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Synthesis and Structural Characterization of Thiolato-Bridged Tetranuclear Palladium(II) Complexes with *N*,*N*,*S*-Tridentate Ligands

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Palladium(II) complexes with 2-[(2-aminoethyl)amino]ethanethiol (HL^1), 2-[(3-aminopropyl)amino]ethanethiol (HL^2), 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3), and 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4), $[Pd_4(L^1)_4]Cl_4$ (**1**), $[Pd_4(L^2)_4]Cl_4$ (**2**), $[Pd_4(L^3)_4](ClO_4)_3Cl$ (**3**), $[Pd_4(L^4)_4][Pd(SCN)_4]Cl_2$ (**4**), and $[Pd_4(L^4)_4](ClO_4)_4$ (**5**), were synthesized and characterized by measurements of the infrared, electronic, and NMR spectra. X-ray crystal structure analyses of **1**, **2**, **3**, and **4** show that these complexes have a thiolato-bridged tetranuclear structure, where each palladium(II) center takes a square-planar N_2S_2 coordination environment.

Thiolato-bridged metal complexes have been the focus of active research for more than 30 years because of their rich chemistry, coming from the distinguishing property of thiolic ligands to react readily with many metals to form complexes containing sulfur-bridges.[1–5] Among thiolato-bridged metal complexes, the chemistry of nickel thiolates is well developed as feasible materials or potential model compounds for biologically significant nickel enzymes.[6,7] In contrast with the case of nickel, the chemistry of its congener palladium thiolates is essentially undeveloped. As part of our continuing interest in the fundamental chemistry of thiolato-bridged metal complexes, we reported on the synthesis and characterization of nickel(II) complexes with thiolic ligands having S and N donor atoms.[8–13] All of the isolated nickel(II) complexes are exclusively dinuclear metal species, while other metals, such as iron(II), afford trinuclear or polynuclear metal species as well as dinuclear metal species with these thiolic ligands.[14–18] In this study, we have extended our efforts on palladium chemistry and isolated tetranuclear metal species. The thiolic ligands utilized in this study were 2-[(2-aminoethyl)amino]ethanethiol (HL^1), 2-[(3-aminopropyl)amino]ethanethiol (HL^2), 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3), and 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4). Herein, we report on the synthesis and structural characterization of palladium(II) complexes with these thiolic ligands (Chart 1). Preliminary results have been reported elsewhere.[19]

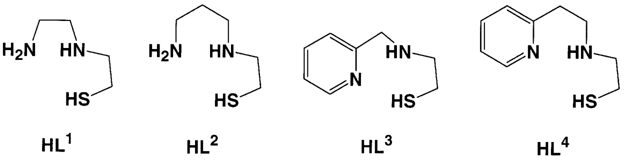

Chart 1.

Experimental

Synthesis of Complexes. The thiolic ligands (HL^1, HL^2, HL^3, and HL^4) were synthesized by applying a method described in the literature.[9] All reactions were performed under an atmosphere of argon using standard Schlenk techniques.

$[Pd_4(L^1)_4]Cl_4$·8H$_2$O ($\mathbf{1}$·8H$_2$O). To a solution of HL^1 (16 mg, 0.13 mmol) in a mixture of methanol (1 cm^3) and acetonitrile (2 cm^3) was added a methanol solution (3 cm^3) of sodium tetrachloropalladate(II) (39 mg, 0.13 mmol) and three drops of triethylamine. The mixture was allowed to stand at room temperature for one week to give yellow prisms. These were collected by filtration and dried in vacuo (yield 12 mg, 31%). Found: C, 16.48; H, 4.94; N, 9.09%. Calcd for $C_{16}H_{60}Cl_4N_8O_8Pd_4S_4$: C, 16.17; H, 5.09; N, 9.43%. IR (KBr) ν/cm^{-1} ν(NH) 3180(m), 3080(m); ν(CH) 2938(m), 2850(m). Diffuse reflectance spectrum λ_{max}/nm 229, 327, 357, 375. Electronic absorption spectrum in MeOH λ_{max}/nm (ε per Pd/dm^3 mol^{-1} cm^{-1}) 245 (7520), 335 (2100). ^{1}H NMR (DMSO-d_6): δ 2.56 (dq, J = 12.0, 3.9 Hz, 1H, C1-H), 2.78 (br, C3–H), 2.81–2.88 (m, br), 2.95 (d, J = 10.7 Hz, C2–H), 3.02 (br, C4–H), 5.55 (s, br, 1H, NH$_2$), 6.28 (s, br, 1H, NH$_2$), 7.78 (s, br, 1H, NH)

$[Pd_4(L^2)_4]Cl_4$·2H$_2$O ($\mathbf{2}$·2H$_2$O). To an *N*,*N′*-dimethylacetamide solution (3 cm^3) of HL^2 (21 mg, 0.16 mmol) was added a solution of sodium tetrachloropalladate(II) (46 mg, 0.16 mmol) in methanol (3 cm^3) and three drops of triethylamine; the mixture was allowed to stand overnight to give yellow prisms. These were collected by filtration and dried in vacuo (yield 28 mg, 62%). Found: C, 21.03; H, 5.32; N, 9.98%. Calcd for $C_{20}H_{56}Cl_4N_8O_2Pd_4S_4$: C, 21.14; H, 4.97; N, 9.86%. IR (KBr) ν/cm^{-1} ν(NH) 3190(m), 3112(m); ν(CH) 2938(m), 2852(m). Diffuse reflectance spectrum λ_{max}/nm 257, 340. Electronic absorption spectrum in MeOH λ_{max}/nm (ε per Pd/dm^3 mol^{-1} cm^{-1}) 258 (8870), 335 (1700). ^{1}H NMR (CD$_3$OD) δ 1.77 (q, J = 12.8, 1H, C4–H), 2.13 (d, J = 16 Hz, 1H, C4–H), 2.41 (dt, J = 13.6 Hz, 3.6Hz, 1H, C1–H), 2.51 (dd, J = 13.6, 3.6 Hz, 1H, C1–H), 2.67 (t, J = 12.4 Hz, 1H, C3–H), 3.01 (m, 2H, C3–H and C5–H), 3.12 (t, J = 11.6 Hz, 1H, C5–H), 3.20 (dt, J = 12.8, 4.0 Hz, 1H, C2-H), and 3.51 (dd, J = 12.4, 3.2 Hz,1H, C2–H). ^{13}C NMR (CD$_3$OD) δ 29.8 (C4), 35.4 (C1), 42.0 (C3), 52.9 (C5), and 61.6 (C2).

