CHEMISTRY OF MATERIALS

VOLUME 20, NUMBER 19 OCTOBER 14, 2008

Communications

Nitric Oxide Disproportionation at Mild Temperatures by a Nanoparticulate Cobalt(II) Complex

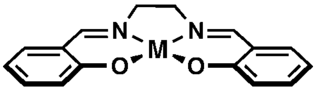
Joseph G. Nguyen,[†] Chad A. Johnson,[‡,§]
Bala Subramaniam,[*,‡,§] and A. S. Borovik[*,∥]

Center for Environmentally Beneficial Catalysis, University of Kansas, 1501 Wakarusa Drive, Lawrence, Kansas 66047, Department of Chemical and Petroleum Engineering and Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, and Department of Chemistry, 1102 Natural Science II, University of California, Irvine, California 92697-2021

Received May 22, 2008
Revised Manuscript Received August 3, 2008

A current challenge in materials chemistry is the design and processing of functional nanoparticles with defined structures.[1] Control of particle morphology governs the physical and chemical properties of the bulk material that can lead to new properties differing from their unprocessed analogs. We recently described a method for the formation of nanoparticles composed of metal complexes[2] containing salen ligands (salen, *N*,*N*′-salicylidiene-1,2-ethylene-diaminato(2-));[3] particle fabrication used precipitation with compressed antisolvent (PCA) technology in which supercritical CO_2 served as the precipitant.[4] A correlation was found between particle architecture and the molecular structure of the precursor metal complexes. Scanning electron microscopy showed that primary particles having rodlike structures with submicrometer-lengths, and diameters of less than 100 nm were obtained from planar [M(salen)] precursors ($M = Co^{II}$, Ni^{II}). These architectures were distinct from the spherical nanoparticles produced from nonplanar complexes. In all cases, spectroscopic and analytical data confirm that the metal complexes remain intact after processing into nanoparticles. For instance, [Co^{II}(salen)] nanoparticles ([Co^{II}(salen)]$_{(P)}$) have identical analytical and electron paramagnetic resonance spectra as their unprocessed [Co^{II}(salen)] analog.

Metal Salen Complexes



M^{II}(salen) M^{II} = Co, Ni

To further probe the properties of the rodlike nanoparticles, we have evaluated their interactions with nitric oxide (NO).

[†] Department of Chemistry, University of Kansas.

[‡] Center for Environmentally Beneficial Catalysis, University of Kansas.

[§] Department of Chemical and Petroleum Engineering, University of Kansas.

[∥] University of California, Irvine.

(1) (a) Johnston, K. P.; Shah, P. S. *Science* **2004**, *303*, 482–483. (b) Leod, M. C.; Anand, M.; Kitchens, C. L.; Roberts, C. B. *Nano Lett.* **2005**, *5*, 461–465. (c) Ogale, S. B.; Ahmad, A.; Pasricha, R.; Dhas, V. V.; Syed, A. *Appl. Phys. Lett.* **2006**, *89*, 263105. (d) Lester, E.; Blood, P.; Denyer, J.; Giddings, D.; Azzopardi, B.; Poliakoff, M. *J. Supercrit. Fluids* **2006**, *37*, 209–214. (e) Eulis, L.; DuPont, J.; DeSimone, J. M. *Chem. Soc. Rev.* **2006**, *35*, 1095–1104. (f) Dahl, J. A.; Maddux, B. L. S.; Hutchison, J. E. *Chem. Rev.* **2007**, *107*, 2228–2269. (g) Jessop, P. G.; Subramaniam, B. *Chem. Rev.* **2007**, *107*, 2666–2694.

(2) For examples of nanoparticles for porphyrin complexes see: (a) Wang, Z.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 15954–15955. (b) Liu, B.; Qian, D.-J.; Chen, M.; Wakayama, T.; Nakamura, C.; Miyake, J. *Chem. Commun.* **2006**, 3175–3177. (c) Wang, Z.; Ho, K. J.; Medforth, C. J.; Shelnutt, J. A. *Adv. Mater.* **2006**, *18*, 2557–2560.

(3) Johnson, C. A.; Sharma, S.; Subramaniam, B.; Borovik, A. S. *J. Am. Chem. Soc.* **2005**, *127*, 9698–9699.

(4) This methodology is also referred to as supercritical antisolvent (SAS) process when supercritical media are used during processing.

10.1021/cm801406y CCC: $40.75

In this report, we demonstrate that $[Co^{II}(salen)]_{(P)}$ have clearly different NO uptake properties than other forms of the complex and appear to disproportionate NO to different nitrogen-containing species at room temperature.

