Catalysis Science & Technology

Accepted Manuscript

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COMMUNICATION

Improving Carbon Capture from Power Plant Emissions with Zinc- and Cobalt-based Catalysts

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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We report homogeneous catalysts that are soluble and stable in primary amine-based CO_2 capture solvents. The zinc(II) and cobalt(III) complexes, which contain electron-donating multidentate anionic ligands, perform catalytic CO_2 hydration at unparalleled observed rates under conditions conducive to industrial post-combustion carbon capture processes.

The control of greenhouse gas emissions is arguably the most complicated environmental policy facing the U.S. and industrialized world.[1,2] An approach that is gaining a significant amount of interest in the control of CO_2 emissions is CO_2 capture from stationary fossil fuel combustion sources using aqueous amine-based solvents such as ethanolamine.[4-12] Such carbon capture systems are estimated to increase the overall costs of electricity by 85% (\$66/ton CO_2 captured) over twenty years levelized cost.[13] Therefore in order to meet the Department of Energy's (DOE) target of \$40/ton of CO_2 captured, new strategies are needed to reduce the large capital and operational costs associated with post-combustion carbon capture. With current technology, only primary and secondary amines have potential to be employed to achieve target costs, but still requires a ~50% reduction in both capital and O&M costs.

CO_2 hydration may be a key step in CO_2 capture using amine-based solvents, the rate of which can be increased through the use of catalyst mimics of carbonic anhydrase (CA) metalloenzymes (Fig. 1a). CAs catalyse the hydration of CO_2 (Fig. 1b) at ambient temperatures and physiological pH with the highest known rate constant (~10^6 $M^{-1}s^{-1}$) of synthetic catalysts and natural enzymes.[14-16] The rate of CO_2 hydration makes CAs an attractive option for improving the efficiency of post-combustion CO_2 capture, but the frailty of these proteins renders them inactive in the harsh conditions associated with industrial processes such as high pH, high ionic concentrations, and temperatures above 100 °C.[17] While CAs cannot be employed in industrial conditions, they serve as a template for development of biomimetic catalysts for carbon capture.

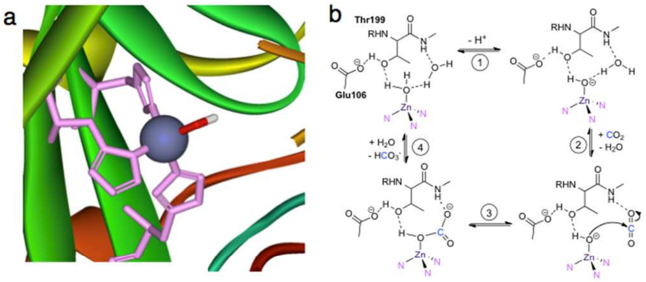

Fig. 1 (a) Representation of the active site of a carbonic anhydrase enzyme, showing three histidine residues and a hydroxide group coordinating to a zinc metal center.[16] (b) Proposed mechanism of CA showing 1) deprotonation, 2) CO_2 activation, 3) bicarbonate formation, and 4) bicarbonate substitution with water in which N atoms come from histidine residues.

Significant catalytic and mechanistic work has been performed on active site mimics, of which $(Zn(cyclen)(H_2O))[ClO_4]_2$ is one of the most well studied and active.[18-23] However, recent results from our laboratory show high levels of inhibition of these catalysts resulting from strong anion coordination, severely limiting their utility in the highly concentrated amine solvents required by post-combustion capture.[24] The zinc center is highly electron deficient, and therefore easily coordinates anions, inhibiting the fourth reaction in Fig. 1b. The cationic complex attracts anionic species such as bicarbonate into its secondary coordination sphere to maintain charge balance, which drives the equilibrium to the bicarbonate bound species. These two factors lead to low catalytic activity of CO_2 hydration under industrial carbon capture conditions.

