Supplementary information

A Square Planar Ni(II) Complex with an N_2S_2 Donor Set Similar to the Active Centre of Nickel-Containing Superoxide Dismutase and Its Reaction with Superoxide

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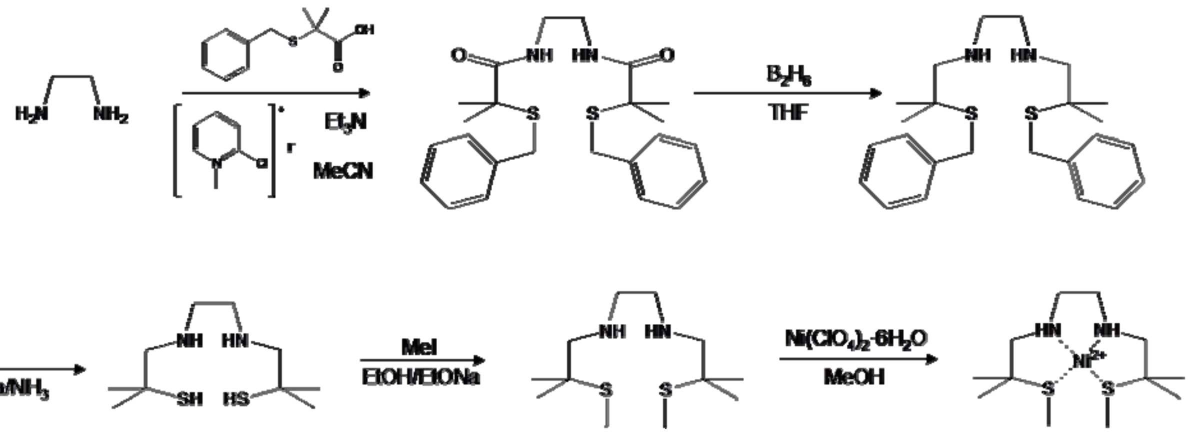
Experimental Section



Scheme S1. Synthetic scheme of ligand and the Ni(II) complex

Materials.

Benzylmercaptane and methyliodide were purchased from Nacalai Tesque. n-Bu_4NBF_4 were purchased from Tokyo Chemical Industry. $Ni(ClO_4)_2{\cdot}6H_2O$ was purchased from Aldrich. All other reagents and solvent were purchased from Wako Pure Chemical Industry and all reagents were highest grade available.

Preparation of Ligands.

2-Benzylmercapto-2-methylpropanoic acid and 2-chrolo-1-methylpyridinium iodide were prepared by the literature methods.[1,2]

N,N'-Bis(2-benzylmercapto-2-methylpropanoyl)-1,2-diaminoethane.

2-Benzylmercapto-2-methylpropanoic acid (2 g, 9.5 mmol), 2-chrolo-1-methylpyridinium iodide (2.4 g, 9.5 mmol), and Et_3N (1 g, 9.5 mmol) were dissolved in MeCN (200 ml) and stirred for 1 h. To this yellow solution, ethylenediamine (0.3 g, 4.7 mmol) and Et_3N (1 g, 9.5 mmol) dissolved in MeCN (50 ml) were added, and the resultant solution was stirred for 3 h. Then, the solvent was removed and dried by evaporation, giving white residual precipitates. The precipitates were suspended in H_2O, filtered out, and washed with a little amount of Et_2O.
(Yield 1.67 g, 80 %)
^{1}H-NMR δ ($CDCl_3$, 300 MHz); 1.53 (s, 12H), 3.19 (t,4H), 3.73 (s, 4H), 7.27 (m, 10+2H).

N,N'-Bis(2-benzylmercapto-2-methylpropyl)-1,2-diaminoethane.

$BF_3{\cdot}Et_2O$ (8.5 g, 60 mmol) was added to the suspended solution of $NaBH_4$ (1.14 g, 30 mmol) in dry THF (50 ml) and stirred for 10 min. The white suspended solution was added to the solution of *N,N'*-bis(2-benzylmercapto-2-methylpropanoyl)-1,2-diaminoethane (1.8 g, 4 mmol) dissolved in dry THF (100 ml). The mixed solution was refluxed for 16 h. At room temperature, a little amount of MeOH was added to the solution to decompose the remaining B_2H_6. After addition of H_2O (100 ml) to this solution, THF and MeOH were removed by evaporation. The product in this residual solution was extracted with Et_2O (50 ml ×3) at pH 9. The Et_2O layer was washed with saturated aqueous NaCl solution and dried with anhydrous sodium sulfate (Na_2SO_4). Et_2O was dried by evaporation to give *N,N'*-bis(2-benzylmercapto-2-methylpropyl)-1,2-diaminoethane as a colorless oil.
(Yield 1.20 g, 72 %)
^{1}H-NMR δ ($CDCl_3$, 300 MHz); 1.34 (s, 12H), 1.90 (br, 2H), 2.52 (s, 4H), 2.57 (s, 4H), 3.70 (s, 4H), 7.31 (m, 10H).

