba}(NCS)]$). The Co(1)−N(1) bond distance decreases significantly upon deprotonation (2.4078(18) and 2.3547(19) Å, respectively). This decrease is believed to result from a twisting of the methylene carbon in each tripodal arm which allows the apical amine to move closer to the metal ion (average dihedral angle of $N_{benz}-Co-N_{amine}-C_{methyl}$ increases from 18.7° to 23.3° upon deprotonation). The terminal isothiocyanato ligand is positioned nearly trans to the apical

---

(10) Lah, M. S.; Moon, M. *Bull. Korean Chem. Soc.* **1997**, *18*, 406.

(11) The reprotonation of the Co(II) complex was done by titration with methonolic HCl and was followed by absorption spectroscopy. For $[Co\mathbf{1}^{tba}(NCS)]^{2-}$, all spectroscopic data suggest that the monomeric Co(II) complex is the only product.

(12) Crystal data for $[CoH_3\mathbf{1}^{tba}(NCS)]BPh_4$: $C_{51}H_{44}BCoN_9S$, $M = 884.75$, $a = 13.3043(2)$ Å, $b = 13.8019(2)$ Å, $c = 14.1322(2)$ Å, $V = 2156.33(5)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$, $T = 173(2)$ K, final R1 = 0.0675, wR2 = 0.1337, GOF (on F^2) = 1.458. For $[CoH_2\mathbf{1}^{tba}(NCS)]$: $C_{31}H_{34}CoN_{10}O_2S$, $M = 669.67$, $a = 15.3530(9)$ Å, $b = 11.0645(6)$ Å, $c = 19.1319(10)$ Å, $V = 3129.1(3)$ Å^3, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 173(2)$ K, final R1 = 0.0664, wR2 = 0.1141, GOF (on F^2) = 1.051.

(13) All benzimidazolyl hydrogen atoms were found in the Fourier difference map and refined positionally while the U_{eq} values were held at relative values.

(14) Buchanan, R. M.; O'Brien, R. J.; Richardson, J. F.; Latour, J.-M. *Inorg. Chim. Acta* **1993**, *214*, 33.

(15) Gomez-Romero, P.; Witten, E. H.; Reiff, W. M.; Jameson, G. B. *Inorg. Chem.* **1990**, *29*, 5211.

(16) Addison, A, W.; Burman, S.; Wahlgren, C. G.; Rajan, O. A.; Rowe, T. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2621.

(17) Linert, W.; Konecny, M.; Renz, F. *J. Chem. Soc., Dalton Trans.* **1994**, 1523.

amine nitrogen atom N(1). Upon deprotonation, the Co(1)−N(8) distance shortens considerably (2.0409(19) and 2.019(2) Å, respectively), and the N(1)−Co(1)−N(8) becomes almost linear with angles of 172.20(7)° for the fully protonated complex and 177.93(8)° for the neutral Co(II) complex, respectively.

In view of the changes in the ligand field around the Co(II) ion, it was initially surprising that the totally deprotonated complex $[\mathrm{Co}\mathbf{1}^{\mathbf{tba}}\mathrm{NCS}]^{2-}$ was completely air stable. Cyclic voltammetry studies on all of the complexes in DMF (glassy carbon electrode, 0.1 M TBAP,[18] scan rate 0.1 Vs^{-1}) showed an irreversible oxidative redox couple which ranged from +0.98 V for $[\mathrm{CoH_3}\mathbf{1}^{\mathbf{tba}}(\mathrm{NCS})]^{+}$ to +0.47 V for $[\mathrm{Co}\mathbf{1}^{\mathbf{tba}}(\mathrm{NCS})]^{-2}$ (vs SCE).[19] This suggests that the introduction of negative charge onto the tripodal ligand shifts the redox potential more negative by an average of 0.17 V per proton. The lack of air sensitivity in these transition metal complexes is similar to the behavior of octahedral iron complexes containing the tridentate ligand 2,6-bis(benzimidazolyl)pyridine.[20,21] However, the magnitude of the electronic shift is considerably smaller in our study than those reported for coordinatively saturated iron complexes containing imidazolyl ligands.[6] Perhaps the high degree of delocalization in the deprotonated benzimidazolylate ligand decreases the electron density available to donate to the metal ion. On the other hand, Haga et al. has studied the effect of deprotonation of coordinated benzimidazole ligands in mixed ruthenium and osmium complexes and has found a 2-fold increase in the reduction potential upon deprotonation than what we have observed.[22,23] This difference could result from the benzimidazolyl acting as a bidentate ligand bridging between the ruthenium and/or osmium ions.

The initial results of this study confirm that distal deprotonation of coordinated benzimidazolyls contained within an unsaturated Co(II) complex can be isolated and characterized. The evidence suggests that the 3-fold symmetric framework formed in metal complexes containing $\mathrm{H_3}\mathbf{1}^{\mathbf{tba}}-[\mathbf{1}^{\mathbf{tba}}]^{3-}$ can sequentially modulate the redox properties of Co(II) complexes by the selective deprotonation of coordinated benzimidazolyls.

Acknowledgment. The authors wish to thank the Research Corporation under Grant CC5286 for support of this research. Professor Brian S. Hammes is a Cottrell Scholar of Research Corporation.

Supporting Information Available: The synthesis of $\mathrm{H_3}\mathbf{1}^{\mathbf{tba}}$ ligand, coordination compounds, the metathesis procedures, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0155885

---

(18) Tetrabutylammonium hexafluorophosphate.

(19) All observed redox events were oxidative in nature. No reductive phenomena were observed for any of the reported complexes between 0 and −1.8 V vs SCE.

(20) Addison, A. W.; Burman, S.; Wahlgren, C. G.; Rajan, O. A.; Rowe, T. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2621.

(21) Rüttimann, S.; Moreau, C. M.; Williams, A. F.; Bernardinelli, G.; Addison, A. W. *Polyhedron* **1992**, *6*, 635.

(22) Haga, M.; Ali, M. M.; Arakawa, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 76.

(23) Haga, M.; Bond, A. M. *Inorg. Chem.* **1991**, *30*, 475.