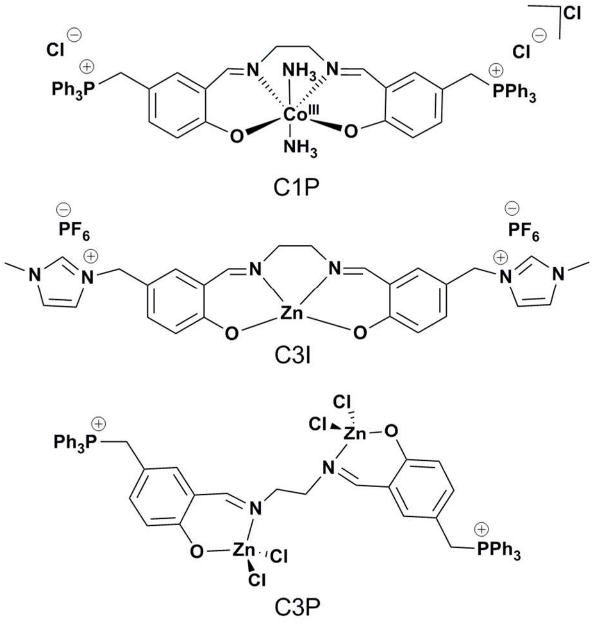

Fig. 2 A depiction of the chemical structures of the cobalt and zinc catalysts core in the solid state.

No reports of homogeneous CO_2 hydration catalysts show activity in concentrated (30 wt%) primary amine-based carbon capture solvents under conditions conducive to post-combustion capture.[25,26] Previous studies have focused on dilute tertiary amine or carbonate solutions (e.g. slow kinetic solvents) and performed under pseudo-first order conditions in CO_2.[18,19,21] Even with the enhancement from a catalyst, those solvents are still ≥ 50% less reactive than primary amines under utility flue gas conditions. Utilization of homogeneous catalysts in primary amines for post-combustion carbon capture is plagued with difficult challenges, including requirements that the catalyst be water soluble, water and air stable, and redox inert. The complexes made here are soluble and stable in concentrated amine solutions over weeks at ambient temperatures and are stable in thermal cycling experiments. Reported herein are the exceptional activities of homogeneous zinc(II) and cobalt(III) complexes containing water soluble and stable salen-like ligands[27] as catalysts that enhance the overall mass transfer of concentrated primary amine solvent absorbents for carbon capture from dilute gas streams.

To assay the effects of water-solubilizing groups on the ligand and the choice of metal center on overall mass transfer enhancements, a series of structurally similar complexes were prepared (Fig. 2). Following reported procedures,[26] a dark brown cobalt(III) complex (**C1P**) was isolated as an octahedral cobalt(III) center with the salen-like ligand occupying the basal plane and two ammonia molecules occupying the apical sites. Utilizing these same methods, zinc(II) complexes were isolated either as a 4-coordiante, bright yellow mono-metallic complex (**C3I**), or as a pale yellow bimetallic species (**C3P**) where each zinc center has tetrahedral geometry, and both complexes contain one ligand molecule. A crystal structure of **C3P** is shown in Fig. S3, and crystallographic data and structure parameters are shown in Table S1 in the Supporting Information.

Flowing a counter current stream of simulated flue gas over a liquid film of 30 wt% MEA in the presence of **C1P**, **C3I**, or **C3P** in a wetted wall column at 40 °C resulted in up to a 34% increase in mass transfer coefficients (Fig. 3) whereas (Zn(cyclen)(H_2O))[SiF_6] showed no enhancement in activity (Data not shown). As seen in Table 1, the overall mass transfer in MEA solutions increased by > 20% over the working range of α = 0.35 - 0.45 (where α is CO_2 loading (mol CO_2/mol MEA)) (Fig. S4). The enhancement in mass transfer remains fairly constant over the working range, even at high CO_2 loadings with a decreased amount of free amines. It is reasonable to expect that a larger enhancement at higher CO_2 loading as the amount of free amine decreases. However, as CO_2 loading increases, the solution viscosity increases causing the physical mass transfer resistance to become more significant. Such increased resistance partially counterbalanced the enhancement by catalyst, which may results in the trend as shown in this work. In addition, the increased ionic strength may have a negative affect the activity of catalyst.

