

metal-carbon bond distances to the carbonyl ligands trans to the iminyl ligand in the ruthenium complex were unusually long.¹⁰ We find that the analogous distances in this osmium complex Os(2)-C(7) and Os(3)-C(8) are also the longest for those carbonyl ligands that are attached to osmium atoms Os(2) and Os(3) (cf. Table III).

There are no unusually short intermolecular contacts. The shortest contacts are between oxygen atoms of the carbonyl ligands, O(5)...O(5) = 3.007 (13) Å and O(4)...O(7) = 3.022 (10) Å. (cf. Table VI).

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Registry No. (μ -H)(μ - η^1 -C=N(H)(*t*-C₄H₉))Os₃(CO)₁₀, 70377-88-7.

Supplementary Material Available: Structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Metal-Metal Interactions in One Dimension. 1. Synthesis and Structural and Spectroscopic Properties of Dithioacetic Acid Derivatives of Palladium(II)

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Three distinct dithioacetato complexes of Pd(II) have been prepared and characterized. They correspond to a common 2:1 ligand to metal ratio but display different structures and spectra. The structures of two derivatives have been solved by X-ray methods. They contain approximately square-planar chromophores, stacking in columns, with the Pd atoms directly over each other. In one structure mononuclear and binuclear units alternate along the *a* axis (monoclinic space group *C2/c*) with metal-repeat separations of 2.754 (1) (in the dimer) and 3.399 (1) Å. The other structure consists of dimers only, stacking along the fourfold axes (tetragonal space group *P4/ncc*) with CS₂ molecules incorporated between different columns. The intra- and interdimer Pd-Pd distances are 2.738 (1) and 3.257 (1) Å, respectively. Monomeric and dimeric molecules coexist not only in the solid state but also in solution, where they are found to be of approximately the same stability, and in the vapor. Vibrational, NMR, vis-UV, and mass spectral data are reported and discussed.

Introduction

One-dimensional inorganic complexes¹ and multinuclear d⁸-d¹⁰ metal ion complexes with sulfur-containing ligands² are receiving considerable attention. One reason these materials are so interesting is that they display a great variety of metal-metal interactions and structural types with consequent wide variations in the physical properties. There is no better example than the metal-chain compounds which span the entire range from localized to collective behavior.³ This outlines the perspective of a systematic chemical control of the unique electronic properties of such systems. Clearly, to understand the important chemical variables to be controlled in inorganic synthesis, in order to construct new molecular systems with specific amounts of a certain physical property associated with them, an adequate theoretical insight into the optical, magnetic, and electron-transport properties of known species is required. Our present understanding of the metal-metal interactions, mainly based on theoretical models of the solid state and MO theories, appears to have poor predictive value when applied to inorganic synthesis and in only few cases has resulted in the enunciation of coherent sets of chemical criteria.^{1,4} The development of experimental chemical trends, therefore, appears useful. In this regard, the dithioacetic acid derivatives of palladium(II), reported in the present paper, have several points of interest. Quite unusual in transition-metal chemistry with sulfur ligands,⁵ several forms

having the same ligand to metal ratio but different structures and physical properties can be isolated. Linear metal chains with short M-M contacts are present in the structures which are the result of a one-dimensional arrangement of either dimeric or dimeric and monomeric units. The coexistence of dimers and monomers is not confined to the solid state, and they are found to be of comparable stability when isolated in solution. A preliminary report of this work has appeared.⁶

Experimental Section

Reagents. Dithioacetic acid (hereafter dtaH) was prepared according to known procedures.^{7,8} K₂PdCl₄ was used as obtained from ICN Pharmaceutical, Inc. Plainview, N.Y.

Preparation of Complexes. Form A. Solid K₂PdCl₄ (2 g, 6 mmol) was added to a solution of dtaH (1.1 g, 12 mmol) in 50 mL of diethyl ether, in the air. After ~48 h of stirring at room temperature, the reaction mixture was filtered. The brick red solid was treated with two 100-mL portions of boiling benzene and the resulting red solution filtered. A small amount of dark, insoluble residue was discarded. Upon cooling of the benzene solution at room temperature, brick-red monoclinic crystals, of composition Pd(CH₃CS₂)₂, were obtained: 1.31 g, 75% yield, referred to original palladium. Anal. Calcd for Pd(CH₃CS₂)₂: C, 16.64; H, 2.10; S, 44.41; Pd, 36.85. Found: C, 16.98; H, 2.20; S, 44.30; Pd, 37.67.

Form B. Upon dissolution of A in carbon disulfide at room temperature, a red solution was obtained which almost instantly became turbid, and, in a few minutes, a green microcrystalline material separated. The residual solution was red. Tetragonal crystals of larger size, suitable for X-ray diffraction studies, were obtained either upon addition of carbon disulfide to a benzene solution (~1:1 volumes) of A or upon slowly cooling (~3 h) a saturated 1:3 carbon di-

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sulfide-toluene solution of A from the boiling point to room temperature. Anal. Calcd for $\text{Pd}(\text{CH}_3\text{CSS})_2 \cdot 1/2 \text{CS}_2$: C, 16.58; H, 1.85; S, 49.02; Pd, 32.54. Found (mean values): C, 17.04; H, 2.11; S, 48.09; Pd, 32.46. Molecular weight in benzene (0.223%) was 623 (calcd for $\text{Pd}_2(\text{CH}_3\text{CSS})_4$: 578).

