Syntheses, Structures, and Magnetic Properties of Di-μ_3-Chloride-Bridged Tripalladium Compounds, $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (HqnS = Quinoline-2(1*H*)-thione) and $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (Et_2dtc = *N*, *N*′-Diethyldithiocarbamate)

Kunihisa Sugimoto, Takayoshi Kuroda-Sowa,* Tamotsu Goto, Masahiko Maekawa,† and Megumu Munakata

Department of Chemistry, Kinki University, Higashi-Osaka, Osaka 577-8502

†Research Institute for Science and Technology, Kinki University, Higashi-Osaka, Osaka 577-8502

(Received September 13, 1999)

Two triangular tripalladium compounds, $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (**1**) (HqnS = quinoline-2(1*H*)-thione), and $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (**2**) (Et_2dtc = *N*, *N*′-diethyldithiocarbamate anion), were prepared. Their single crystal X-ray structure analyses revealed they have a similar trigonal bipyramidal framework of $Pd_3(\mu_3\text{-}Cl)_2$ with two chlorine atoms in apical positions. Each Pd atom in all clusters has two additional coordination sites to establish a square planar *cis*-$PdL_2(\mu_3\text{-}Cl)_2$ geometry. In compound **1**, six sulfur atoms of six HqnS ligands with thion form are coordinated to the vacant sites of the $Pd_3(\mu_3\text{-}Cl)_2$ core. Two coordination sites of one of the three Pd atoms in **2** are occupied by two triphenylphosphines and those of the other two are coordinated by two S atoms of Et_2dtc. Although both compounds have 50 valence electrons, only **1** shows paramagnetic behavior. Crystallographic data are as follows. **1**: $Pd_3Cl_4S_6N_6C_{54}H_{42}$, triclinic, $P\bar{1}$, $a = 14.988(5)$, $b = 17.328(3)$, $c = 12.642(1)$ Å, $\alpha = 93.61(1)$, $\beta = 96.06(2)$, $\gamma = 71.79(2)^\circ$, $V = 3099(1)$ Å^3, and $Z = 2$. **2**: $Pd_3Cl_2P_2S_4N_2C_{52}H_{56}$, monoclinic, $P2_1$, $a = 12.278(5)$, $b = 17.426(6)$, $c = 12.630(3)$ Å, $\beta = 94.65(3)^\circ$, $V = 2693(2)$ Å^3, and $Z = 2$.

Since group 10 transition-metal ions in low oxidation states prefer square planar coordination, there are two types of core frameworks for trinuclear triangular compounds of these metal ions.[1] One has all equatorial ligands in coplanar coordination to the M_3 equilateral triangle and the other dose not have them in such coordination. A series of trimetal compounds bridged by bis(diphenylphosphino)methane (dppm), $[M_3(\mu_3\text{-}CO)(dppm)_3]^{2+}$ system (M = Ni, Pd, Pt) affords a typical example of the former type. Their reactivity and their potential utilization as catalysts have been extensively explored by Puddephatt and co-workers[2] and by others.[3,4] μ_3-Bridging carbonyls in this type of compound are labile and are easily replaced by other two-electron donors.[2] On the other hand, the core framework of $[M_3(\mu_3\text{-}E)_2(L)_6]^{2+}$ (M = Ni, Pd; E = O, S, or $Se(SiMe_3)_2$; L = P- or S-centered ligands or halogenide ions)[5—12] is an example of the latter type, which can be described as three square planar *cis*-ME_2L_2 moieties having two E ligands in common. The role of μ_3-bridging ligands in this case is important to maintain the structure: each E ligand donates three lone pairs to three metal ions and is regarded as bearing of a waterwheel with three fliers. In this type of compound, metal–metal separations are fairly large compared to those of the former type or of bulk metals. As far as we know,[13,14] only chalcogen atoms[2] have been reported for bridging E atoms. As chalcogen-bridged system has 48 valence electrons, replacing two E atoms from chalcogen to halogen causes an addition of two electrons to the trimetal compound, forming a compound with 50-valence electrons. Trimetal compounds with more than 49 valence electrons are rare. To our knowledge, only those containing electronegative cyclopentadienyl (Cp) ligands in cobalt and nickel systems[1] are reported. During the course of our study in trimetal cluster chemistry,[15,16] we have found that two new tripalladium compounds with bis-μ_3-bridging chlorides, $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (**1**) and $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (**2**), can be synthesized. Their crystal structures and magnetic properties are reported.

