This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

New Synthetic Techniques for Incorporation of Thiolate Donation in Transition Metal Complexes

David M. Eichhorn; Niranjan Goswami

Online publication date: 24 June 2010

To cite this Article Eichhorn, David M. and Goswami, Niranjan(2003) 'New Synthetic Techniques for Incorporation of Thiolate Donation in Transition Metal Complexes', Comments on Inorganic Chemistry, 24: 1, 1 — 13
To link to this Article: DOI: 10.1080/02603590390228164
URL: http://dx.doi.org/10.1080/02603590390228164

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Comments on Inorganic Chemistry, 24: 1–13, 2003
Copyright © Taylor & Francis Inc.
ISSN: 0260-3594 print
DOI: 10.1080/02603590390228164

Taylor & Francis
Taylor & Francis Group

New Synthetic Techniques for Incorporation of Thiolate Donation in Transition Metal Complexes

David M. Eichhorn* and Niranjan Goswami[‡]
Wichita State University, Wichita, KS 67260-0051

A new method for the synthesis of metal complexes containing mixed nitrogen/sulfur coordination spheres is discussed. The use of 2,2′-dithiodibenzaldehyde as the source of the sulfur donors obviates the need for protection of the thiolate moiety. The reaction involves a concerted Schiff-base condensation and disulfide bond reduction. Mononuclear and dinuclear complexes of Ni(II), Cu(II), Fe(III), and Co(III) have been prepared by this method, including the first mononuclear Ni(II) complex of a non-porphyrinic tetradentate N_3S ligand.

Keywords: Metal-thiolate complexes, iron complexes, nickel complexes, copper complexes, cobalt complexes, disulfides

Downloaded At: 12:16 15 January 2011

Among the twenty naturally occurring amino acids that make up proteins, two have side chains that contain sulfur atoms. Both the thioether from methionine and, especially, the thiolate from cysteine are incorporated as donor atoms to the metal ions at the active sites of metalloproteins and metalloenzymes. Among the metalloenzymes that have sulfur atom donors to the active-site metal ions are the iron-sulfur proteins (S_4 coordination sphere),[1] the blue copper enzymes (N_2S_2),[2] the Ni-Fe (NiS_4-FeO_3S_2)[3] and Fe only [Fe_4S_4-$Fe(S_2[CO]_2)(CN)$][4] hydrogenases, Zn alcohol dehydrogenase (NOS_2),[5] Mo sulfite oxidase (S_3O_2),[6] Fe[7] and Co[8] nitrile hydratase (N_2S_3O), and CO dehydrogenase [(NiS_4)-(FeS_4)$_3$-(FeS_3N)].[9]

An important tool in unraveling and understanding the mechanisms by which metalloenzymes operate is the synthesis and study of small-molecule synthetic analogs. These models fall into two categories—structural analogs, which closely reproduce the identity and disposition of the donor atoms

*Corresponding author.
[‡]Current Address: Department of Chemistry, Kaskaskia College, Centralia, IL 62801.

around the active-site metal, and functional analogs, which reproduce or improve upon the catalytic activity of the enzyme. Ideally, but not necessarily, a structural model will also serve as a functional model, but both types of models are useful on their own. Structural models often find their greatest utility in cases where a crystal structure does not exist for an enzyme. In such cases, comparison of spectroscopic data from the enzyme with those from well-characterized model complexes can help to define the nature of the metal's coordination sphere in the natural system. In cases where a crystal structure of the enzyme does exist, structural models still have a role to play. Comparison of models that very closely reproduce the structure of the natural system with models in which one or more features have been altered can help to identify which structural features are most important for establishing the necessary electronic environment for the active-site metal. In addition, a structural model will serve, at least, as a starting point for the ultimate design as functional models. Functional models are important because they provide the opportunity to investigate the mechanism of a system that performs the same chemistry of the natural system and may be able to give insight into the mechanism of the actual enzyme. In addition, functional models can ultimately lead to synthetic catalytic systems.

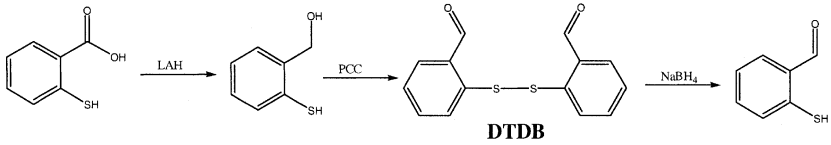
Downloaded At: 12:16 15 January 2011

The first truly successful models for metalloenzyme active sites actually involved sulfur coordination—Holm's models for rubredoxin and the two- and four-iron ferredoxins.[10] Although subsequent generations of models have been more involved, the initial models used simple thiophenolate ligands to reproduce the cysteine thiolate coordination. As a general rule, however, models for enzyme active sites containing sulfur coordination lag far behind models for enzyme active sites containing only nitrogen and oxygen coordination, as metal-sulfur coordination chemistry generally lags behind metal-nitrogen and metal-oxygen coordination chemistry. A simple manifestation of this discrepancy can be seen by recognizing that there are 173 published crystal structures for metal complexes of the N_2O_2 salen[11] ligand, but only nine published crystal structures of its N_2S_2 analog, tsalen.[12] The most obvious explanation for this discrepancy is the extreme air-sensitivity of thiols, making it necessary to work under an inert atmosphere and, more importantly, to incorporate protection and deprotection steps in the synthetic procedure. We have developed a novel procedure for the synthesis of metal complexes with mixed imine nitrogen/sulfur coordination spheres using an air-stable disulfide synthon, which obviates the need for protection of the thiol moiety.