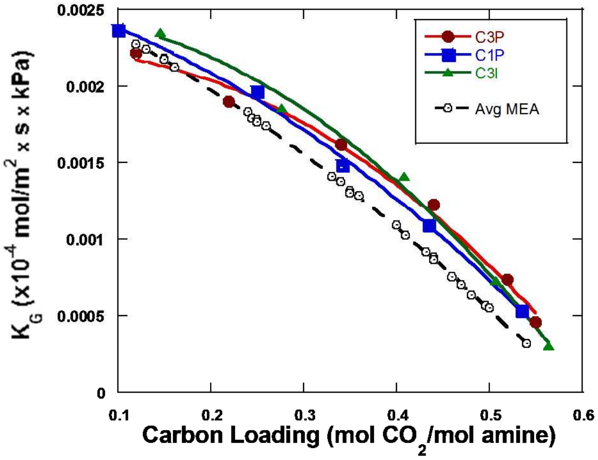

Fig. 3 Overall mass transfer coefficients vs. CO_2 loading of 30 wt% MEA (black line) and 30 wt% MEA containing with 2.3 g/L C1P (blue line), C3I (green line), or C3P (red line) obtained using the wetted-wall column set-up at 40 °C.

Table 1. Mass transfer enhancements from CAER catalysts.

Entry	Solvent[a]	[Catalyst] (g/L)	Mass Transfer[b]
1	MEA	0	1
2	MEA + **C1P**	2.3	1.23
3	MEA + **C3I**	2.3	1.34
4	MEA + **C3P**	2.3	1.34

[a] 30 wt% aqueous MEA. [b] Average mass transfer over the solvent working range of α = 0.35 - 0.45 normalized to MEA set as 1.0.

The overall mass transfer of the system is approximated using a pseudo first order approximation (eq 1), where the catalysts contribution is bundled into the k_2 term (eq 2) where k is ~6000 $M^{-1}s^{-1}$ and [amine] is ~5 M[18,28]

$$\sqrt{\frac{D_{CO2} \bullet k_2 \bullet [amine]}{H_{CO2}}} \qquad (1)$$

$$k_2[amine] = k_{obs} = k[amine] + k'[cat] \qquad (2)$$

therefore, with a catalyst loading of 2-3 mM, k' needs to be ~1 x 10^5 $M^{-1}s^{-1}$ in order to contribute to the overall k_{obs} (eq. 1 and eq. 2) This rate estimate is approximately two orders of magnitude larger than