Experimental

All chemicals and solvents used were reagent grade, purchased from Wako Chemicals Co., Ltd. and Aldrich Co., Ltd. Most of manipulations were carried out under argon with Schlenk-type flasks. Solvents were dried and purified in the usual manner before use and stored under argon.

Physical Measurements. Infrared spectra were recorded on a JASCO FT/IR-8000E spectrometer using KBr disks. NMR spectra were recorded by using a JEOL GSX-270 spectrometer with use of $Si(CH_3)_4$ as an internal standard for ^1H or 30 wt% aqueous solution of H_3PO_4 as an external standard for ^{31}P. ESR spectra were obtained on a JEOL JES-TE200 ESR spectrometer. Variable-temperature magnetic susceptibility data were collected between 4.2 and 270 K using a Quantum Design $MPMS_2$ system with an applied magnetic field of 1.0 T.

Synthesis of $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (1). A 15 ml CH_2Cl_2 solution of $[Pd(dba)_2]$ (23 mg, 0.04 mmol, dba = dibenzylideneacetone) was cooled at −40 °C and HqnS (13 mg, 0.08 mmol) was added to the solution. After being stirred for a few minutes, the reaction mixture was allowed to warm to room temperature. The mixture was filtered and the filtrate was sealed in glass tubes which were kept at room temperature. After three days, red crystals of $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (**1**) were obtained. Yield 10 mg (52.5% based on Pd). Main IR bands 3200 cm^{-1} (m, br), 1582 cm^{-1} (s), 1100 cm^{-1} (m). Found: C, 45.7; H, 3.04; N, 6.00%. Calcd for $Pd_3Cl_4S_6N_6C_{54}H_{42}$: C, 45.41; H, 2.96; N, 5.88%.

Synthesis of $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (2) A mixture of $[Pd(PhCN)_2Cl_2]$ (46 mg, 0.12 mmol), $NaEt_2dtc$ (28 mg, 0.12 mmol), and PPh_3 (32 mg, 0.12 mmol) were stirred in 16 ml of benzene/methanol mixed solvent (v/v: 3/5) under argon at room temperature. $NaBH_4$ (27 mg, 0.72 mmol) was added to the suspension and this mixture was stirred until the color of the suspension became brown. The mixture was then filtered and the filtrate was sealed in glass tubes which were allowed to stand at room temperature. After one week, red crystals of $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (**2**) were obtained. Yield 31 mg (60.1% based on Pd). IR 1519 cm^{-1} (ν_{CN}). ^{1}H NMR ($(CD_3)CO$) δ = 7.70 (m), 7.57 (m), 7.36 (m) (Ph), 3.77 (q), 1.27 (t) (Et_2dtc). ^{31}P NMR ($(CH_3)_2CO$) δ = 25.73 (s). Found: C, 48.89; H, 4.65; N, 2.17%. Calcd for $Pd_3Cl_2P_2S_4N_2C_{52}H_{56}$: C, 48.44; H, 4.38; N, 2.17%.

X-Ray Data Collections, Reductions, and Structure Determinations. X-Ray measurements of **1** and **2** were made with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) on Rigaku AFC6S and AFC5R diffractometers, respectively. The intensities of three representative reflections were measured after every 150 reflections. These results showed a good stability of the intensities. An empirical absorption correction based on ψ scan[17] was applied for compounds **1** and **2**. The data were corrected for Lorentz and polarization effects. All structures were solved by heavy-atom Patterson methods[18] and expanded using Fourier techniques.[19] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but were not refined. The refinements (on F^2) were performed by using full-matrix least-squares method, where the unweighted and weighted agreement factors of $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ are used. Neutral atomic scattering factors were taken from Cromer and Waber.[20] All calculations were performed using the teXsan[21] crystallographic software package of Molecular Structure Corporation. Crystal data and details of the structure determination for the compounds **1** and **2** are summarized in Table 1. Relevant bond length and bond angles for compounds **1** and **2** are given in Tables 2 and 3, respectively.