N,N'-Bis(2-mercapto-2-methylpropyl)-1,2-diaminoethane.

To a solution of *N,N'*-bis(2-benzylmercapto-2-methylpropyl)-1,2-diaminoethane (1 g, 2.4 mmol) dissolved in dry THF (5 ml), liquid NH_3 (200 ml) and Na (1 g, 43.5 mmol) were added and the solution color was turned from pale yellow to dark blue. After stirring for 30 min., NH_4Cl was added until the solution color disappeared. NH_3 was removed by evaporation to give white precipitate of the product. This white precipitate was dissolved in H_2O (50 ml) and extracted with Et_2O (50 ml ×3) at pH 8. The Et_2O layer was washed with aqueous saturated NaCl solution and dried with anhydrous sodium sulfate. Removal of Et_2O in this layer by evaporation gave colorless oil of *N,N'*-bis(2-mercapto-2-methylpropyl)-1,2-diaminoethane.
(Yield 0.43 g, 76 %)
^{1}H-NMR δ ($CDCl_3$, 300 MHz); 1.38 (s, 12H), 1.75 (br, 2H), 2.62 (s, 4H), 2.79 (s, 4H).

N,N'-Bis(2-methylmercapto-2-methylpropyl)-1,2-diaminoethane.

To the solution of *N,N'*-bis(2-mercapto-2-methylpropyl)-1,2-diaminoethane (0.7 g, 3 mmol) dissolved in EtOH (50 ml), Na (0.2 g, 6.5 mmol) was added and the suspended solution was stirred for 15 min. CH_3I (0.9 g, 6.5 mmol) was added to this solution and stirred for 2 h at 40 ºC. After removal of the solvent by evaporation, the residual white precipitate was dissolved in H_2O (100 ml) and the product was extracted with Et_2O (50 ml ×3) at pH 12. The Et_2O layer was dried by evaporation, giving *N,N'*-bis(2-methylmercapto-2-methylpropyl)-1,2-diaminoethane as colorless oil. The product was purified by silica gel column chromatography with $CHCl_3$
(Yield 0.56 g, 70 %)
^{1}H-NMR δ ($CDCl_3$, 300 MHz); 1.29 (s, 12H), 1.58 (br, 2H), 1.98 (s, 6H), 2.57 (s, 4H), 2.77 (s, 4H).

Preparation of Ni(II) complex of *N,N'*-Bis(2-methylmercapto-2-methylpropyl)-1,2-diaminoethane (1).

Addition of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) in MeOH (10 ml) to a stirring solution of *N,N'*-bis(2-methylmercapto-2-methylpropyl)-1,2-diaminoethane (0.26 g, 1 mmol) in MeOH (10 ml) gave orange precipitate of **1**. The pure crystalline product was obtained by slow diffusion of Et_2O into the acetone solution. (Yield 0.41 g, 78 %). Anal. Calcd. for $C_{12}H_{28}Cl_2N_2NiO_8S_2$: C, 27.61; H, 5.41; N, 5.37 %. Found: C, 27.72; H, 5.66; N, 5.50 %. Absorption spectral data (in MeOH): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 221 (7600), 278 (8300), 474 (210).

Measurements of samples

Electronic absorption spectra were taken on a JASCO U-best V-550 spectrometer. ^{1}H-NMR spectra were taken on a Varian Gemini-300 NMR spectrometer. X-band EPR spectra of frozen solutions were recorded at 77 K by using a JEOL JES-RE 1X ESR spectrometer. Cyclic voltammetric measurements were performed using ALS/CH Instruments Electrochemical Analyzer Model 600A. Glassy-carbon, Ag/Ag^+, and Pt-wire electrode were used as working, reference, and counter electrodes, respectively. All measurements were performed in acetone solution containing 0.1 M $(n\text{-}Bu)_4NBF_4$ electrolyte at r.t. under Ar atmosphere. All potentials are reported relative to the normal hydrogen electrode (NHE) using Cp_2Fe/Cp_2Fe^+ as a standard.[3] Resonance Raman (rR) spectrum were recorded by using Ritsu Oyo Kogaku Model MC-100DG spectrometer using Kr^+ laser. The sample was prepared as 10 mM solution of 1:1 MeOH/MeCN mixture. KO_2 (1 mg) was added to 1 ml of the solution of **1**, and the Raman data were reported by using laser excitation of 364 nm at -80 ˚C.