$[Pd_4(L^3)_4](ClO_4)_3Cl·5H_2O$ (3·5H_2O). To a solution of HL^3 (23 mg, 0.14 mmol) in a mixture of methanol (2 cm^3) and *N*,*N′*-dimethylacetamide (1 cm^3) was added a methanol solution (3 cm^3) of sodium tetrachloropalladate(II) (40 mg, 0.14 mmol), sodium perchlorate (33 mg, 0.27 mmol), and three drops of triethylamine. The mixture was allowed to stand overnight to give greenish-brown needles. These were collected by filtration and dried in vacuo (yield 47 mg, 88%). Found: C, 25.36; H, 3.49; N, 7.19%. Calcd for $C_{32}H_{54}Cl_4N_8O_{17}Pd_4S_4$: C, 25.31; H, 3.58; N, 7.38%. IR (KBr) ν/cm^{-1} ν(NH) 3022(m); ν(CH) 2844(m); ν(ClO4) 1139(s), 1111(s), 1081(s), 1031(s). Diffuse reflectance spectrum λ_{max}/nm 250, 354, 588 sh (weak). Electronic absorption spectrum in DMSO λ_{max}/nm (ε per Pd/dm^3 mol^{-1} cm^{-1}) 338 (2800). ^{1}H NMR(CD_3CN) δ 3.10 (m, 2H, C1–H), 3.53 (m, 1H, C2–H), 3.75 (m, 1H, C2–H), 4.32 (dd, *J* = 16.0, 4.8 Hz, 1H, C3–H), 4.68 (dd, *J* = 16.4, 10.8 Hz, 1H, C3–H), 6.74 (m, br, 1H, NH), 7.09 (t, *J* = 6.4 Hz, 1H, C7–H), 7.36 (d, *J* = 7.6 Hz, 1H, C5–H), 7.75 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H, C6–H), and 8.27 (d, *J* = 5.6 Hz, 1H, C8–H).

$[Pd_4(L^4)_4][Pd(SCN)_4]Cl_2$·$2H_2O$ (4·2H_2O). To a solution of HL^4 (25 mg, 0.14 mmol) in a mixture of methanol (2 cm^3) and *N*,*N′*-dimethylacetamide (1 cm^3) was added a methanol solution (3 cm^3) of sodium tetrachloropalladate(II) (40 mg, 0.14 mmol), sodium thiocyanate (22 mg, 0.27 mmol), and three drops of triethylamine. The mixture was allowed to stand for one week to give red prisms. These were collected by filtration and dried in vacuo (yield 17 mg, 32%). Found: C, 29.71; H, 3.51; N, 10.28%. Calcd for $C_{40}H_{56}Cl_2N_{12}O_2Pd_5S_8$: C, 30.09; H, 3.54; N, 10.53%. IR (KBr) ν/cm^{-1} ν(NH) 3028(m); ν(CH) 2862(m); ν(SCN) 2100(s), 768. Diffuse reflectance spectrum λ_{max}/nm 249, 311, 350, 503.

$[Pd_4(L^4)_4](ClO_4)_4$·H_2O (5·H_2O). To a solution of HL^4 (22 mg, 0.12 mmol) in a mixture of methanol(2 cm^3) and *N*,*N′*-dimethylacetamide (1 cm^3) was added a methanol solution (3 cm^3) of sodium tetrachloropalladate(II) (36 mg, 0.12 mmol), sodium perchlorate (29 mg, 0.24 mmol), and three drops of trietylamine. The mixture was allowed to stand overnight to give orange prisms. These were collected by filtration and dried in vacuo (yield 25 mg, 53%). Found: C, 27.61; H, 3.23; N, 6.89%. Calcd for $C_{36}H_{54}Cl_4N_8O_{17}Pd_4S_4$: C, 27.60; H, 3.47; N, 7.15%. IR (KBr) ν/cm^{-1} ν(NH) 3042(m); ν(CH) 2860(m); ν(ClO_4^-) 1132(s), 1110(s), 1085(s). Diffuse reflectance spectrum λ_{max}/nm 244, 355. Electronic absorption spectrum in DMSO λ_{max}/nm (ε per Pd/dm^3 mol^{-1} cm^{-1}) 343 (2810). ^{1}H NMR(DMSO-*d*$_6$) δ 2.39 (d, *J* = 13.6 Hz, 1H, C1–H), 2.97 (m, br, C2–H), 3.05–3.23 (m, br, C1–H and C2–H), 3.37 (m, C4–H), 3.64 (m, br, 2H, C3–H), 7.19 (t, *J* = 6.8 Hz, 1H, C8–H), 7.27 (m, br, 1H, NH), 7.78 (d, *J* = 8.0 Hz, 1H, C6–H), 8.17 (t, *J* = 7.6 Hz, 1H, C7–H), 8.80 (d, *J* = 5.6 Hz, 1H, C9–H).