Complete listings of the atomic coordinates and bond parameters as well as a listing of observed and calculated structure factors have been deposited as Document No. 73018 at the Office of the Editor of Bull. Chem. Soc. Jpn. and available from the Cambridge Crystallographic Data Centre.

Results and Discussion

Structure of $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (1). Figure 1 shows an ORTEP drawing of **1**, which also provides the atomic numbering scheme for important atoms. The core framework of $Pd_3(\mu_3\text{-}Cl)_2S_6$, now having a pseudo D_{3h} symmetry, is constructed from three square planar *cis*-$PdCl_2S_2$ moieties, which have two chlorine atoms in common. The average Pd–Cl distance of 2.312 Å is similar to 2.311(1) Å observed for a Pd–Cl distance in $Pd(HqnS)(PMe_3)Cl_2$[22] in which two chlorine atoms have *cis*-orientation. The Pd–S distance of 2.351 Å in average is a little longer than 2.297(1) Å observed in $Pd(HqnS)(PMe_3)Cl_2$.[22]

Table 1. Crystallographic Data for $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]$-$Cl_2$ (**1**) and $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (**2**)

	1	**2**
Formula	$Pd_3Cl_4S_6N_6C_{54}H_{42}$	$Pd_3Cl_2P_2S_4N_2C_{52}H_{56}$
Formula weight	1428.34	1289.32
Crystal color	Red	Red
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a/Å	17.328(3)	12.278(5)
b/Å	14.988(5)	17.426(6)
c/Å	12.642(1)	12.630(3)
α/deg	83.94(2)	90
β/deg	86.39(1)	94.65(3)
γ/deg	71.79(2)	90
V/Å^3	3099(1)	2693(2)
Z	2	2
D_{calcd}/g cm^{-3}	1.530	1.590
Radiation	Mo $K\alpha$	Mo $K\alpha$
μ/cm^{-1}	12.74	13.41
$R1$[a)]	0.052	0.045
$wR2$[b)]	0.131	0.112
GOF	1.07	0.99

a) $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.
b) $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Relevant Bond Lengths (Å) and Angles (°) with the Estimated Standard Deviations in Parentheses for $[Pd_3(\mu_3\text{-}Cl)_2(HqnS)_6]Cl_2$ (**1**)

	(a) Bond lengths (Å)		
Pd(1)–Cl(1)	2.317(2)	Pd(1)–Cl(2)	2.306(2)
Pd(1)–S(1)	2.341(2)	Pd(1)–S(2)	2.354(2)
Pd(2)–Cl(1)	2.312(2)	Pd(2)–Cl(2)	2.315(2)
Pd(2)–S(3)	2.353(2)	Pd(2)–S(4)	2.354(2)
Pd(3)–Cl(1)	2.316(1)	Pd(3)–Cl(2)	2.308(2)
Pd(3)–S(5)	2.358(2)	Pd(3)–S(6)	2.348(2)
S(1)–C(1)	1.704(6)	S(2)–C(10)	1.701(7)
S(3)–C(19)	1.693(8)	S(4)–C(28)	1.703(8)
S(5)–C(37)	1.724(7)	S(6)–C(46)	1.683(8)
Pd(1)···Pd(2)	3.1864(6)	Pd(2)···Pd(3)	3.0647(7)
Pd(1)···Pd(3)	3.1536(7)		
	(b) Bond angles (°)		
Pd(2)–Pd(1)–Pd(3)	57.81(1)	Pd(1)–Pd(2)–Pd(3)	60.56(2)
Pd(2)–Pd(1)–Pd(3)	61.63(1)	Pd(1)–Cl(1)–Pd(2)	87.02(5)
Pd(1)–Cl(1)–Pd(3)	85.80(5)	Pd(2)–Cl(1)–Pd(3)	82.94(5)
Pd(1)–Cl(2)–Pd(2)	87.18(5)	Pd(1)–Cl(2)–Pd(3)	86.23(5)
Pd(2)–Cl(2)–Pd(3)	83.05(5)	Cl(1)–N(1)–C(9)	124.4(5)
C(10)–N(2)–C(18)	123.8(5)	C(19)–N(3)–C(27)	125.5(6)
C(28)–N(4)–C(36)	124.8(7)	C(37)–N(5)–C(45)	124.1(6)
C(46)–N(6)–C(54)	125.6(8)		

