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Synthesis, Properties, and Crystal Structure of Binuclear Nickel(II) and Palladium(II) Complexes of Tridentate Thiolic Ligands with NNS-Donor Set

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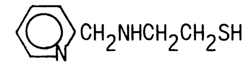
Nickel(II) and palladium(II) complexes with tridentate thiolic ligands of the NNS-donor set have been prepared and characterized on the basis of elemental analyses, IR and electronic spectra, molar conductances, and magnetic susceptibilities. The crystal structure of the nickel(II) perchlorate of 3-[2-(2-pyridyl)ethylamino]-1-propanethiol was determined by single-crystal X-ray diffraction method. The structure consists of thiolate-bridged binuclear units. Each metal ion is coordinated by the amino nitrogen, pyridine nitrogen, and two bridging sulfur atoms, forming an essentially planar coordination unit, and the two N_2S_2 planes are connected at the S1–S2 edge with a dihedral angle of 136.1°.

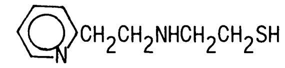
Tridentate alcoholic ligands have been extensively utilized for synthesizing binuclear metal complexes bridged by their deprotonated alcoholic oxygens. As reported in the previous papers, we carried out systematic investigations on binuclear copper(II) complexes of tridentate alcoholic ligands of NSO-,[1-6] SNO-,[4,6,7] or SSO-donor set,[4,8] and revealed that the substitution of thioether sulfur for nitrogen donor atom substantially affects the formation, structure, magnetism, and electrochemical and spectral properties of the complexes. In this study the interest is focused on the effect of the change of the bridging atom from alcoholic oxygen to thiolic sulfur on the structure and physicochemical properties of binuclear complexes. All attempts to synthesize binuclear copper(II) complexes with thiolate-bridge have been unsuccessful, because thiols in general reduce copper(II) to copper(I) ($2R\text{-}S^- + 2Cu^{2+} \rightarrow R\text{-}SS\text{-}R + 2Cu^+$). However, formation of thiolate-bridged metal complexes is feasible by the use of other transition metal ions. In spite of great interests in structure and properties of such thiolate-bridged complexes, investigation on binuclear metal complexes with tridentate thiolic ligands is very limited.[9-12] Thus, we have initiated a systematic investigation on thiolate-bridged binuclear complexes using tridentate thiolic ligands.

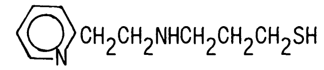
In this study we have examined binuclear nickel(II) and palladium(II) complexes of thiolic ligands of NNS-donor set. The ligands utilized in this study are 2-(2-aminoethylamino)ethanethiol (HL^1), 2-(3-aminopropylamino)ethanethiol (HL^2), 2-(2-pyridylmethylamino)ethanethiol (HL^3), 2-[2-(2-pyridyl)ethylamino]ethanethiol (HL^4), and 3-[2-(2-pyridyl)ethylamino]-1-propanethiol (HL^5). Of these ligands, HL^1 and HL^2

HL^1: $NH_2CH_2CH_2NHCH_2CH_2SH$

HL^2: $NH_2CH_2CH_2CH_2NHCH_2CH_2SH$

HL^3:


HL^4:


HL^5:


