A Square-planar NiS₄ Unit with an Aliphatic Thiolato–Thioether Donor Set: a Carbon Monoxide Dehydrogenase Model that Binds CO

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Ni⁺–CO was generated by using a newly prepared square-planar nickel compound with an aliphatic thiolato–thioether sulfur ligand, with relevance to the nickel centre of carbon monoxide dehydrogenase.

In the modelling of the metal sites of metallo-enzymes, aliphatic thiolate and thioether ligands conform more strictly to the metal–sulfur centres in proteins than other types of sulfur ligands, corresponding to the cysteinate and methionyl residues in proteins. The chemistry of mononuclear nickel with such ligands is concerned with the active centres of CO dehydrogenase (CODH) and hydrogenase (H₂-ase).[1] The so-called NiFe complex of Clostridium thermoaceticum CODH catalyses the synthesis of acetyl-CoA from CO, Me (bound to the corrinoid/iron–sulfur protein[2]) and coenzyme A.[3–5] The nickel adopts NiS₄[6] or NiS₂(O)₂[7] mononuclear coordination with distorted square-planar or pyramidal geometry, linked with an iron–sulfur cluster.[4] However, the exact site for CO binding (Fe or Ni) and the valence state of the metal ion are not yet known. The reduced state of the biological[8] and abiological[9] iron–sulfur cluster, Fe₄S₄⁺, is known to interact with CO. Low-valent nickel complexes with π-acid ligands, as well as the nickel in H₂-ase,[10] are well known to form Ni–CO. In model chemistry, however, examples of Ni–CO for NiS₄, NiS₂N(O)₂ or other types of nickel complexes with thiolato and thioether ligands are limited,[11] because of the instability of the low-valent nickel complexes.[12–14] We now report the synthesis and structure of a square-planar NiS₄ compound which, surrounded by a thiolato–thioether ligand, generates Ni–CO when reduced.
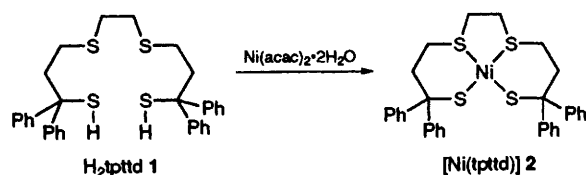
In order to stabilize the reduced state of such a nickel unit, and thereby to discuss the ability for Ni–CO bond formation, we introduced bulky groups near the thiolato-sulfur atoms of the 1,5,8,12-tetrathiadodecane ligand (Scheme 1). The bulky groups were expected to protect the anionic thiolato-sulfur atoms and the reduced nickel from oxidants in solutions. For this purpose, 2,2,11,11-tetraphenyl-1,5,8,12-tetrathia-dodecane, H₂tpttd 1,† was prepared by use of the sulfhydryl protection method with pyran.[15] Compound 1 was treated with Ni(acac)₂·2H₂O (Hacac = pentane-2,4-dione) in toluene to give [Ni(tpttd)] 2† (Scheme 1). Complex 2 was recrystal-lized from 1,1,2-trichloroethane–ether as dark violet needles.

As seen in Fig. 1, the X-ray crystallographic results‡ show that 2 adopts a square-planar NiS₄ coordination. The deviations of Ni, S(1), S(2), S(3) and S(4) from the least-squares plane are −0.015(1), +0.265(2), −0.255(2), +0.269(2) and −0.264(2) Å, respectively; hence, the NiS₄ core is slightly

H₂tpttd 1   [Ni(tpttd)] 2

Scheme 1

distorted from square planar. Not only the thiolato-sulfur atoms, but also the axial positions of the nickel, are covered by the benzene rings at least in the solid state. The distances between the nickel and the ring protons are about 3.3 Å.

