Bridged Mercaptide Complexes of Nickel(II) and Palladium(II) with Metal–Metal Interactions

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Abstract: The structural features of three bridged mercaptide complexes, $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$ (A), $Pd_2[SC(CH_3)_3]_2[S_2CSC(CH_3)_3]_2$ (B), and $Pd_3(SC_2H_5)_3(S_2CSC_2H_5)_3$ (C), are described. Each compound contains a distorted planar MS_4 coordination geometry with trigonally bound bridging sulfur atoms in the bridging mercaptide groups. A displays a nonplanar syn-endo Ni_2S_2 rhombus and B a nonplanar anti Pd_2S_2 rhombus. The trimer shows a substantial distortion from the potential trigonal symmetry for the "chair" form of the Pd_3S_3 ring. The dimers A and B have metal–metal distances of 2.795 and 3.162 Å, respectively, while C shows Pd–Pd distances of 3.655, 3.307, and 3.303 Å. The metal–metal distances in the dimers are not consistent with a metal–metal bond alone being the feature controlling the gross stereochemistry of these complexes. Sulfur–sulfur interactions also appear to occur. Data were obtained diffractometrically with Cu $K\bar{\alpha}$ radiation. Refinement produced a final R of 0.062, 0.087, and 0.058 respectively for A, B, and C. The unit cells are as follows with space groups found to be respectively $I2$, $Pnma$ and $P\bar{1}$: A, a = 16.459 (7); b = 4.6041 (5), c = 22.116 (5) Å, β = 97.04°, z = 2; B, a = 11.719 (1), b = 23.186 (1), c = 10.806 Å, z = 4; C, a = 11.573 (1), b = 16.778 (2), c = 9.873 (1) Å, α = 93.18 (1), β = 104.24 (1), γ = 122.29 (1)°, z = 2.

Much has been learned during the past decade about the chemical properties of sulfur containing complexes.[1-3] However, detailed knowledge of structural features and chemical reactivity, particularly of the mercaptide ligand species, is still quite limited. In spite of the importance of metal–mercaptide species in biological chemistry, few nonorganometallic prototype[4] compounds have been studied, largely because of the problems inherent in their synthesis.

Our work[5] has established that certain neutral metal–mercaptide complexes may be synthesized by solution decomposition of the metal thioxanthates (eq I). The

$$2M(S_2CSR)_n \longrightarrow 2CS_2 + [M(SR)(S_2CSR)_{n-1}]_2 \qquad (I)$$

elimination of CS_2 by this route, orginally used by Knox, *et al.*,[6] generally affords crystalline materials. The metal thioxanthates themselves are easily prepared[5] and can be stored. Thioxanthate ligands which remain coordinated to the metal in the mercaptide products are themselves candidates for further reaction chemistry.[7] Lippard and coworkers[8,9] utilized this synthetic technique to prepare and structurally study $Fe_2(SR)_2(S_2CSR)_4$ and $Co_2(SR)_2(S_2CSR)_4$, two compounds containing mercaptide bridges. These compounds display a planar M_2S_4 rhombus. Roussin's salt,[10] $Fe_2(SC_2H_5)_2(NO)_4$, also has a planar Fe_2S_4 rhombus. With[11] $Fe_2(SR)_2(CO)_6$ and[12] $[Fe_2(C_5H_5)_2(SCH_3)_2(CO)_2]^+$, a folded rhombus is found, suggestive of Fe–Fe bonding.

With metal complexes in which the metal ion can be described electronically by [core]nd,[8] any metal–metal interactions assumed generally have been thought to be rather weak.[13] However, the situation has become confused recently by some apparent structural contradictions. Both[14] $Ni_2(S_2CCH_2C_6H_5)_4$ and[13] $Pt_2(S_2CC_6H_4C_3H_7)_4$ show short metal–metal distances (2.56 and 2.87 Å, respectively). Also[15] $Ni_6(SC_2H_5)_{12}$ and[16] $Ni_2[S(CH_2CH_2S)_2]_2$ display folded Ni_2S_2 quadrangles, with Ni–Ni distances of ~2.8 Å. Yet the Pd_2S_2 rhombus[17] in $Pd_2(SC_6F_5)_4(P(C_6H_5)_3)_2$ is planar. After our work had begun, Villa, *et al.*,[18] reported the structure of $Ni_2(SC_2H_5)_2(S_2CSC_2H_5)_2$ and suggested that the 2.76 Å Ni–Ni distance represented "the first example of binuclear planar Ni^{II} complex with Ni–Ni bonds."

In this study we report the crystal and molecular structures of three bridged mercaptide complexes, $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$ (A), an analog of the complex studies by Villa, *et al.*,[18] $Pd_2(SC(CH_3)_3)_2(S_2CSC(CH_3)_3)_2$ (B), a compound with aliphatic bridging mercaptide ligands, and $Pd_3(SC_2H_5)_3(S_2CSC_2H_5)_3$ (C), a trimeric bridged mercaptide species. Added impetus for study of C comes from the fact that a related compound,[19] $Pd_3[(SCH_2CH_2)_2S]_3$, contains a distinctly nontrigonal (3.66, 3.49, and 3.41 Å) arrangement of palladium atoms with Pd–Pd distances averaging close to

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Table I. Crystal and Data Collection Parameters

	A	B	C
Molecular formula	$Ni_2S_8C_{30}H_{28}$	$Pd_2S_8C_{18}H_{36}$	$Pd_3S_{12}C_{15}H_{30}$
Color	Brown	Orange	Orange
Crystal size, mm^3	0.1 × 0.3 × 0.1	0.5 × 0.3 × 0.2	0.4 × 0.1 × 0.1
Radiation used	Nickel filtered Cu $K\bar{\alpha}$ (1.5418 Å)		
Cell dimensions (ambient temp) a	16.459 (7)	11.719 (1)	11.573 (1)
b	4.6041 (5)	23.186 (1)	16.778 (2)
c	22.116 (5)	10.806 (1)	9.873 (1)
α,β,γ	97.04 (2)		93.18 (1), 104.24 (1), 122.29 (1)
Systematic absences	$h + k + l = 2n + 1$	$h0l, h = 2n + 1$; $0kl, k + l = 2n + 1$	
Space group	$I2(C2;\ C_2^3$, No. 5)	$Pnma(D_{2h}^{16}$, No. 62)	($P\bar{1}$ No. 2)
Molecules/unit cell	2	4	2
Density calcd [found]	1.52 [1.51 (1)]	1.63 [1.65 (2)]	1.98 [2.01 (2)]
Scan	θ–2θ	θ–2θ	θ–2θ
Scan speed, deg/min	1	2	2
Background, sec	15	15	10
No. of reflections	1763	2346	4200
Nonzero reflections	1200	2000	3769
μ_λ, cm^{-1}	59.5	186	218
Transmission coeff	a	0.09–0.32	0.14–0.40

[a] Absorption corrections not performed. While the theoretical range in the transmission coefficient is 0.2–0.5 for the crystal used, the actual range for the cylindrical crystal is probably much smaller.