Table 3. Relevant Bond Lengths (Å) and Angles (°) with the Estimated Standard Deviations in Parentheses for $[Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2]\cdot C_6H_6$ (**2**)

	(a) Bond lengths (Å)		
Pd(1)–Cl(1)	2.343(2)	Pd(1)–Cl(2)	2.363(2)
Pd(2)–Cl(1)	2.306(2)	Pd(2)–Cl(2)	2.313(3)
Pd(3)–Cl(1)	2.312(3)	Pd(3)–Cl(2)	2.317(2)
Pd(1)–P(1)	2.297(3)	Pd(1)–P(2)	2.324(3)
Pd(2)–S(1)	2.337(3)	Pd(2)–S(2)	2.340(3)
Pd(3)–S(3)	2.336(3)	Pd(3)–S(4)	2.332(3)
Pd(1)···Pd(2)	3.129(1)	Pd(2)···Pd(3)	3.162(1)
Pd(1)···Pd(3)	3.016(1)		
	(b) Bond angles (°)		
Pd(2)–Pd(1)–Pd(3)	61.91(3)	Pd(1)–Pd(2)–Pd(3)	52.27(3)
Pd(1)–Pd(3)–Pd(2)	60.79(3)	Pd(1)–Cl(1)–Pd(2)	84.61(8)
Pd(1)–Cl(1)–Pd(3)	80.77(8)	Pd(2)–Cl(1)–Pd(3)	86.45(9)
Pd(1)–Cl(2)–Pd(2)	84.00(9)	Pd(1)–Cl(2)–Pd(3)	80.22(8)
Pd(2)–Cl(2)–Pd(3)	86.15(9)		

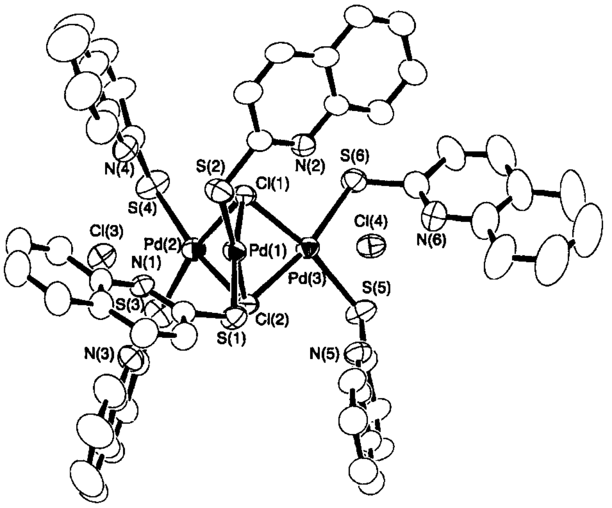

Fig. 1. Molecular structure of **1** showing the atom numbering scheme.

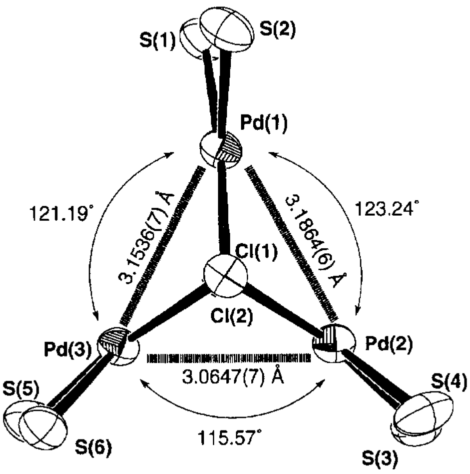

Fig. 2. A top view of the core framework of **1**.