Measurements. Elemental analyses (C, H, and N) were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer (Model IR 700) in the region 4000–400 cm^{-1} on KBr disks. The diffuse reflectance spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). The ^{1}H(400MHz) and ^{13}C(100.58MHz) NMR spectra were recorded on a JEOL Alpha-400 spectrometer. Chemical shifts were reported relative to a tetramethylsilane internal standard.

X-Ray Crystal Structure Analyses. Single crystals suitable for X-ray work were collected from each solution and were not dried. Each crystal was sealed in a glass capillary together with the mother liquor and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. Crystal data and details concerning data collection are given in Table 1. The lattice constants were calculated by a least-squares refinement based on 25 reflections with $20 \le 2\upsilon \le 30°$. The intensity data were corrected for Lorentz-polarization effects. The structures were solved by direct methods. Refinements were performed by full-matrix least-squares methods. In the course of the refinement, it became apparent that the S3 and S4 atoms of **4**·2CH_3OH were disordered. These atoms were divided into two positions with occupancy factors of 75 and 25%, respectively. The water oxygen atoms of **1**·3/2CH_3OH·13/8H_2O were also disordered and assigned an occupancy factor of 50%. Hydrogen atoms of **2** and **4** were located from difference Fourier maps. The other hydrogen atoms

Table 1. Crystal Data and Data Collection Details

Complex	$[Pd_4(L^1)_4]Cl_4$·3/2CH_3OH ·13/8H_2O (**1**·3/2CH_3OH ·13/8H_2O)	$[Pd_4(L^2)_4]Cl_4$·4CH_3OH (**2**·4CH_3OH)	$[Pd_4(L^3)_4](ClO_4)_2Cl$·2CH_3OH·H_2O (**3**·2CH_3OH·H_2O)	$[Pd_4(L^4)_4][Pd(SCN)_4]Cl_2$·2$CH_3OH$ (**4**·2CH_3OH)
Formula	$C_{35}H_{106.5}Cl_8N_{16}O_{6.25}Pd_8S_8$	$C_{24}H_{68}Cl_4N_8O_4Pd_4S_4$	$C_{34}H_{54}Cl_4N_8O_{15}Pd_4S_4$	$C_{42}H_{60}Cl_2N_{12}O_2Pd_5S_8$
F. W.	2243.3	1228.6	1510.6	1624.6
Crystal system	monoclinic	tetragonal	orthorhombic	monoclinic
Space group	*C/c*	$I4_1/a$	*P*bca	*C/c*
a/Å	26.206(8)	18.916(3)	27.592(5)	23.645(8)
b/Å	21.364(3)		25.308(2)	14.697(3)
c/Å	33.688(9)	12.693(3)	15.457(1)	16.797(5)
β/°	93.00(1)			101.42(2)
V/Å^3	18834(8)	4541(1)	10794(2)	5721(3)
Z	8	4	8	4
D_c/g cm^{-3}	1.88	1.80	1.86	1.89
D_m/g cm^{-3}	1.86	1.81	1.87	1.89
μ(Mo $K\alpha$)/cm^{-1}	19.27	19.91	17.08	19.43
Crystal size/mm	0.50 × 0.45 × 0.30	0.40 × 0.30 × 0.22	0.50 × 0.45 × 0.10	0.57 × 0.40 × 0.20
2θ range/°	1.0–44.0	1.0–50.0	1.0–48.0	1.0–49.0
Total no. of reflections measured	8990	2109	9244	4958
No. of unique Reflections with $I \ge 3\sigma(I)$	6674	1190	5150	3658
R	0.043	0.045	0.045	0.036
R_w	0.066	0.050	0.055	0.040

were inserted into their calculated positions. These hydrogen atoms were fixed at their positions with the isotropic thermal parameters set at 1.3-times those of the atoms to which they are attached. A weighting scheme, $w = 1/[\sigma^2(|F_o|) + (0.02|F_o|)^2 + 1.0]$, was employed. The final discrepancy factors, $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$, are listed in Table 1. All of the calculations were performed on a VAX station 4000(90A) using a MolEN program package.[20] The X-ray analysis data have been deposited as Document No. 74012 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 152326–152329.