Table II. Refinement Information

	A	B	C
Compound	$Ni_2S_8C_{30}H_{28}$	$Pd_2S_8C_{18}H_{36}$	$Pd_3S_{12}C_{15}H_{30}$
Initial solution	Patterson, Harker section	Patterson	Patterson, gradient sharpened
Isotropic convergence[a]			
R_1	0.11	0.14	0.10
R_2	0.13		
Anisotropic convergence			
R_1	0.062[b]	0.087	0.058
R_2	0.082	0.113	0.076
Error at unit wt[c]	0.67	0.91	0.86
Diff Fourier max int, e/Å^3	0.2	1.5	0.5
Final max shifts in units of σ		0.3	0.6

[a] Least-squares minimized on $\Sigma(|F_o| - |F_c|)^2$; $R_1 = \Sigma w|(|F_o| - |F_c|)/|F_o|)|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [b] Hydrogen atoms included at 0.95 Å. [c] A Cruickshank $1/[\sigma(F)]^2$ weighting scheme[28] was used for refinement near convergence.

the 3.5 Å value reported for the bridging pentafluorothiophenol dimer.[16] Yet Tiethof, *et al.*,[20] report $[Cu((CH_3)_3PS)Cl]_3$, ostensibly a [core]$3d^{10}$ metal ion system, to contain a similar M_3S_3 chair-form cyclohexane type ring but with nearly equal (3.545, 3.545, and 3.610 Å) Cu^I–Cu^I distances.

Experimental Section

Bis(benzyl trithiocarbonato)di-μ-(benzylthio)-dinickel(II), $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$ (A). Data Collection. A crystal (Table I) prepared as described[5] (mp 214–215°; mol wt calcd 762, found 791, osmometrically in $CHCl_3$) was mounted parallel to b on a glass fiber. Precession photographs with Mo $K\bar{\alpha}$, oscillation, and Weissenberg photographs with Cu $K\bar{\alpha}$ established the lattice. Centering was done with 17 reflections. Data subsequently were collected on a Picker four-circle automatic diffractometer with two intensity standards each 50 reflections.

Solution and Refinement of Structure. Initial refinement was performed in[21] space group $I2$. The groups Im and $I2/m$, which also are acceptable from the systematic absences, were discounted because of the probable molecular structure. Refinement (Table II) established the choice to be correct. Scattering factors of Cromer and Waber[22] for Ni, C, and S and those of Stewart, *et al.*,[23] for H were used. The nickel atoms were located at $2x$, 0, $2y$. Unobserved reflections were not included in the final structure factor calculation.[24] Positional parameters and thermal parameters are presented in Tables III and IV. See paragraph at end of paper regarding supplementary material.

Table III. Atomic Positional Parameters for $[Ni(SCH_2C_6H_5)(S_2CSCH_2C_6H_5)]_2$[a,b]

Atom	x	y	z
Ni	0.4379 (1)	0.5000 (0)	0.4509 (1)
S1	0.3170 (2)	0.7141 (7)	0.4413 (2)
S2	0.4308 (1)	0.6933 (7)	0.3589 (2)
S3	0.5600 (2)	0.3086 (5)	0.4584 (1)
S4	0.2788 (2)	0.0112 (8)	0.3184 (2)
CL	0.1899 (10)	0.1095 (20)	0.3554 (10)
CM	0.6258 (8)	0.5201 (22)	0.4118 (6)
CT	0.3390 (8)	0.8172 (20)	0.3727 (6)
Ca	0.123 (1)	−0.113 (3)	0.354 (1)
Cb	0.094 (1)	−0.216 (5)	0.406 (1)
Cc	0.029 (1)	−0.420 (5)	0.401 (1)
Cd	−0.002 (1)	−0.502 (7)	0.346 (2)
Ce	0.023 (1)	−0.409 (6)	0.295 (1)
Cf	0.086 (1)	−0.206 (4)	0.298 (1)
C1	0.688 (1)	0.321 (3)	0.391 (1)
C2	0.676 (1)	0.182 (4)	0.336 (1)
C3	0.732 (2)	−0.008 (7)	0.313 (1)
C4	0.800 (2)	−0.072 (5)	0.351 (1)
C5	0.817 (1)	−0.064 (6)	0.405 (1)
C6	0.760 (1)	0.246 (4)	0.427 (1)

[a] Numbers in parentheses in tables are estimated standard deviations in the least significant figure. [b] The coordinates are expressed as fractions of the unit cell edge.

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Table IV. Anisotropic Thermal Parameters for $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.0032 (1)	0.0454 (11)	0.0020 (1)	0.0000 (3)	0.0000 (0)	−0.0008 (2)
S1	0.0038 (1)	0.0792 (30)	0.0024 (1)	0.0029 (6)	0.0001 (1)	−0.0012 (4)
S2	0.0044 (2)	0.0885 (33)	0.0021 (1)	0.0000 (3)	0.0002 (1)	0.0018 (5)
S3	0.0033 (1)	0.0383 (19)	0.0025 (1)	0.0000 (4)	0.0010 (1)	0.0000 (3)
S4	0.0049 (2)	0.0767 (39)	0.0039 (1)	−0.0001 (4)	−0.0003 (1)	0.0070 (6)
CL	0.005 (1)	0.082 (14)	0.006 (1)	0.007 (2)	0.000 (1)	0.001 (2)
CM	0.004 (1)	0.065 (8)	0.003 (1)	−0.002 (1)	0.002 (1)	0.000 (1)
CT	0.003 (1)	0.066 (9)	0.002 (1)	0.000 (2)	−0.001 (1)	−0.001 (1)
Ca	0.004 (1)	0.041 (8)	0.004 (1)	0.004 (1)	0.000 (0)	−0.001 (1)
Cb	0.010 (1)	0.095 (15)	0.003 (1)	0.020 (4)	0.001 (1)	0.005 (2)
Cc	0.008 (1)	0.067 (15)	0.007 (1)	0.011 (3)	0.004 (1)	0.007 (3)
Cd	0.006 (1)	0.083 (17)	0.008 (1)	0.001 (1)	0.001 (1)	−0.006 (3)
Ce	0.005 (1)	0.089 (18)	0.006 (1)	0.008 (3)	0.060 (1)	0.001 (1)
Cf	0.004 (1)	0.085 (13)	0.004 (1)	0.006 (2)	0.001 (1)	−0.003 (2)
C1	0.004 (1)	0.046 (8)	0.002 (1)	−0.001 (1)	0.001 (1)	0.002 (1)
C2	0.007 (1)	0.048 (8)	0.003 (1)	−0.003 (2)	0.002 (1)	0.000 (1)
C3	0.014 (2)	0.059 (13)	0.005 (1)	−0.004 (2)	0.004 (1)	−0.001 (1)
C4	0.011 (2)	0.082 (16)	0.008 (1)	0.012 (4)	0.009 (1)	0.003 (2)
C5	0.006 (1)	0.099 (20)	0.009 (1)	0.014 (4)	0.004 (1)	0.015 (4)
C6	0.006 (1)	0.065 (12)	0.004 (1)	0.003 (2)	0.001 (1)	0.005 (2)

[a] The expression for the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The choice of phasing[25] used for refinement of this noncentric structure appears correct based on (1) the reasonableness of the bond distances and angles (compare Ni–S1 and Ni–S2 or Ni–S3 and Ni–S3′, for example) and (2) the fact that the agreement parameters R_1 and R_2 using unweighted data are slightly poorer for the opposite phasing (0.0918 and 0.0902 *vs.* 0.0935 and 0.0917). The small effect of the anomalous dispersion, however, suggests that refinement with opposite phasing will not lead to significant changes in the sulfur and nickel atom positions. The chirality of the crystal in this polar space group is not assumed to have been unequivocally determined[26] in this study, although the reported stereochemistry is probably correct.