SYNTHESIS OF 2,2′-DITHIODIBENZALDEHYDE (DTDB)

The syntheses of H_2tsalen and related Schiff-base ligands containing the thiophenolate group begin with the synthesis of thiosalicylaldehyde, which is then combined with the appropriate amine to yield the desired ligand.

Thiosalicylaldehyde is an air-sensitive compound that is not commercially available. It can be made by reduction of commercially available thiosalicylic acid to the alcohol and then reoxidation of the alcohol to the aldehyde using pyridinium chlorochromate (Scheme 1).[13] The oxidation step also results in the oxidation of the thiol to the disulfide, yielding 2,2′-dithiodibenzaldehyde (DTDB). Thiosalicylaldehyde can then be isolated by a borohydride reduction of the disulfide. The intermediate product, DTDB, is an air-stable white powder that can be produced in multigram quantities and stored indefinitely on the benchtop. It seemed reasonable to investigate the utility of this convenient compound as a source of thiophenolate donors for metal complexes.



SCHEME 1. Synthesis of thiosalicylaldehyde.

Downloaded At: 12:16 15 January 2011

METAL-DISULFIDE COMPLEXES

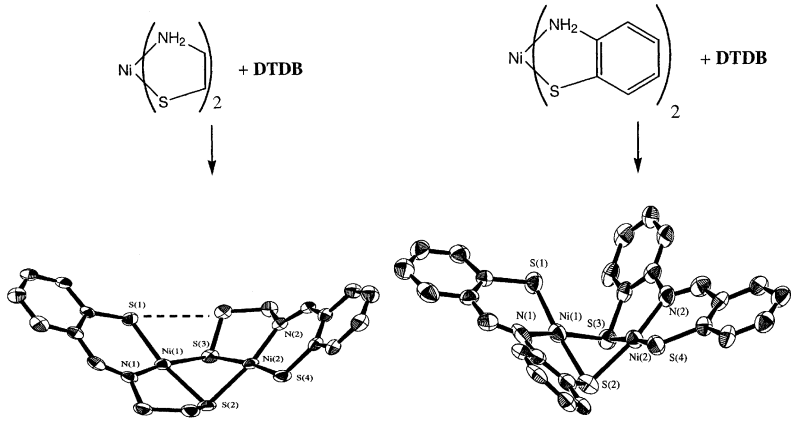
There are a number of literature reports concerning metal complexation of organic disulfides, demonstrating both coordination of the intact disulfide ligand and reduction of the disulfide to the thiolate. Seff and coworkers reported an Ni complex of bis[(2-(2-pyridylmethyl)imino)phenyl]disulfide, which was initially isolated by oxidation of the corresponding thiolate complex.[14] In this compound the disulfide is coordinated to the Ni via one of the sulfur atoms. Belluco and coworkers reported the reaction of $PdCl_4^{2-}$ with diphenyldisulfide in methanol, which led to the isolation of a polymer containing Pd atoms bridged by Cls and thiophenolates. Alternatively, reaction of $Pd(CH_3CN)_2Cl_2$ with diphenyldisulfide in benzene produced a dimeric complex with the intact disulfide ligand bridging the two metals.[15] Livingstone and Nolan reported formation of Ni(II) complexes of 2,2′-dithiodianiline (dta) with the intact disulfide coordinated to the metal, as well as metal complexes of the bis(pyridinecarboxaldehyde) Schiff-base adduct of dta with intact disulfides and with cleaved disulfide bonds.[16] Studies on the reaction of 2,2′-dithiodipyridine (DTDP) have produced examples of coordination of the intact disulfide via one S atom and a pyridyl N atom[17] and of reductive cleavage of the disulfide to produce the N,S-chelating 2-pyridinethiolate ligand.[18] Thus, a disulfide ligand has been shown to react with metal complexes to produce either the disulfide complex or the thiolate complex. The only example of the reaction of an organic disulfide with a ligand on a metal complex is the report by Datta and coworkers of the reaction of

DTDP with $[Co(NH_3)_4(H_2O)_2]^{3+}$, which resulted in the insertion of a coordinated ammonia ligand between the two sulfur atoms to give a complex in which the three nitrogen atoms of the resulting ligand serve as donors to the cobalt, but the sulfur atoms are not coordinated.[19]