Results and Discussion

In the earlier report,[9] only one palladium complex, Pd(L^2)ClO_4, was isolated for the system of palladium compounds with the *N,N,S*-tridentate thiolic ligands, (HL^1, HL^2, HL^3, and HL^4). The complex was obtained after a few steps, starting from a reaction with palladium(II) chloride in water. In this study, we improved the synthetic method to a one-pot reaction in an organic solvent by using sodium tetrachloropalladate(II) in place of palladium(II) chloride. The reaction of HL^1 with sodium tetrachloropalladate(II) in methanol–acetonitrile gave yellow crystals of $[Pd_4(L^1)_4]Cl_4 \cdot 8H_2O$ (**1**·$8H_2O$). The crystallization process afforded a solvated species, **1**·3/2CH_3OH·13/8H_2O. The X-ray crystallography reveals that there are two crystallographycally independent tetranuclear complex cations, $[Pd_4(L^1)_4]^{4+}$, in the crystal structure. Both of the two cations are similar to each other. A perspective view of one of the two cations, $[Pd_4(L^1)_4]^{4+}$, is illustrated in Fig. 1. The cation is an aggregate comprised of four Pd(L^1) units having an eight-membered Pd_4S_4 ring with a boat-like conformation of alternating Pd and S atoms. Each palladium ion is in an approximately square-planar N_2S_2 coordination environment with two amino-nitrogen atoms and one thiolato-sulfur atom of L^1 and one thiolato-sulfur atom of the neighbouring unit. The deviations of the donor atoms from each least-squares plane of N_2S_2 donor atoms are less than 0.11 Å and the deviation of each Pd atom from the plane is 0.11–0.17 Å. The dihedral angle of the two coordination planes are 93.5° for the S1–S2–N1–N2 and S2–S3–N3–N4 planes, 90.6° for the S1–S2–N1–N2 and S1–S4–N7–N8 planes, 164.4° for the S1–S2–N1–N2 and S3–S4–N5–N6 planes, 90.8° for the S2–S3–N3–N4 and S3–S4–N5–N6 planes, 164.7° for the S2–S3–N3–N4 and S1–S4–N7–N8 planes, and 92.0° for the S3–S4–N5–N6 and S1–S4–N7–N8 planes, respectively. The Pd–Pd distances via a bridging sulfur atom are 3.842(2)–3.996(2) Å, while the Pd–Pd distances without bridging groups are 3.500(2)–3.793(2) Å (Table 2). These distances are longer than the metal-metal distances in thiolato-briged dinuclear nickel(II) complexes with related thiolic ligands [2.733(5)–3.134(2) Å][8,9,11,13] and exclude any possibility for metal-metal bonding. The Pd–S–Pd angles are 115.0(2)–122.2(2)°. In the case of the nickel(II) complexes, the Ni–S–Ni angles are 76.7(2)–92.5(1)°.[8,9,11,13] These differences may come from the ring size; the former takes an eight-membered *cyclo*-$(Pd–S)_4$ ring, while the latter has a four-membered *cyclo*-$(Ni–S)_2$ ring. The Pd–S bond lengths [2.267(5)–2.320(4) Å] and S–Pd–S angles [94.7(2)–97.6(2)°] fall within the observed ranges for Pd–S bond distances [2.260(2)–2.365(2) Å] and S–Pd–S angles [79.8(1)–100.0(1)°], respectively, in thiolato-bridged palladium(II) complexes.[21–27] The Pd–N bond lengths [2.038(13)–2.093(13) Å] are comparable to those observed for thiolato-bridged palladium(II) complexes having N donor atoms [2.086(6)–2.220(5) Å].[21,25]

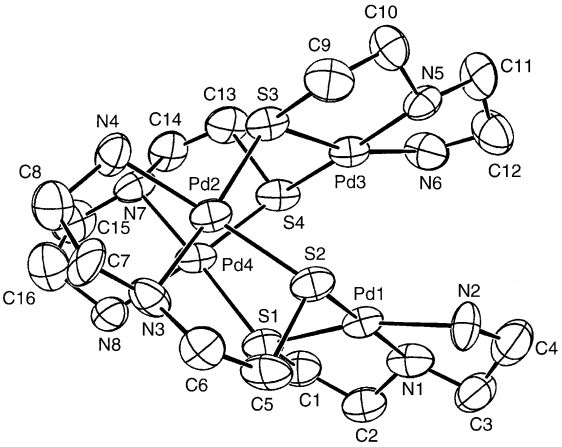

Fig. 1. ORTEP drawing of the structure of the cation in **1**·3/2CH_3OH·13/8H_2O showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

A similar reaction of a related thiolic ligand, 2-[(3-aminopropyl)amino]ethanethiol (HL^2), with sodium tetrachloropalladate(II) in methanol–*N,N′*-dimethylacetoamide afforded an analogous complex, $[Pd_4(L^2)_4]Cl_4 \cdot 2H_2O$ (**2**·$2H_2O$). The crystal structure of **2**·4CH_3OH consists of a tetranuclear cation, $[Pd_4(L^2)_4]^{4+}$, four chloride ions, and four methanol molecules. A perspective view of $[Pd_4(L^2)_4]^{4+}$ is illustrated in Fig. 2. The molecular structure is very similar to that of **1**, except that the cation has a crystallographically imposed S_4 symmetry. The deviations of atoms from the least-squares plane of N_2S_2 are less than 0.07 Å and the deviation of Pd from the plane is only 0.06 Å. The dihedral angle of the two coordination planes is 87.4 or 155.2°. The Pd–Pd′ [prime refers to the equivalent position (y+3/4, 5/4−x, 5/4−z)] distance and the Pd–S–Pd‴ [triple prime refers to the equivalent position (−y+5/4, −3/4+x, 5/4−z)] angle are 3.738(1) Å and 109.4(1)°, respectively. The Pd–S bond lengths [2.270(3), 2.311(3) Å], S–Pd–S angle [93.8(1)°], and Pd–N bond lengths [2.084(9), 2.091(9) Å] compare with those that are observed for **1**. The chloride ion is in the vicinity of the amino-nitrogen atoms of the ligand, as indicated by the distances Cl···N1 3.201(9) Å and Cl···N2‴ 3.36(1) Å [triple prime refers to the equivalent position (5/4−y, x−3/4, 5/4−z)], which suggest the occurrence of hydrogen bondings. The chloride ion is further hydrogen-bonded to the methanol molecule, as implied by the Cl···O (CH_3OH) distance of 3.04(1) Å.