X-ray crystallography

A single crystal of complex **1** was mounted on a glass fiber. X-ray measurement was made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100 ± 1°C to a maximum 2θ value of 25.0°. A total of 1200 oscillation images were collected. The structure was solved by direct methods[4] and expanded using Fourier techniques.[5] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Fourier map showed the high peak (ca. 1.37 e/Å^3) to remain around the chloride atom of perchlorate anion, but it was judged to be essentially festureless. The lager temperature factors of oxygen atoms of perchlorate anion, which are sometimes found in the crystals containing perchlorate anion due to the disorder of the molecule. It caused a short contact of perchlorate anions in the crystal; O(4)···O(4) = 2.708(4) Å, but this is also essentially no problem.

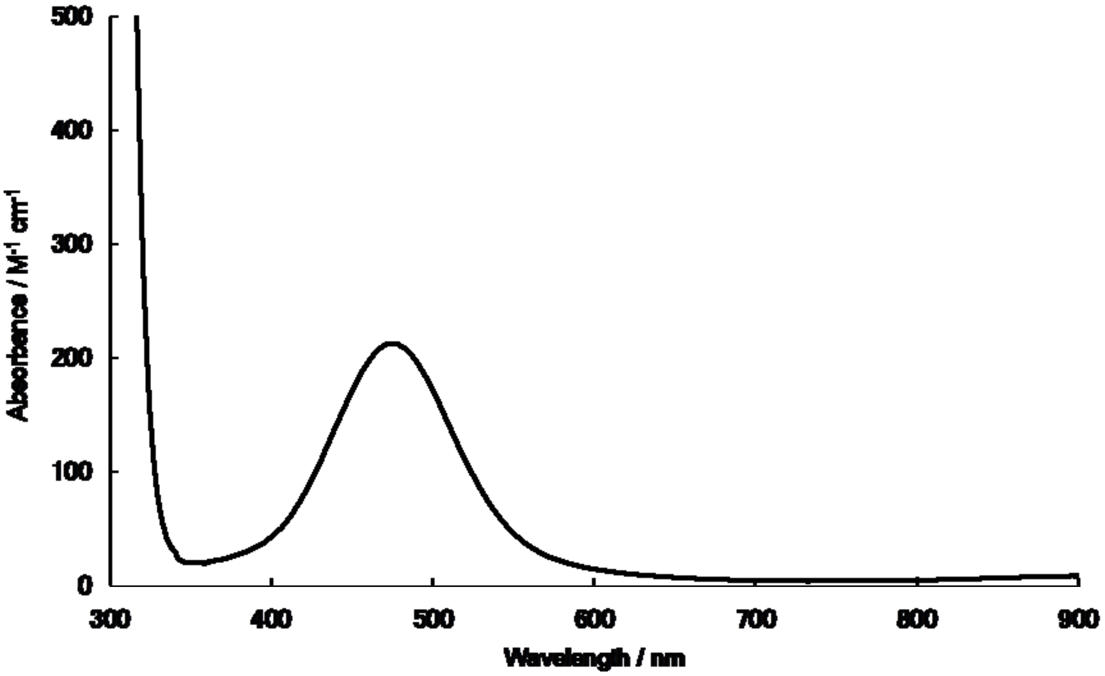


Figure S1. UV-vis spectrum of the Ni(II) complex **1** in MeOH

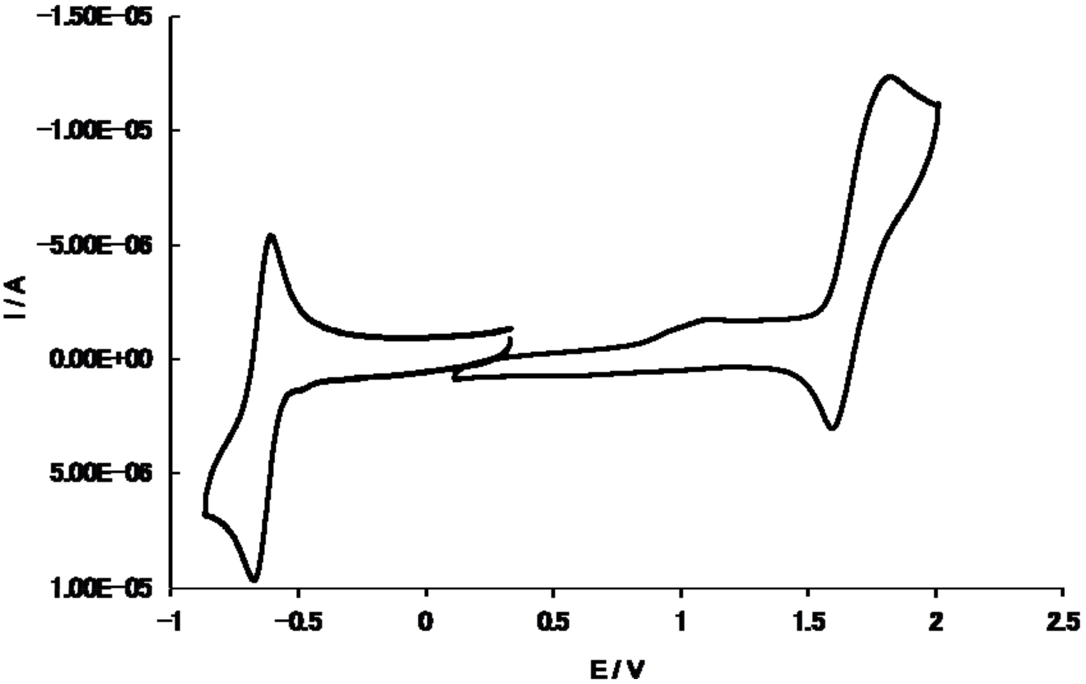


Figure S2. Cyclic voltammogram of Ni(II) complex **1** in reducing and oxidizing process.

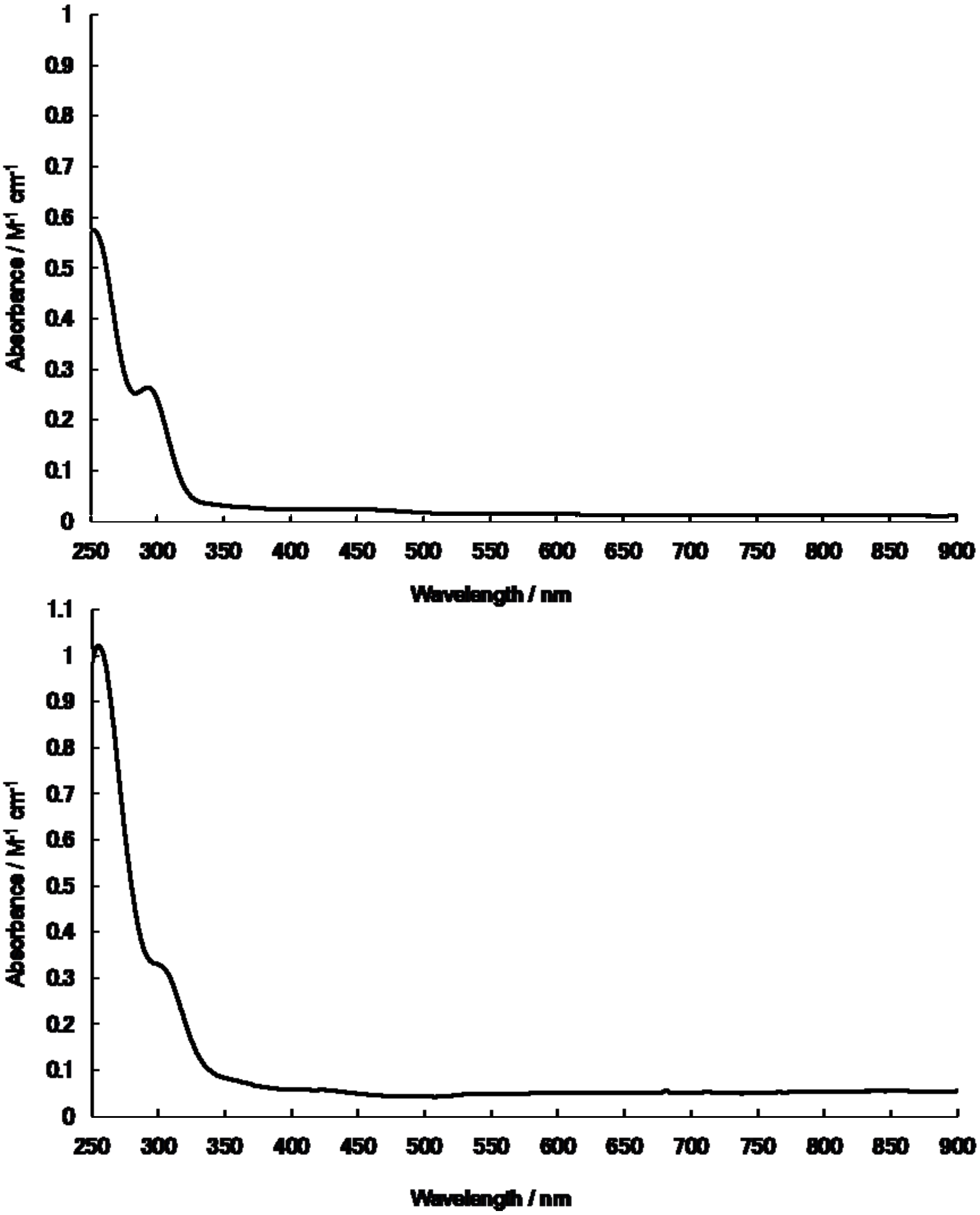


Figure S3. UV-vis spectra obtained by the reactions between the reduced Ni(I) complex and O_2 (upper), and between the Ni(II) complex and KO_2 (bottom).