REACTION OF DTDB WITH $Ni(NS)_2$ COMPLEXES

The first set of reactions attempted with DTDB was the reaction of DTDB with nickel(II) complexes of the chelating NS ligands 2-aminoethanethiolate and *o*-aminothiophenolate.[20] The relatively insoluble nickel complexes were suspended in methanol and a solution of DTDB in CH_2Cl_2 was added. The products that were isolated and crystallized showed the formation of a Schiff base by reaction of the aldehyde functionality of DTDB with the coordinated primary amine of the NS ligand. In addition, the disulfide bond was cleaved, resulting in a thiolate sulfur atom that is coordinated to the nickel. The structures of these compounds revealed them to be dimeric complexes **1** and **2** (Figure 1), with each nickel atom in a square-planar NS_3 coordination sphere made up of the imine nitrogen, two bridging thiolates that came from the originally coordinated NS ligands, and a terminal thiolate that resulted from the reductive cleavage of the DTDB disulfide bond. The reaction, therefore, is a nickel-templated formation of the NS_2 ligands 2-thiosalicylideneimineethanethiolate and N-thiosalicylideneimine-2-thiophenolate. These nickel complexes were reported at about the same time by Bouwman, et al., with a synthesis that involved the reaction of *t*-butyl–protected thiosalicylal-

Downloaded At: 12:16 15 January 2011



(a) (b)

FIGURE 1. Reactions leading to and ORTEP drawings of (a) **1** and (b) **2** showing the 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

dehyde with the appropriate nickel starting material.[21] The complexes, as with many dimeric complexes of group 10 metals, feature edge-sharing, square-planar coordination spheres with a bend along the S-S axis of the bridging sulfur atoms. The dihedral angles between the two NS_3 planes are 72.7° and 74.6° for **1** and **2**, respectively. The bending of the dimer in **1** allows for a relatively close contact between a methylene hydrogen atom and the phenylthiolate sulfur atom of the ligand on the other nickel atom (dashed line in Figure 1a). The H-S distance of 2.71 Å is indicative of a weak bonding interaction between hydrogen and sulfur,[22] which is borne out by coupling of the methylene hydrogen to some of the phenyl hydrogens in the ^1H-^1H COSY spectrum.

REACTION OF DTDB WITH Ni(N-N-N)$_2$ COMPLEXES

Reaction of DTDB with nickel(II) complexes containing linear triamine ligands resulted in quite different products from those described above.[20] The nickel complexes of diethylenetriamine and 3,3′-diamino-N-methyldipropylamine clearly have two coordinated primary amines on each ligand that should be capable of engaging in a Schiff-base condensation with an aldehyde group. However, the products isolated from these reactions, tetraphenylborate salts of complexes **3** and **4** (Figure 2), were mononuclear complexes of the tetradenate N_3S ligands resulting from the condensation of one

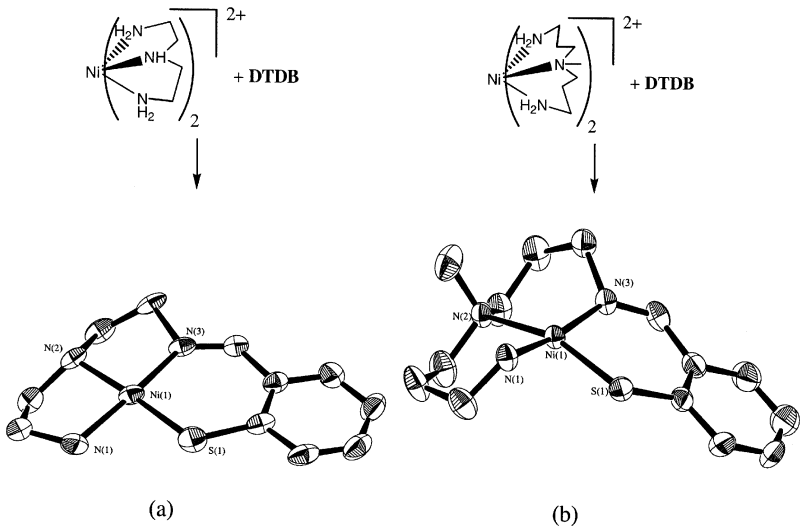


FIGURE 2. Reactions leading to and ORTEP drawings of the cations in (a) **3** and (b) **4** showing the 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Downloaded At: 12:16 15 January 2011

thiosalicylaldehyde equivalent on one side of the linear triamine, leaving the other primary amine unreacted. These were the first structurally characterized four-coordinate nickel complexes with N_3S coordination spheres provided by a single non-porphyrinic tetradentate ligand. At the same time, Bouwman, et al., reported the synthesis of **3** and the crystal structure of its chloride salt, again using a process involving a *t*-butyl–protected thiolate.[23] The structures of **3** and **4** are very similar, but show two significant differences. The first is the bond length between Ni and the middle nitrogen atom, N(2). In complex **4**, in which this is a tertiary amine nitrogen, the Ni-N bond length of 2.036 Å is $\approx$0.1 Å longer than the analogous bond length to the secondary amine nitrogen in **3**. In complex **3**, in which the Ni-N-N chelate rings contain five atoms, the nickel coordination geometry deviates very little from square planar, while complex **4**, with six-membered chelate rings (one boat configuration and one chair), deviates significantly more from a regular square-planar geometry. This deviation toward a tetrahedral geometry is evidenced in the electronic spectrum of complex **4**, which displays a band at 1022 nm that can be attributed to the pseudotetrahedral geometry.