Bis(*tert*-butyl trithiocarbonato)di-μ-(*tert*-butylthio)-dipalladium(II), $Pd_2[SC(CH_3)_3]_2[S_2CSC(CH_3)_3]_2$ (B). Data Collection. Orange crystals were obtained by slow evaporation from pentane. Precession photographs with Mo K$\bar{\alpha}$ showed symmetry which was confirmed diffractometrically (Table I). The density was obtained by flotation in aqueous zinc chloride. Centering and lattice parameters were obtained with 17 reflections. Two intensity standards were positioned after each 100 reflections during the automatic data collection on a crystal mounted in a capillary. A linear decrease of $\sim$30% occurred over the run, and the data were appropriately scaled. Several symmetry related reflections were monitored and found to be identical ($\pm$6%). Six high-intensity data were collected using nickel foil attenuation.

Selection and Refinement of Structure. Intensity statistics implicated the centrosymmetric[21] group *Pnma* (Table I). Palladium and bridging sulfur atom vectors readily appeared on the Patterson map. Scattering factors were obtained as for the nickel compound with anomalous dispersion of Cromer.[27] Hydrogen atoms were not included. Positional parameters and thermal parameters are presented in Tables V and VI.

Tris(ethyl trithiocarbonato)tri-μ-(ethylthio)-tripalladium(II), $Pd_3(SC_2H_5)_3(S_2CSC_2H_5)_3$ (C). Synthesis. In general, bridged mercaptide complexes were synthesized by allowing 0.1 mol of *n*-butyllithium in hexane (27%, Alfa Inorganics) to react with the mercaptan in tetrahydrofuran. The solution was cooled to $\sim$0° and flushed with N_2. CS_2 (0.1 mol) was added dropwise, producing a yellow solution to which metal chloride in water (saturated) was added. The monomeric bis(alkyl trithiocarbonato) complex formed was oligomerized by allowing a chloroform solution of the monomer to stand undisturbed for up to 72 hr. Recrystallization was accomplished in CS_2 on addition of pentane.

Data Collection. A crystal was mounted parallel to *c* on a glass fiber. Precession and Weissenberg photographs indicated only $\bar{1}$ symmetry. Twenty-eight reflections were centered and used as data input for diffractometer settings and lattice parameters. Delauney[28] reduction failed to produce additional symmetry. A standard monitored after every $\sim$50 data varied only $\pm$2% over the entire run. Twenty-two attenuated reflections were included with the data after being remeasured with calibrated nickel foils. Background, Lorentz, and polarization effects were treated as described by Duesler and Raymond.[29]

Solution and Refinement of Structure. Wilson statistics[28] indicated the centrosymmetric triclinic space group which was verified by refinement. Scattering factors as above were used with Patterson map positions to generate structure factors for the data with sin θ/λ $\sim$0.37. Nine sulfur atoms were located from the Fourier synthesis. The entire data set was used in isotropic least-squares cycles to convergence. After anisotropic parameters and anomalous dispersion corrections, refinement converged to the values indicated (Table II). Positional and thermal parameters are listed in Tables VII and VIII.

Reactions. Benzyl bromide reacts with a suspension of [1]$[(C_2H_5)_4N]_2Ni(CS_3)_2$ in CS_2 upon reflux for 12 hr to produce[7] $Ni_2(SC_2H_5)_2(S_2CSC_2H_5)_2$, mp 215°.

Table V. Atomic Positional Parameters[a,b] for $Pd_2[SC(CH_3)_3]_2[S_2CSC(CH_3)_3]_2$

Atom	*x*	*y*	*z*
Pd	0.20321 (6)	0.31818 (3)	−0.01050 (7)
S1	0.3475 (3)	0.2500 (0)	−0.0308 (3)
S2	0.1237 (3)	0.2500 (0)	0.1201 (3)
S3	0.0546 (3)	0.3835 (1)	0.00411 (3)
S4	0.05425 (3)	0.4820 (1)	−0.16248 (3)
S5	0.2472 (3)	0.3921 (1)	−0.14851 (3)
CT	0.1213 (9)	0.4226 (5)	−0.1068 (9)
C1	0.1409 (12)	0.5157 (5)	−0.2875 (11)
C2	0.0675 (15)	0.5663 (7)	−0.32353 (16)
C3	0.2532 (12)	0.5354 (6)	−0.24170 (17)
C4	0.1538 (17)	0.4726 (8)	−0.3957 (14)
CA	0.4181 (13)	0.2500 (0)	−0.1879 (13)
CB	0.4935 (12)	0.3048 (6)	−0.1905 (15)
CC	0.3331 (16)	0.2500 (0)	−0.2917 (17)
CA′	0.1910 (16)	0.2500 (0)	0.2756 (15)
CB′	0.1402 (19)	0.3052 (7)	0.3419 (15)
CC′	0.3185 (16)	0.2500 (0)	0.2764 (18)

[a] Numbers in parentheses in tables are the estimated standard deviations in the last significant figure. [b] The coordinates are expressed as functions of the unit cell edge.

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Table VI. Anisotropic Thermal Parameters for $Pd_2(SC(CH_3)_3)_2(S_2CSC(CH_3)_3)_2$[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	65.5 (9)	10.8 (9)	46.2 (9)	−0.1 (9)	6.8 (9)	−0.3 (9)
S1	58 (3)	16 (1)	53 (3)	0	4 (2)	0
S2	62 (3)	12 (1)	63 (3)	0	13 (2)	0
S3	82 (2)	14 (1)	73 (3)	4 (1)	21 (2)	3 (1)
S4	91 (3)	19 (1)	106 (3)	9 (1)	28 (2)	18 (1)
S5	77 (2)	15 (1)	87 (3)	3 (1)	18 (2)	8 (1)
CT	75 (8)	13 (2)	37 (8)	1 (3)	14 (6)	1 (3)
C1	109 (12)	17 (2)	67 (11)	4 (4)	14 (9)	10 (4)
C2	154 (18)	22 (3)	140 (19)	22 (6)	−0 (1)	26 (7)
C3	74 (10)	22 (3)	204 (22)	8 (5)	14 (10)	30 (7)
C4	190 (21)	33 (4)	78 (14)	15 (8)	22 (13)	−1 (3)
CA	71 (12)	20 (3)	32 (11)	0	−1 (3)	0
CB	87 (11)	23 (3)	140 (18)	−17 (5)	−5 (6)	7 (6)
CC	66 (14)	39 (6)	73 (17)	0	6 (8)	0
CA′	107 (17)	18 (3)	69 (16)	0	40 (12)	0
CB′	231 (25)	19 (3)	95 (16)	−5 (7)	26 (16)	−11 (6)
CC′	47 (14)	111 (17)	55 (18)	0	−42 (12)	0

[a] The expression for the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Thermal parameters with zero values are symmetry required.