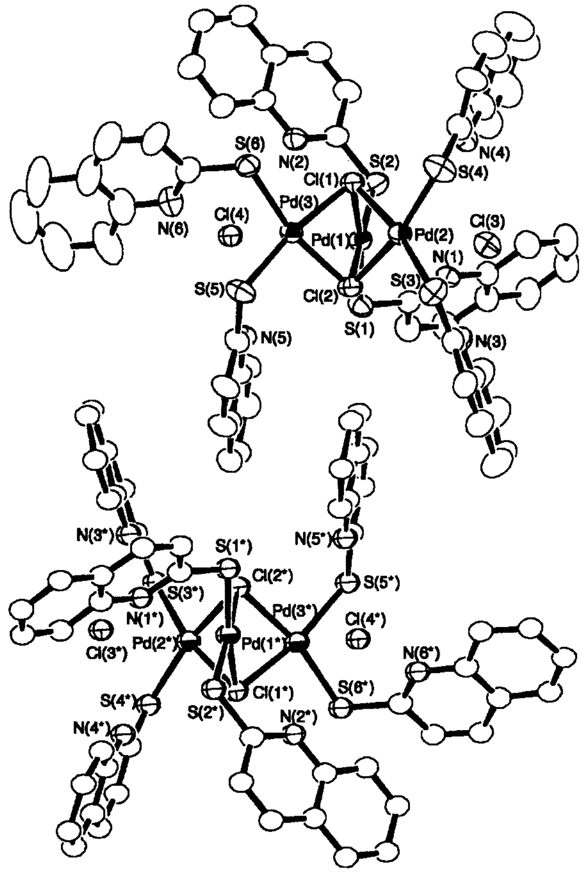

Fig. 3. Molecular packing of **1** viewed from *b*-axis.

A top view of the core framework of **1** is shown in Fig. 2 together with their Pd···Pd distances and dihedral angles between each pair of Pd square planes. The Pd···Pd distances in **1** are 3.1864(6), 3.0647(7), and 3.1536(7) Å for Pd(1)···Pd(2), Pd(2)···Pd(3), and Pd(1)···Pd(3), respectively. The variation of these Pd···Pd distances is again difficult to explain by intramolecular interactions only. Figure 3 shows an arrangement of two molecules viewed from a vertical direction to a Pd(2)···Pd(3) vector. Two HqnS containing N(5) atom are parallel to each other and show a π–π interaction with the nearest carbon-to-carbon distance of 3.55 Å. Additionally, HqnS containing N(3) atom is located near the aforementioned HqnS of the neighboring molecule (the nearest carbon-to-carbon distance of 3.40 Å) although the planes are not completely coplanar (dihedral angle of 25.4°). This π–π interaction column extends in the direction of a Pd(2)···Pd(3) vector. Compression along this direction results in the shorter Pd(2)···Pd(3) distance than the others, which is a reasonable explanation for the observed variation of Pd···Pd distances. Two, non-coordinating chloride anions are incorporated in the crystal as counter anions. The existence of them is important not only for the charge compensation but also for determination of orientations of HqnS ligands. As can be seen from Fig. 3, Cl(3) and Cl(4) are surrounded by nitrogen atoms of HqnS ligands. Six Cl···N distances are in the range of 3.151(7) to 3.242(5) Å, indicating the existence of significant N–H···Cl hydrogen bonding interaction. As for the tautomarization between thione (–C(S)–NH–) and thiole (–C(SH)=N–) forms in HqnS, most of the HqnS ligands are considered to have thione forms because of the following reasons: 1) the observation of ν_{NH} at around 3400 cm^{-1} and the lack of ν_{SH} at around 2600 cm^{-1} strongly suggest that HqnS has a thione form rather than a thiole form, 2) the existence of the above-mentioned N–H···Cl hydrogen bonding interaction supports the existence of N–H bonds, and 3) the averaged C–S distance of 1.70 Å in **1** is comparable with those reported for C=S double bond distances of HqnS (1.696(6)—1.713(3) Å)[22] or pySH (1.68(2)—1.730(9) Å).[23,24] Since one C–S distance (S(5)–C-(37): 1.724(7) Å) is a little longer than the others and is falling in the range of C–S single bond distances (1.712—1.763 Å),[14] we can not exclude the possibility that the HqnS ligand has the thiole form. However, we can safely say it is not thiolate form (–C(S$^-$)=N–) on the basis of the magnetic property with S = 1 (vide infra).