were used for the preparation of chloride and tetraphenylborate complexes of nickel(II) by Rose et al.[9] The chloride complexes were practically diamagnetic, whereas the tetraphenylborate complexes showed a subnormal magnetic moment in solid state (1.07 B.M. for $Ni(L^1)B(C_6H_5)_4$ and 1.29 B.M. for $Ni(L^2)B(C_6H_5)_4$). They presumed that the tetraphenylborate complexes were polymeric and contained both diamagnetic nickel(II) of square plane and paramagnetic nickel(II) of a coordination number larger than four. However, the structures of the tetraphenylborate and chloride complexes have not been confirmed yet. Thus, we have reinvestigated the nickel(II) complexes (perchlorate and tetrafluoroborate) of HL^1 and HL^2 together with the new complexes of HL^3, HL^4, and HL^5. During the course of this study, we found the X-ray structural data of $Ni(L^4)ClO_4$ had been already reported by Seff et al.[10] In this complex, a five-membered chelate ring is formed by the mercapto group with Ni(II), whereas $Ni(L^5)ClO_4$ has a six-membered chelate ring. The difference in the chelate ring size may affect the thiolate-bridged binuclear structure. Therefore we have determined the X-ray crystal structure of $Ni(L^5)ClO_4$ in order to compare the structure with that of $Ni(L^4)ClO_4$.

Experimental

Preparations. The ligands except HL^5 were prepared by the literature methods.[9,13] HL^1, HL^3, and HL^4 were

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purified by distillation under reduced pressure and HL^2 was purified by sublimation. HL^5 was prepared by the application of the method of Murase et al.[14] 3-[2-(2-pyridyl)ethylamino]-1-propanol[8] was converted to *N*-[2-(2-pyridyl)ethyl]-3-bromopropylamine (**1**) according to the standard method.[15] Conversion of **1** to the corresponding thiol ($HL^5 \cdot 2HBr$) was proceeded via the phosphorothioate, which was obtained by the reaction of **1** with trisodium phosphorothioate.[14] $HL^5 \cdot 2HBr$ was used for the preparation of the complex without purification.

$Ni(L)ClO_4$ ($L=L^1$, L^2, L^3, L^4). To a solution of nickel(II) perchlorate hexahydrate (1 mmol) in methanol (10 cm^3) was added a methanolic solution of the ligand (1 mmol), and the mixture was stirred for 30 min to give violet microcrystals. They were collected, washed with methanol, and dried over P_2O_5 in a vacuum desiccator.

$Ni(L^5)ClO_4$. Crude ligand ($HL^5 \cdot 2HBr$, 1.4 g, ca. 4 mmol) and nickel(II) perchlorate hexahydrate (3.0 g, 8 mmol) were dissolved in 30 cm^3 of water and the pH of the solution was adjusted to ca. 9 by the addition of triethylamine. The resulting deep brown solution was heated on a water bath for ten minutes and undissolved material was filtered off. Addition of excess sodium perchlorate to the filtrate resulted in the precipitation of reddish brown crystals, which were recrystallized from an acetonitrile-ethanol mixture and dried over P_2O_5 under vacuum.

$Ni(L)BF_4$ ($L=L^2$, L^4). To an aqueous solution (10 cm^3) of nickel(II) acetate tetrahydrate (1 mmol) was added a solution of the ligand (1 mmol) in water (10 cm^3) to form a red solution. A saturated aqueous solution of $NaBF_4$ (2 mmol) was added to this solution to give violet microcrystals, which were collected, washed with methanol, and dried over P_2O_5 in a vacuum desiccator.

$Pd(L^2)ClO_4$. An aqueous solution of $[PdCl_4]^{2-}$ was prepared by dissolving $PdCl_2$ (2 mmol) in water containing NaCl (4.4 mmol). To this were added HL^2 (2 mmol) and NaOH pellets (2.2 mmol), and the mixture was stirred for a half hour. Then, an aqueous solution of $NaClO_4 \cdot H_2O$ (large excess) was added to give a yellow precipitate. It was recrystallized from water as yellow microcrystals.

Elemental analyses of the complexes are given in Table 1.