Table VII. Positional Parameters for $Pd_3(SC_2H_5)_3(S_2CSC_2H_5)_3$[a,b]

Atom	x	y	z
Pd	0.04316 (11)	0.14852 (6)	0.08372 (10)
Pd′	0.028786 (9)	0.36070 (6)	0.07544 (10)
Pd′′	0.01687 (9)	0.25796 (6)	0.35209 (10)
S1	−0.0771 (4)	0.2056 (2)	−0.0560 (4)
S2	−0.1339 (3)	0.2911 (2)	0.2012 (3)
S3	−0.1209 (4)	0.1024 (2)	0.2076 (4)
S4	0.1717 (4)	0.0874 (3)	0.1968 (4)
S5	0.2247 (4)	0.1922 (2)	−0.0209 (4)
S6	0.1863 (4)	0.2468 (2)	0.5222 (4)
S7	0.1764 (3)	0.4104 (2)	0.5080 (4)
S8	0.2051 (4)	0.4471 (2)	−0.0318 (4)
S9	0.1432 (4)	0.5233 (2)	0.1824 (4)
S10	0.3749 (4)	0.6605 (2)	0.0591 (4)
S11	0.4176 (4)	0.4256 (3)	0.7429 (4)
S12	0.4128 (4)	0.1267 (3)	0.0820 (5)
C10	0.2462 (13)	0.5495 (8)	0.0749 (13)
C11	0.2673 (12)	0.3658 (8)	0.5944 (12)
C12	0.2721 (14)	0.1340 (9)	0.0895 (14)
C1A	−0.0268 (15)	0.2151 (10)	−0.2213 (16)
C1B	−0.1201 (20)	0.2323 (13)	−0.3332 (20)
C2A	−0.1286 (13)	0.3873 (8)	−0.3044 (13)
C2B	0.12259 (15)	0.3455 (10)	0.3978 (16)
C3A	−0.0996 (15)	0.0212 (10)	0.3172 (15)
C3B	−0.19672 (18)	−0.0013 (12)	0.4176 (18)
C10A	0.3758 (16)	0.7431 (11)	0.1836 (17)
C10B	0.4621 (18)	0.7549 (12)	0.3411 (19)
C11A	0.4671 (14)	0.5503 (9)	0.7730 (15)
C11B	0.5529 (17)	0.6062 (11)	0.6732 (18)
C12A	0.4086 (24)	0.0532 (15)	0.2124 (33)
C12B	0.5009 (35)	0.0303 (21)	0.2124 (33)

[a] The numbers in parentheses represent the estimated standard deviation in the last significant figure. [b] The coordinates are expressed as fractions of the unit cell edge.

Iodine, bromine, and $AlBr_3$ (in CS_2) react with A in CCl_4 to produce $Ni(S_2CSCH_2C_6H_5)_2$ and oxidized benzyl mercaptide including $(C_6H_5CH_2S)_2$, as established by chemical analysis and proton magnetic resonance spectra.

$Ni(S_2CN(C_2H_5)_2)_2$ reacts with A in $CHCl_3$ over 2 days to produce $Ni(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)_2$, mp 222–224°. The product was characterized by comparison with an authentic sample.[7]

The dimer, A, reacts with $Zn(S_3CC_6H_5)_2$ overnight at room temperature in CCl_4 to produce[30] $Ni(S_3CC_6H_5)(S_2CC_6H_5)$, mp 200–201°, and other products including dibenzyl disulfide.

Results

Chemical Studies. It is apparent that bridged mercaptide complexes readily react with oxidants to form disulfides. No evidence was achieved in this work for the formation of stable cation complexes of the nickel triad species. Oxidation to cations has been reported[12] with $Fe_2(SR)_2(CO)_2(C_5H_5)_2$. Metal sulfur atom bond rupture and ligand exchange appear to be facile with the nickel dimer.

(30) J. P. Fackler, Jr., J. A. Fetchin, and D. C. Fries, *J. Amer. Chem. Soc.*, **94**, 7323 (1972).

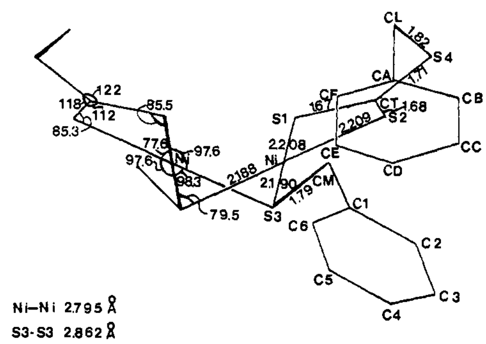


Figure 1. A view of A showing the numbering system.

Crystallographic Studies. $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_6$. A stick drawing of A including the asymmetric unit is presented in Figure 1. Appropriate bond distances and angles are included in Table IX. A stereopair drawing including thermal ellipsoids presented at the 50% level is seen in Figure 2. The twofold axis of the molecule is coincidental with the short axis *b* of the unit cell. The molecules pack in this lattice as "stacks of irregular bowls" with closest intermolecular contacts of ~4 Å.

$Pd_2(SC(CH_3)_3)_2(S_2CSC(CH_3)_3)_2$. A sketch of the molecular structure of the palladium dimer B is presented in Figure 3. This material with its nonplanar anti[5] $Pd_2(SR)_2$ structure packs in the unit cell, Figure 4, differently from the nickel material. A thermal ellipsoid drawing of the molecular configuration, Figure 5, suggests that the methyl groups in the bridged mercaptide ligands librate significantly about the threefold axis of the ligand. Intermolecular distances and angles are presented in Table X.

$Pd_3(SC_2H_5)_3(S_2CSC_2H_5)_3$. The trimeric palladium(II) compound, C, is sketched in Figure 6. Interatomic distances and angles are presented in Tables XI

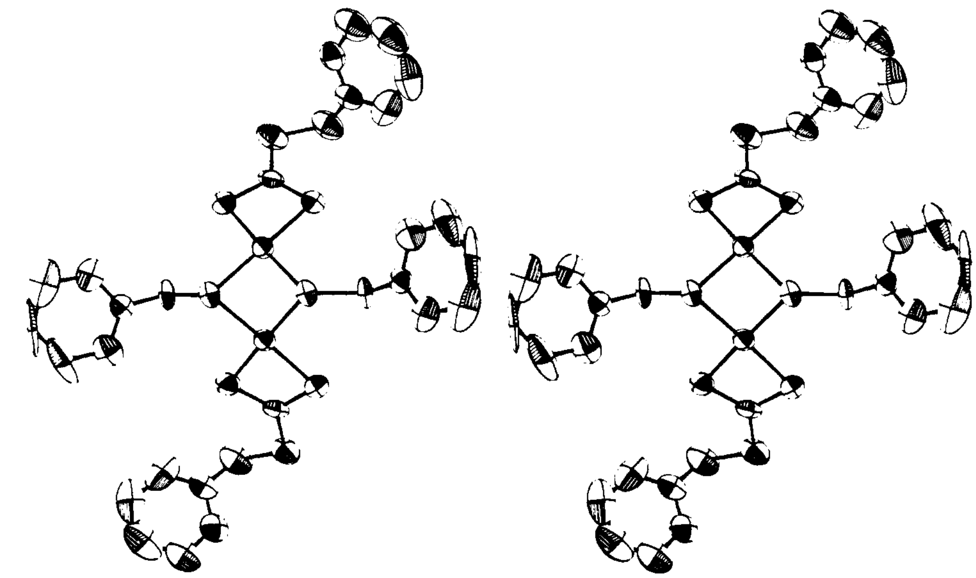


Figure 2. A stereodrawing of the dimer A as viewed along the "*b*" axis of the unit cell. Thermal ellipsoids are drawn at the 50% level.