When 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3) was al-

Table 2. Selected Bond Distances (Å) and Angles (°) with Their Estimated Standard Deviations in Parentheses

$[Pd_4(L^1)_4]Cl_4\cdot3/2CH_3OH\cdot13/8H_2O$ (**1**$\cdot3/2CH_3OH\cdot13/8H_2O$)

Pd1	Pd2	3.898(2)		Pd3	N5	2.038(13)	
Pd1	Pd3	3.500(2)		Pd3	N6	2.09(2)	
Pd1	Pd4	3.940(2)		Pd4	S1	2.306(4)	
Pd2	Pd3	3.971(2)		Pd4	S4	2.271(5)	
Pd2	Pd4	3.520(2)		Pd4	N7	2.057(12)	
Pd3	Pd4	3.842(2)		Pd4	N8	2.078(14)	
Pd5	Pd6	3.951(2)		Pd5	S5	2.272(5)	
Pd5	Pd7	3.510(2)		Pd5	S6	2.297(5)	
Pd5	Pd8	3.928(2)		Pd5	N9	2.039(14)	
Pd6	Pd7	3.926(2)		Pd5	N10	2.09(2)	
Pd6	Pd8	3.793(2)		Pd6	S6	2.268(5)	
Pd7	Pd8	3.996(2)		Pd6	S7	2.300(4)	
Pd1	S1	2.277(4)		Pd6	N11	2.059(11)	
Pd1	S2	2.291(5)		Pd6	N12	2.075(14)	
Pd1	N1	2.057(14)		Pd7	S7	2.277(5)	
Pd1	N2	2.089(14)		Pd7	S8	2.289(4)	
Pd2	S2	2.267(4)		Pd7	N13	2.052(13)	
Pd2	S3	2.320(4)		Pd7	N14	2.093(13)	
Pd2	N3	2.052(13)		Pd8	S5	2.308(5)	
Pd2	N4	2.082(13)		Pd8	S8	2.275(4)	
Pd3	S3	2.278(5)		Pd8	N15	2.037(13)	
Pd3	S4	2.285(4)		Pd8	N16	2.083(12)	
S1	Pd1	S2	95.8(2)	S1	Pd4	N8	93.8(4)
S1	Pd1	N1	87.3(4)	S4	Pd4	N7	86.8(4)
S1	Pd1	N2	167.0(4)	S4	Pd4	N8	166.0(4)
S2	Pd1	N1	174.5(4)	N7	Pd4	N8	83.7(5)
S2	Pd1	N2	92.7(4)	S5	Pd5	S6	96.5(2)
N1	Pd1	N2	83.6(6)	S5	Pd5	N9	86.7(4)
S2	Pd2	S3	95.9(2)	S5	Pd5	N10	167.1(4)
S2	Pd2	N3	87.0(4)	S6	Pd5	N9	173.2(4)
S2	Pd2	N4	164.4(4)	S6	Pd5	N10	92.1(4)
S3	Pd2	N3	176.3(4)	N9	Pd5	N10	83.8(6)
S3	Pd2	N4	93.7(4)	S6	Pd6	S7	95.7(2)
N3	Pd2	N4	83.1(5)	S6	Pd6	N11	87.2(4)
S3	Pd3	S4	94.7(2)	S6	Pd6	N12	167.8(4)
S3	Pd3	N5	87.4(4)	S7	Pd6	N11	175.1(4)
S3	Pd3	N6	166.6(4)	S7	Pd6	N12	92.4(4)
S4	Pd3	N5	175.0(4)	N11	Pd6	N12	84.1(5)
S4	Pd3	N6	93.7(4)	S7	Pd7	S8	96.1(2)
N5	Pd3	N6	83.4(6)	S7	Pd7	N13	87.5(4)
S1	Pd4	S4	95.2(2)	S7	Pd7	N14	165.5(4)
S1	Pd4	N7	176.2(4)	S8	Pd7	N13	173.0(3)
S8	Pd7	N14	91.9(4)	Pd1	S1	Pd4	118.5(2)
N13	Pd7	N14	83.3(5)	Pd1	S2	Pd2	117.6(2)
S5	Pd8	S8	97.6(2)	Pd2	S3	Pd3	119.4(2)
S5	Pd8	N15	175.6(4)	Pd3	S4	Pd4	115.0(2)
S5	Pd8	N16	92.9(4)	Pd5	S5	Pd8	118.1(2)
S8	Pd8	N15	86.6(4)	Pd5	S6	Pd6	119.9(2)
S8	Pd8	N16	165.4(4)	Pd6	S7	Pd7	118.2(2)
N15	Pd8	N16	82.8(5)	Pd7	S8	Pd8	122.2(2)

$[Pd_4(L^2)_4]Cl_4\cdot4CH_3OH$ (**2**$\cdot4CH_3OH$)[a)]

Pd	Pd′	3.738(1)		Pd	S′	2.311(3)	
Pd	Pd″	3.842(1)		Pd	N1	2.091(9)	
Pd	S	2.270(3)		Pd	N2	2.084(9)	
S	Pd	S′	93.8(1)	S′	Pd	N1	179.6(3)
S	Pd	N1	86.6(3)	S′	Pd	N2	87.8(3)
S	Pd	N2	174.0(3)	N1	Pd	N2	91.8(4)

$[Pd_4(L^3)_4](ClO_4)_3Cl\cdot2CH_3OH\cdot H_2O$ (**3**$\cdot2CH_3OH\cdot H_2O$)