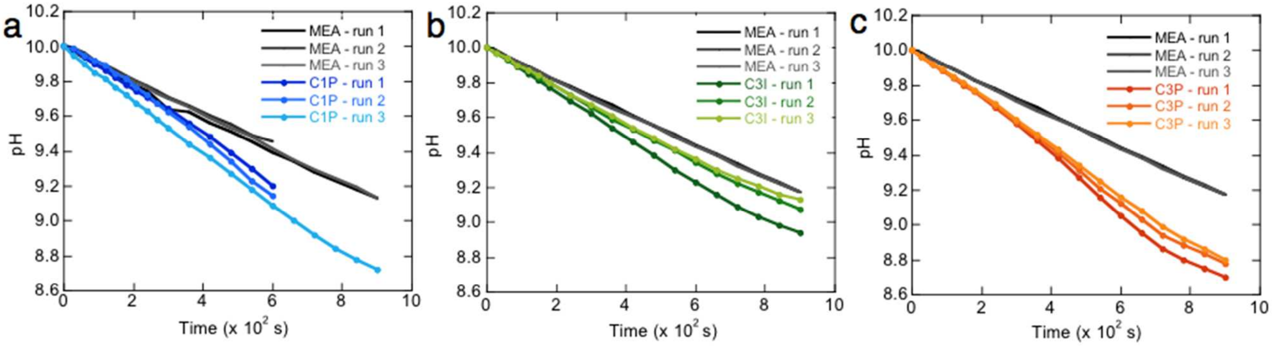

Fig. 4 Three CO_2 loading and solvent regeneration via heat cycles in 5M MEA (black and grey lines) in the presence of 2.3 g/L **C1P** (a, dark and light blue lines), **C3I** (b, dark and light green lines), and **C3P** (c, red and orange lines).

the current state-of-art $[Zn(cyclen)(H_2O)]^{2+}$ catalyst system at catalyst concentrations and reaction conditions consistent with post-combustion capture. When the active zinc center is replaced with cobalt, approximately a one third drop in mass transfer is observed. This follows the same trend observed in human CA when a Co(II) is substituted for the Zn(II) in the active site, and is most likely caused by a drop in the Lewis acidity of the metal center as well as the more favourable coordination of Lewis bases to the cobalt center.[20] Analysis of these reactions mixtures post CO_2 loading by UV-vis spectroscopy gave > 90% spectroscopic yield of catalyst. No enhancement is observed in the presence of the metal salts $ZnCl_2$ or $CoCl_2$, suggesting that the increase in mass transfer is not catalysed by decomposition products. No enhancement is observed in overall mass transfer in the presence of the enzyme, carbonic anhydrase, when tested in the breakthrough solvent evaluation apparatus, showing another limitation of CA that is not observed with our catalyst: activity in concentrated primary amines (Fig. S5). The addition of catalyst has a negligible effect on solvent pH, viscosity, and surface tension. The sum of these data suggest that the enhanced mass transfer is attributed to the catalytic activity of C1P, C3I, and C3P, and not to physical changes in the solvent with catalyst addition (see Table S2).

At high CO_2 loadings ($\alpha > 0.40$ where α is CO_2 loading in mol CO_2 / mol MEA), carbon capture solutions contain a large concentration of anions such as carbamates and bicarbonates. These species are known catalyst inhibitors and are typically the main cause of poor catalytic activity.[29,30] The addition of up to 100 eq. of $NaH^{13}CO_3$ to D_2O solutions of C1P, C3P, or C3I show only 1 peak for the bicarbonate-derived peak in the ^{13}C NMR spectra, suggesting that these complexes strongly disfavour bicarbonate coordination and that the equilibrium lies heavily to the left. Titration of up to 100 equiv. bicarbonate into H_2O solutions of C1P, C3P, or C3I showed no change in their respective UV-vis spectra. However, addition of a large excess (10^4-10^5 eq.) of sodium bicarbonate to a C3I solution resulted in a decrease the absorbance at 355 nm corresponding to the metal complex, and the appearance of a shoulder at 395 nm (Fig. S6). The addition of large excess of sodium bicarbonate to C1P or C3P showed no observable change in the UV-visible spectra. An isosbestic point is observed at 375 nm suggesting a simple A → B process without the formation of intermediates. The most likely explanations for the change in the UV-vis spectra are 1) coordination of $[HCO_3]^-$ to the zinc center, a scenario that suggests strongly disfavoured bicarbonate coordination, or 2) deprotonation of the $[Zn\text{-}OH_2]^{2+}$ core to generate $[Zn\text{-}OH]^+$, resulting in a change in the electronic structure. This scenario is plausible considering the pKa of bicarbonate to carbonic acid is ~6.5 and would suggest that the metal bound aqua proton is less acidic.

