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Synthesis and the Structure of Bis(tetraphenylphosphonium) [Ni(1,2-*trans*-dimercaptocyclohexane)$_2$]. A New Addition to the Ni^{3+} Generating Thiolato Nickel Complexes

Takeshi YAMAMURA,* Hiroki ARAI, Hiroaki KURIHARA, and Reiko KURODA†
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162
†Department of Chemistry, Faculty of Science and Art, The University of Tokyo, Komaba, Meguro-ku, Tokyo 256

1,2-*trans*-Dimercaptocyclohexane and $NiCl_2 \cdot 6H_2O$ reacted in aqueous alkaline solution to give [Ni(1,2-*trans*-dimercaptocyclohexane)$_2$]$^{2-}$, which generated Ni^{3+} in a reversible manner on electrodes. X-ray crystallography has shown that the coordination unit of this compound is NiS_4 square planar. Ni K-edge XANES spectrum of this compound, which was almost superimposable to that of [Ni(SCH_2-CH_2S)$_2$]$^{2-}$, was similar to those of Ni atoms in hydrogenases and CO-dehydrogenases.

In a recent paper, we have shown that [Ni(edt)$_2$]$^{2-}$ (H_2edt = 1,2-dimercaptoethane or 1,2-ethanedithiole), a member of [Ni(SR)$_4$]$^{2-}$ (RS^-; alkane-thiolate), adopts a square planar NiS_4 geometry as its coordination unit.[1] From the resemblance of its Ni K-edge XANES spectrum to those of hydrogenases[2] (and CO-dehydrogenases[3]), as well as the low spin feature[4] and the low Ni^{3+}/Ni^{2+} oxidation potential (-0.7 V vs. SCE),[4,5] [Ni(edt)$_2$]$^{2-}$ was considered mimicing the coordination environment of the nickel in hydrogenases. However, the Ni^{3+} species generated from [Ni(edt)$_2$]$^{2-}$ was not stable.[1] More recently Millar has presented [Ni(ndt)$_2$]$^{2-}$ (H_2ndt = bicyclo[2.2.1]heptane-*exo*-*cis*-2,3-dithiol or 1,2-*cis*-norbornanedithiole; abbreviated as S_2-norbornane in the literature[6]) as generating Ni^{3+} in a reversible manner.

We report here the synthesis, structural study (X-ray and XAFS analyses) and the redox behavior of [Ni(cdt)$_2$]$^{2-}$ (H_2cdt = 1,2-*trans*-dimercaptocyclohexane or 1,2-*trans*-cyclohexanedithiole[7]). This also generates Ni^{3+} reversibly on electrodes. The new ligand is of *trans*-ethanedithiole type differently from the *cis* structure of H_2ndt.

0.27 g (4.1 mmol) of KOH and 0.3 g (2.0 mmol) of 1,2-*trans*-cyclohexanedithiol were dissolved into a 20 ml of water, to which was added slowly the aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.24 g; 1.0 mmol) and tetraphenylphosphonium chloride (0.76 g; 2.1 mmol). The resulting mixture was passed through a glass frit to remove the insoluble tarry material (red brown color). Standing the greenish filtrate at room temperature we obtained the block crystals of the purpose compound (yield; 200 mg (18%), reddish brown). UV-vis. (DMF[8]) 482 nm (ε326), 652 nm (sh, 154). Calcd. for $C_{60}H_{64}O_2P_2S_4Ni$ or $(PPh_4)_2[Ni(cdt)_2]$: C 67.60; H 6.05%. Found: C 67.84; H 5.86% (the sample was dried in vacuo at 40 deg. prior to the analysis). ^{1}H-NMR (DMSO-d_6) δ=1.666, 1.363, 1.951 (10H, cyclohexane).