Pd1	Pd2	3.636(1)		Pd2	S3	2.308(3)	
Pd1	Pd3	3.649(1)		Pd2	N3	2.032(10)	
Pd1	Pd4	3.647(1)		Pd2	N4	2.079(9)	
Pd2	Pd3	3.668(1)		Pd3	S3	2.269(3)	
Pd2	Pd4	3.659(1)		Pd3	S4	2.313(3)	
Pd3	Pd4	3.682(1)		Pd3	N5	2.048(9)	
Pd1	S1	2.277(3)		Pd3	N6	2.054(10)	
Pd1	S2	2.315(3)		Pd4	S1	2.315(3)	
Pd1	N1	2.051(9)		Pd4	S4	2.283(3)	
Pd1	N2	2.070(10)		Pd4	N7	2.045(9)	
Pd2	S2	2.276(3)		Pd4	N8	2.075(9)	
S1	Pd1	S2	96.0(1)	S3	Pd3	N6	166.8(3)
S1	Pd1	N1	87.8(3)	S4	Pd3	N5	176.6(3)
S1	Pd1	N2	167.2(3)	S4	Pd3	N6	97.5(3)
S2	Pd1	N1	176.0(3)	N5	Pd3	N6	79.8(4)
S2	Pd1	N2	95.8(3)	S1	Pd4	S4	95.9(1)
N1	Pd1	N2	80.5(4)	S1	Pd4	N7	176.4(3)
S2	Pd2	S3	95.5(1)	S1	Pd4	N8	96.1(3)
S2	Pd2	N3	87.6(3)	S4	Pd4	N7	87.1(3)
S2	Pd2	N4	167.6(3)	S4	Pd4	N8	167.3(3)
S3	Pd2	N3	175.6(3)	N7	Pd4	N8	81.0(4)
S3	Pd2	N4	95.9(3)	Pd1	S1	Pd4	105.2(1)
N3	Pd2	N4	81.4(4)	Pd1	S2	Pd2	104.7(1)
S3	Pd3	S4	95.0(1)	Pd2	S3	Pd3	106.5(1)
S3	Pd3	N5	87.8(3)	Pd3	S4	Pd4	106.5(1)

$[Pd_4(L^4)_4][Pd(SCN)_4]Cl_2\cdot2CH_3OH$ (**4**$\cdot2CH_3OH$)[b)]

Pd1	Pd1′	3.755(1)		Pd2	S1′	2.310(2)	
Pd1	Pd2	3.770(1)		Pd2	S2	2.257(2)	
Pd1	Pd2′	3.884(1)		Pd2	N3	2.092(6)	
Pd2	Pd2′	3.880(1)		Pd2	N4	2.090(5)	
Pd1	S1	2.289(2)		Pd3	S3B	2.322(11)	
Pd1	S2	2.299(2)		Pd3	S3A	2.327(3)	
Pd1	N1	2.071(5)		Pd3	S4B	2.330(10)	
Pd1	N2	2.062(5)		Pd3	S4A	2.307(3)	
Pd1	S1	Pd2′	115.2(1)	S1′	Pd2	S2	90.3(1)
Pd1	S2	Pd2	111.7(1)	S1′	Pd2	N3	176.5(2)
S1	Pd1	S2	97.3(1)	S1′	Pd2	N4	92.6(2)
S1	Pd1	N1	88.2(2)	S2	Pd2	N3	87.4(2)
S1	Pd1	N2	170.6(1)	S2	Pd2	N4	177.1(2)
S2	Pd1	N1	174.1(2)	N3	Pd2	N4	89.8(2)
S2	Pd1	N2	89.1(1)	S3A	Pd3	S4A	87.6(1)
N1	Pd1	N2	85.2(2)	S3B	Pd3	S4B	89.5(4)

a) Primes and double primes refer to the equivalent position (*y* + 3/4, 5/4 − *x*, 5/4 − *z*) and (2 − *x*, 1/2 − *y*, *z*), respectively.

b) Primes refer to the equivalent position (1 − *x*, *y*, 1/2 − *z*).

lowed to react with sodium tetrachloropalladate(II) in methanol–*N*,*N*′-dimethylacetoamide, we could not isolate the palladium(II) compound. Therefore, sodium perchlorate was added to the reaction mixture to give a palladium(II) complex, $[Pd_4(L^3)_4](ClO_4)_3Cl\cdot5H_2O$ (**3**$\cdot5H_2O$). In the infrared spectrum of this complex, the ν(Cl–O) bands of the perchlorate ion appear at 1031–1139 cm^{-1} with a small splitting. This is consistent with no coordination of the perchlorate ion to the metal ion in **3**.[28] The crystal structure of **3**$\cdot2CH_3OH\cdot H_2O$ consists of a tetranuclear cation, $[Pd_4(L^3)_4]^{4+}$, three perchlorate ions, a chloride

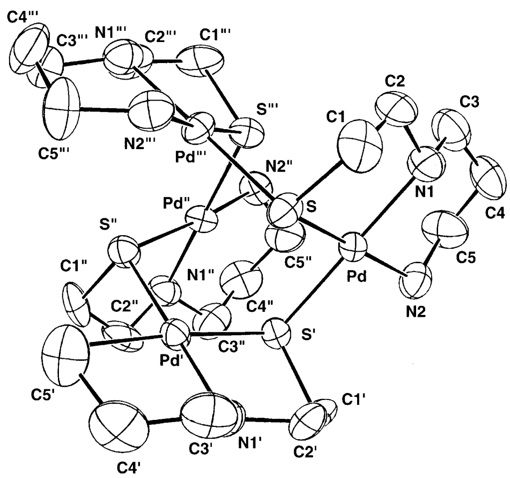

Fig. 2. ORTEP drawing of the structure of the cation in **2**·4CH$_3$OH showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