The complexes discussed here contain anionic ligands that donate electron density into the metal center, thereby facilitating bicarbonate/anion dissociation and increasing CO_2 hydration rates. The higher electron density of the catalyst core as well as the covalently attached cationic water solubilizing groups may serve to remove anionic bicarbonates/carbamates from the secondary coordination sphere and away from the metal center. We propose the above as key features in achieving catalytic rates large enough to contribute to the overall mass transfer in concentrated primary amine-based solvents, thereby increasing the rate of CO_2 absorption. Two possible mechanisms of action can explain the increased rate of absorption: either the catalysis of CO_2 hydration (eq 3) or the conversion of bicarbonate to carbamate in the presence of primary amines (eq 4). The increase in rate could be due to either of these reactions or both and cannot be determined easily without altering the reaction conditions, moving them away from actual carbon capture process conditions.

$$H_2O + CO_2 \rightarrow [HCO_3]^- + H^+ \qquad (3)$$

$$RNH_2 + [HCO_3]^- \rightarrow [RNHCO_2]^- + H_2O \qquad (4)$$

The cobalt(III) and zinc(II) complexes effects rapid absorption of CO_2 into the amine solvent to afford captured CO_2. The mechanism for CO_2 absorption and catalyst speciation is difficult to determine due to the complex nature of performing the reactions in concentrated amines, and in a dilute gas stream (14% CO_2) in order to mimic conditions observed in industrial settings. The capture solvent contains a complex mixture of amines, carbonates, and carbamates in equilibrium. Efforts to experimentally determine a mechanism will fundamentally change this equilibrium and the behaviour of the reaction. For example, stop-flow UV-vis and NMR experiments would require dilute solutions and/or be saturated in CO_2.

The rate of CO_2 absorption is measureable in tertiary amines using a delta pH method.[31] The use of tertiary amines removes the ability of the amine to react with CO_2 directly, therefore simplifying the solution speciation, and any enhancement will most likely come from the direct reaction of CO_2 with the catalyst complexes, similar to the proposed mechanism for CO_2 hydration by CA. Flowing a 14% CO_2 gas stream through a methyldiethanolamine (MDEA) solution containing 1 mol% C1P afforded a rapid drop in pH, while the pH drop in the absence of C1P was significantly slower (Fig. S7). Tertiary amines are unable to react directly with aqueous CO_2 and serve as a proton sink (eq. 3). Catalysts C3P and C3I were only slightly soluble in 0.2 M aqueous MDEA solutions and formed a fine suspension which was unsuitable for CO_2 absorption studies.

A second possible mechanistic pathway could be direct insertion of CO_2 into the amine to form a carbamate. These complexes have a rigid ligand scaffold imparting a semi-rigid, 4-coordinate geometry. This orientation would make it difficult for the complexes to assume the required octahedral geometry with a cis-amine and -CO_2 ligand needed for direct insertion of CO_2 into the amine. A migratory insertion pathway would require the amine to be coordinated as a deprotonated, anionic species that is highly unlikely given the pH of the system. There are no reported examples of zinc(II) complexes performing a CO_2 insertion reaction under conditions similar to those observed in carbon capture. There are examples of CO_2 insertion into zinc hydride bonds. However, it is not well precedented, and the only examples involve monomeric zinc hydride complexes such as $[k^3\text{-Tptm}]$ZnH and $[\text{Tp}^R]$ZnH derivatives.[32-37] To test this mechanistic possibility, we removed H_2O from the system in order to shut down the hydration pathway. For this purpose, we performed CO_2 breakthrough investigations in 30 wt% MEA in DMSO. When water is removed from the system, there is no observed enhancement in mass transfer (Fig. S8). However, this possibility cannot be ruled out at the current state. The sum of the experimental data reported herein is most consistent with the CO_2 hydration mechanism proposed for CAs. A more detailed investigation is required to fully understand and delineate the mechanism and speciation of the metal catalysts in complex solution environments observed at conditions conducive to industrial carbon capture and is the subject matter for a future manuscript.