Downloaded At: 12:16 15 January 2011

REACTION OF DTDB WITH METAL COMPLEXES OF ETHYLENEDIAMINE

In the first set of complexes described above, each ligand in the nickel starting materials has only one primary amine that could react with DTDB. In the second set of complexes, however, each triamine ligand has two primary amines that could react with DTDB, but only one reacts. This can be explained by the fact that nickel(II) is satisfied with four coordination, especially with a sulfur donor. In order to investigate the ability of DTDB to add two thiosalicylaldehyde equivalents to the same ligand, simple ethylenediamine metal complexes were combined with DTDB.[24] Reaction of $[Ni(en)_3]Cl_2$ with DTDB resulted in the isolation of golden crystals of **5**, [Ni(tsalen)] (Figure 3a). This complex has been previously synthesized by a process involving the *t*-butyl–protected tsalen ligand.[25] The reaction of DTDB with $[Cu(en)_2]Cl_2$ also results in the isolation of the [Cu(tsalen)] complex (**6**) in good yield (Figure 3b). Although this complex has also been known for years, it had never been crystallographically characterized, due in large part to the difficulty in accomplishing a clean deprotection of the *t*-butyl–protected ligand.[26] The crystal structure of **6** was somewhat surprising. Whereas **5** displays a relatively undistorted square-planar coordination geometry, the structure of **6** shows a significant deviation toward a tetrahedral geometry, with twist angles of 21° and 25° in the two independent molecules. This structural feature is interesting as it relates to the reduction potential of [Cu(tsalen)]. In 1975, Patterson and Holm published a paper discussing the reduction potentials of a number of copper(II) complexes demonstrating the general trend toward an increase in reduction potential as

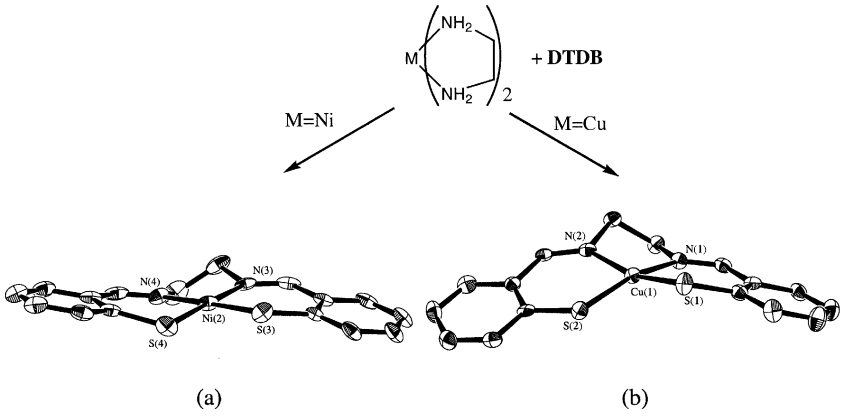


FIGURE 3. Reactions leading to and ORTEP drawings of (a) **5** and (b) **6** showing the 50% thermal ellipsoids. In both cases, one of the two independent molecules has been shown and hydrogen atoms have been omitted for clarity.

Downloaded At: 12:16 15 January 2011

the coordination geometry tends toward tetrahedral.[27] Included in this discussion were a few comparisons of compounds in which the only difference was the substitution of donor atoms. Two such comparisons were the N_2O_2 [Cu(salen)] with the N_2S_2 [Cu(tsalen)] and the N_2O_2 [Cu(acacen)] with the N_2S_2 [Cu(sacacen)]. In both cases, the N_2O_2 complexes had been crystallographically characterized and shown to have virtually planar coordination geometries while the N_2S_2 complexes had not been structurally characterized and were assumed to have planar geometries. The reduction potentials of the N_2S_2 complexes are ≈ 40 mV higher than for the N_2O_2 complexes, a phenomenon that was attributed to the change in donor atom. Our results demonstrate that the [Cu(tsalen)] complex does not, in fact, display undistorted square-planar geometry, a fact that must be considered in analyzing the elevated reduction potential. In fact, the crystal structure of [Cu(sacacen)] has also since been reported and it shows a similar 28.6° deviation from a square-planar geometry.[28]