The source of the chlorine atoms in compound **1** is probably from CH_2Cl_2 used as a solvent. It has been reported that a photochemical reaction of $Pd(S_2C_2O_2)(PMe_3)_2$ in CH_2Cl_2 results in the formation of a $PdCl_2(PMe_3)_2$ complex.[11] Since we did not protect the samples from exposure to room light, similar photo-induced chlorination might occur in this case.

Structure of [$Pd_3(\mu_3\text{-}Cl)_2(Et_2dtc)_2(PPh_3)_2$]·$C_6H_6$ (2). The ORTEP drawing of the molecular structure of **2** is shown in Fig. 4, which also provides an atomic numbering scheme for important atoms. The core framework of $Pd_3(\mu_3\text{-}Cl)_2P_2S_4$ is similar to that of **1**, except for the absence of the three-fold symmetry axis. Three square planar *cis*-$PdCl_2L_2$ moieties (L = P or S) are connected through two bridging chlorine atoms. Two PPh_3 coordinate to Pd(1) at the Pd–P distance of 2.311 Å in average, while two sulfur atoms of Et_2dtc coordinate to Pd(2) or Pd(3) in chelating fashion with a Pd–S distance of 2.336 Å in average. The Pd(1)–Cl distance of 2.353 Å in average for Cl(1) and Cl(2) is slightly longer than 2.312 Å averaged for other four Pd–Cl distances, due to the *trans* effect of a phosphorous atom being stronger than that of a sulfur atom. Figure 5 shows a top view of the core framework of $Pd_3(\mu_3\text{-}Cl)_2P_2S_4$ together with an incorporated benzene molecule is located near one of Et_2dtc. The three Pd···Pd distances are 3.129(1), 3.162(1), and 3.016(1) Å for Pd(1)···Pd(2), Pd(2)···Pd(3), and Pd(1)···Pd(3), respectively. The effect of coordination of triphenylphosphine to Pd(1) directly appears in the distorted bridging mode of chlorine atoms (vide supra), which induces elongation of the Pd(2)···Pd(3) distance, this prediction is consistent with the observations. The reason for a longer Pd(1)···Pd(2) distance compared to that of Pd(1)···Pd(3) is ascribed to a benzene molecule located near Et_2dtc being coordinated to Pd(2) atom. The nearest carbon (C(51): benzene) to sulfur (S(1): Et_2dtc) distance of 3.56(2) Å is an indication of a weak π–π interaction between Et_2dtc and benzene, as shown in Fig. 5. The existence of a benzene molecule within an arc between planes defined by Pd(1)–Cl(1)–Cl(2) and by Pd(2)–Cl(1)–Cl-(2) induces steric repulsion between the benzene and phenyl groups of PPh_3, which probably contributes to the elongation of the Pd(1)···Pd(2) distance.