Electrochemical reduction of 2 was examined in several organic solvents in order to study the stability of the reduced state. Fig. 2 shows the comparison of the cyclic voltammograms (CV) of 2 and [Ni(ttu)] 3[14] in acetonitrile in the
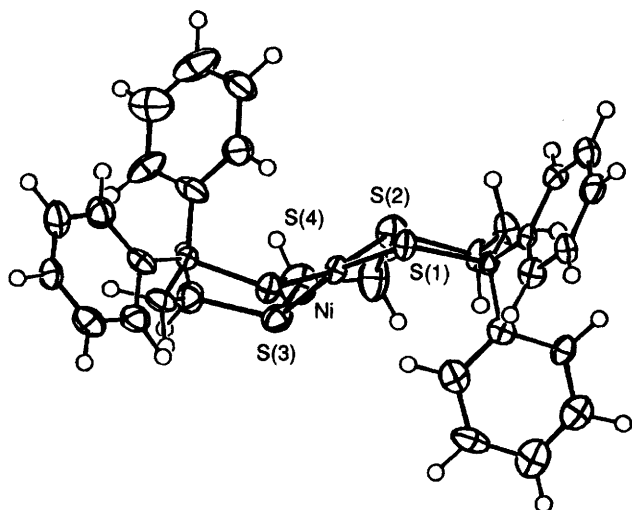

Fig. 1 Structure of complex 2 with 50% thermal ellipsoids. Selected bond distances (Å) and bond angles (°): S(1)–Ni, 2.199(3); S(2)–Ni, 2.159(3); S(3)–Ni, 2.156(3); S(4)–Ni, 2.207(3); S(1)–Ni–S(2), 94.8(1); S(1)–Ni–S(3), 164.8(1); S(1)–Ni–S(4), 86.6(1); S(2)–Ni–S(3), 89.9(1); S(2)–Ni–S(4), 167.1(1); S(3)–Ni–S(4), 91.9(1).
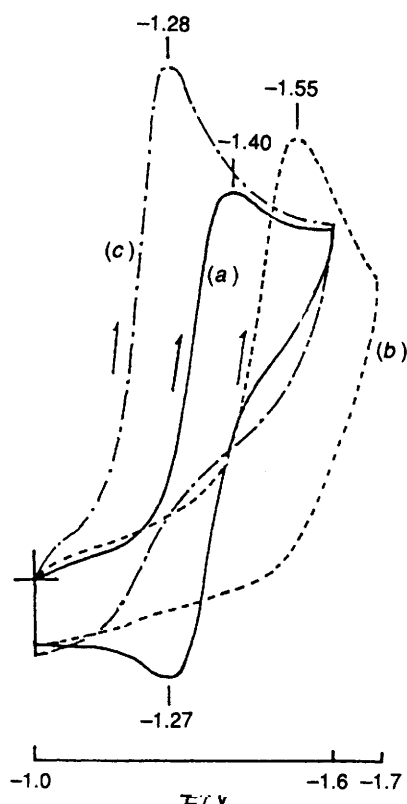
potential region of the Ni^{2+}/Ni^{+} redox couple for the neutral bis(thiolato)nickel core.[14,16] Complex 3 possesses a thiolato–thioether square-planar NiS_4 unit also, but no bulky groups near the sulfur atoms.§ Both 2 and 3 show reduction waves (Fig. 2); however, in comparison with the irreversible behaviour of 3, 2 gives a reversible CV wave (E_{cp} = −1.40 V, E_{ap} = −1.27 V), and so it achieves a fairly stable reduced state, as we expected. However, this reversibility is lost under a carbon monoxide atmosphere, where only the reduction wave is observed at −1.28 V with a slight current increase. This positive shift and the current increase of the reduction wave suggest that the electrode process is accompanied by the reaction[17] in eqn. (1).

$$[Ni(tpttd)] \overset{e^-}{\longleftrightarrow} [Ni(tpttd)]^- + \overset{CO}{\longleftrightarrow} [Ni(tpttd)(CO)]^- \quad (1)$$
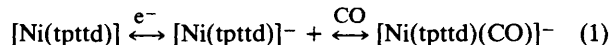
Although [Ni(tpttd)]⁻ seemed stable on the electrode, it was not stable to chemical reduction. The addition of sodium acenaphthylenide to 2 caused quenching of the absorption maxima at 476 nm (ε 697 mol^{-1} dm^3 cm^{-1}) and 573 (ε 464) even in strictly purified dimethylacetamide (well dried and treated with sodium acenaphthylenide prior to use). The rate of this decomposition was suppressed under CO, not completely but partially, suggesting that CO increases the stability of the reduced species. Fig. 3 shows the v_{CO} region of the IR spectrum of 2, as well as that obtained by drying the reduced solution of 2 under CO. The band at 1940 cm^{-1} of the latter is characteristic of CO ligated to a metal ion. Therefore, it can be said that [Ni(tpttd)]⁻ generates an Ni–CO binding species. This Ni–CO compound was paramagnetic in contrast to 2 (from NMR).