Reaction of $[Fe(en)_3]Cl_3$ and $[Co(en)_3]Cl_3$ with DTDB results in different products from those seen in the nickel(II) and copper(II) systems. Instead of adding a thiosalicylaldehyde equivalent to each side of the ethylenediamine ligand, these systems return to the pattern seen with the linear triamine ligands—Schiff-base condensation at only one side with the second primary amine remaining unreacted. This produces the tridentate N_2S ligand aetsaln$^-$, two of which are bound to the Fe(III) or Co(III) in the isolated isostructural octahedral complexes. $[Fe(aetsaln)_2]^+$ (**7**) has been reported previously, synthesized by the reaction of $FeCl_3$, thiosalicylaldehyde, and ethylenediamine,[29] but $[Co(aetsaln)_2]$ (**8**)[30] has not appeared in the literature. Both complexes have an octahedral coordination geometry with each

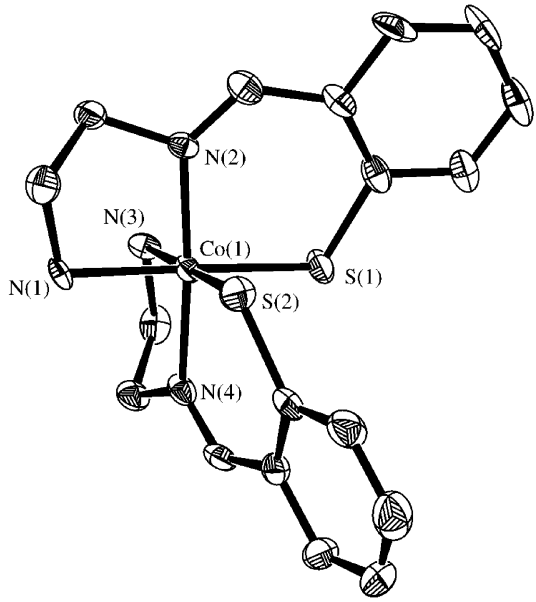


FIGURE 4. ORTEP drawing of the cation in **8** showing the 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Downloaded At: 12:16 15 January 2011

tridentate ligand binding in a meridional fashion (Figure 4). The two sulfur atoms are, therefore, *cis* to each other. Both complexes are low-spin, the cobalt complex being diamagnetic.

In order to ascertain the utility of the DTDB reaction in the presence of other functional groups, a reaction was carried out involving a nickel(II) complex of 2-hydroxy-1,3-diaminopropane.[30] The presence of the alcohol functionality on the ligand did not hamper the progress of the reaction, and the crystallized product, **9**, was found to be analogous to [Ni(tsalen)], with a thiosalicylaldehyde equivalent added to each side of the diamine ligand (Figure 5). Unlike [Ni(tsalen)], this complex has a significant distortion from square-planarity with a twist angle of 24°. It is not entirely obvious why this molecule displays such a large deviation from square planarity. The other structurally characterized Ni(II) complexes of related ligands with three-carbon backbones show coordination geometries much closer to square-planar, with twist angles ranging from 2.24° to 10.60°.[31]

MECHANISM OF THE DTDB REACTION

A detailed mechanistic study of this reaction has not been carried out, so it is only possible at this point to speculate on the mechanism of the reaction.