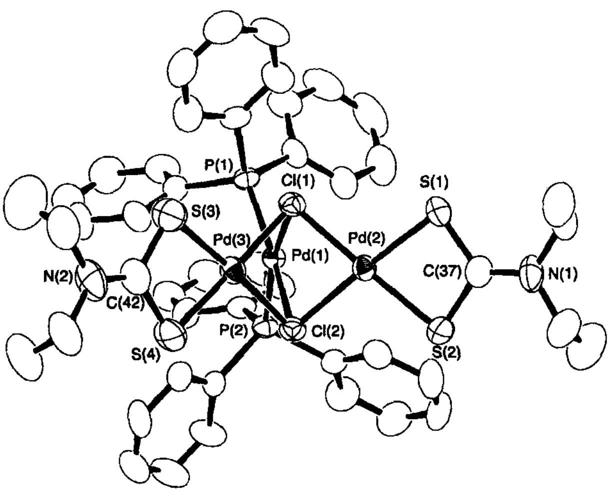

Fig. 4. Molecular structure of **2** showing the atom numbering scheme.

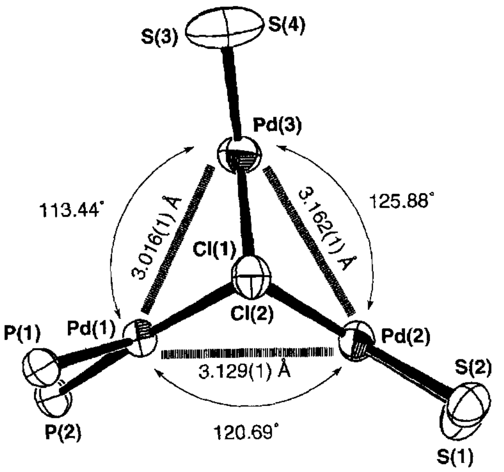

Fig. 5. A top view of the core framework of **2**.

Magnetic Properties. In contrast to the chalcogen-bridged trimetal compounds,[10—12] **1** shows paramagnetic behavior. The solid state powder ESR spectrum of **1** shows an extremely broadened signal expanding from zero field to ca. 500 mT. The temperature dependence of the effective magnetic moment (μ_{eff}) per molecule is shown in Fig. 6. The room temperature value of about 3 μ_B decreases with decreasing temperature, which is well simulated by using the spin Hamiltonian (1) and the S = 1 ground state model, as shown in "calc1" in Fig. 6, with a large positive zero-field splitting

$$H = \mu_B S\cdot g\cdot H + D[S_z^2 - S(S+1)/3], \qquad (1)$$

parameter (D = 420 cm^{-1}). The fairly large D value can be ascribed to the large spin-orbit coupling constant of Pd-(II) (1460 cm^{-1})[25] together with a probably large difference between g-values. We have examined another possibility, that the ground state is S = 0 with a low-lying S = 1 state near in energy. The plot "calc2" in Fig. 6 is the best fit obtained by using Bleaney–Bowers equation,[26] where the g-value is fixed to that obtained by "calc1" (2.38). As can be seen from the figure, it is difficult to reproduce the experimental data.

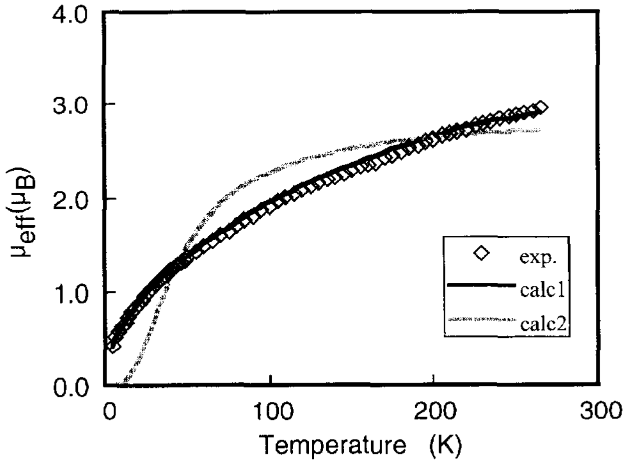

Fig. 6. Temperature dependence of the effective magnetic moment of **1** measured at external magnetic field of 1.0 T. The solid line ("calc1") shows the best fit calculated by using the spin Hamiltonian (1) with $g = 2.38$ and $D = 420$ cm^{-1} and matrix diagonalization method. The g-value was assumed to be isotropic. The doted line ("calc2") is the best fit obtained by using Bleaney–Bowers equation[29] with $g = 2.38$ (fixed) and $J = -56$ cm^{-1}. In both cases, the parameters were obtained by the least-squares fitting.