[Ni(tpttd)] 2 still lacks the minimum conditions for modelling of the NiFe complex in CODH, in that the nickel is not linked with an iron–sulfur cluster, and that the Ni^{2+}/Ni^{+} redox
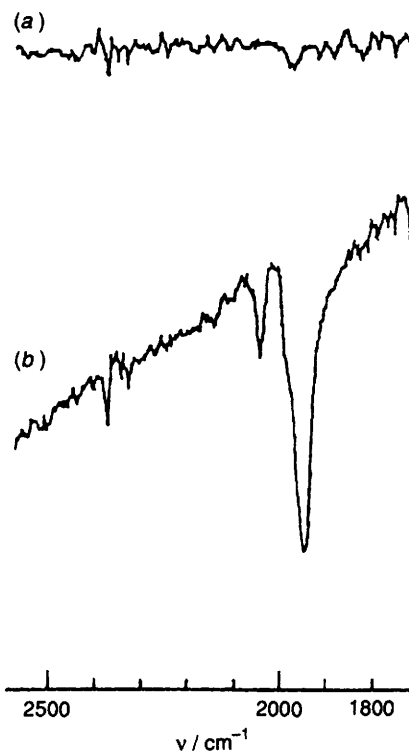

Fig. 2 Electrochemical measurements, performed with a glassy carbon electrode (working), a Pt wire (auxiliary), and an Ag/AgCl reference electrode. Comparison of the CV for Ni^{2+}/Ni^{+} redox couples: (a) [Ni(tpttd)] under argon; (b) [Ni(ttu)] under argon; (c) [Ni(tpttd)] under CO.
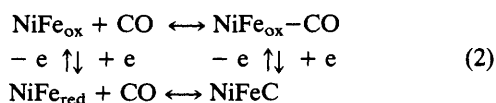

Fig. 3 IR spectra of (a) [Ni(tpttd)] and (b) its reduced species under CO atmosphere {probably [Ni(tpttd)(CO)]⁻}, as KBr pellets

§ H_2ttu = 1,4,8,11-tetrathiaundecane. Although the skeletons of [Ni(tpttd)] 2 and Ni(ttu) are not exactly the same, they are similar, both being linear tetrathia alkanes, and hence are expected to be comparable.

potential (-1.34 V *vs.* Ag$^+$/Ag) is far lower than that of *C. thermoaceticum* (-541 mV *vs.* normal hydrogen electrode).[18] Satisfaction of these conditions will no doubt change the behaviour of the nickel and iron–sulfur cluster. However, our result does indicate the potential of the square-planar NiS$_4$ unit as the CO binding site of CODH.

Shin and Lindahl proposed eqn. (2) for the NiFe complex.[5]

$$NiFe_{ox} + CO \longleftrightarrow NiFe_{ox}-CO$$
$$-e \uparrow\downarrow +e \qquad -e \uparrow\downarrow +e \qquad (2)$$
$$NiFe_{red} + CO \longleftrightarrow NiFeC$$

Considering the magnetic properties of [Ni(tpttd)], its Ni–CO species, NiFe$_{ox}$, and NiFeC ($S = 0$, paramagnetic, $S = 0$,[5] $S = 1/2$,[5] respectively), and ignoring the difference in the linkage to the iron–sulfur cluster between the synthetic and natural systems, it might be possible to assign [Ni(tpttd)]$^-$ and its Ni–CO species probably [Ni(tpttd)(CO)]$^-$ to NiFe$_{red}$ and NiFeC in eqn. (2). However, this correspondence conflicts with the Shin and Lindahl's proposal which assumes NiFe$_{ox}$–CO as the intermediate.