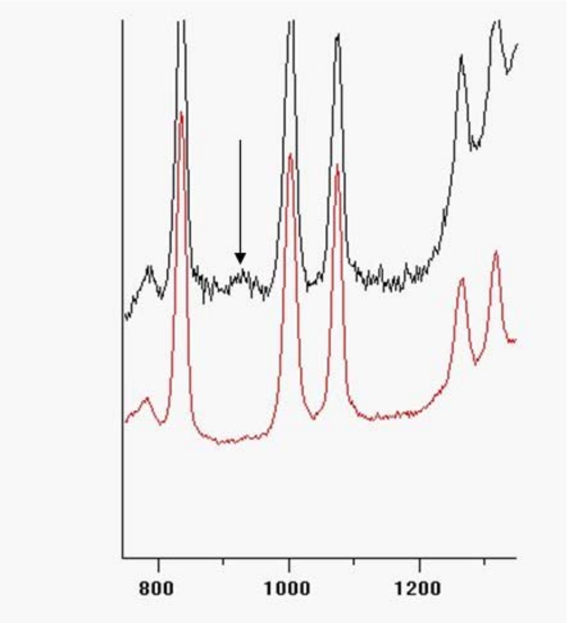


Figure S4. rR spectra of oxidized product obtained by the reaction between Ni(II) complex **1** and KO_2 at -80 ˚C (upper) and at r. t. (bottom). The sample was prepared as 10 mM solution of 1:1 MeOH/MeCN mixture. The Raman data were reported by using laser excitation of 364 nm.

References

1. R. H. Mach, H. F. Kung, *Organic Mass Spectrometry*, 1991, **26**, 528-530.
2. K. Saigo, M. Usui, K. Kikuchi, E. Shimada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.,* 1977, **50**, 1863-1866.
3. R. R. Gange, C. A. Coval, G. C. Lisensky, *Inorg. Chem.,* 1980, **19**, 2854-2855.
4. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M.Camalli, *J. Appl. Cryst.,*1994, **27**, 435-436.
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Sample:

X-ray Structure Report

for

December 1, 2009

Experimental

Data Collection

An orange platelet crystal of $C_{12}H_{28}Cl_2N_2NiO_8S_2$ having approximate dimensions of 0.20 x 0.20 x 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 0 images that were exposed for 0 seconds. The crystal-to-detector distance was 45.22 mm.

Cell constants and an orientation matrix for data collection corresponded to a C-centered monoclinic cell with dimensions:

a = 17.864(4) Å
b = 8.569(2) Å β = 107.176(3)^o
c = 13.909(3) Å
V = 2034.2(8) Å^3

For Z = 4 and F.W. = 522.09, the calculated density is 1.705 g/cm^3. Based on the systematic absences of:

hkl: h+k ± 2n
h0l: l ± 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

C2/c (#15)

The data were collected at a temperature of -100 $\pm$ 1^{o}C to a maximum 2θ value of 55.0^o. A total of 1200 oscillation images were collected. A sweep of data was done using ω scans from -70.0 to 110.0^o in 0.3^o step, at χ=45.0^o and ϕ = 0.0^o. The exposure rate was 16.7 [sec./^{o}]. The detector swing angle was 20.09^o. A second sweep was performed using ω scans from -70.0 to 110.0^o in 0.3^o step, at χ=45.0^o and ϕ = 90.0^o. The exposure rate was 16.7 [sec./^{o}]. The detector swing angle was 20.09^o. The crystal-to-detector distance was 45.22 mm. Readout was performed in the 0.273 mm pixel mode.

Data Reduction

Of the 7832 reflections that were collected, 2297 were unique (R_{int} = 0.019); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows:

$$F^2 = [\Sigma(P_i - mB_{ave})] \cdot Lp^{-1}$$

where P_i is the value in counts of the i^{th} pixel
m is the number of pixels in the integration area
B_{ave} is the background average
Lp is the Lorentz and polarization factor

$$B_{ave} = \Sigma(B_j)/n$$

where n is the number of pixels in the background area
B_j is the value of the j^{th} pixel in counts

$$\sigma^2(F^2_{hkl}) = [(\Sigma P_i) + m((\Sigma(B_{ave} - B_j)^2)/(n-1))] \cdot Lp \cdot errmul + (erradd \cdot F^2)^2$$

where erradd = 0.00
errmul = 1.00

The linear absorption coefficient, μ, for Mo-Kα radiation is 14.635 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.824 to 0.929. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques[3]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 2297 observed reflections and 124 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.0452$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2} = 0.1452$$

The standard deviation of an observation of unit weight[5] was 1.02. A Sheldrick weighting scheme was used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.37 and -0.46 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf" were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL-97[11].