Table VIII. Anisotropic Thermal Parameters[a] for the Palladium Trimer, C

Atom	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Pd	152.8 (14)	46.1 (8)	110.7 (14)	38.8 (8)	42.0 (11)	11.3 (8)
Pd′	117.2 (12)	49.6 (8)	104.7 (13)	38.7 (8)	37.0 (10)	19.5 (8)
Pd′′	108.5 (12)	40.0 (8)	104.4 (13)	32.4 (8)	29.1 (9)	13.1 (8)
S1	157 (5)	56 (2)	111 (5)	39 (2)	49 (4)	15 (2)
S2	115 (4)	45 (2)	113 (4)	33 (2)	30 (3)	13 (2)
S3	166 (5)	45 (2)	125 (5)	38 (3)	42 (4)	17 (2)
S4	209 (7)	80 (3)	191 (7)	77 (4)	80 (5)	50 (3)
S5	177 (5)	61 (2)	146 (5)	51 (3)	63 (4)	22 (3)
S6	152 (5)	55 (2)	163 (5)	56 (3)	26 (4)	19 (3)
S7	122 (4)	48 (2)	148 (5)	41 (2)	−4 (3)	1 (2)
S8	184 (5)	64 (2)	170 (6)	59 (3)	89 (5)	34 (3)
S9	149 (5)	55 (2)	169 (6)	42 (3)	71 (4)	22 (3)
S10	152 (5)	60 (2)	193 (6)	50 (3)	75 (4)	47 (3)
S11	161 (5)	73 (2)	147 (5)	62 (3)	34 (4)	64 (3)
S12	188 (6)	77 (3)	223 (8)	66 (4)		
C10	134 (17)	64 (8)	111 (18)	53 (10)	34 (14)	38 (9)
C11	115 (16)	57 (8)	106 (16)	40 (10)	26 (13)	10 (9)
C12	160 (21)	49 (7)	135 (18)	38 (11)	27 (16)	3 (9)

Isotropic Thermal Parameters

Atom	B	Atom	B
C1A	5.7 (3)	C10A	6.2 (3)
C1B	8.8 (5)	C10B	7.4 (4)
C2A	4.5 (2)	C11A	5.3 (3)
C2B	6.0 (3)	C11B	7.0 (4)
C3A	5.4 (3)	C12A	8.3 (5)
C3B	7.4 (4)	C12B	12.7 (7)

[a] The anisotropic thermal parameter (T) is expressed as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

and XII, respectively. The thermal ellipsoid stereopair, Figure 7, clearly displays the chair form for the $(Pd\text{–}S)_3$ ring and the totally syn-endo[5] mercaptide bridge configuration. The coordination geometry about each metal atom remains essentially square. The distortion of the molecule from an equilateral to an isosceles triangle of palladium atoms is significant. The metal–sulfur atom distances are only slightly affected by this distortion. Intermolecular contacts, see Figure 8, are well removed from the metal–ligand portion of the molecule.

Discussion

The Dimers. The reaction of bridged mercaptide thioxanthate complexes of nickel with oxidants leads to disulfide formation and product decomposition. In view of iron–sulfur studies[12] it had been thought that the $Ni_2(SR)_2$ rhombus might remain intact upon oxidation. This did not happen.

The molecular structures of A and B consist of metal–thioxanthate units bridged by mercaptide groups resulting in the formation of a four-membered M_2S_2 ring. The metal atoms in both compounds have planar, four-coordinate geometries and the planes containing the metal atoms are folded with respect to each other in both structures. The angle between planes is 114.3° in A and 131.8° in B. The metal–metal separation in A is 2.795 (2) Å while in B the distance between palladium atoms is 3.162 (1) Å. The bridging units of A are

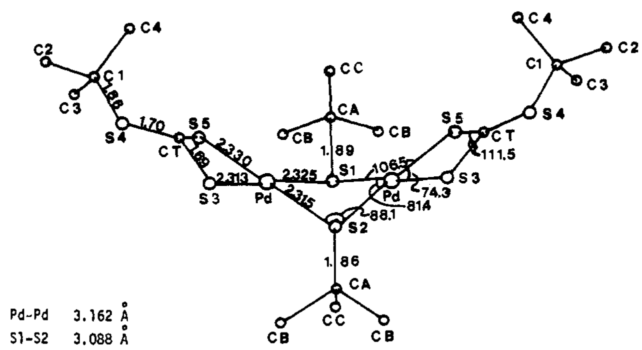


Figure 3. A view of B showing the atom labels.

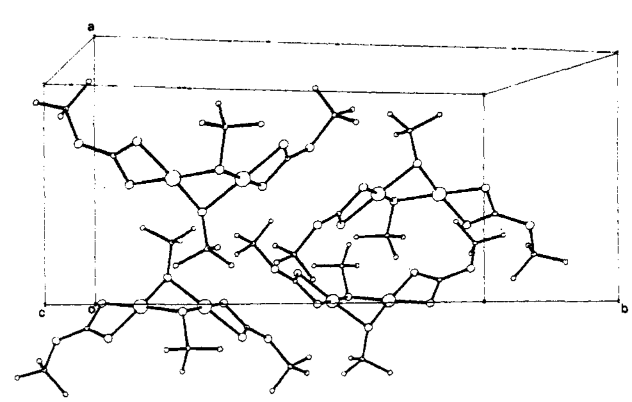


Figure 4. Packing of B in the unit cell.

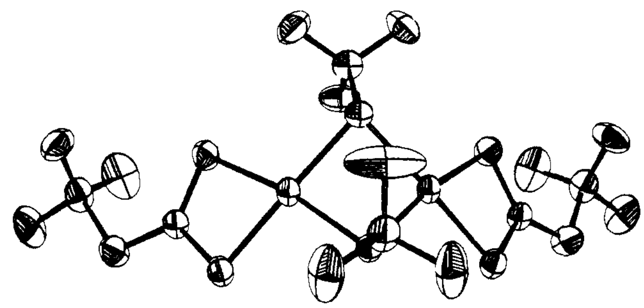


Figure 5. The molecular configuration of B showing associated thermal ellipsoids, at 50% probability level.