The cyclic (thermal) stability of the catalyst was tested by performing multiple carbon loading and solvent regeneration cycles. The rate of accelerated CO_2 hydration was measured using a delta pH method while the solvent regeneration was performed by bubbling N_2 through the heated (80 °C), carbon loaded solution for 75 min.[33] The cobalt-based catalyst **C1P** maintains its activity for five cycles over the typical solvent window (three cycles are shown in Fig. 4a). However, the zinc-based catalysts **C3I** and **C3P** showed steady decreases in activity after each regeneration cycle until no enhancement was observed after cycles 3 and 5, respectively; three cycles are shown in Fig. 4b and 4c. Analysis of the deactivated reaction mixture by UV-vis spectroscopy confirms the presence of unmetallated ligand. This result suggests that the most probable cause for the drop in activity is from demetallation of the zinc center at elevated temperatures.

The apparent stability of C1P was very encouraging and warranted further investigation at higher temperatures relevant to those observed in the stripper column of carbon capture systems, i.e. 120 °C. Heating solutions of 30 wt% MEA in the presence of C1P at 120 °C for 145 h resulted in no observable decomposition of the complex when analyzed by UV-vis spectroscopy (Fig. S9). The activity of the catalyst, post-heating, was assayed via pH-drop, and no loss in activity was observed (Fig. 5). Assuming a 10% resonance time in the stripper, this process would correlate to *ca.* 2 months of continuous operation. At this point, the thermal reclaiming of the solvent to remove heat-stable degradation products will remove the small amount of catalyst additive. The catalyst will therefore be required to be added with the capture solvent during solvent makeup.

The economics, cost, and environmental impact of the complexes discussed here will play a major role in the decision making process for industrial use in carbon capture systems. The synthesis of complexes C1P, C3P, and C3I utilize easily acquired, and cost effective, reagents and do not require complicated workups for isolation or purification. These complexes are isolated in high yield and purity via simple filtration from the reaction mixtures. The simplicity of the synthesis will allow for simple scale-up utilizing currently practiced industrial synthetic processes. We estimate the cost of the catalyst to be ~\$0.25/L of carbon capture solvent, which roughly equates to \$100/MW of electricity generated. The low cost of the catalyst is a requirement, as it would be removed in the thermal reclaiming process of the solvent. Since our catalysts are low cost they do not add a significant increase to the overall cost of the solvent, and the benefit outweighs the added cost. It is also important to consider the potential environmental implications of adding metal complexes to the solvent, which will, at some point, need to be disposed. The carbon capture solvent will most likely contain metal salts of Fe, Cr, As, Se, and Mn derived from the coal and corrosion products, which will classify the solvent as a hazardous waste and be required to follow proper disposal procedures. The addition of small amounts of our cobalt or zinc catalysts will not change this classification, and will not add any additional requirements in case of a spill or leak.

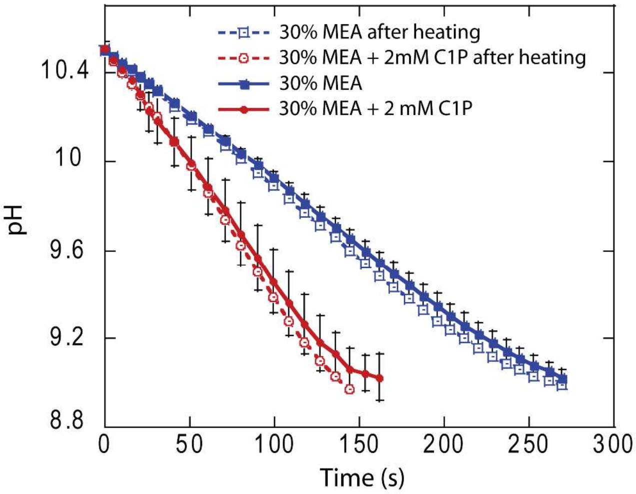

Fig. 5 CO_2 hydration activity via delta-pH of 30% MEA baseline (blue —■—) and 30% MEA in the presence of 2 mM C1P (red —●—) without exposure to high temperatures, and 30% MEA (blue --□--) and 30% MEA in the presence of 2 mM C1P (red --○--) after being heated at 120 °C for 145 h.