Nitric oxide has various functions, ranging from its adverse role in the environment[5] to its importance in mammalian biology,[6] in which it has been linked to regulatory processes involving the cardiovascular, respiratory, and nervous systems. These needs have led to an increase in the development of substances that interact with NO, including nanoparticles coated with compounds that bind or produce NO.[7] Metal complexes processed as nanoparticles offer a possible alternative to the norm because the facile formation of M-NO units can alleviate the need for coatings. In solution, $Co^{II}(salen)$ is known to bind NO, forming the $Co^{II}(salen)NO$ complex; in the presence of dioxygen, this complex irreversibly converts to $Co^{III}(salen)NO_2$ species.[8] In contrast, there is little evidence that amorphous or crystalline $Co^{II}(salen)$ binds NO,[9] in fact, only when the complex is immobilized within a porous organic hosts does it definitely bind NO with no evidence of NO disproprotionation.[10] A major objective of this work was to investigate if a similar behavior is possible with $[Co^{II}(salen)]_{(P)}$.

We have monitored NO uptake using a tapered element oscillating microbalance (TEOM), which can detect mass changes of a solid sample at the microgram level.[11] Flowing NO at 7 sccm over a sample of $[Co^{II}(salen)]_{(P)}$ produces a reproducible mass increase of approximately 32% (Figure 1), which corresponds to 3.5 NO per cobalt center. This finding eliminates the simple binding of NO to each $Co^{II}(salen)$ molecule within the particles, as is found when the complex is in the condensed phase—a 9% mass gain would be expected from this type of uptake.

The larger than expected mass gain with NO appears to be specific for $[Co^{II}(salen)]_{(P)}$. Under the same experimental conditions, TEOM measurements of the unprocessed $Co^{II}(salen)$ showed less than a 0.5% mass change in the presence of flowing NO (Figure 1, inset (red line))—a finding that supports previous observations that $Co^{II}(salen)$ normally does not interact with NO in the solid state. In addition, we do not attribute the large mass change solely to the morphology of the nanoparticles. As illustrated in Figure 1 (inset, blue line), the structurally identical nanoparticles of $Ni^{II}(salen)$ display a mass change of less than 0.8% when exposed to flowing NO in a TEOM. Note that this result is in accordance with known chemistry of $Ni^{II}(salen)$, which to our knowledge does not bind NO in either the solution or the solid-state.

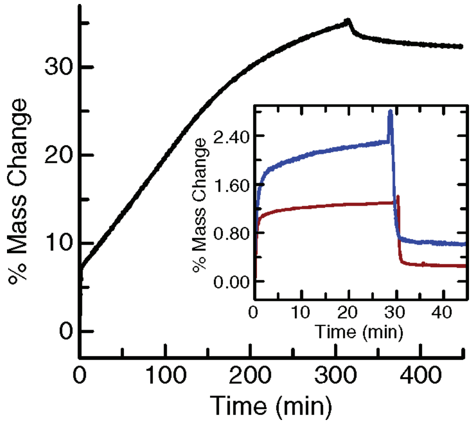


Figure 1. TEOM profile for NO uptake by $[Co^{II}(salen)]_{(P)}$. A different, lower baseline is attained when the flow is switched from flowing NO to flowing He. The difference between this baseline value and that prior to NO introduction is the net weight gain because of NO uptake. Inset: TEOM profiles of NO uptake by $Co^{II}(salen)$ (red) and $[Ni^{II}(salen)]_{(P)}$ (blue).

Table 1. Results from Elemental Analyses[a]

	% C	% H	% N	% Co	no. of N atoms
$Co^{II}(salen)$	57.08	4.25	8.25	17.02	2.04
$[Co^{II}(salen)]_{(P)}$	56.92	4.13	8.11	16.66	2.05
$Co^{II}(salen)$ + NO	58.16	4.24	8.45	16.17	2.20
$[Co^{II}(salen)]_{(P)}$ + NO	35.36	2.18	14.63	10.83	5.68

[a] Calculated values for $Co^{II}(salen)$: % C, 59.09; % H, 4.35; % H, 8.61; % Co, 18.12.

The large mass change of $[Co^{II}(salen)]_{(P)}$ in flowing NO is supported by analytical data obtained from elemental analyses (Table 1). The elemental compositions of $[Co^{II}(salen)]_{(P)}$ and its unprocessed analogue are identical within measurement accuracy and agree closely with the calculated theoretical percentages. Similar results were found for $Co^{II}(salen)$ when treated with NO, again indicating that the complex does not bind nitric oxide in the solid state. In contrast, there is a large change in the elemental percentages for $[Co^{II}(salen)]_{(P)}$ when exposed to flowing NO. The percentage of nitrogen atoms changes from 8.11% to 14.63%, an increase that corresponds to the addition of 3.5 nitrogen atoms per cobalt complex, which can be attributed to the uptake of approximately four NO molecules.