Finally, cyclic voltammetry of [Ni(tpttd)] under carbon dioxide showed a strong increase of the irreversible cathodic wave. This result indicates the catalytic reduction of CO$_2$ by [Ni(tpttd)]. The activity of [Ni(tpttd)]$^-$ for such reaction may be related to the reversible CO$\longleftrightarrow$CO$_2$ reaction in CODH.[5]

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References

1 *The Bioinorganic Chemistry of Nickel*, ed. J. R. Lancaster, Jr., VCH, New York, 1988.
2 W.-P. Lu, S. R. Harder and S. W. Ragsdale, *J. Biol. Chem.*, 1990, **265**, 3124.
3 S. W. Ragsdale, H. G. Wood and E. Antholine, *Proc. Natl. Acad. Sci. USA*, 1985, **82**, 6811; E. Pezacka and H. G. Wood, *J. Biol. Chem.*, 1986, **261**, 1609; D. G. Grahame, *J. Biol. Chem.*, 1991, **261**, 22227.
4 P. A. Lindahl, E. Munck and S. W. Ragsdale, *J. Biol. Chem.*, 1990, **265**, 3873; P. A. Lindahl, S. W. Ragsdale and E. Munck, *J. Biol. Chem.*, 1990, **265**, 3880.
5 W. Shin and P. A. Lindahl, *J. Am. Chem. Soc.*, 1992, **114**, 9718; *Biochemistry*, 1992, **31**, 12870; *Biochem. Biophys. Acta*, 1993, **1161**, 317.
6 N. R. Bastian, G. Diekert, E. C. Niederhoffer, B-K. Teo, C. T. Walsh and W. H. Orme-Johnson, *J. Am. Chem. Soc.*, 1988, **110**, 5581.
7 S. P. Cramer, M. K. Eidsness, W.-H. Pan, T. A. Morton, S. W. Ragsdale, D. V. DerVartanian, L. G. Ljungdahl and R. A. Scott, *Inorg. Chem.*, 1987, **26**, 2477.
8 M. W. W. Adams, *J. Biol. Chem.*, 1987, **262**, 15054.
9 R. S. McMillan, J. Renaud, J. G. Reynolds and R. H. Holm, *J. Inorg. Biochem.*, 1979, **11**, 213.
10 G. Fauque, H. D. Peck, Jr., J. J. G. Moura, B. H. Huynh, Y. Berliel, D. V. DerVartanian, L. G. Ljungdahl and R. A. Scott, *FEMS Microbiol. Rev.*, 1988, **54**, 299.
11 P. Stavropoulos, M. Carrie, M. C. Muetterties and R. H. Holm, *J. Am. Chem. Soc.*, 1990, **112**, 5385.
12 T. Yamamura, H. Kurihara and R. Kuroda, *Chem. Lett.*, 1990, 101; T. Yamamura, H. Arai, H. Kurihara and R. Kuroda, *Chem. Lett.*, 1990, 1975; S. Fox, Y. Wang, A. Silver and M. Millar, *J. Am. Chem. Soc.*, 1990, **112**, 3218.
13 W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 4694; P. H. Davis, L. K. White and R. L. Belford, *Inorg. Chem.*, 1975, **14**, 1753; J. M. Desper, S. H. Gellman, R. E. Wolf, Jr., and S. R. Cooper, *J. Am. Chem. Soc.*, 1991, **113**, 8663.
14 T. Yamamura, H. Arai, N. Nakamura and H. Miyamae, *Chem. Lett.*, 1990, 212.
15 J. M. Berg and R. H. Holm, *J. Am. Chem. Soc.*, 1985, **107**, 917.
16 A. L. Balch, F. Rohrscheid and R. H. Holm, *J. Am. Chem. Soc.*, 1965, **87**, 2301; H.-J. Cruger and R. H. Holm, *Inorg. Chem.*, 1989, **28**, 1148; T. Yamamura, M. Tadokoro, K. Tanaka and R. Kuroda, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1.
17 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
18 C. M. Gorst and S. W. Ragsdale, *J. Biol. Chem.*, 1991, **266**, 20687.