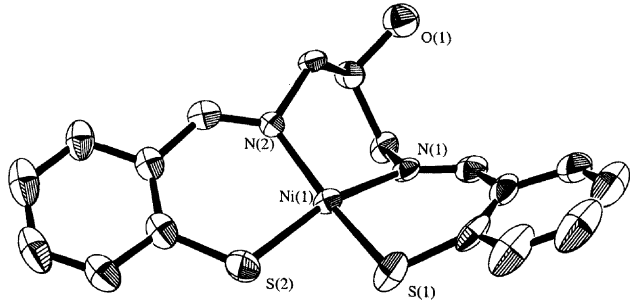


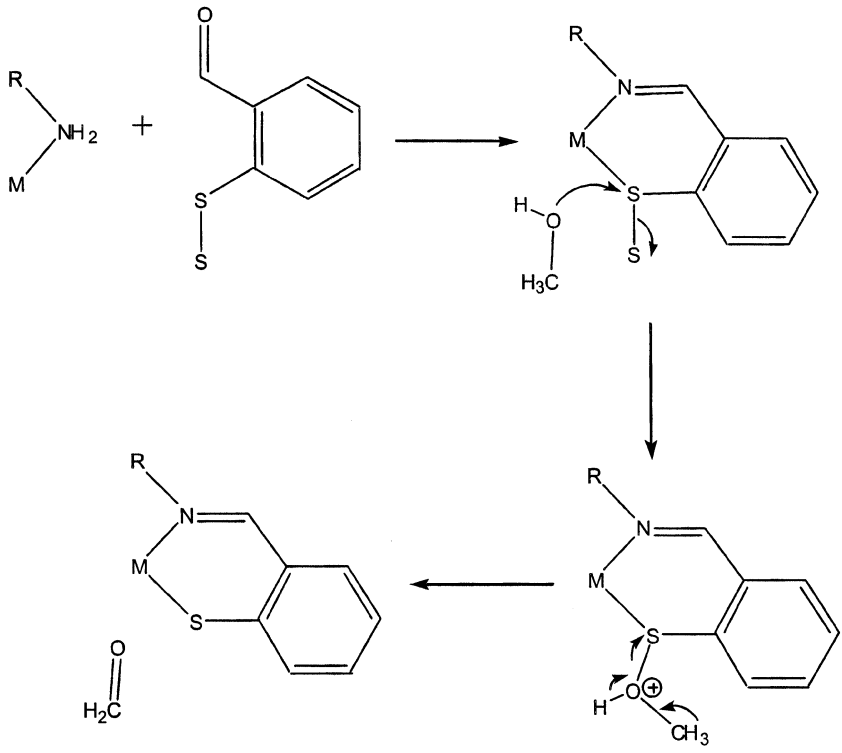
FIGURE 5. ORTEP drawing of **9** showing the 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Downloaded At: 12:16 15 January 2011

One possibility hearkens back to the work of Belluco and coworkers.[15] As mentioned above, reaction of $PdCl_4^{2-}$ with diphenyl disulfide in methanol resulted in the cleavage of the disulfide bond and formation of a polymeric species with bridging phenylthiolates. On the other hand, reaction of $Pd(CH_3CN)_2Cl_2$ with diphenyldisulfide in benzene resulted in the isolation of a dimeric species containing intact diphenyldisulfide ligands. Subsequent refluxing of this latter compound in methanol led to the isolation of the same polymeric species as in the first reaction. The authors propose a mechanism for the disulfide bond cleavage that involves formation of an intermediate complex with the coordinated disulfide followed by nucleophilic attack of CH_3OH on the sulfur atom. A similar mechanism is supported in the DTDB reactions by the fact that no reaction is evident when carried out in non-alcoholic solvents, such as DMF and acetonitrile. In addition, although the reaction occurs in ethanol, it proceeds at a slower rate than in methanol. Thus, a possible mechanism (Scheme 2) is initial formation of a Schiff base by condensation of the aldehyde moiety with a coordinated primary amine, with coordination of the disulfide to the metal atom. This is followed by nucleophilic attack of the methanol solvent on the activated sulfur atom and fission of the S-S bond.

OXIDATION OF THE TSALEN LIGAND BY $FeCl_3$

Whereas the tsalen ligand was synthesized in the above reactions by reductive cleavage of a disulfide bond, an unexpected oxidation of the coordinated tsalen ligand was realized by treatment of [Ni(tsalen)] with $FeCl_3$.[32] This reaction was carried out in the hopes of isolating a complex containing nickel(II) and iron(III) bridged by sulfur atoms, which would be interesting in terms of its relationship to the active sites of the nickel-iron hydrogenase enzymes. Instead, an unusual product (**10**) was isolated, which, when



SCHEME 2. Possible mechanism of DTDB reaction.

Downloaded At: 12:16 15 January 2011

characterized crystallographically, was shown to contain four molecules of [Ni(tsalen)], two $FeCl_4^-$ anions, and the 1,2-bis(1,2-benzisothiazol-2-yl)ethane dication ($BBITE^{2+}$). The cation derives from a four-electron oxidation of the $tsalen^{2-}$ ligand with decomplexation of the ligand and ring closure by formation of an S-N bond. The overall structure of the isolated crystalline material (Figure 6) shows the four [Ni(tsalen)] molecules forming a channel into which the $BBITE^{2+}$ is inserted. Apparent π-π interactions between the phenyl rings on the $BBITE^{2+}$ and the phenyl rings on the [Ni(tsalen)] molecules seem to be involved in organizing this structure.

CONCLUSION

The reaction of DTDB with metal complexes containing coordinated primary amines is a convenient method for incorporating thiolate donation into the coordination sphere of a metal ion. DTDB is easily synthesized in multigram quantities and can be conveniently stored and accessed without need for