The molecular structure of $[Ni(cdt)_2]^{2-}$ by X-ray analysis and the significant molecular parameters are presented in Fig. 1.[9] The Ni complex resides on an inversion center, thus the coordination geometry is exactly square planar. The ligand is disordered, and the two ligands of opposite handedness are related by a pseudo mirror plane going through $NiS_1S_2C_3C_6$. Only the structure belonging one handedness is shown in the figure. The mean Ni-S distance of $[Ni(cdt)_2]^{2-}$ is 2.192 Å. This is close to 2.195 Å of $[Ni(edt)_2]^{2-}$, and longer than 2.184 Å of $[Ni(ndt)_2]^{2-}$. Similarly, S-S bite distances for $[Ni(cdt)_2]^{2-}$ and $[Ni(edt)_2]^{2-}$, 3.140 and 3.139 Å[10] respectively, are longer than that (3.092 Å) of $[Ni(ndt)_2]^{2-}$.[6] These results would be explained by the difference in configuration for the two adjacent sulfur atoms on the ligands. In $[Ni(ndt)_2]^{2-}$, the sulfur

$Ni-S_1$, 2.187(3) Å
$Ni-S_2$, 2.196(3)
S_1-C_1, 1.88(3)
S_2-C_2, 1.83(2)
C_1-C_2, 1.57(3)
S_1-Ni-S_2, 91.5(1) deg.
$S_1-Ni-S_2^*$, 88.5(1)

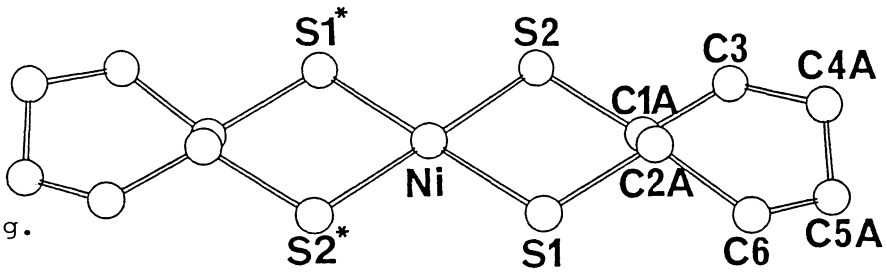

Fig. 1. ORTEP drawing of $[Ni(cdt)_2]^{2-}$ and the important bond lengths and bond angles.

atoms are in *cis* position,[6,11] whereas in $[Ni(cdt)_2]^{2-}$ they are in *trans* position.[7] As for $[Ni(edt)_2]^{2-}$, we could not decide the configuration because of disorder,[1] however, this is also expected to take *trans* configuration. It may be that the contraction of the central coordination unit in $[Ni(ndt)_2]^{2-}$, manifested in short S-S bite and Ni-S distances, is the result of the *cis* configuration, which promotes the electron delocali-

zation over NiSCCS five membered ring. If this is true, it is expected that $[Ni(ndt)_2]^{2-}$ is more stable than $[Ni(edt)_2]^{2-}$ and $[Ni(cdt)_2]^{2-}$ in some stages on reactivity. In fact, $[Ni(cdt)_2]^{2-}$ was converted to $[Ni_2(cdt)_3]^{2-}$ by the presence of H^+, as $[Ni(edt)_2]^{2-}$ was.[12] This is in contrast to the robust feature of $[Ni(ndt)_2]^{2-}$.[6]

The site geometry of Ni in hydrogenases has been considered to be distorted pseudo-octahedron on the basis of EPR measurements.[13] Eidsness has supported this for *D.gigas* hydrogenase because of the absence of 1s→4p absorption in Ni K-edge XANES spectra.[14] However, in our study, the shape resonances[15] of the XANES spectra published for *D. gigas* hydrogenase situates clearly in the square planar area of the "energy/peak hight" plottings involving 30 compounds within which are 10 Ni/S cases (the back scatterers of the nickel in hydrogenase are 3 - 4 sulfurs[2,3,16]).

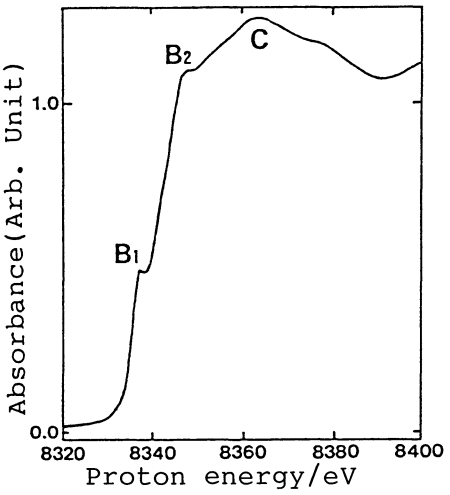

Fig. 2. XANES Spectrum of $[Ni(cdt)_2]^{2-}$.