Measurements. Infrared spectra were measured on a Hitachi 215 infrared spectrometer, and electronic spectra were recorded on a Shimadzu UV-VISIBLE recording spectrometer Model UV-240 in acetone or water. Reflectance

Table 1. Elemental Analyses of Complexes

	Found(%)			Calcd(%)		
	C	H	N	C	H	N
$Ni(L^1)ClO_4 \cdot 1/2H_2O$	16.72	4.18	9.77	16.78	4.22	9.78
$Ni(L^2)ClO_4$	20.65	4.49	9.59	20.61	4.50	9.61
$Ni(L^2)BF_4$	21.34	4.57	9.90	21.55	4.70	10.05
$Ni(L^3)ClO_4 \cdot 1/2H_2O$	28.63	3.51	8.10	28.73	3.62	8.38
$Ni(L^4)ClO_4$	31.66	3.96	7.92	31.85	3.86	8.25
$Ni(L^4)BF_4$	32.87	3.95	8.62	33.08	4.01	8.57
$Ni(L^5)ClO_4$	34.05	4.31	7.94	33.98	4.28	7.93
$Pd(L^2)ClO_4$	17.49	3.79	8.12	17.71	3.86	8.26

Table 2. Atomic Coordinates (×10^4) and Thermal Parameters

Atom	x	y	z	$B_{eq}/Å^2$ [b]	Atom	x	y	z	$B_{eq}/Å^2$ [b]
Ni1	4088(1)	3530(1)	−1217(1)	3.0	N4	486(5)	4046(2)	−162(7)	3.4
Ni2	1430(1)	3599(1)	−964(1)	3.2	C1	3256(9)	4300(4)	989(20)	10.1
Cl1	−2009(2)	3186(1)	704(3)	5.4	C2	4442(9)	4480(3)	1121(14)	6.5
Cl2	2708(2)	4940(1)	5396(3)	6.5	C3	5512(8)	4169(3)	1020(12)	5.8
S1	3063(2)	3715(1)	734(2)	4.0	C4	5660(8)	4230(3)	−2011(11)	5.0
S2	2550(2)	3107(1)	−1834(3)	3.5	C5	5160(8)	4045(3)	−3726(11)	4.8
O1	−2066(6)	3524(2)	−452(9)	7.1	C6	5479(7)	3567(3)	−3877(10)	3.9
O2	−3203(8)	3090(3)	955(11)	10.1	C7	6235(7)	3412(3)	−4962(10)	4.6
O3	−1694(12)	2822(4)	−115(18)	18.4	C8	6455(8)	2984(3)	−5034(11)	5.1
O4	−1295(12)	3252(4)	2050(16)	20.8	C9	5941(7)	2703(3)	−4020(10)	4.7
O5[a]	2553(11)	5454(4)	5508(16)	7.6	C10	5184(7)	2874(3)	−2964(10)	3.9
O5′[a]	1862(17)	4746(6)	4375(24)	8.2	C11	2099(8)	3160(3)	−4122(10)	5.1
O6[a]	2977(9)	4772(3)	7008(14)	6.1	C12	880(8)	2969(3)	−4654(12)	6.0
O6′[a]	3387(14)	4929(5)	6925(20)	6.1	C13	−14(8)	3015(3)	−3370(13)	5.7
O7[a]	3298(11)	4968(4)	4091(16)	8.1	C14	−431(8)	3791(3)	−3744(10)	5.2
O7′[a]	3940(15)	4951(6)	4787(21)	6.7	C15	40(8)	4230(3)	−3089(10)	4.6
O8[a]	1482(10)	4969(4)	5231(15)	7.3	C16	−179(7)	4293(2)	−1310(9)	3.4
O8′[a]	2485(17)	4404(7)	4887(24)	8.3	C17	−1008(7)	4592(3)	−875(10)	4.0
N1	5427(5)	3925(2)	−598(8)	4.1	C18	−1130(7)	4631(3)	826(11)	4.5
N2	4975(5)	3295(2)	−2871(7)	3.1	C19	−428(8)	4383(3)	1986(11)	4.6
N3	8(5)	3439(2)	−2550(8)	4.1	C20	358(7)	4086(3)	1464(10)	4.2

a) Atoms refined with occupancy factors of 0.5. b) $B_{eq}=4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

spectra were recorded on Shimadzu multipurpose spectrophotometer Model MPS-5000. Conductance measurements were carried out with a Yanagimoto Conductivity Outfit Model MY-8 in acetone or in water. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.16) The diamagnetic corrections were made with Pascal's constants17) and magnetic moments were calculated by the equation, $\mu_{eff}=(8\chi_A T)^{1/2}$.