Form C. This was obtained, as a bright red microcrystalline material, upon sublimation of either A or B. Various combinations of temperatures, in the range 170–220 °C, and pressures, between 10^{-1} and 10^{-3} torr, were used in an attempt to obtain single crystals suitable for X-ray analysis. These attempts were not successful. The composition of the sublimation product did not vary with the temperature and pressure conditions. Anal. Calcd for $\text{Pd}(\text{CH}_3\text{CSS})_2$: C, 16.64; H, 2.10; S, 44.41; Pd, 36.85. Found (mean values): C, 17.46; H, 2.32; S, 43.08; Pd, 37.18. Molecular weight: 429 in benzene (0.026%); 468 in chloroform (0.020%). Carbon disulfide solutions of C separate B, but, unlike those of A, they remain clear and require several hours (~4) to form the first green microcrystals, at room temperature.

Molecular Weight Measurements. Molecular weights were determined by using a Mechrolab Model 301 A vapor pressure osmometer.

Chemical Analyses. These were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, and by B.M.A.C., Middlesex, U.K.

Mass Spectra. The mass spectra of A were recorded with a AEI MS-9 mass spectrometer at an ionizing voltage of 70 V and sample temperatures in the range 140–190 °C. Samples were introduced into the ionization chamber via the direct-insertion lock. Perfluorokerosene was used as a mass reference.

Infrared Spectra. Infrared spectra were recorded, in the region 5000–250 cm^{-1} , with a Perkin-Elmer 521 spectrophotometer. The compounds were studied as KBr pellets or Nujol mulls and, in the case of C, as carbon disulfide solutions in 0.1-mm cesium bromide cells.

Visible-UV Spectra. These were recorded on a Cary 17 spectrophotometer.

NMR Spectra. Proton chemical shifts were measured, at ambient temperature (~37 °C) and at 100 °C, with a Perkin-Elmer R12 60-MHz spectrometer.

X-ray Powder Diffraction. X-ray powder photographs were obtained by using a Difflex II camera (Co $K\alpha$ radiation).

Crystal Data and Intensity Measurements. **Form A.** A red needle $0.52 \times 0.03 \times 0.03 \text{ mm}^3$ was mounted on the goniometer head of a Philips PW1100 four-circle diffractometer equipped with graphite monochromator and employing Mo radiation. Crystals were monoclinic; the unit cell parameters were refined by a least-squares method to give the best fit between calculated and observed settings χ , φ , and 2θ , measured at 20 °C for 25 reflections. The results are $a = 9.553$ (2) Å, $b = 17.875$ (2) Å, $c = 16.141$ (2) Å and $\beta = 107.30$ (1)°. From systematic absences the space group is either Cc or $C2/c$, further investigation confirmed the latter one. The calculated density for 12 $\text{Pd}(\text{dta})_2$ molecules in the cell is 2.11 g cm^{-3} , in agreement with the measured value of 1.95 g cm^{-3} (by the flotation method). The linear absorption coefficient $\mu(\text{Mo } K\alpha)$ has a value of 27.94 cm^{-1} . Intensities were measured by the ω - 2θ scan technique within a sphere of radius $2\theta \leq 60^\circ$. Each reflection was measured with a scan width of 1.2° and a scan speed of $0.05^\circ \text{ s}^{-1}$ and two background measurements for 10 s on each side of the reflection. Three reflections were monitored after every 180 min and no apparent decay in intensity was detected. A unique data set of 3926 reflections was collected. Reflections with $I \leq 3\sigma(I)$ were considered to be unobserved and were excluded from further computations. Corrections were applied to the data for Lorentz and polarization effects but no absorption correction was applied.²⁹

Form B. A green needle crystal $0.86 \times 0.12 \times 0.11 \text{ mm}^3$ was employed for the collection of intensity data by using the same measurement procedure described for form A and led to the following results: crystals are tetragonal, space group $P4/ncc$, with $a = 12.803$ (2) and $c = 11.995$ (2) Å. With a cell content of eight $\text{Pd}(\text{dta})_2 \cdot 1/2 \text{CS}_2$ units, the calculated density is $D_x = 2.127 \text{ g cm}^{-3}$ and the linear absorption coefficient is $\mu(\text{Mo } K\alpha) = 27.86 \text{ cm}^{-1}$. A total of 2458 independent reflections were collected out to $2\theta = 70^\circ$, 1213 of which had $I \geq 3\sigma(I)$ and were retained for subsequent computations. The intensities were corrected for Lorentz and polarization effects but not for absorption.²⁹

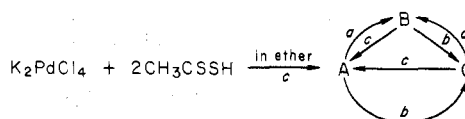
Crystal data for A and B are summarized in Table I.

Table I. Crystal Data for the A and B Forms of Bis(dithioacetato)palladium(II)

form A	form B
monoclinic, $C2/c$	tetragonal, $P4/ncc$
$a = 9.553$ (2) Å	$a = 12.803$ (2) Å
$b = 17.875$ (2) Å	$c = 11.995$ (2) Å
$c = 16.141$ (2) Å	$\mu(\text{Mo } K\alpha) = 27.79 \text{ cm}^{-1}$
$\beta = 107.30$ (1)°	$V = 1966.18 \text{ Å}^3$
$\mu(\text{Mo } K\alpha) = 28.87 \text{ cm}^{-1}$	$\text{mol wt } 326.8^a$
$V = 2631.54 \text{ Å}^3$	$Z = 8, D_{\text{calcd}} = 2.207 \text{ g cm}^{-3}$
$\text{mol wt } 288.7^a$	
$Z = 12, D_{\text{calcd}} = 2.185 \text{ g cm}^{-3}$	

^a Molecular weights refer to the asymmetric unit, $\text{Pd}(\text{dta})_2$ in A and $\text{Pd}(\text{dta})_2 \cdot 1/2 \text{CS}_2$ in B.

Scheme I



^a Crystallization in the presence of CS_2 . ^b Sublimation. ^c Crystallization from C_6H_6 , CH_2Cl_2 , etc.