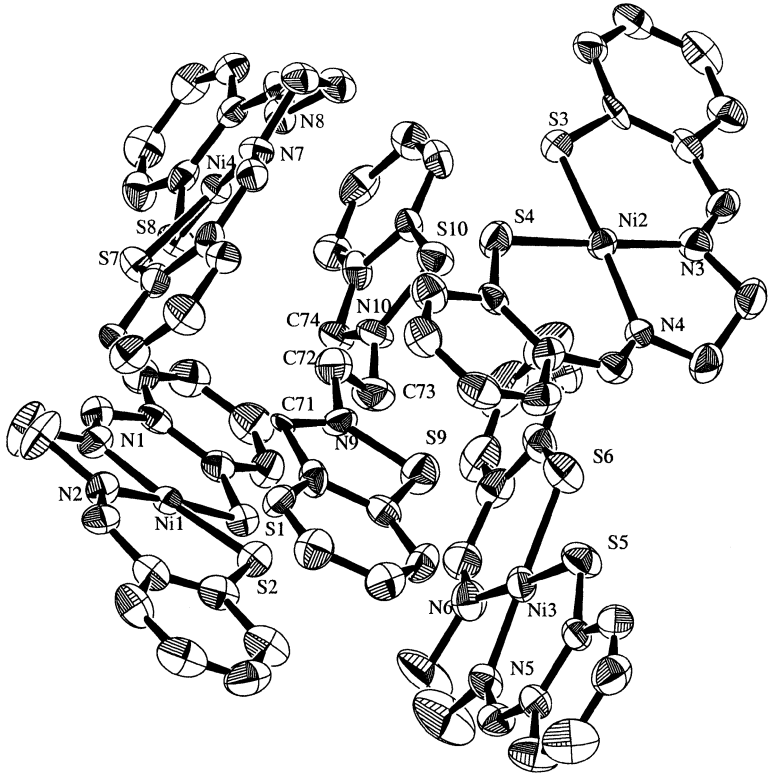


FIGURE 6. ORTEP drawing of the $[Ni(tsalen)]_4BBITE^{2+}$ unit in **10**. Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms have been omitted for clarity.

Downloaded At: 12:16 15 January 2011

an inert atmosphere. The reaction is capable of producing a variety of Schiff base/thiolate ligands, depending on the identity of the ligands in the metal starting material. Ligands with NS_2, N_3S, N_2S_2 and N_2S donor sets have been synthesized and the reaction has been shown to proceed with nickel(II), copper(II), iron(III) and cobalt(III). This and related reactions have the potential to be very useful in allowing access to thiolate coordination without the need for cumbersome protection and deprotection steps for the generally air-sensitive thiol moiety.

ACKNOWLEDGMENTS

The research reported herein was supported by the National Science Foundation (Grant EPS-9550), the American Chemical Society—Petroleum

Research Fund (Grant 35214-G3), and by the Kansas EPA-EPSCoR program through a grant from the U.S. Environmental Protection Agency and Kansas Technology Enterprise Corporation.

REFERENCES

1. see Carter, C. W. 1977. In *Iron-Sulfur Proteins*, W. Lovenberg, ed., New York: Academic Press, 157.
2. Colman, P. M., Freeman, H. C., Guss, J. M., Murata, M., Norris, V. A., Ramshaw, J. A. M., Venkatappa, M. P. 1978. *Nature* 272, 319.
3. (a)Volbeda, A., Charon, M. H., Piras, C., Hatchikian, E. C., Frey, M., Fontecilla-Camps, J. C. 1995. *Nature* 373, 580. (b) Volbeda, A., Garcin, E., Piras, C., de Lacey, A. L., Fernandez, V. M., Hatchikian, E. C., Frey, M. Fontecilla-Camps, J. C. 1996. *J. Am. Chem. Soc*. 118, 12989.
4. (a) Nicolet, Y., Piras, C., Legrand, P., Hatchikian, E. C., Fontecilla-Campus, J. C. 1999. *Structure* 7, 13. (b) Peters, J. W., Lanzilotta, W. N., Lemon, B. J., Seefeldt, L. C. 1998. *Science* 282, 1853.
5. (a) Eklund, H., Nordstrom, B., Zeppezauer, E., Soderlund, G., Ohlsson, I., Bowie, T., Soderberg, B.-O., Tapia, O., Branden, C.-I., Akeson, A. 1976. *J. Mol. Biol.* 102, 27. (b) Cedergren-Zeppezauer, E. 1983. *Biochemistry* 22, 5761. (c) Eklund, H., Plapp, B. V., Samama, J.-P., Branden, C.-I. 1982. *J. Biol. Chem.* 257, 14349. (d) Eklund, H., Samara, J.-P., Jones, T. A. 1984. *Biochemistry* 23, 5982.
6. (a) Hille, R. 1997. *J. Biol. Inorg. Chem.* 2, 804. (b) Fischer, B., Enemark, J. H., Basu, P. 1998. *J. Inorg. Biochem.* 72, 13. (c) Rajagopalan, K. V. 1991. *Adv. Enzymol. Relat. Areas Mol. Biol.* 64, 215. (d) Rajagopalan, K. V., Johnson, J. L. 1992. *J. Biol. Chem.* 267, 10199.
7. (a) Huang, W., Jia, J., Cummings, J., Nelson, M., Schneider G., Lindovist, Y. 1997. *Structure* 5, 691. (b) Nagashima, S., Nakasako, M., Dohmae, N., Tsujimura, M., Takio, K., Odaka, M., Yohda, M., Kamiya, N., Endo, I. 1998. *Nat. Struct. Biol.* 5, 347.
8. (a) Nagasawa, T., Takeuchi, K., Yamada, H. 1988. *Biochem. Biophys. Res. Comm.* 155, 1008–1016 (b) Nagasawa, T., Takeuchi, K., Yamada, H. 1991. *Eur. J. Biochem.* 196, 581–589. (c) Brennan, B. A., Alms G., Nelson, M. J., Durney, L. T., Scarrow, R. C. 1996. *J. Am. Chem. Soc.* 118, 9194. (d) Payne, M. S., Wu, S., Fallon, R. D., Tudor, G., Stieglitz, B., Turner, Jr., I. M., Nelson, M. J. 1997. *Biochemistry* 36, 5447.
9. Dobbek, H., Svetlitchnyi, V., Gremer, L., Huber, R., Meyer, O. 2001. *Science* 293, 1281.
10. see Holm, R. H. and Ibers, J. A. 1977. In *Iron-Sulfur Proteins*, W. Lovenberg, ed., Academic Press, 205.
11. abbreviations used in this paper: H_2salen:N,N′-ethylenebis(salicylideneimine); H_2tsalen: N,N′-ethylenebis(thiosalicylideneimine); DTDB:2,2′-dithiodibenzaldehyde; en:ethylenediamine; H_2acacen:N,N′-ethylenebis(acetylacetonimine); H_2sacacen:N,N′-ethylenebis (thioacetylacetonimine); Haetsaln:2-[(2-aminoethyl)imino]methyl]benzenethiol; DMF: N,N-dimethylformamide
12. Cambridge Crystallographic Database, v. 2.54, 2002 (Cambridge Crystallographic Data Centre).
13. Kasmai, H. S., Mischke, S. G. 1989. *Synthesis* 763.
14. Warner, L. G., Ottersen, T., Seff, K. 1974. *Inorg. Chem.* 13, 2529.
15. Bosci, T., Crociani B., Toniolo, L., Belluco, U. 1970. *Inorg. Chem.* 9, 532.
16. Livingstone, S. E., Nolan, J. D. 1973. *Aust. J. Chem.* 26, 961.
17. Kadooka, M. M., Warner L. G., Seff, K. 1976. *J. Am. Chem. Soc.* 98, 7569.