The comparison of these simulations clearly eliminates the latter model.

On the other hand, **2** is NMR active and ESR silent, indicating that it has an $S = 0$ ground state. Although the valence electron count of 50 is the same as for **1**, the lower symmetry (C_{2v}) compared to **1** will lift the orbital degeneracy and the $S = 0$ ground state can be realized.

This work was supported in part by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research on Priority Areas (Metal-assembled compounds), No. 10016743, 1998, and Scientific Research (C), No. 11640591, 1999.

References

1 In "The Chemistry of Metal Cluster Complexes," ed by D. F. Shriver, H. D. Kaesz, and R. D. Adams, VCH Publishers, Inc., New York (1990).

2 R. J. Puddephatt, L. Manojlovic-Muir, and K. W. Muir, *Polyhedron*, **9**, 2767 (1990).

3 A. L. Balch, B. J. Davis, and M. M. Olmstead, *J. Am. Chem. Soc.*, **112**, 8592 (1990).

4 D. A. Morgenstern, G. M. Ferrence, J. Washington, J. I. Henderson, L. Rosenhein, J. D. Heise, P. E. Fanwick, and C. P. Kubiak, *J. Am. Chem. Soc.*, **118**, 2198 (1996).

5 C. A. Ghilardi, S. Midollini, and L. Sacconi, *Inorg. Chim. Acta*, **31**, L431 (1978).

6 C. A. Ghilardi, S. Midollini, A. Orlandini, C. Battistoni, and G. Mattogno, *J. Chem. Soc., Dalton Trans.*, **1984**, 939.

7 C. A. Ghilardi, P. Innocenti, S. Midollini, and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, **1985**, 2209.

8 E. Carmona, J. M. Marin, P. Palma, M. Paneque, and M. L. Poveda, *Organometallics*, **4**, 2053 (1985).

9 F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, and J. A. Ramirez, *J. Chem. Soc., Dalton Trans.*, **1980**, 773.

10 H. Werner, W. Bertleff, and U. Schubert, *Inorg. Chim. Acta*, **43**, 199 (1980).

11 R. L. Cowan, D. B. Pourreau, A. L. Rheingold, S. J. Geib, and W. C. Trogler, *Inorg. Chem.*, **26**, 259 (1987).

12 D. Fenske, H. Fleischer, H. Krautscheid, and J. Magull, *Z. Naturforsh. B*, **45b**, 127 (1990).

13 F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).

14 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.

15 M. Maekawa, M. Munakata, T. Kuroda-Sowa, and K. Hachiya, *Inorg. Chem. Acta*, **231**, 213 (1995).

16 M. Maekawa, M. Munakata, T. Kuroda-Sowa, and K. Hachiya, *Inorg. Chim. Acta*, **233**, 1 (1995).

17 C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **A24**, 351 (1968).

18 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, and C. Smykalla, "PATTY" (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

19 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, "DIRDIF94," (1994), The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

20 "International Tables for X-Ray Crystallography," ed by D. T. Cromer, and J. T. Waber, The Kynoch Press, Birmingham, England (1974), Vol. IV.

21 "teXsan" Crystal Structure Analysis Package, Molecular Structure Corporation, (1985 & 1999).

22 E. M. Padilla, J. H. Yamamoto, and C. M. Jensen, *Inorg. Chim. Acta*, **174**, 209 (1990).

23 S. C. Kokkou, S. Fortier, P. J. Rentzeperies, and P. Karagiannidis, *Acta Crystallogr., Sect. C*, **39C**, 178 (1983).

24 G. Valle, U. Ettore, V. Vettori, V. Peruzzo, and G. Plazzogna, *J. Chem. Soc., Dalton Trans.*, **1987**, 815.

25 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, **13**, 135 (1970).

26 B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. (London), Ser. A*, **214**, 451 (1952).