Structure Solution and Refinement. **Form A.** Patterson and Fourier methods revealed the presence of monomeric and dimeric units in the crystal. A difference Fourier synthesis revealed that the dimer is affected by some positional disorder: maxima were found corresponding to sulfur atoms of a molecule with a different orientation. This second orientation is related to the first one by an inversion through a center on the twofold axis midway between the Pd atoms; this operation leaves unchanged the positions of the Pd and C atoms. The refinement was accomplished by a full-matrix least-squares technique. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with weights, w , assigned as $4F_o^2/\sigma^2(F_o^2)$. The two orientations found for the dimer were refined together, by varying the occupancy of the sulfur atoms. The best agreement between observed and calculated structure factors was obtained when the ratio between orientation A and orientation B was 4:1. The sulfur atoms in orientation B were given isotropic thermal parameters. All the other atoms were refined anisotropically. The final agreement index, $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, was 0.058 for 1483 observed reflections. R_w , defined as $(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, resulted 0.066. The atomic scattering factors for the neutral Pd, S, and C atoms were taken from ref 10. Corrections for anomalous dispersion were included for Pd and S atoms.¹¹ Tables of observed and calculated structure factors are available as supplementary material. The final positional and anisotropic thermal parameters are given in Table II. Interatomic bond lengths and angles are listed in Table III.

Form B. An analysis of the Patterson map showed that the Pd atoms lie in special positions on fourfold axes and yielded the coordinates of the two independent Pd and four S atoms; subsequent structure factor calculation gave $R = 0.30$. Then, successive difference Fourier syntheses revealed all the other nonhydrogen atoms and also a CS_2 molecule on the special position 222 of the space group. The refinement was carried out with the same computational procedure as that employed for form A. Full-matrix least-squares calculations with isotropic thermal parameters yielded $R = 0.067$, and, after several anisotropic cycles, the discrepancy index refined to 0.032. R_w was 0.044. An anomalous dispersion correction was applied to the scattering factors of the Pd and S atoms, as before. The final atomic coordinates and thermal parameters are listed in Table IV; interatomic bond lengths and angles are given in Table V. Observed and calculated structure factors are available as supplementary material.

Results

Three solid phases formed by palladium(II) and the dithioacetato ligand have been isolated according to Scheme I.

Analytical data are in agreement with a 2:1 ligand to metal ratio for each phase, and in the case of B they suggest the presence of one additional CS_2 molecule for every two PdL_2 units. A and C can be kept unaltered in the air for a long time while the surface of B turns from green to red, within ap-

Table II. Fractional Atomic Coordinates and Thermal Parameters^a in Form A^b

Atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃	B, Å ²
Pd(1)	0.0	0.12499 (13)	0.25	2.58 (6)	2.63 (8)	3.14 (8)	0	0.90 (6)	0	
Pd(2)	0.35586 (8)	0.12504 (8)	0.25002 (7)	1.50 (4)	2.36 (5)	3.11 (5)	0.06 (6)	0.84 (6)	0.18 (6)	
S(1)	0.0578 (5)	0.0469 (3)	0.3711 (3)	3.3 (2)	2.4 (3)	3.4 (2)	-0.1 (1)	0.7 (2)	0.1 (2)	
S(2)	0.0630 (5)	0.2031 (3)	0.3711 (3)	3.5 (2)	2.7 (3)	3.2 (2)	-0.3 (1)	1.1 (2)	-0.4 (2)	
S(3)	0.3613 (6)	0.2521 (3)	0.2772 (5)	2.7 (2)	2.4 (3)	4.7 (3)	0.0 (2)	1.9 (2)	-0.6 (2)	
S(4)	0.3338 (5)	-0.0020 (3)	0.2229 (4)	1.7 (2)	2.3 (3)	4.9 (4)	-0.3 (1)	0.3 (2)	0.0 (2)	
S(5)	0.4240 (6)	0.0999 (4)	0.3978 (4)	2.5 (2)	4.5 (4)	3.2 (3)	-0.9 (2)	1.2 (2)	0.2 (2)	
S(6)	0.2746 (6)	0.1497 (4)	0.1019 (4)	2.1 (2)	4.2 (4)	3.1 (3)	-0.9 (2)	0.7 (2)	0.4 (2)	
C(1)	0.0928 (14)	0.1243 (15)	0.4321 (11)	2.2 (5)	2.8 (8)	3.9 (9)	-0.9 (9)	0.6 (5)	2.0 (10)	
C(2)	0.1394 (20)	0.1256 (18)	0.5275 (11)	6.2 (10)	5.8 (11)	2.2 (8)	0.9 (13)	0.8 (7)	1.4 (13)	
C(3)	0.4016 (14)	0.1255 (15)	0.0531 (9)	2.4 (5)	3.1 (8)	2.8 (7)	0.1 (9)	0.7 (5)	-1.5 (9)	
C(4)	0.3535 (17)	0.1267 (18)	-0.0432 (11)	3.7 (7)	7.2 (12)	2.8 (8)	-2.2 (12)	0.9 (6)	0.0 (12)	
C(5)	0.5	0.2944 (14)	0.25	0.9 (7)	2.8 (11)	3.6 (12)	0	0.2 (7)	0	1.9 (3)
C(6)	0.5	0.3787 (22)	0.25	3.6 (9)	1.3 (9)	4.5 (12)	0	1.7 (8)	0	2.1 (4)
C(7)	0.5	-0.0450 (13)	0.25	3.9 (10)	1.4 (11)	2.3 (10)	0	1.3 (10)	0	2.2 (4)
C(8)	0.5	-0.1272 (24)	0.25	4.0 (10)	1.4 (11)	5.4 (14)	0	0.2 (10)	0	2.1 (3)
S(3)B	0.3670 (21)	-0.0013 (13)	0.2819 (15)							
S(4)B	0.3354 (22)	0.2514 (13)	0.2196 (16)							
S(5)B	0.4229 (23)	0.1532 (15)	0.3981 (15)							
S(6)B	0.2778 (21)	0.0948 (14)	0.0993 (15)							

^a Estimated standard deviations in parentheses refer to the last digit. The form of the anisotropic thermal parameter is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. ^b Sulfur atoms from S(3) to S(6) have occupancy factor 0.8. Those labeled S(3)B to S(6)B have occupancy 0.2.