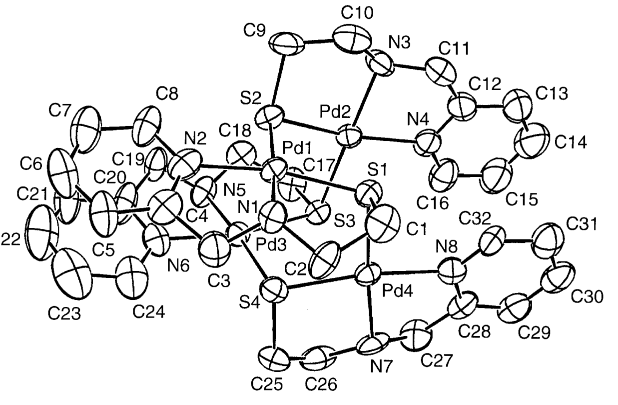

Fig. 3. ORTEP drawing of the structure of the cation in **3**·2CH$_3$OH·H$_2$O showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

ion, two methanol molecules and a water molecule. A perspective view of [Pd$_4$(L^3)$_4$]$^{4+}$ is illustrated in Fig. 3. The structure of the cation is similar to those found in **1** and **2**. Each palladium ion adopts an essentially planar configuration with aliphatic amino-nitrogen, pyridyl-nitrogen, and bridging thiolato-sulfur atoms. The deviations of atoms from the least-squares plane of N$_2$S$_2$ are less than 0.10 Å and the deviation of Pd from the plane is 0.02–0.04 Å. The dihedral angles of the two coordination planes are 88.5–89.6° or 171.9–172.4°. The Pd–Pd distances [3.636(1)–3.682(1) Å] and the Pd–S–Pd angles [104.7(1)–106.5(1)°] are similar to those of **1** and **2**. The Pd–S bond lengths [2.269(3)–2.315(3) Å] and S–Pd–S angle [95.0(1)–96.0(1)°] fall within the observed ranges for Pd–S bond distances [2.267(5)–2.320(4) Å] and S–Pd–S bond angles [94.7(2)–97.6(2)°], respectively, in **1** and **2**. The Pd–N bond lengths of aliphatic amine (N1, N3, N5, N7) [2.032(10)–2.048(9) Å] compare with those of pyridyl-nitrogen (N2, N4, N6, N8) [2.054(10)–2.079(9) Å].

In attempting to prepare analogous compounds with 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4), two compounds, [Pd$_4$(L^4)$_4$][Pd(SCN)$_4$]Cl$_2$·2H$_2$O (**4**·2H$_2$O) and [Pd$_4$(L^4)$_4$](ClO$_4$)$_4$·4H$_2$O (**5**·4H$_2$O), could be isolated. The presence of thiocyanate and perchlorate ions in these complexes could be confirmed by their infrared spectra, which show the ν(N–C) band at 2100 cm^{-1} and the ν(Cl–O) bands at 1085–1132 cm^{-1}, respectively. The crystal structure of **4**·2CH$_3$OH consists of a tetranuclear cation, [Pd$_4$(L^4)$_4$]$^{4+}$, a tetrakis(thiocyanato)palladate(II) ion, [Pd(SCN)$_4$]$^{2-}$, two chloride ions, and two methanol molecules. A perspective view of [Pd$_4$(L^4)$_4$]$^{4+}$ is illustrated in Fig. 4. The cation has C_2 symmetry with the crystallographic two-fold axis passing through the two midpoints of Pd1–Pd1′ and Pd2–Pd2′. The coordination environment of each palladium ion is similar to that of **3**. The deviations of atoms from the least-squares plane of N$_2$S$_2$ are less than 0.06 Å and the deviations of Pd1 and Pd2 from the plane are 0.08 and 0.03 Å, respectively. The Pd–Pd distances [3.770(1)–3.884(1) Å] are slightly longer than those found in **3** [3.636(1)–3.682(1) Å]. The Pd–S–Pd angles [115.2(1), 111.7(1)°] are more obtuse compared with those of **3**. The expansion of the Pd$_4$S$_4$ core in **4** may be ascribed to the larger chelate ring of L^4. The Pd–S distances [2.257(2)–2.310(2) Å] are comparable to those of **1**, **2**, and **3**. The Pd–N (amino) [2.071(5), 2.092(6) Å] and the Pd–N (pyridyl) [2.062(5), 2.090(5) Å] are also comparable to the corresponding Pd–N distances of **1**, **2**, and **3**. In the Pd(SCN)$_4^{2-}$ ion, each thiocyanato ligand is bonded to the palladium atom through the sulfur atom in a square-planar configuration. The infrared spectrum of **4** [ν(C–N) 2100 cm^{-1}, ν(C–S) 768 cm^{-1}] is compatible with this fact.[28] The tetrakis(thiocyanato)palladate(II) anion is in the shape of a gammadion, but with some disorder, as is usual for S-bonded thiocyanates.[29–31] The chloride ion is in the vicinity of the amino-nitrogen atom of the ligand, as indicated by the distance Cl···N1″ 3.215(6) Å [double prime refers to the equivalent position (1−x, y, 1/2−z)], which suggests the occurrence of hydrogen bonding. The chloride ion is further hydrogen-bonded to the methanol molecule,

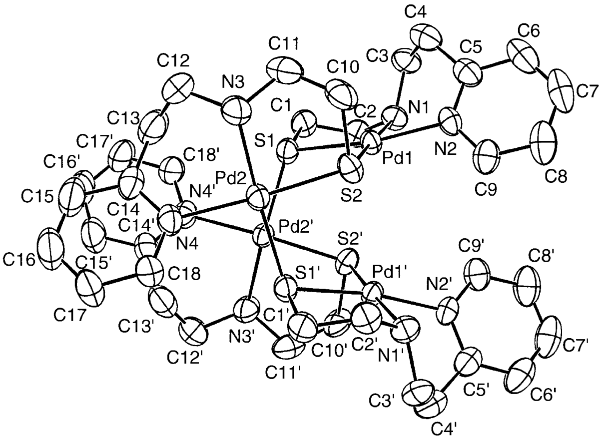

Fig. 4. ORTEP drawing of the structure of the cation in **4**·2CH$_3$OH showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

as implied by the Cl···O (CH_3OH) distance of 3.06(1) Å. Although the X-ray crystallographic work was unsuccessful for **5**, it is reasonable to assume that the complex has a tetranuclear structure similar to those of **3** and **4** based on the analytical data and the similarity of the infrared and electronic spectra to those of **3**.