One possible explanation for the observed mass gain at room temperature is that $[Co^{II}(salen)]_{(P)}$ disproportionates NO: this process often consumes 4 equiv of NO to produce other nitrogen-containing species.[12] Metal complexes are known to promote this type of reaction; however, it typically occurs in the condensed phase at room temperature.[13,14] Solid-state systems, such cobalt-

---

(5) Armor, J. N. *Catal. Today* **1995**, *26*, 99–105.

(6) (a) *Nitric Oxide: Biology and Pathobiology*; Ignarro, L. J., Ed.; Academic Press: New York, 2000. (b) Lincoln, J.; Hoyle, C. H. V.; Burnstock, G. *Nitric Oxide in Health and Disease*; Cambridge University Press: New York, 1997. (c) Wink, D. A.; Mitchell, J. B. *Free Radical Biol. Med.* **1998**, *25*, 434–456.

(7) (a) Rothrock, A. R.; Donkers, R. L.; Schoenfisch, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 9362–9363. (b) Shin, J. H.; Metzger, S. K.; Schoenfisch, M. H. *J. Am. Chem. Soc.* **2007**, *129*, 4612–4619. (c) Polizzi, M. A.; Stasko, N. A.; Schoenfisch, M. H. *Langmuir* **2007**, *23*, 4938–4943. (d) Neuman, D.; Ostrowski, A. D.; Absalonson, R. O.; Strouse, G. F.; Ford, P. C. *J. Am. Chem. Soc.* **2007**, *129*, 4146–4147.

(8) Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528–1534.

(9) The only references on NO binding to solid $Co^{II}(salen)$ contain limited information on the properties and formulation of the final complexes: (a) Diehl, H.; Hach, C. C.; Harrison, G. C.; Liggett, L. M.; Chao, T. S. *Iowa State Colloid J. Sci.* **1947**, *21*, 287–309. (b) Earnshaw, A.; Hewelett, P. C.; Larkworthy, L. F. *Chem. Soc.* **1965**, 4712–4723.

(10) Padden, K. M.; Krebs, J. F.; MacBeth, C. E.; Scarrow, R. C.; Borovik, A. S. *J. Am. Chem. Soc.* **2001**, *123*, 1072–1079.

(11) See, for example: Zhu, W.; van de Graaf, J. M.; van den Broeke, L. J. P.; Kapteijn, F.; Moulijn, J. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 1934–1942.

(12) Tsukahara, H.; Ishida, T.; Todoroki, Y.; Hiraoka, M.; Mayumi, M. *Free Radical Res.* **2003**, *37*, 171–177.

(13) (a) Franz, K. J.; Doerrer, L. H.; Spingler, B.; Lippard, S. J. *Inorg. Chem.* **2001**, *40*, 3774–3780. (b) Hilderbrand, S. A.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 4674–4682.

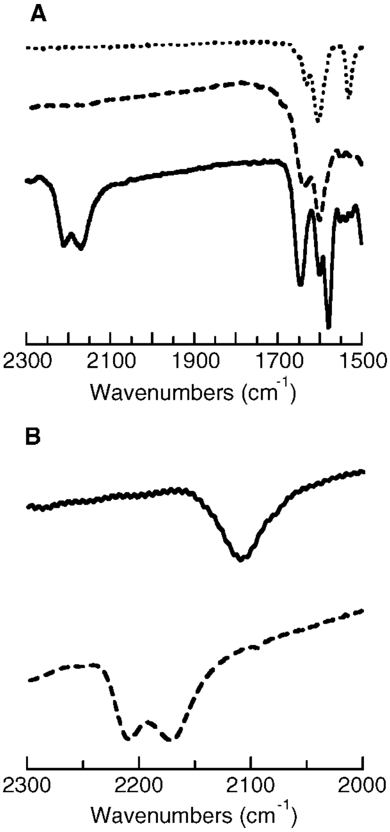


Figure 2. Solid-state FTIR spectra: (A) [Co^{II}(salen)]$_{(P)}$ (dotted line), [Co^{II}(salen)]$_{(P)}$ + NO (solid line), and NO exposed Co^{II}(salen)$_{(P)}$ placed under vacuum at 120 °C for 2 h (dashed line); (B) [Co^{II}(salen)]$_{(P)}$ + ^{15}NO (solid line) and [Co^{II}(salen)]$_{(P)}$ + ^{14}NO (dashed line). All measurements were performed on KBr pellets.

doped zeolites, disproportionate NO but *only at elevated temperatures that are greater than 400 °C*.[15] To our knowledge, there are no reports of [Co^{II}(salen)] complexes being able to disproportionate NO.