Table III. Main Interatomic Distances (Å) and Angles (deg) in the Mono- and Binuclear Units of Form A^a

Pd(1)-S(1)	2.331 (5)	S(1)-Pd(1)-S(2)	73.6 (2)
Pd(1)-S(2)	2.331 (5)	S(1)-Pd(1)-S(1)'	106.4 (3)
S(1)-C(1)	1.67 (2)	S(2)-Pd(1)-S(2)'	106.4 (3)
S(2)-C(1)	1.69 (2)	Pd(1)-S(1)-C(1)	87.4 (7)
C(1)-C(2)	1.47 (2)	Pd(1)-S(2)-C(1)	86.9 (7)
Pd(1)-Pd(2)	3.399 (1)	S(1)-C(1)-S(2)	112.1 (10)
S(1)-S(2)	2.792 (7)	S(1)-C(1)-C(2)	125.1 (21)
		S(2)-C(1)-C(2)	122.8 (21)
Pd(2)-S(3)	2.311 (5)	S(3)-Pd(2)-S(4)	176.1 (2)
Pd(2)-S(4)	2.310 (5)	S(3)-Pd(2)-S(5)	90.7 (3)
Pd(2)-S(5)	2.322 (6)	S(3)-Pd(2)-S(6)	89.5 (3)
Pd(2)-S(6)	2.326 (6)	S(4)-Pd(2)-S(5)	89.2 (2)
S(3)-C(5)	1.69 (1)	S(4)-Pd(2)-S(6)	90.4 (2)
S(4)-C(7)	1.70 (1)	S(5)-Pd(2)-S(6)	176.9 (2)
S(5)-C(3)'	1.68 (1)	Pd(2)-S(3)-C(5)	111.4 (8)
S(6)-C(3)	1.69 (2)	Pd(2)-S(4)-C(7)	111.7 (7)
C(3)-C(4)	1.48 (5)	Pd(2)-S(5)-C(3)'	111.6 (7)
C(5)-C(6)	1.51 (5)	Pd(2)-S(6)-C(3)	111.4 (6)
C(7)-C(8)	1.47 (5)	S(3)-C(5)-S(3)'	126.9 (10)
Pd(2)-Pd(2)'	2.754 (1)	S(4)-C(7)-S(4)'	126.2 (10)
S(3)-S(3)'	3.028 (8)	S(5)-C(3)'-S(6)'	126.8 (11)
S(4)-S(4)'	3.033 (9)	S(3)-C(5)-C(6)	116.5 (21)
S(5)-S(6)'	3.012 (9)	S(4)-C(7)-C(8)	116.9 (22)
		S(5)-C(3)'-C(4)	116.9 (22)
		S(6)-C(3)-C(4)	116.3 (22)

^a Estimated standard deviations in parentheses refer to the last digit.

proximately 1 week, if not preserved in a sealed tube.

Structure of Form A. Structural information about form A is reported in Figures 1-3 and Tables II and III. The crystal structure consists of mononuclear and binuclear units which alternate along the *a* axis. There are therefore an infinite

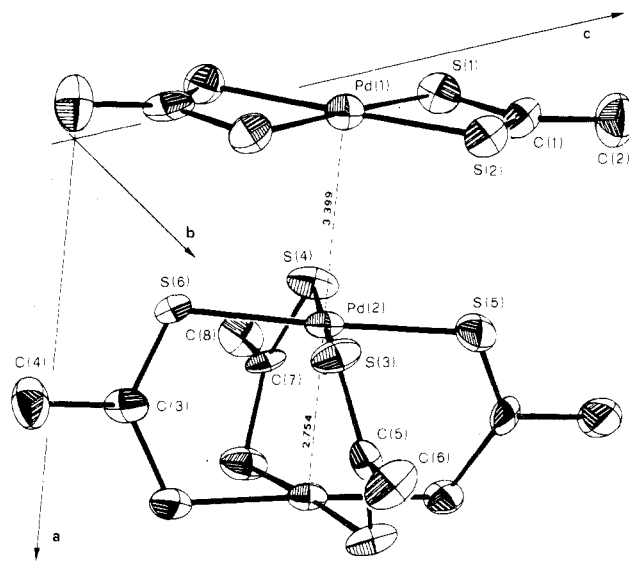


Figure 1. The asymmetric units in the structure of form A, showing the labeling of the atoms.

number of directly interacting metal atoms arranged in linear chains throughout the crystal lattice. Each metal atom is surrounded by four sulfur atoms in an approximately square-planar arrangement. Successive S₄ planes along the columns are essentially parallel and normal to the *a* axis, as shown by the angles S(1)Pd(1)Pd(2) = 90.7 (1)° and S(2)Pd(1)Pd(2) = 89.4 (1)°. The Pd-Pd distance between two different units is 3.399 (1) Å; this may be compared with

Table IV. Fractional Atomic Coordinates^a and Thermal Parameters^b in Pd₂(CH₃CSS)₄CS₂ (Form B)

Atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Pd(1)	0.25	0.25	0.54808 (4)	1.70 (1)	1.70	1.21 (2)	0	0	0
Pd(2)	0.25	0.25	0.31977 (4)	2.10 (1)	2.10	1.21 (2)	0	0	0
S(1)	0.42740 (9)	0.21155 (10)	0.55370 (9)	1.8 (1)	2.6 (1)	2.0 (1)	0.1 (1)	-0.2 (1)	-0.1 (1)
S(2)	0.39663 (10)	0.14243 (10)	0.31494 (9)	2.7 (1)	2.9 (1)	2.0 (1)	0.6 (1)	-0.2 (1)	0.4 (1)
S(3)	0.66494 (19)	0.16494	0.75	6.3 (1)	6.3	5.5 (1)	0.0 (1)	-0.3 (1)	0.3
C(1)	0.4639 (3)	0.1542 (3)	0.4350 (3)	2.1 (1)	1.7 (1)	2.2 (1)	0.2 (1)	0.3 (1)	0.2 (1)
C(2)	0.5723 (4)	0.1068 (5)	0.4352 (4)	1.7 (2)	4.2 (2)	3.3 (2)	0.8 (2)	0.2 (1)	0.2 (2)
C(3)	0.75	0.25	0.75	5.4 (4)	5.4	3.1 (4)	2.0 (6)	0	0

^a Coordinates are referred to the origin at $\bar{1}$. ^b Estimated standard deviations in parentheses refer to the last digit. The form of the anisotropic thermal parameters is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Main Interatomic Distances (Å) and Angles (deg) in $\text{Pd}_2(\text{CH}_3\text{CSS})_4$ (Form B)

Pd(1)-Pd(2)	2.738 (1)	Pd(2)-Pd(1)-S(1)	91.7 (1)
Pd(1)-S(1)	2.325 (1)	Pd(1)-Pd(2)-S(2)	91.4 (1)
Pd(2)-S(2)	2.329 (1)	Pd(1)-S(1)-C(1)	110.0 (1)
S(1)-C(1)	1.669 (4)	Pd(2)-S(2)-C(1)	109.7 (1)
S(2)-C(1)	1.685 (4)	S(1)-C(1)-S(2)	128.7 (2)
C(1)-C(2)	1.515 (7)	S(1)-C(1)-C(2)	115.7 (3)
S(3)-C(3)	1.540 (2)	S(2)-C(1)-C(2)	115.7 (3)
S(1)-S(2)	3.023 (2)		
Pd(1)-Pd(2)'	3.257 (1)		

^a Estimated standard deviations in parentheses refer to the last digit.

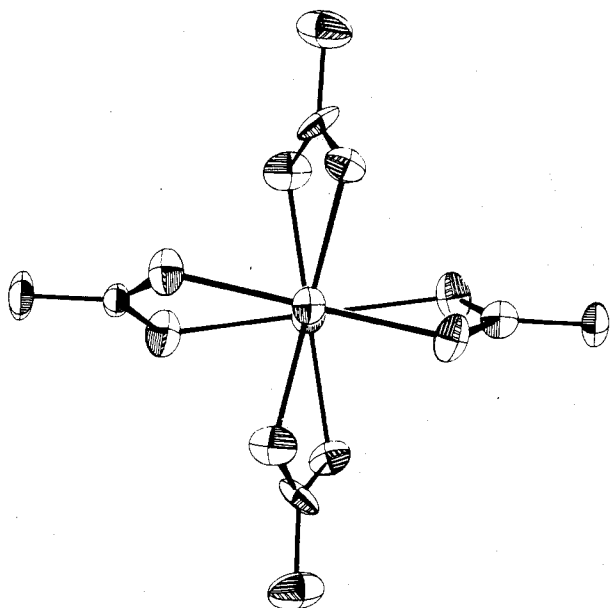


Figure 2. An ORTEP¹² view of the binuclear unit in the structure of form A, along the pseudo-fourfold axis.

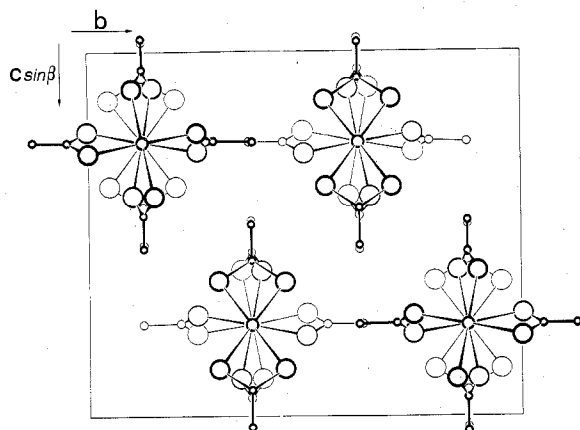


Figure 3. Atomic arrangement in the structure of the A form, projected along the *a* axis.

those observed in classical one-dimensional systems with direct M-M interactions such as the tetracyano complexes (3.25–3.63 Å)^{1,13,14} or the bis(α,β -dione dioximato) derivatives (3.20–3.52 Å).^{4,13,14} Other intermolecular contacts are in the range of normal van der Waals distances. The monomeric units lie on crystallographic twofold axes and are nearly planar (maximum deviation from the least-squares plane is 0.02 Å). The dimer contains four bridging ligands and involves a Pd-Pd distance of 2.754 (1) Å, even shorter than those found in palladium and platinum bis(ethylene-1,2-dithiolene),¹⁵ 2.79 and 2.77 Å, respectively, or in bis(dithiocumato)platinum(II) (2.87 Å),¹⁶ which have been taken as examples of direct M-M bonding,

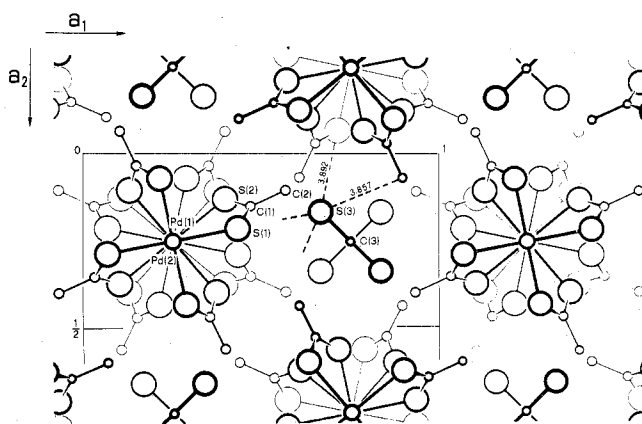


Figure 4. Atomic arrangement in the structure of the B form, projected along the *c* axis. The system of coordinates is left-handed.

and slightly longer than that (2.715 (3) Å) in bis(phenyldithioacetato)palladium(II).¹⁷ The distance between the centers of the S_4 planes is 0.14 Å longer than the Pd-Pd distance; this "inward" distortion reinforces the view of a strong Pd-Pd attractive interaction.