References

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000.J.W.Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(3) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(4) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2-F_c^2)^2 \qquad \text{where } w = \text{Least Squares weights.}$$

(5) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$$

where: N_o = number of observations
N_v = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

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(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.

(11) SHELX97: Sheldrick, G.M. (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{12}H_{28}Cl_2N_2NiO_8S_2$
Formula Weight	522.09
Crystal Color, Habit	orange, platelet
Crystal Dimensions	0.20 X 0.20 X 0.05 mm
Crystal System	monoclinic
Lattice Type	C-centered
Detector Position	45.22 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 17.864(4) Å b = 8.569(2) Å c = 13.909(3) Å β = 107.176(3) ^{o} V = 2034.2(8) Å^3
Space Group	C2/c (#15)
Z value	4
D_{calc}	1.705 g/cm^3
F_{000}	1088.00
μ(MoKα)	14.635 cm^{-1}

B. Intensity Measurements

Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	1200 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-70.0 - 110.0^{o}
Exposure Rate	16.7 sec./^{o}
Detector Swing Angle	20.09^{o}
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0^{o}
Exposure Rate	16.7 sec./^{o}
Detector Swing Angle	20.09^{o}
Detector Position	45.22 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0^{o}
No. of Reflections Measured	Total: 7832 Unique: 2297 (R_{int} = 0.019)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.824 - 0.929)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0902 \cdot P)^2$ $+ 6.7128 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2297
No. Variables	124
Reflection/Parameter Ratio	18.52
Residuals: R1 ($I>2.00\sigma(I)$)	0.0452
Residuals: R (All reflections)	0.0525
Residuals: wR2 (All reflections)	0.1452
Goodness of Fit Indicator	1.018
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	1.37 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.46 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Ni(1)	1.0000	0.30211(7)	0.7500	1.708(16)	1/2
Cl(2)	1.14054(4)	0.15313(9)	1.01313(6)	1.750(17)	
S(1)	0.93274(5)	0.47399(10)	0.80785(7)	1.962(18)	
O(1)	1.1957(2)	0.0445(5)	0.9938(3)	6.30(10)	
O(2)	1.1244(2)	0.2753(4)	0.9431(2)	4.96(8)	
O(3)	1.1740(2)	0.2091(4)	1.1140(2)	4.82(8)	
O(4)	1.06986(18)	0.0684(4)	1.0076(2)	3.88(6)	
N(1)	0.95127(17)	0.1396(3)	0.8059(2)	1.71(4)	
C(1)	0.8637(2)	0.5555(5)	0.6972(3)	3.19(7)	
C(2)	0.8728(2)	0.3362(4)	0.8595(2)	1.87(5)	
C(3)	0.7907(2)	0.3982(4)	0.8453(3)	2.96(7)	
C(4)	0.9177(2)	0.3261(4)	0.9713(2)	2.80(7)	
C(5)	0.8711(2)	0.1826(4)	0.8038(2)	1.97(5)	
C(6)	0.9592(2)	-0.0114(4)	0.7562(2)	2.19(6)	

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B $_{iso}$ involving hydrogens/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
H(1)	0.8921	0.5988	0.6529	3.83	
H(2)	0.8336	0.6384	0.7172	3.83	
H(3)	0.8280	0.4735	0.6615	3.83	
H(4)	0.7598	0.3873	0.7745	3.55	
H(5)	0.7935	0.5085	0.8645	3.55	
H(6)	0.7658	0.3387	0.8876	3.55	
H(7)	0.9187	0.4291	1.0023	3.36	
H(8)	0.9714	0.2914	0.9792	3.36	
H(9)	0.8916	0.2514	1.0042	3.36	
H(10)	0.8484	0.0997	0.8361	2.37	
H(11)	0.8379	0.1935	0.7332	2.37	
H(12)	0.9190	-0.0196	0.6899	2.63	
H(13)	0.9529	-0.1005	0.7985	2.63	
H(14)	0.9801	0.1300	0.8732	2.05	