Conclusions

In conclusion, we have demonstrated for the first utilization of homogeneous catalysts for the enhancement of CO_2 absorption into concentrated amine-based aqueous solvents. Compared to previously reported CO_2 hydration catalyst systems, we observed enhancements of up to 34% in the highly concentrated primary amine solutions, which requires unprecedented second order rate constants. Key to success is the use of anionic, water-soluble salen-like ligands that donate electron density into the metal center. The electron donation facilitates the dissociation of the formed bicarbonate, typically the rate limiting step, regenerating the catalytically active species, under basic conditions. The increase in mass transfer by our catalyst would translate to *ca.* 30% reduction in the volume of the absorber tower for a 550 MW plant which relates to *ca.* 15% reduction in capital costs. Assuming a cost of \$300/kw for the construction of the absorber tower, this correlates to savings of ~\$25M.

Acknowledgements

We thank the University of Kentucky's Office for the Vice President for Research and the College of Arts and Sciences, the US-China Clean Energy Research Center – Advanced Coal Technology Collaboration for funding under award number DE-PI10000017.

Notes and references

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[b] *University of Kentucky, Department of Chemistry, Lexington, KY 40506-0055*

1 *Advancing the Science of Climate Change*. National Research Council. The National Academies Press, Washington, DC, USA, 2010.
2 U.S. Energy Information Administration, Monthly Energy Review, November 2013.
3 Standards of Performance for Greenhouse Gas Emissions from New Stationary Sources: Electric Utility Generating Units, Environmental Protection Agency, 2013.
4 U. Desideri and R. Corbelli, *Energ. Convers. Manage.,* 1998, **39**, 857.
5 P. Riemer, H. Audus, and A. Smith, *Carbon Dioxide Capture from Power Stations*; IEA Greenhouse Gas R&D Programme: Cheltenham, United Kingdom, 1993.
6 C. Hendriks, *Carbon Dioxide Removal from Coal-fired Power Plants;* Kluwer Academic Publishers: The Netherlands, 14-223, 1994.
7 T. Mimura, S. Satsumi, M. Iijima, and S. Mitsuoka, Developments on Energy Saving Technology for Flue Gas Carbon Dioxide Recovery by the Chemical Absorption Method and Steam System in Power Plant. In *Greenhouse Gas Control Technologies*, Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies, 30 August-2 September 1998; Eliasson, B., Riemer, P., Wokaun, A., Eds.; Elsevier Science Ltd.: Interlaken, Switzerland, 1994.
8 D. Jeremy, M.S. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 2000.
9 H. Audus, Leading Options for the Capture of CO_2 at Power Stations. Presented at the Fifth International Conference on Greenhouse Gas Control Technologies, Cairns, Australia, August 13-16, 2000.
10 A. B. Rao and E. S. Rubin, *Environ. Sci. Technol*., 2002, **36**, 4467.
11 Carbon Sequestration: Research and Development; A U.S. Department of Energy Report; Office of Science, Office of Fossil Energy, U.S. Department of Energy, 1999.