X-Ray Crystal Structure Analysis of Ni(L^5)ClO$_4$. A crystal with dimensions 0.12×0.30×0.31 mm^3 was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The intensity data were collected by the ω scan technique with a scan rate of 4° min^{-1}.

Crystal Data: $C_{20}H_{28}Cl_2N_4Ni_2O_8S_2$, F.W.=704.9; monoclinic, $P2_1/n$; a=11.303(2), b=31.142(5), c=8.104(1) Å, β=98.17(1)°; D_c=1.66 g cm^{-3}; Z=4; μ(Mo $K\alpha$)=17.2 cm^{-1}.

A total of 4254 reflections with $2\theta<46°$ were collected. The intensity data were corrected for Lorentz-polarization effects and for absorption. Independent 3125 reflections with $|F_o|>3\sigma(F_o)$ were considered as "observed" and were used for structure analysis. The structure was solved by the direct method. Refinements were carried out by the block-diagonal least-squares method. The weighting scheme $w=[\sigma_{count}{}^2+(0.015|F_o|)^2]^{-1}$ was employed. Hydrogen atoms were inserted in their calculated positions and fixed at their positions. The final discrepancy factors are $R=\sum||F_o|-|F_c||/\sum|F_o|=0.059$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.076$.

All the calculations were carried out on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using a local version of the MULTAN 78, UNICS-III, and ORTEP programs.18) Atomic coordinates and thermal parameters of nonhydrogen atoms are listed in Table 2. The anisotropic thermal parameters of nonhydrogen atoms, the atomic coordinates and thermal parameters of hydrogen atoms, and the F_o–F_c tables have been deposited as a Document No. 8841 at the Office of the Editor.

Results and Discussion

Nickel(II) complexes with the general formula NiLX (X=ClO$_4^-$, L=L^1, L^2, L^3, L^4, L^5; and X=BF$_4^-$, L=L^2, L^4) were obtained. As for the palladium(II) complex, only Pd(L^2)ClO$_4$ could be isolated as crystals. Magnetic moments at room temperature and molar conductance data are given in Table 3.

The magnetic moments of the complexes are not zero. These residual paramagnetism can be ascribed to the temperature independent paramagnetism of nickel atom. Thus, we can conclude that all these complexes are diamagnetic. The S–H vibration near 2500 cm^{-1} of the free ligands was absent in the IR spectra of the complexes. This suggests that the thiol is deprotonated and coordinated to the metal. IR spectra also suggested no coodination of the perchlorate and tetrafluoroborate ions to the metal; ClO$_4^-$ and BF$_4^-$ vibrations appeared as a broad band at ca. 1100 and ca. 1050 cm^{-1}, respectively. Molar conductance data indicated that all the complexes are 2:1 electrolyte in acetone or water. Based on these facts, the complexes are presumed to be binuclear bridged by the mercaptide sulfur atoms.

The crystal structure of Ni(L^5)ClO$_4$ consists of binuclear complex cations and perchlorate ions. Perchlorate ions do not participate in any coordination as suggested from IR spectra. A perspective drawing of the binuclear cation is illustrated in Fig. 1. Selected bond distances and angles are given in Table 4. Both the nickel ions adopt an essentially planar configuration with aliphatic amino nitrogen, pyridine nitrogen, and bridging sulfur atoms. The deviations of atoms from the least-squares planes of N$_2$S$_2$ are less than 0.11 Å and the deviations of Ni1 and Ni2 from the planes are only 0.05 and 0.01 Å, respectively. The Ni–S