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	0.0221(3)	0.0189(3)	0.0238(3)	0.0000	0.0066(2)	0.0000
Cl(2)	0.0203(3)	0.0279(4)	0.0177(4)	-0.0068(2)	0.0047(2)	-0.0005(2)
S(1)	0.0263(4)	0.0226(4)	0.0262(4)	-0.0007(3)	0.0085(3)	-0.0020(3)
O(1)	0.058(2)	0.086(3)	0.106(3)	0.014(2)	0.039(2)	-0.020(2)
O(2)	0.060(2)	0.070(2)	0.048(2)	-0.0223(18)	-0.0002(17)	0.0265(18)
O(3)	0.088(2)	0.055(2)	0.0301(17)	-0.0132(19)	0.0030(17)	-0.0045(14)
O(4)	0.0353(15)	0.0558(19)	0.052(2)	-0.0102(14)	0.0066(14)	0.0186(15)
N(1)	0.0253(13)	0.0193(12)	0.0187(14)	-0.0002(10)	0.0041(10)	0.0003(10)
C(1)	0.048(2)	0.041(2)	0.033(2)	0.0187(18)	0.0128(18)	0.0103(17)
C(2)	0.0231(15)	0.0273(16)	0.0207(16)	-0.0021(13)	0.0065(13)	-0.0019(13)
C(3)	0.0269(18)	0.036(2)	0.051(2)	-0.0030(15)	0.0139(17)	-0.0066(18)
C(4)	0.046(2)	0.037(2)	0.0214(18)	0.0001(17)	0.0075(16)	-0.0045(15)
C(5)	0.0261(16)	0.0264(16)	0.0218(17)	-0.0074(13)	0.0060(13)	-0.0010(12)
C(6)	0.0361(19)	0.0211(15)	0.0284(18)	-0.0055(14)	0.0131(15)	-0.0035(13)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ni(1)	S(1)	2.1981(10)	Ni(1)	S(1)$^{1)}$	2.1981(10)
Ni(1)	N(1)	1.924(3)	Ni(1)	N(1)$^{1)}$	1.924(3)
Cl(2)	O(1)	1.437(5)	Cl(2)	O(2)	1.401(3)
Cl(2)	O(3)	1.435(3)	Cl(2)	O(4)	1.439(3)
S(1)	C(1)	1.804(4)	S(1)	C(2)	1.874(3)
N(1)	C(5)	1.470(4)	N(1)	C(6)	1.494(4)
C(2)	C(3)	1.516(5)	C(2)	C(4)	1.528(4)
C(2)	C(5)	1.523(4)	C(6)	C(6)$^{1)}$	1.517(5)

Symmetry Operators:

(1) -X+2,Y,-Z+1/2+1

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N(1)	H(14)	0.930	C(1)	H(1)	0.980
C(1)	H(2)	0.980	C(1)	H(3)	0.980
C(3)	H(4)	0.980	C(3)	H(5)	0.980
C(3)	H(6)	0.980	C(4)	H(7)	0.980
C(4)	H(8)	0.980	C(4)	H(9)	0.980
C(5)	H(10)	0.990	C(5)	H(11)	0.990
C(6)	H(12)	0.990	C(6)	H(13)	0.990

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
S(1)	Ni(1)	S(1)$^{1)}$	95.85(4)	S(1)	Ni(1)	N(1)	88.60(9)
S(1)	Ni(1)	N(1)$^{1)}$	173.97(8)	S(1)$^{1)}$	Ni(1)	N(1)	173.97(8)
S(1)$^{1)}$	Ni(1)	N(1)$^{1)}$	88.60(9)	N(1)	Ni(1)	N(1)$^{1)}$	87.26(13)
O(1)	Cl(2)	O(2)	111.4(2)	O(1)	Cl(2)	O(3)	106.8(2)
O(1)	Cl(2)	O(4)	107.6(2)	O(2)	Cl(2)	O(3)	111.8(2)
O(2)	Cl(2)	O(4)	110.1(2)	O(3)	Cl(2)	O(4)	109.1(2)
Ni(1)	S(1)	C(1)	104.89(16)	Ni(1)	S(1)	C(2)	98.87(11)
C(1)	S(1)	C(2)	104.27(18)	Ni(1)	N(1)	C(5)	111.4(2)
Ni(1)	N(1)	C(6)	108.9(2)	C(5)	N(1)	C(6)	115.6(2)
S(1)	C(2)	C(3)	111.7(2)	S(1)	C(2)	C(4)	103.8(2)
S(1)	C(2)	C(5)	106.1(2)	C(3)	C(2)	C(4)	110.4(3)
C(3)	C(2)	C(5)	111.3(2)	C(4)	C(2)	C(5)	113.2(2)
N(1)	C(5)	C(2)	109.5(2)	N(1)	C(6)	C(6)$^{1)}$	106.2(2)

Symmetry Operators:

(1) -X+2,Y,-Z+1/2+1

Table 7. Bond angles involving hydrogens (^{o})

atom	atom	atom	angle	atom	atom	atom	angle
Ni(1)	N(1)	H(14)	106.8	C(5)	N(1)	H(14)	106.8
C(6)	N(1)	H(14)	106.8	S(1)	C(1)	H(1)	109.5
S(1)	C(1)	H(2)	109.5	S(1)	C(1)	H(3)	109.5
H(1)	C(1)	H(2)	109.5	H(1)	C(1)	H(3)	109.5
H(2)	C(1)	H(3)	109.5	C(2)	C(3)	H(4)	109.5
C(2)	C(3)	H(5)	109.5	C(2)	C(3)	H(6)	109.5
H(4)	C(3)	H(5)	109.5	H(4)	C(3)	H(6)	109.5
H(5)	C(3)	H(6)	109.5	C(2)	C(4)	H(7)	109.5
C(2)	C(4)	H(8)	109.5	C(2)	C(4)	H(9)	109.5
H(7)	C(4)	H(8)	109.5	H(7)	C(4)	H(9)	109.5
H(8)	C(4)	H(9)	109.5	N(1)	C(5)	H(10)	109.8
N(1)	C(5)	H(11)	109.8	C(2)	C(5)	H(10)	109.8
C(2)	C(5)	H(11)	109.8	H(10)	C(5)	H(11)	108.2
N(1)	C(6)	H(12)	110.5	N(1)	C(6)	H(13)	110.5
C(6)$^{1)}$	C(6)	H(12)	110.5	C(6)$^{1)}$	C(6)	H(13)	110.5
H(12)	C(6)	H(13)	108.7				

Symmetry Operators:

(1) -X+2,Y,-Z+1/2+1

Table 8. Torsion Angles(^{o})

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
S(1)	Ni(1)	S(1)$^{1)}$	C(1)$^{1)}$	72.57(16)	S(1)	Ni(1)	S(1)$^{1)}$	C(2)$^{1)}$	-179.99(7)
S(1)$^{1)}$	Ni(1)	S(1)	C(1)	72.57(16)	S(1)$^{1)}$	Ni(1)	S(1)	C(2)	-179.99(9)
S(1)	Ni(1)	N(1)	C(5)	32.4(2)	S(1)	Ni(1)	N(1)	C(6)	161.14(18)
N(1)	Ni(1)	S(1)	C(1)	-111.50(17)	N(1)	Ni(1)	S(1)	C(2)	-4.07(12)
S(1)	Ni(1)	N(1)$^{1)}$	C(5)$^{1)}$	170.1(7)	S(1)	Ni(1)	N(1)$^{1)}$	C(6)$^{1)}$	-61.2(9)
N(1)$^{1)}$	Ni(1)	S(1)	C(1)	-64.9(8)	N(1)$^{1)}$	Ni(1)	S(1)	C(2)	42.6(8)
S(1)$^{1)}$	Ni(1)	N(1)	C(5)	170.1(7)	S(1)$^{1)}$	Ni(1)	N(1)	C(6)	-61.2(9)
N(1)	Ni(1)	S(1)$^{1)}$	C(1)$^{1)}$	-64.9(8)	N(1)	Ni(1)	S(1)$^{1)}$	C(2)$^{1)}$	42.6(8)
S(1)$^{1)}$	Ni(1)	N(1)$^{1)}$	C(5)$^{1)}$	32.4(2)	S(1)$^{1)}$	Ni(1)	N(1)$^{1)}$	C(6)$^{1)}$	161.14(18)
N(1)$^{1)}$	Ni(1)	S(1)$^{1)}$	C(1)$^{1)}$	-111.50(17)	N(1)$^{1)}$	Ni(1)	S(1)$^{1)}$	C(2)$^{1)}$	-4.07(12)
N(1)	Ni(1)	N(1)$^{1)}$	C(5)$^{1)}$	-143.2(2)	N(1)	Ni(1)	N(1)$^{1)}$	C(6)$^{1)}$	-14.47(19)
N(1)$^{1)}$	Ni(1)	N(1)	C(5)	-143.2(2)	N(1)$^{1)}$	Ni(1)	N(1)	C(6)	-14.47(19)
Ni(1)	S(1)	C(2)	C(3)	-143.9(2)	Ni(1)	S(1)	C(2)	C(4)	97.1(2)
Ni(1)	S(1)	C(2)	C(5)	-22.5(2)	C(1)	S(1)	C(2)	C(3)	-36.0(3)
C(1)	S(1)	C(2)	C(4)	-154.9(2)	C(1)	S(1)	C(2)	C(5)	85.5(2)
Ni(1)	N(1)	C(5)	C(2)	-56.5(3)	Ni(1)	N(1)	C(6)	C(6)$^{1)}$	39.5(2)
C(5)	N(1)	C(6)	C(6)$^{1)}$	165.8(2)	C(6)	N(1)	C(5)	C(2)	178.5(2)
S(1)	C(2)	C(5)	N(1)	49.3(3)	C(3)	C(2)	C(5)	N(1)	171.0(3)
C(4)	C(2)	C(5)	N(1)	-63.9(4)	N(1)	C(6)	C(6)$^{1)}$	N(1)$^{1)}$	-51.0(3)

Symmetry Operators:

(1) -X+2,Y,-Z+1/2+1

The sign is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.