12 E. A. Parson and D. W. Keith, *Science*, 1998, **282**, 1053.
13 J. P. Ciferno, T. E. Fout, A. P. Jones, and J. T. Murphy, Capturing Carbon from Existing Coal-Fired Power Plants. Chemical Engineering Progress, April, 2009.
14 K. M. Merz, A. M. Murcko, and P. A. Kollman, *J. Am. Chem. Soc.*, 1989, **111**, 5636.
15 V. M. Krishnamurthy, G. K. Kaufman, A. R. Urbach, I. Fitilin, K. L. Gudiksen, D. B. Weibel, and G. M. Whitesides, *Chem. Rev.*, 2008, **108**, 946.
16 A. E. Eriksson, T. A. Jones, and A. Liljas, *Proteins*, 1988, **4**, 274.
17 D. Matulis, J. K. Kranz, R. Salemme, and M. J. Todd, *Biochemistry***,** 2005, **44***,* 5258.
18 X. Zhang, R. van Eldik, T. Koike, and E. Kimura, *Inorg. Chem.*, 1993, **32**, 5749.
19 X. Zhang and R. Van Eldik, *Inorg. Chem.*, 1995, **34**, 5606-5614.
20 R. Davy, *Energy Procedia*, 2009, **1**, 885.
21 N. L. Zastrow, A. F. A. Peacock, J. A. Stuckey, and V. L. Pecoraro, *J. Inorg. Biochem*., 2002, **89**, 255.
22 D. Huang, O. V. Makhlynets, L. T. Tan, S. C. Lee, E. V. Rybak-Akimova, and R. H. Holm, *Proc. Natl. Acad. Sci. USA*, 2011, **108**, 4, 1222.
23 D. Huang, O. V. Makhlynets, L. T. Tan, S. C. Lee, E. V. Rybak-Akimova, and R. H. Holm, *Inorg. Chem*. 2011, **50**, 20, 10070.
24 C. A. Lippert, D. Gupta, A. Wishrojwar, J. P. Selegue, J. E. Remias, and K. Liu, unpublished results.
25 C. A. Lippert, R. A. Burrows, S. R. Parkin, J. E. Remias, K. Liu, and S. A. Odom, unpublished results.
26 C. W. Floyd *et al.*, *Environ. Sci. Technol*., 2013, **47**, 10049.
27 S. Sonar, K. Ambrose, D. A. Hendsbee, J. D. Masuda, and R. D. Singer, *Can. J. Chem.*, 2012, **90**, 60.
28 N. McCann, D. Phan, X. Wang, W. Conway, R. Burns, M. Attalla, G. Puxty, and M. Maeder, *J. Phys. Chem. A*, 2009, **113**, 5022.
29 K. Nakata, N. Shimomura, N. Shiina, M. Izumi, K. Ichikawa, and M. Shiro, *J. Inorg. Biochem.*, 2002, **89**, 255.
30 Y. E. Lau, S. E. Wong, S. E. Baker, J. P. Bearinger, L. Koziol, C. A. Valdez, J. H. Satcher Jr., R. D. Aines, and F. C. Lightstone, *PLoS One*, 2013, **8**, e66187.
31 G. M. Bond, J. Stringer, D. K. Brandvold, F. A. Simsek, M.-G. Medina, and G. Egeland, *Energ. Fuel,* 2001, **15**, 309.
32 R. Han, I. B. Gorrell, A. G. Looney, and G. Parkin, *J. Chem. Soc., Chem. Commun*. **1991**, 717.
33 W. Sattler and G. Parkin, *J. Am. Chem. Soc*., 2011, **133**, 9708.
34 A. Looney, R. Han, I. B. Gorrell, M. Cornebise, K. Yoon, G. Parkin, and A. L. Rheingold, *Organometallics*, 1995, **14**, 274.
35 M. Rombach, H. Brombacher, and H. Vahrenkamp, *Eur. J. Inorg. Chem*., 2002, 153.
36 K. Merz, M. Moreno, E. Löffler, L. Khodeir, A. Rittermeier, K. Fink, K. Kotsis, M. Muhler, and M. Driess, *Chem. Commun*., 2008, 73.
37 S. Schulz, T. Eisenmann, S. Schmidt, D. Bläaser, U. Westphal, and R. Boese, *Chem. Commun.*, 2010, **46**, 7226.

Electronic Supplementary Information (ESI) available: catalyst synthesis and characterization, including single crystal x-ray analysis and cif files, description of catalyst testing and stability measurements. See DOI: 10.1039/c000000x/