To test whether [Co^{II}(salen)]$_{(P)}$ is capable of this type of reactivity, we examined the vibrational properties of the nanoparticles for signals typically associated with products formed from NO disproportionation (e.g., N_2O, NO_2, and N_2). Preliminary Fourier transform infrared (FTIR) spectral results on samples treated with flowing NO reveal the presence of several new bands that are assigned to nitrogen-based products (Figure 2): N_2O (2210 cm^{-1}) and NO_2 (1580 cm^{-1}).[16] In addition, the peak at 1640 cm^{-1} is similar to signals found in complexes with Co-NO units.[7] We also observe a band at 2170 cm^{-1}, which is tentatively assigned to a vibration from N_2.[14] These bands disappear when heating the NO-exposed nanoparticles under vacuum for 2 h, producing a FTIR spectrum approaching that of [Co^{II}(salen)]$_{(P)}$ (Figure 2A). Further evidence to support the formation of N_2O and N_2 comes from labeling studies with ^{15}NO. The bands at 2210 and 2170 cm^{-1} are replaced with a broadband centered at 2110 cm^{-1} in the ^{15}NO treated nanoparticles, which is attributed to overlapping vibrations from $^{15}N_2$ and $^{15}N_2O$.[17] The observed shifts are expected based on a classical harmonic N−N oscillator model that predicts each band should be lowered in energy by ~75 cm^{-1}. In addition, the band at 1640 cm^{-1} shifts a small amount to 1635 cm^{-1} in the ^{15}N-isotopomer—a shift that is substantially smaller than the predicted value of 30 cm^{-1} for $\nu(^{15}NO)$. While this change indicates that the vibration is sensitive to the isotope of nitrogen in the sample, we are still uncertain as to why such a relatively small shift was observed.

In summary, we have discovered a new function for [Co^{II}(salen)] complexes, in which exposure to NO leads to disproportionation. Large mass changes were found when [Co^{II}(salen)] nanoparticles were treated with flowing NO. Analytical and vibrational studies support that N_xO_y products were formed—these compounds are associated with NO disproportionation reactions. Moreover, this reactivity is observed at *room temperature*, which is significantly lower than previously found for cobalt-containing substances in the solid state. Furthermore, NO disproportionation only occurs when the [Co^{II}(salen)] complexes are processed into nanoparticles. Control experiments found that unprocessed [Co^{II}(salen)] *does not bind NO in the solid state*, further illustrating that [Co^{II}(salen)]$_{(P)}$ have different functional properties compared to its molecular precursor. We do not yet understand the cause(s) for the new NO reactivity in [Co^{II}(salen)]$_{(P)}$ or to what extent the products bind to the nanoparticles. Nonetheless, our findings show that this bottom-up approach of fabricating nanoparticulates of metal complexes produces systems that have distinct structural and functional properties.

Acknowledgment. Financial support for this work was provided by the NSF-Engineering Research Centers program (NSF-EEC 0310689) and the University of California, Irvine. We thank Professor Reg Penner for helpful advice.

Supporting Information Available: Full experimental details for NO uptake and ^{15}NO labeling studies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM801406Y

---

(14) (a) Hilderbrand, S. A.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 4674–4682. (b) Potter, W. T.; Cho, J.; Sublette, K. L. *Fuel Process. Technol.* **1994**, *40*, 355–360. (c) Rossi, M.; Sacco, A. *Chem. Commun.* **1971**, (13), 694. (d) Miki, E.; Tanaka, M.; Sarro, K.; Maejima, T.; Mizumachi, K.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1642–1645.

(15) (a) Shimokawabe, M.; Okumura, K.; Ono, H.; Takezawa, N. *React. Kinet. Catal. Lett.* **2001**, *73*, 267–274. (b) Minming, H.; Chunhua, Y.; Kunsong, C. *J. Mol. Catal.* **1991**, *69*, L7−L13. (c) Agnew, S. F.; Swanson, B. I.; Jones, L. H.; Mills, R. L. *J. Phys. Chem.* **1985**, *89*, 1678–1682. (d) Chao, C. C.; Lunsford, J. H. *J. Am. Chem. Soc.* **1971**, *93* (1), 71–77. (e) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; John Wiley & Sons, Inc.: New York, 1997.

(16) Franz, K. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 10504–10512.

(17) Similar shifts have been observed for these isotopomers: see ref 13.