The diffuse reflectance spectra of **1** and **4** are shown in Fig. 5. Chloride and perchlorate complexes **1**, **2**, and **5** are yellow or orange and have no distinct absorption band in the visible region, although complex **3** has a weak shoulder around 588 nm. On the other hand, the thiocyanate complex **4** is red and shows an absorption band at 503 nm. This band is absent in the chloride and perchlorate complexes; such an absorption seems to be characteristic of $[Pd(SCN)_4]^{2-}$ and may be assigned to d-d transitions for the PdS_4 chromophores. The present palladium(II) complexes show one or two intense bands (229–257 nm, 311–327 nm) in the ultraviolet region and one band (340–357 nm) at near-ultraviolet region. The former bands may be assigned to the charge-transfer transitions from the bridging S atoms to the Pd atoms and the latter due to the d-d transitions for the PdN_2S_2 chromophores.[32] Complexes **1**, **2**, **3**, and **5** are soluble in organic solvents. The absorption spectra of these complexes are essentially similar to those of the diffused reflectance spectra, respectively. The ^{1}H NMR spectra were measured for these complexes. A comparison of the ^{1}H NMR chemical shifts is shown in Fig. 6. The NMR spectra, which can be assigned to only one set of ligand resonances, indicate that the complexes are stable and all thiolic ligands are symmetrically equivalent in solution.

In this study, the four *N*,*N*,*S*-tridentate thiolic ligands (HL) have proved to form a thiolato-bridged tetranuclear $[Pd_4(L)_4]^{4+}$ core containing a *cyclo*-(Pd–S)$_4$ ring. All of the eight-membered rings have a boat-like conformation and there are no significant differences in these tertranuclear cores, except for the Pd-S-Pd angles; the angles are 115.0(2)–122.2(2)°, 109.4(1)°, 104.7(1)–106.5(1)°, 111.7(1)–115.2(1)°, for **1**, **2**, **3**, and **4**, respectively. The Pd–S–Pd angles of **3** are the smallest among the present complexes. This may be ascribed to the smallest chelate ring of L^{3-}. The Pd_4S_4 ring formation is a marked contrast with the case for nickel(II), where the dinuclear $[Ni_2(L)_2]^{2+}$ core containing *cyclo*-(Ni–S)$_2$ ring forms exclusively. In both cases, the coordination environment around the metal center is an N_2S_2 square-plane. The unique Pd_4S_4 core formation may be ascribed to the preference for ring formation in palladium(II) thiolates. This kind of Pd_4S_4 core appeared in the literature recently.[23,26,27]

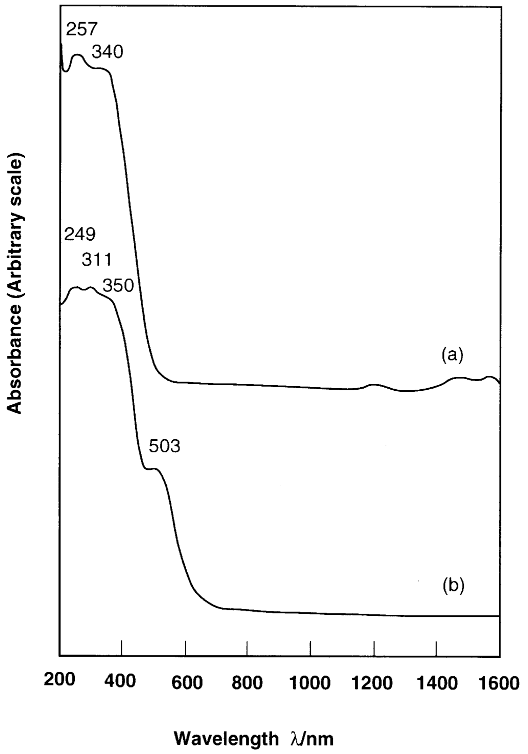

Fig. 5. Diffuse reflectance spectra of complexes. (a) **2** and (b) **4**.

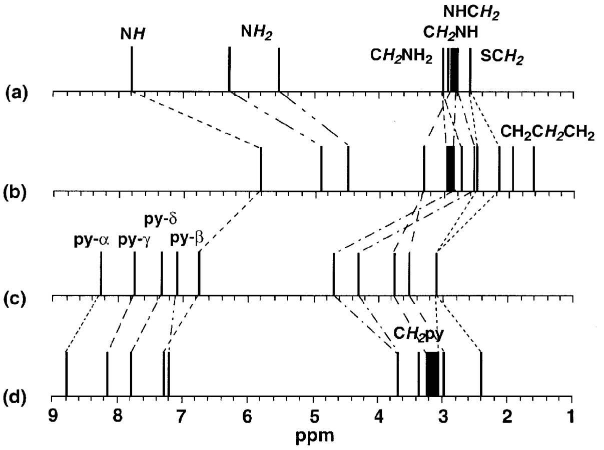

Fig. 6. Comparison of ^{1}H NMR chemical shifts of complexes, (a) **1**, (b) **2**, (c) **3**, and (d) **5**.

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