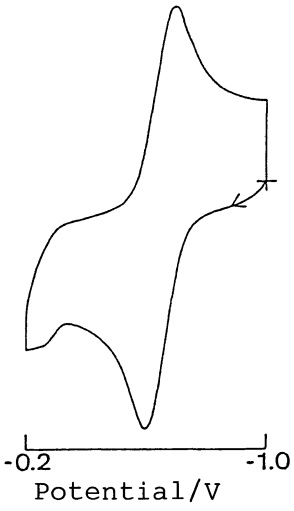

Fig. 3. Cyclic voltammogram of $[Ni(cdt)_2]^{2-}$ in DMF.

$[Ni(cdt)_2]^{2-}$ provides a Ni K-edge XANES spectrum[17] typical to a square planar geometry(peak; B1, B2, C). It was superimposed well to that of $[Ni(edt)_2]^{2-}$ (Fig. 2). The energy position (8360 eV) and the hight of the shape resonance (peak C in Fig. 2) relative to the normalization point, which was taken on the background curve of the EXAFS at 8390 eV, was just the same as those of the XANES spectra reported for *D. gigas* hydrogenase and *C. thermoaceticum* CO-dehydrogenase.[14]

$[Ni(cdt)_2]^{2-}$ is reversibly oxidized to a Ni^{3+} species on electrodes (platinum and glassy carbon, in DMF, vs. Ag^+/Ag). The cyclic voltammogram (Fig. 3) shows $E_{1/2}(Ni^{3+}/Ni^{2+})$ at -0.65 V. This value is slightly shifted toward positive side in comparison with -0.72 V[18] of $[Ni(ndt)_2]^{2-}$. In contrast to the case of $[Ni(ndt)_2]^{2-}$, which resists to air oxidation, $[Ni(cdt)]^{2-}$ was oxidized to decompose when exposed to air in DMF and the color changed from red-brown to golden-yellow. This fragility of $[Ni(cdt)_2]^{2-}$ or the robustness of $[Ni(ndt)_2]^{2-}$,[6] probably depends on the absence or the presence of the cap for the Ni atom, that is to say, in the latter compound Ni is protected by the methylene groups of the two

norbornanes.

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8)$[Ni(cdt)_2]^{2-}$ decomposes spontaneously even in a strictly dried DMF probably due to the water involved in the crystals.
9)Crystallographic data for $(PPh_4)_2[Ni(cdt)_2]$: F.W.=1102.08, monoclinic $P2_1/c$, Mo Kα(λ=0.71069 Å), a=11.788(3), b=13.841(2), c=18.236(2) Å, β=105.57(1) , V=2866.1(8) $Å^3$, Z=2, D_c=1.277 g cm^{-3}, μ(Mo Kα)=5.77 cm^{-1}. The structure was solved by direct method for total 6462 reflections (ω-2θ scan, $2\theta_{max}$=55.0° , 6140 unique). The final cycle of full-matrix least squares refinement was based on 1914 observed reflections (I>3.00 σ(I)) and 198 variables. R=0.074 (R_w=0.081) for all non-hydrogen atoms.
10)In paper 1), we have misreported the S-S bite distance of $[Ni(edt)_2]^{2-}$ as 3.09 Å on an erroneous calculation.
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12)$[Ni_2(cdt)_3]^{2-}$: $\lambda_{max}(\varepsilon)$; 476 nm(1781), 618 nm(548).
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17)XAFS data were acquisited in transmittance mode for polyethylene pelletts on the beam line BL-7C of the Photon Factory of the National Institute of High Energy Physics at Tsukuba by using the EXAFS facilities. The results were analyzed with EXAFS1 programme (N. Kosugi and H. Kuroda, Research Center for Spectrochemistry, The University of Tokyo).
18)Converted from -0.76 V (vs. SCE)[6] to the value for vs. Ag^+/Ag.

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