Table IX. Bond Distances and Angles for A[a,b]

Atom	Distance, A	Atom	Angle, deg
Ni–Ni′	2.795 (3)	S1–Ni–S2	77.6 (2)
Ni–S1	2.208 (4)	S1–Ni–S3	175.1 (3)
Ni–S2	2.209 (4)	S2–Ni–S3	97.6 (3)
Ni–S3	2.188 (4)	S3–Ni–S3′	98.3 (3)
Ni–S3′	2.190 (4)	Ni–S1–CT	85.5 (6)
S1–S2	2.768 (5)	Ni–S2–CT	85.3 (6)
S3–S3′	2.862 (5)	Ni–S3–CM	112.2 (7)
S1–CT	1.67 (1)	S1–CT–S2	111.6 (8)
S2–CT	1.68 (1)	S1–CT–S4	122 (1)
S3–CM	1.79 (1)	S2–CT–S4	118 (1)
S4–CT	1.71 (1)	S3–CM–C1	108 (1)
S4–CL	1.82 (2)	CT–S4–CL	104 (1)
CL–CA	1.50 (2)	S4–CL–CA	116 (1)
CM–C1	1.50 (2)	C–C–C(PhA)$_{av}$	120 (1)
C–Cl(PhA)$_{av}$	1.37 (3)	C–C–C(Ph1)$_{av}$	120 (1)
C–C(Ph1)$_{av}$	1.37 (3)		

[a] The primed atoms refer to those in symmetry related positions. [b] PhA refers to the phenyl group on the thioxanthate ligand and Ph1 to that on the mercaptide group.

Table X. Intermolecular Distances for B[a]

Atoms	Distance, Å	Atoms	Angle, deg
Pd–Pd*	3.162 (1)	Pd–S1–Pd*	85.6 (1)
Pd–S1	2.325 (3)	Pd–S2–Pd*	86.1 (1)
Pd–S2	2.315 (3)	S1–Pd–S2	83.4 (1)
Pd–S3	2.313 (3)	Pd–S1–CA	113.8 (5)
Pd–S5	2.330 (3)	Pd–S2–CA′	112.4 (6)
S1–S2	3.088 (5)	S3–Pd–S5	74.3 (1)
S1–CA	1.89 (1)	Pd–S3–CT	87.4 (4)
S2–CA′	1.86 (1)	Pd–S5–CT	86.7 (4)
S3–CT	1.69 (1)		
S4–CT	1.70 (1)		
S5–CT	1.70 (1)	S1–Pd–S3	177.5 (1)
S4–C1	1.86 (1)	S1–Pd–S5	106.1 (1)
C1–C2	1.50 (2)	S2–Pd–S3	95.9 (1)
C1–C3	1.48 (2)	S2–Pd–S5	169.1 (1)
C1–C4	1.54 (2)	S3–CT–S4	118.2 (6)
CA–CB	1.55 (2)	S5–CT–S4	130.3 (6)
CA–CC	1.50 (2)	S3–CT–S5	111.5 (6)
CA′–CB′	1.55 (2)	CT–S4–C1	110.2 (6)
CA′–CC′	1.50 (2)		

[a] The asterisk refers to those atoms in symmetry related positions.

present in a syn-endo configuration, whereas B exhibits a folded anti disposition of these groups.

It has been suggested[18] that $Ni_2(SC_2H_5)_2(S_2CSC_2H_5)_2$, an analog of A with a 2.763 (3) Å Ni–Ni distance, Table XIII, contains a metal–metal bond. Structural evidence for metal–metal bonding certainly is not lacking;[31] however, with A and its ethyl analog, the

(31) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 328 (1963).

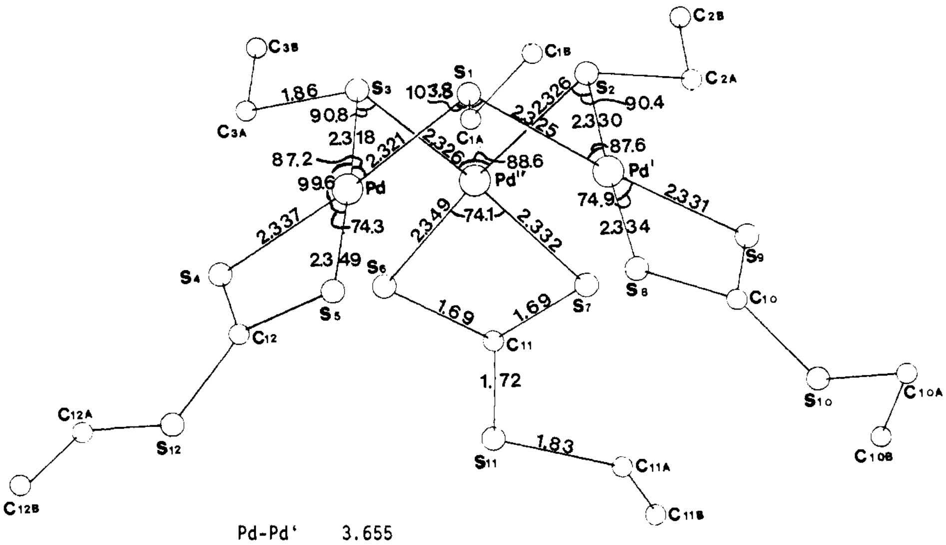
Table XI. Interatomic Distances for the Palladium Trimer, C

Atoms	Distance, Å	Atoms	Distance, Å
Pd–Pd′	3.655 (2)	S4–S5	2.829 (8)
Pd–Pd′′	3.307 (2)	S6–S7	2.822 (8)
Pd′–Pd′′	3.303 (2)	S8–S9	2.836 (9)
Pd–S1	2.321 (6)	S1–C1A	1.85 (2)
Pd–S3	2.318 (5)	S2–C2A	1.83 (2)
Pd–S4	2.337 (6)	S3–C3A	1.86 (2)
Pd–S5	2.349 (6)	S4–C12	1.70 (2)
Pd′–S1	2.325 (4)	S5–C12	1.67 (2)
Pd′–S2	2.330 (4)	S6–C11	1.69 (2)
Pd′–S8	2.334 (5)	S7–C11	1.69 (2)
Pd′–S9	2.331 (4)	S8–C10	1.70 (2)
Pd′′–S2	2.326 (6)	S9–C10	1.70 (2)
Pd′′–S3	2.326 (4)	S10–C10	1.71 (1)
Pd′′–S6	2.349 (5)	S11–C11	1.72 (1)
Pd′′–S7	2.332 (3)	S12–C12	1.71 (2)
S1–S2	3.222 (8)	S10–C10A	1.79 (2)
S1–S3	3.198 (6)	S11–C11A	1.83 (2)
S2–S3	3.249 (9)	S12–C12A	1.88 (3)

Bridging mercaptide ethyl groups: (C–C)$_{av}$ = 1.54 (3)
Thioxanthate ethyl groups: (C–C)$_{av}$ = 1.52 (3)

existence of a metal–metal bond must be viewed with considerable skepticism.

There are a number of factors, including metal–metal interaction, that can lead to the specific metal–metal distances observed in A and its ethyl analog. The pyramidal stereochemistry normally expected about the tricoordinate bridge sulfur atom[5] and the S···S distance in the bridge are two very important factors which must be considered. If, for example, the bridge Ni–S–Ni angle would open to ~106°, the maximum possible S···S distance across the bridge (for a symmetric planar Ni_2S_2 rhombus) at an Ni–S distance of 2.19 Å is 2.63 Å. This is very short compared with an



Pd-Pd' 3.655
Pd-Pd'' 3.307
Pd'-Pd'' 3.303

Figure 6. The trimer C showing its chair configuration.