The two nearly parallel PdS_4 squares of the dimer, related by a twofold axis, are rotated by 22.5° in a tetragonal twist from the eclipsed D_{4h} structure. There is no significant difference between the palladium-sulfur, sulfur-carbon, and carbon-carbon bond lengths in the monomer and the dimer. That the bonding within the two different units differs considerably, however, is clearly indicated by the SPdS angle which increases from 73.6° in the monomer to 90.0° in the dimer, by the PdSC angle (from 87.2 to 111.5°), and also by the SCS and SCC angles (from 112.1 and 124.1 to 126.7 and 116.7°, respectively).

Structure of Form B. In accordance with the analytical and molecular weight results, the crystal structure of B (Figure 4; Tables IV, V) comprises $\text{Pd}_2(\text{CH}_3\text{CSS})_4$ and carbon disulfide molecules in a 1:1 ratio.

The dimeric molecules involve four bridging ligands, as in A, and form linear chains of directly interacting metal atoms through the stacking in columns along the fourfold axes. The metal-repeat separations along the columns of B are shorter than those along the columns of A: 2.738 (1) Å within the dimer and 3.257 (1) Å between successive dimers. The shorter intradimer Pd-Pd distance in B involves only small changes of the other structural parameters with respect to the dimers in A; e.g., the tetragonal twist of the two PdS_4 squares is 25°, the SCS angle increases to 128.7°, etc. Adjacent PdS_4 squares of two different units are rotated by ~39°.

The carbon disulfide molecules occupy the 222 position of the space group. Intermolecular contacts involving the carbon disulfide sulfur atoms are >3.8 Å.

Vibrational Spectra. The vibrational spectra of the dithioacetato complexes of palladium(II) and the parent ligand, in the KBr region, are presented in Table VI. The bands due to the aliphatic substituent either remain unchanged or are shifted slightly when the free ligand is converted into its metal complexes. They will not be discussed here. The assignments of the stretching frequencies of the chelated rings have been made following previous lines of discussion.¹⁸ There are no striking differences, either in energy or in intensity, between the bands of the dithioacetic acid derivatives of Pd(II) and those of other transition metals with different oxidation states and molecular geometry, e.g., $\text{V}(\text{dta})_4$,¹⁹ $\text{Ni}_2(\text{dta})_4$,¹⁸ or $\text{M}^{\text{III}}(\text{dta})_3$ (M = Fe, Co, Cr, etc.).²⁰ It is worth noting that dithioaromatic complexes with the same metal ions show the carbon-sulfur stretching modes at considerably different energies and with markedly smaller energy separations.^{16,18,21} In this respect the dithiocarboxylates differ from other 1,1-

Table VI. Infrared Frequencies (cm^{-1}) and Assignments of the Absorptions of the A, B, and C Forms and the Parent Ligand

CH_3CSSH^a	B^b	A^b	C^b	C^c	assign ^t
1216 $s^{d,f}$					
1192 m					
	1168 vs	1172 vs	1180 sh	1173 s	$\bar{\nu}_{\text{as}}(\text{CSS})(\text{bridging})$
			1172 vs		
		1132 ms	1150 s	1133 s	$\bar{\nu}_{\text{as}}(\text{CSS})(\text{terminal})$
			1132 s		
1107 s	1085 m	1088 m	1088 m	1110 s	$\rho(\text{CH}_3)$
				1095 s	
1010 vw	1010 vw	1005 w, br	1010 w, br		$\gamma(\text{CH}_3)$
	950 w				
903 m		890 sh	900 sh		$\bar{\nu}(\text{C}-\text{C})$
	898 vs	900 vs	890 vs	900 mw	$\bar{\nu}_{\text{s}}(\text{CSS})(\text{bridging})$
860 s^e		832 vs	830 s	835 s	$\bar{\nu}_{\text{s}}(\text{CSS})(\text{terminal})$
			825 sh		
	720 vw	720 vw	720 vw		not assigned
	600 vw	598 vw	590 vw	650 w	
581 s^f				610 m	$\bar{\nu}(\text{C}-\text{S})$
450 m	448 m	448 m	445 mw		$\omega(\text{CSS})$
			430 vw		
406 vw	402 mw	400 sh	390 w	400 w, br	$\bar{\nu}(\text{MSS})(\text{bridging}) + \text{def modes}$
	392 mw	390 mw	370 ms		
		345 m	345 s		
		311 w	310 w		$\bar{\nu}(\text{MSS})(\text{terminal})$

^a Nujol; ref 18. ^b KBr pellets. ^c Carbon disulfide solution; not measured below 400 cm^{-1} . ^d At $1210, 1180 \text{ cm}^{-1}$ in CD_3CSSH . ^e $\bar{\nu}(\text{S}-\text{H})$. ^f At 550 cm^{-1} in CD_3CSSH .

dithiolates such as the dithiocarbamates or dithiocarbonates, which show C-S bands almost insensitive to the nature of the substituent attached to the $\text{N}-\text{CS}_2^-$ or $\text{O}-\text{CS}_2^-$ group.