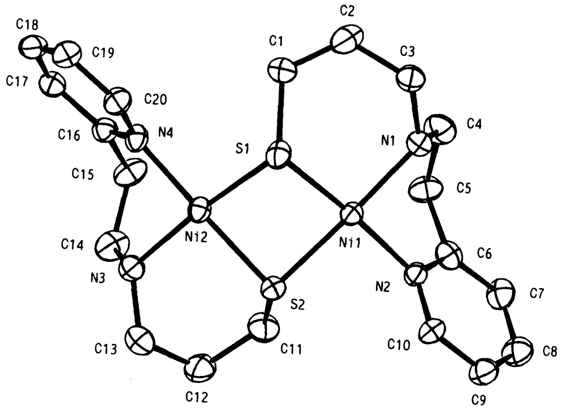

Fig. 1. A perspective view of $[Ni_2(L^5)_2]^{2+}$ ion.

Table 3. Magnetic Moments and Molar Conductances of Complexes

	μ_{eff}/B.M.a)	λ_M/Ω^{-1} cm^{-2} mol^{-1}
Ni(L^1)ClO$_4$·1/2H$_2$O	0.28	204b)
Ni(L^2)ClO$_4$	0.21	183b)
Ni(L^2)BF$_4$	0.28	198b)
Ni(L^3)ClO$_4$·1/2H$_2$O	0.67	154b)
Ni(L^4)ClO$_4$	0.40	214b)
Ni(L^4)BF$_4$	0.26	231b)
Ni(L^5)ClO$_4$	0.28	223b)
Pd(L^2)ClO$_4$	0.23	214c)

a) Magnetic moment at room temperature. Temperature-independent paramagnetism is not included for the calculation of μ_{eff}. b) In acetone. c) In water.

distances are 2.166(2)—2.180(2) Å, which are common for other thiolate-bridged bi- and oligonuclear nickel(II) complexes.[19—24] The Ni1–Ni2 distance is 3.047(1) Å, making a contrast with that of Ni(L^4)ClO$_4$ (2.739(1) Å)[10] and other thiolate-bridged binuclear nickel(II) complexes,[19—21] whose structurtes are characterized by the small dihedral angle (82.3—114.3°) between the two NiN$_2$S$_2$ planes sharing the S–S′ edge and by the small Ni–S–Ni angle (76.7—79.5°). As the result, the Ni–Ni′ distances are very short (2.733—2.795 Å).[25] In Ni(L^5)ClO$_4$, the two N$_2$S$_2$ planes are bent at the S1–S2 edge with a dihedral angle of 136.1° and the Ni–S–Ni angles are 89.02(8) and 89.27(8)°. This may be ascribed to the steric requirement of the six-membered chelate ring which favors the coplanar structure. A similar structural feature was observed in [Ni$_2${SCH(CH$_2$CH$_2$NH$_2$)$_2$}$_2$]Br$_2$ which contains two adjacent six-membered chelate rings.[24]

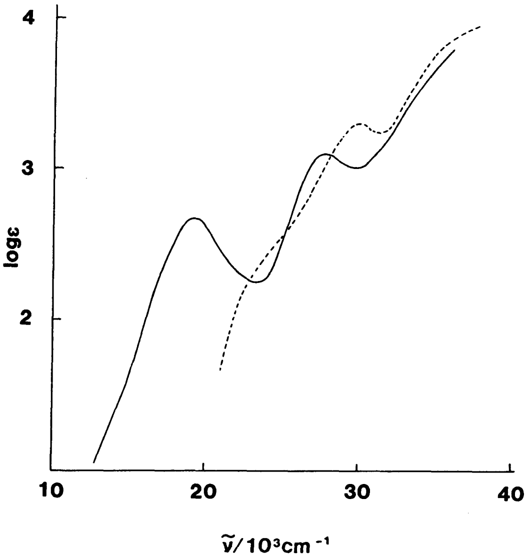

Fig. 2. Electronic spectra of (——) Ni(L^2)ClO$_4$ and (-----) Pd(L^2)ClO$_4$.