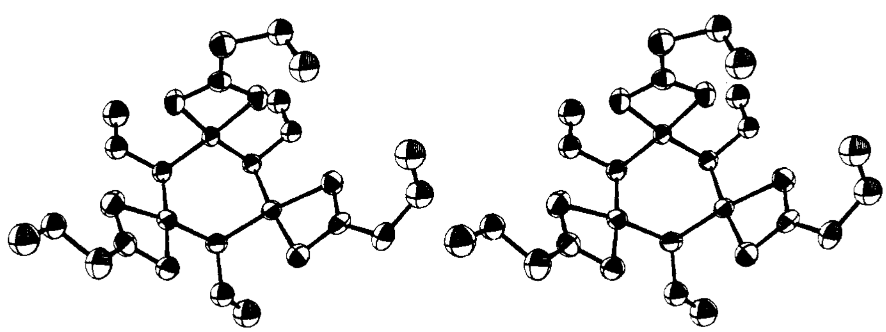


Figure 7. A stereopair drawing of the timer, C, at 50% probability for the thermal ellipsoids.

Table XII. Interatomic Angles for C

Atoms	Angle, deg	Atoms	Angle, deg
Pd–Pd′–Pd′′	56.49 (8)	S2–Pd′–S9	18.8 (3)
Pd′–Pd′′–Pd	67.14 (8)	S1–Pd′–S9	172.9 (2)
Pd′–Pd–Pd′′	56.38 (8)	S2–Pd′–S8	173.5 (3)
Pd–S1–Pd′	103.8 (2)	S2–Pd′′–S7	97.9 (2)
Pd′–S2–Pd′′	90.4 (3)	S3–Pd′′–S6	99.4 (2)
Pd′′–S3–Pd	90.8 (2)	S2–Pd′′–S6	172.0 (3)
S3–Pd–S1	87.2 (2)	S3–Pd′′–S7	173.2 (2)
S1–Pd′–S2	87.6 (3)	S4–C12–S5	114 (1)
S2–Pd′′–S3	88.6 (3)	S4–C12–S12	126 (1)
S4–Pd–S5	74.3 (3)	S5–C12–S12	120 (1)
S5–Pd′–S9	74.9 (2)	S6–C11–S7	113 (1)
S6–Pd′′–S7	74.1 (2)	S6–C11–S11	120 (1)
S1–Pd–S5	99.1 (2)	S7–C11–S11	126 (1)
S3–Pd–S4	99.6 (3)	S8–C10–S9	113 (1)
S1–Pd–S4	172.2 (3)	S8–C10–S10	120 (1)
S3–Pd–S5	173.6 (2)	S9–C10–S10	127 (1)
S1–Pd′–S8	98.8 (2)		
Bridging Mercaptides			(average values)
M–S–CA	107.3 (8)		(6)
S–CA–CB	109 (1)		(3)
Thioxanthate Mercaptides			(average values)
C–S–CA	103.7 (9)		(3)
S–CA–CB	110 (1)		(3)

expected nonbonding S···S distance of ~3.2 Å. The M–S–M angle does open to ~104° in the trimer, C, where the S···S distance is ~3.2 Å.

Of course, in order to have M–S–M become ~106° in a planar rhombus, the S–M–S angle would have to be rather small. In fact, simple steric arguments suggest that the small S–Ni–S angle of 77.6° produced by the terminal bidentate thioxanthate ligand causes the internal S–M–S angle in the rhombus to be greater than 90° (as observed). With an S–Ni–S angle of 90° or larger in a planar Ni_2S_2 rhombus, S···S contacts must be at least 3.1 Å. Both S···S and Ni···Ni interactions are likely to be involved in influencing the fold of the molecule.

If one compares the stereochemical features of the palladium dimer B to the nickel dimer A, it is noted that the increased M–M distance is achieved by an increase in the M–S–M angle and an increase in the length of the M–S bond. The Ni/Pd ratio is about the same for both parameters. The bridge S···S distance is increased in B but not proportionally to the increase in the M–M distance. This may mean that S···S attractive forces are as important as M···M interactions in describing the bonding. (Alternatively, any reductive metal–metal coupling must be accompanied by oxidative coupling such as indicated by S···S interactions.)

It should be recognized that the Ni–Ni distances in A and its ethyl analog are substantially larger than the Ni–Ni distances of 2.39 and 2.38 Å, respectively,[32] in

(32) A. A. Hock and O. S. Mills in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, pp 640–648.

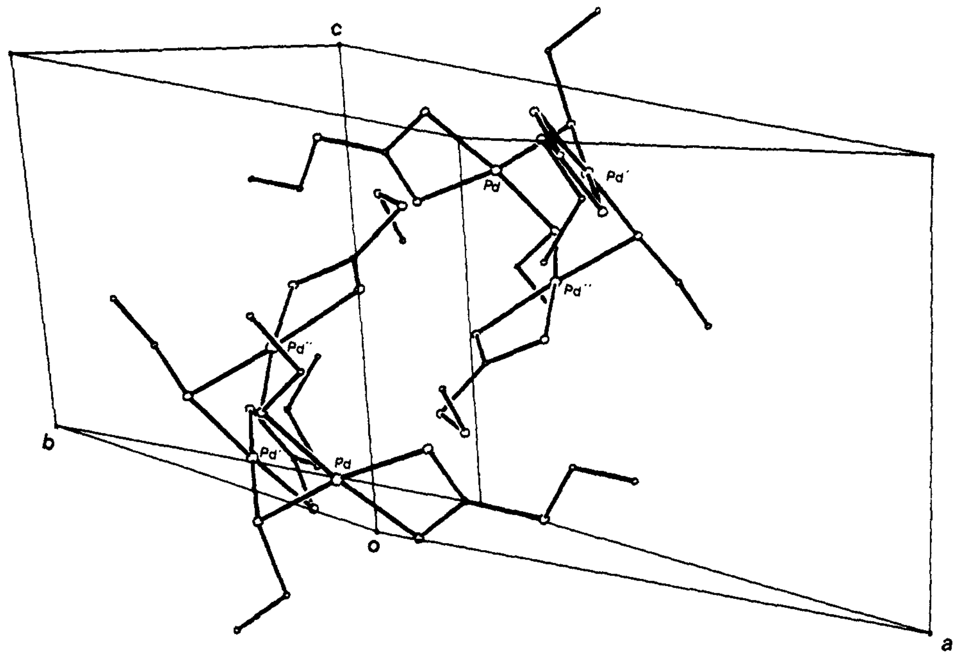


Figure 8. Unit cell of the palladium trimer, C.

($(\pi\text{-}C_6H_5)_3Ni_3(CO)_2$ and $(C_6H_5N_3C_6H_5)_4Ni_2$. The distance observed (2.733 Å) for the trinuclear[33] Ni[Ni-$(NH_2CH_2CH_2S)_2]_2Cl_2$ is ~4% shorter than that found in the neutral benzyl and ethyl mercaptide dimers, while the distance in the hexamer[15] (Table XIII) is somewhat larger.