Downloaded At: 12:16 15 January 2011

18. Kita, M., Yamanari, K., Shimura, Y. 1989. *Bull. Chem. Soc. Jpn.* 62, 3081.
19. Nakayama, H., Prout, K., Hill, H. A. O., Datta, D. 1999. *J. Chem. Soc., Chem. Commun.* 695.
20. Goswami, N., Eichhorn, D. M. 1999. *Inorg. Chem.* 38, 4329.
21. Bouwman, E., Henderson, R. K., Powell, A. K., Reedijk, J., Smeets, W. J. J., Spek, A. L., Veldman, N., Wocadlo, S. 1998. *J. Chem. Soc., Dalton Trans.* 1245.
22. (a) Shoner, S. C., Olmstead, M. M., Kovacs, J. A. 1994. *Inorg. Chem.* 33, 7. (b) Kruger, H.-J., Peng, G., Holm, R. H. 1991. *Inorg. Chem.* 30, 734.
23. Bouwman, E., Henderson, R. K., Reedijk, J., Veldman, N., Spek, A. L. 1999. *Inorg. Chim. Acta* 287, 105.
24. Goswami, N., Eichhorn, D. M. 2000. *Inorg. Chim Acta* 303, 272.
25. Yamamura, T., Tadokoro, M., Tanaka, K., Kuroda, R. 1993. *Bull. Chem. Soc. Jpn.* 66, 1984.
26. (a) Nation, D. A., Reibenspies, J. H., Taylor, M. R., Wainwright K. P. 1997. *Inorg. Chim. Acta.* 258, 161. (b) Corrigan, M. F., Murray, K. S., West, B. O. 1977. *Aust. J. Chem.* 30, 2455.
27. Patterson, G. S., Holm, R. H. 1975. *Bioinorg. Chem.* 4, 257.
28. Cini, R., Cinquantini, A., Orioli, P., Sabat, M. 1980. *Cryst. Struct. Commun.* 9, 865.
29. (a) Marini, P. J., Murray, K. S., West, B. O. 1983. *J. Chem. Soc., Dalton Trans.* 143. (b) Fallon, G. D., Gatehouse, B. M. 1975. *J. Chem. Soc., Dalton Trans* 1344.
30. Goswami, N., Eichhorn, D. M. unpublished work.
31. (a) Gomes, L., Pereira, E., de Castro, B. 1999. *Acta Crstallogr., Soct. C: Cryst. Struct. Commun.* 55, 1061. (b) Christensen, A., Jensen, H. S., McKee, V., McKenzie, C. J., Munch, M. 1997. *Inorg. Chem.* 36, 6080.
32. Goswami, N., Van Stipdonk, M. J., Eichhorn, D. M. 2003. *Inorg. Chem. Commun.* 6, 86.

Downloaded At: 12:16 15 January 2011