Table 4. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°)

Ni1–Ni2	3.047(1)	Ni1–N1	1.960(6)
Ni1–S1	2.167(2)	Ni1–N2	1.928(6)
Ni1–S2	2.180(2)	Ni2–N3	1.974(6)
Ni2–S1	2.170(2)	Ni2–N4	1.923(6)
Ni2–S2	2.166(2)		
Ni1–S1–Ni2	89.27(8)	N1–Ni1–N2	87.5(3)
Ni1–S2–Ni2	89.02(8)	S1–Ni2–S2	80.9(1)
S1–Ni1–S2	80.6(1)	S1–Ni2–N4	97.3(2)
S1–Ni1–N1	96.9(2)	S2–Ni2–N3	94.0(2)
S2–Ni1–N2	95.1(2)	N3–Ni2–N4	87.9(3)

Electronic spectra of the nickel(II) complexes in acetone exhibit a d–d band near 19×10^3 cm^{-1} (ε: 400—500 dm^3 mol^{-1} cm^{-1}) (Fig. 2 and Table 5), characteristic of planar nickel(II). The spectra were also characterized by an absorption in a near-ultraviolet region (27—28×10^3 cm^{-1}), whose extinction coefficient is more than 10^3 dm^3 mol^{-1} cm^{-1}. Judging from its frequency and intensity it can not be a d–d transition band, but should be assigned to a charge-transfer transition. Such a near-ultraviolet band was also observed for other thiolate-bridged binuclear nickel(II) complex.[14]

The electronic spectrum of Pd(L^2)ClO$_4$ in water shows absorption bands at ca. 24×10^3 and 30×10^{3}cm^{-1}, which can be assigned to a d–d and a charge-transfer transitions, respectively.

Electronic spectra of the nickel(II) complexes in water (immediately after the dissolution) were essentially the same as the spectra in acetone. However, the purple color of the aqueous solutions faded gradually and the solutions became pale green in a day or two, suggesting the decomposition of the complexes in water. The tendency to decompose in water was prominent in Ni(L^1)ClO$_4$ and Ni(L^3)ClO$_4$, whereas the complexes with (L^2)$^-$, (L^4)$^-$, and (L^5)$^-$ were fairly stable in water. The low stability of the former complexes seems to be due to the strain in the 5–5 fused-ring system.

Each powder spectrum of the nickel(II) complexes resembles that in acetone solution in the region 14—30×10^3 cm^{-1} (Table 5). Thus, the magnetic, electronic spectral, and X-ray structural results indicate that the coordination geometries are invariably planar in solution as well as in solid state for all the present nickel complexes.

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Table 5. Electronic Spectral Data ($\tilde{\nu}$/10^3 cm^{-1} (ε))

	Absorption		Reflectance	
Ni(L^1)ClO$_4$·1/2H$_2$O	19.6(420)	27.7(1100)[a]	19.4	26.7
Ni(L^2)ClO$_4$	19.3(470)	27.6(1230)[a]	19.0	27.2
Ni(L^2)BF$_4$	19.3(480)	27.7(1230)[a]	18.9	27.0
Ni(L^3)ClO$_4$·1/2H$_2$O	19.3(460)	ca. 28(1800)[a]	19.0	ca. 27
Ni(L^4)ClO$_4$	19.3(500)	ca. 27(1480)[a]	19.0	ca. 27
Ni(L^4)BF$_4$	19.4(490)	ca. 27(1390)[a]	19.1	ca. 27
Ni(L^5)ClO$_4$	20.1(450)	26.8(2030)[a]	20.2	26.7
Pd(L^2)ClO$_4$	ca. 24(200)	30.0(2000)[b]		

a) In acetone. b) In water.

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