Table XIII. Comparison of Some Distances and Angles in Bridged Mercaptide Complexes[a] of Nickel

Atoms	A	Ni_2–Et	Ni_6–Et	Ni_3SN
Ni–Ni	2.795	2.763	2.92	2.733
Ni–S_{bridge}	2.188	2.183	2.20	2.212
S···S	2.862	~2.84[b]	~2.9[b]	2.89
S_{bridge}–Ni–S_{bridge}	81.7°	81.6°	~83°	81.4°
Ni–S_{bridge}–Ni	79.5	78.4	~83	77.5
Stereochemistry	syn-endo	syn-endo	anti	syn-endo

[a] Ni_2–Et[18] = $Ni_2(SC_2H_5)_2(S_2CSC_2H_5)_2$; Ni_6–Et[15] = $Ni_6(SC_2H_5)_{12}$; Ni_3SN[30] = $Ni[Ni(NH_2CH_2CH_2S)_2]Cl_2$. [b] Distance approximated from limited data presented.

The stereochemistry of the bridging mercaptide groups relative to each other and the fold is not well-defined. While syn-endo[5] structures appear for the nickel and palladium trimers, the nickel hexamer has a folded anti configuration.[15] The folded anti structure appears also with the palladium dimer B. The $Pd_2(SC_6F_5)_4(P(C_6H_5)_3)_2$ has[17] an anti stereochemistry. Physical measurements of the bridged mercaptide compounds in solution (proton magnetic resonance, infrared spectra, etc.) have to date failed to give evidence for more than one (or an averaged) structural configuration.

A comparison of $Pd_2(SC_6F_5)_4(P(C_6H_5)_3)_2$ with B further emphasizes the structural relationships occurring in the M_2S_2 quadrangles which control interatom distances. In the pentafluorothiophenol derivative the Pd–Pd distance is ~3.54 Å with S···S being ~3.2 Å. *The rhombus is planar.* In B, the Pd–Pd and S···S distances are significantly shorter and the rhombus is folded to ~132° between SMS′ planes.[34]

The gross stereochemical differences between $Pd_2(SC_6F_5)_4(P(C_6H_5)_3)_2$ and B appear to be related to the ability of the sulfur atom in the pentafluorothiophenol to conjugate with the pentafluorophenyl ring. The short C–S distance of 1.66 Å (shorter by 0.04–0.12 Å than the C–S distance in the terminal thiophenols) is to be compared with the 1.89 Å distance in B for the aliphatic mercaptide. By distributing the negative charge over the aromatic ring, electron density in the Pd_2S_2 rhombus is reduced. In B the electron density cannot be delocalized over the bridged ligands. Instead it can be distributed effectively over the Pd_2S_2 rhombus by partial reductive Pd···Pd and oxidative S···S coupling. This is consistent with the observed short Pd···Pd and S···S distances in B and the fold of the rhombus. Indeed oxidative S···S interactions may be important in general in metal–sulfur systems which display relatively short metal–metal distances. Certainly in the mercaptide dimers studied here it is apparent that any metal–metal interaction (reductive coupling) is accompanied by sulfur–sulfur interaction (oxidative coupling).

The Trimer. The distorted triangular metal atom arrangement found in C and[19] $Pd_3[(SCH_2CH_2)_3S]_3$ merits comment. Intermolecular interactions (crystal forces) are unlikely to be totally responsible. An electronic explanation arises out of the fact that palladium(II) contains an empty (antibonding) d orbital. In $[CuSP(CH_3)_3Cl]_3$ the d orbitals in the copper(I)

(33) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

(34) It is interesting to note that orbital symmetries in the syn-endo nickel complexes permit positive S···S overlap. Such overlap is expected to be smaller in the anti bridged mercaptide species. In addition to the compounds reported by Lippard,[7,8] the compounds $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2$, N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7470 (1970), and $[(\pi\text{-}C_5H_5)_2Nb(SCH_3)_2]_2Ni(PF_6)_2$, W. E. Douglas, M. C. H. Green, C. K. Prout, and G. V. Rees, *Chem. Commun.*, 896 (1971), contain anti mercaptide bridges. (The latter compound has a tetrahedral NiS_4 geometry.)

atoms form a closed shell. In this latter compound the copper atoms form a triangle with $\sim D_3$ symmetry.[20]

Assuming that some metal–metal interaction occurs in the trimers, an asymmetric mixing of empty orbitals energetically close to the filled ground orbitals, a second-order Jahn–Teller interaction,[35] may account for the distortions observed. An asymmetric mixing is possible between empty and filled d orbitals of the palladium atoms. If, for example, one assumes that the dominant orbital splitting of palladium d orbitals is caused by a square arrangement of sulfur atoms, the metal $d_{x^2-y^2}$ orbitals are empty but only an electron volt or so removed from the filled d orbitals. In D_3 symmetry these $d_{x^2-y^2}$ orbitals transform as A_2 and E. The highest filled orbital set is likely d_{z^2} which transforms as A_1 and E. The vibrational coordinates which change the metal–metal distances transform as A_1 and E, also. Consequently this model would lead to an asymmetric mixing of the filled d_{z^2} with the empty $d_{x^2-y^2}$ orbitals by means of the e vibrational coordinate. Displacement along this coordinate leads to removal of the trigonal symmetry. While it is impossible at present to determine quantitatively the magnitude of the effect, the features required qualitatively are present in the trimeric palladium complexes.

(35) R. Mason, *Chem. Soc. Rev.*, **1**, 431 (1972), and references therein.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8566.

^{13}C Nuclear Magnetic Resonance Studies of Organometallic Compounds. I. *trans*-Methylplatinum(II) Derivatives[1]

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Abstract: The ^{13}C nmr spectra have been obtained for three series of *trans*-methylplatinum(II) complexes of the type *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$, *trans*-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$, and *trans*-$(CH_3)Pt(P(CH_3)_2(C_6H_5))_2X$, where L is a neutral ligand and X is an anionic substituent. The ^{13}C shieldings and $^{13}C-^{195}Pt$ coupling constants are discussed and compared with data derived from ^{1}H nmr spectra of the complexes. Evidence is obtained which supports the rehybridization theory of the nmr trans influence.

In principle, there are certain distinct advantages of using ^{13}C nmr rather than ^{1}H nmr spectroscopy for the investigation of organometallic compounds. ^{13}C nmr parameters have been demonstrated to exhibit considerably greater sensitivity to changes in bonding and molecular structure.[3] The use of off-resonance and noise-modulated proton decoupling enables first-order assignments to be made without the sometimes tedious spectral analysis. Moreover, ^{13}C nmr offers a unique method of directly observing the effects of stereochemical and bonding alterations of coordinated groups such as acetylenes, carbonyls, isocyanides, and olefins, which contain carbon atoms immediately bonded to a transition metal.

Our preliminary ^{13}C nmr investigations[4,5] have attempted to exploit this potential. In those studies, we examined a number of organoplatinum derivatives and were able to show that valuable information could be derived from the coupling of the ^{195}Pt ($I = 1/2$, 34% natural abundance) and ^{13}C nuclei, as well as from the ^{13}C shieldings. Although ^{13}C nmr investigations of organometallic compounds are now relatively common, few reports[6-11] have appeared which involve detailed examination of series of closely related complexes.

We now wish to describe a *systematic* study of three series of σ-bonded platinum(II) complexes, (I) *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$, (II) *trans*-$[(CH_3)Pt$-

(1) This work may also be regarded as part 35 of the series ^{13}C Nmr Studies. Part 34: J. B. Stothers and C. T. Tan, *Can. J. Chem.*, in press.

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