Bridging and terminal ligands in the present complexes are clearly discernible through the infrared spectra. The X-ray structures of A and B show that the bridging ligands have an SCS angle approximately 16° larger than the same angle in the terminal ligands. Further, the SPdS angle in the dimer is $\sim 16^\circ$ larger than in the chelated part of the monomer. The assignments made in Table VI take this into account. The spectrum of A shows, in the carbon-sulfur and metal-sulfur stretching regions, bands which are almost superimposable on those of B (containing only bridging ligands) and additional, lowest energy bands which are clearly attributable to the terminal ligands. It seems unlikely that the additional bands arise from the splitting of single bands due to solid-state effects. Intermolecular interactions should have to be negligible in B as compared to those in A, in contrast to the crystallographic results, and they would have to produce the observed $40\text{--}50\text{-cm}^{-1}$ separations, leaving the bands sharp. There are striking similarities between the solution spectrum of C and the solid-state spectrum of A (Table VI), not only in band positions but also in band intensities, in both the C-S and the M-S regions. Additional bands are instead present in the solid-state spectrum of C.

Mass Spectra of Form A. Table VII lists only the observed palladium-containing ions; these can be clearly distinguished by a consideration of the isotopic abundances. The reported m/e ratios are based on the most intense peak, and intensities are given relative to a palladium-containing base peak of 100 units. We have not considered the organic ions produced so the individual ion abundances will not approximate to the percentage of total ion current carried. Unlike fragments containing one or two palladium atoms, which are easily discernible upon comparison of the observed and calculated²² isotopic patterns, fragments containing three or four palladium atoms are not always easy to distinguish, due to the high mass and the insufficient resolution.

The principal species in the vapor is the monomer, the even-electron ion $\text{Pd}(\text{CH}_3\text{CSS})^+$ being the basic peak. However, it appears that the solid does not fragment solely into monomeric units; ions of appreciable intensity containing

Table VII. Palladium-Containing Ions in the Mass Spectra of Form A ($\text{R} = \text{CH}_3$)

ion	m/e	RI	ion	m/e	RI
Pd^+	106	66	$\text{Pd}_3(\text{dta})_2\text{S}_2^+$	565	0.88
PdS^+	138	37	$\text{Pd}_4(\text{dta})\text{CS}_2^+$	593	0.77
PdCS^+	150	30	$[\text{Pd}_3(\text{dta})_3]^+$		
PdRCS^+	165	34	$\text{Pd}_4(\text{dta})\text{SCS}_2^+$	625	0.31
PdS_2^+	170	33	$[\text{Pd}_3(\text{dta})_3\text{S}]^+$		
PdCS_2^+	182	5	$\text{Pd}_4(\text{dta})\text{S}_2\text{CS}_2^+$	657	0.26
$\text{Pd}(\text{dta})^+$	197	100	$[\text{Pd}_3(\text{dta})_3\text{S}_2]^+$		
$\text{Pd}(\text{dta})(\text{CR})^+$	224	1.4	$\text{Pd}_4(\text{dta})_2\text{CS}_2^+$	684	0.37
$\text{Pd}(\text{dta})\text{S}^+$	230	4.7	$[\text{Pd}_3(\text{dta})_3]^+$		
$\text{Pd}(\text{dta})(\text{RCS})^+$	256	0.7	$\text{Pd}_4(\text{dta})_4^+$	791	0.02
$\text{Pd}(\text{dta})(\text{CS}_2)^+$	273	0.9	$[\text{Pd}_3(\text{dta})_3\text{SCS}_2]^+$		
$\text{Pd}(\text{dta})_2^+$	288	44	$\text{Pd}_4(\text{dta})_4\text{S}^+$	822	0.02
$\text{Pd}_2(\text{dta})_2^+$	397	9.4	$\text{Pd}_4(\text{dta})_4(\text{RCS})^+$	850	0.01
$\text{Pd}_2(\text{dta})_2(\text{RCS})^+$	456	8.4	$\text{Pd}_4(\text{dta})_4(\text{RCS})^+$	876	0.01
$\text{Pd}_2(\text{dta})_2^+$	488	16.5	$\text{Pd}_4(\text{dta})_4(\text{RCS}_2\text{CR})^+$	908	0.01
$\text{Pd}_3(\text{dta})(\text{CS})\text{S}_2^+$	519	1.38			

two palladium atoms and even ions, of very low intensity, containing three or four palladium atoms are detected in the mass spectra, showing that more highly associated molecules are present in the vapor albeit in low concentration.

Solution Behavior. Solubility. A, B, and C are practically insoluble in polar solvents such as water or ethanol and are slightly soluble in nonpolar or weakly polar organic solvents such as benzene, chloroform, or dichloromethane. With the obvious exception of carbon disulfide, the solubility follows the order $\text{B} > \text{C} > \text{A}$ and, in terms of PdL_2 units, is in the range $10^{-2}\text{--}5 \times 10^{-4} \text{ M}$, at room temperature. Solutions in the above solvents are quite stable at room temperature (vide infra).

Molecular Weights. Molecular weight data indicate that benzene solutions of B contain only dimeric species. Solution electronic spectra reinforce this view and show that it holds also for solutions of B in solvents other than benzene.

Measurements for C are scarcely reliable because of the low solubility. However, benzene and chloroform solutions gave similar results, suggesting the presence in solution of both monomeric and polynuclear species. A is so sparingly soluble as to prevent significant measurements.

¹H NMR Spectra. We have had considerable difficulty in obtaining reliable data. At room temperature (36°C) the

Table VIII. Chemical shifts (ppm from Me₄Si) of A, B, and C

compd	solvent	temp, °C	time, min	methyl τ^a
A	C ₆ D ₆	36		7.58
B	C ₆ D ₆	36		7.50
C	C ₆ D ₆	36		7.47, 7.85, 7.90 ⁱ
A	C ₆ D ₆	100	40	7.36, 7.65
B	C ₆ D ₆	100	40	7.31, 7.60
C	C ₆ D ₆	100	40	7.33, 7.59
A	C ₆ D ₆ + 10% CS ₂	36		7.58
C	CDCl ₃	36		7.60, 7.70, 7.78 ⁱⁱ
C	CS ₂	36		7.33, 7.49, 7.56 ⁱⁱⁱ

^a Relative intensities: (i) 1:2:3; (ii) 1:1.3:1; (iii) 1:1.5:1.

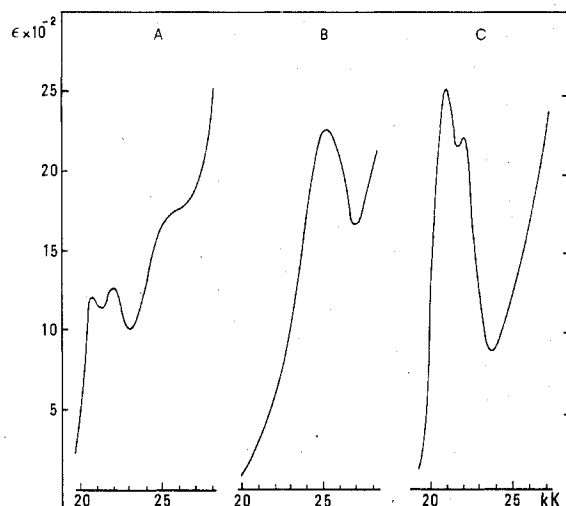


Figure 5. Electronic absorptions of A, B, and C, between 20 and 28 $\text{cm}^{-1} \times 10^3$, in benzene. (1 kK = $1 \text{ cm}^{-1} \times 10^3$.)

resolution of the signals is very poor (except for B) because of the low solubility. At 100 °C, both the number of peaks and their relative intensities change with time. After ~30 min the chemical shifts are roughly reproducible but the intensities of the signals do not show any significant trend. The chemical shifts are reported in Table VIII. At 36 °C all three compounds exhibit a singlet at approximately the same τ , ~7.50, and C exhibits two more peaks. At 100 °C two signals are observed for each species and at not significantly different τ . It appears, therefore, that after ~30 min at 100 °C, solutions of A, B, and C contain variable amounts (the intensities of the peaks vary) of the same chemical species, irrespective of the original content of the solutions. The electronic spectral behavior of A, B, and C in solution leads to the same conclusion.

Electronic Spectra. Both solid-state⁶ (Nujol mull and reflectance) and solution spectra were recorded, and, for each species, there are significant differences between them. Preliminary single-crystal polarized spectra of A and B show properties which can be related to the one-dimensional character of the crystal lattices and to the different metal-repeat separations along the columns of A and B.

The present electronic spectral information has the limited aim of describing, together with other data, how the individual units constituting the solid stacks behave when isolated in solution. In this regard, the transitions occurring in the range between ~20 and ~28 $\text{cm}^{-1} \times 10^3$ are the most revealing. Our attention will be confined to this spectral region. Figure 5 shows the electronic absorptions of A, B, and C when they are dissolved in, e.g., benzene (a solvent for which molecular weight and NMR data are available), at room temperature. The spectrum of C refers to a sample obtained upon sublimation of A at 190 °C and 10^{-3} torr. Samples from sublimations at different conditions show sometimes a shoulder at

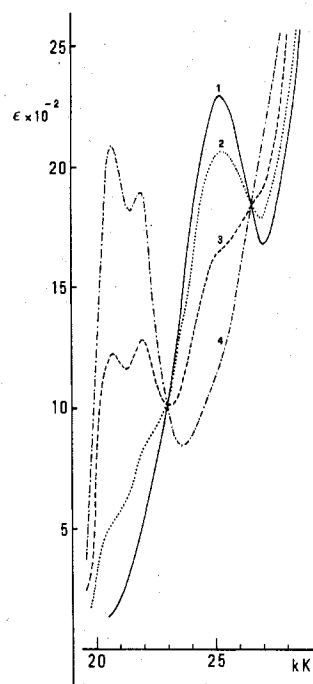


Figure 6. Spectral changes with time undergone by a cyclohexane solution of B at 100 °C. The curves refer to increasing times: 1 < 2 < 3 < 4.

~26 $\text{cm}^{-1} \times 10^3$, of variable intensity. How the presence and the intensity of this absorption might be related to the temperatures and pressures at which the samples are obtained remains obscure. A exhibits two sharp absorptions at 20.8 (log $\epsilon = 3.09$) and 22.0 $\text{cm}^{-1} \times 10^3$ (log $\epsilon = 3.11$), followed by a well-defined shoulder (~25 $\text{cm}^{-1} \times 10^3$, log $\epsilon \approx 3.23$) at an energy which closely corresponds with that of the single maximum observed for B (25.2 $\text{cm}^{-1} \times 10^3$, log $\epsilon = 3.36$). When compared with each other and related to the crystallographic and molecular weight results, these spectral data seem to leave little doubt that the band at ~25 $\text{cm}^{-1} \times 10^3$ originates from a transition in the dimer and that those at ~21 and ~22 $\text{cm}^{-1} \times 10^3$ arise from transitions in the monomeric species. Further, the fact that such bands can still be recognized in the crystalline phases⁶ suggests that the D_{2h} and D_{2d} symmetries revealed by the X-ray structures for the monomeric and dimeric units, respectively, are retained in solution. If the solution spectrum of A is regarded as resulting from the superposition of the spectra of corresponding quantities of monomers and dimers, the transition frequencies of C (20.8 $\text{cm}^{-1} \times 10^3$, log $\epsilon = 3.40$; 21.9 $\text{cm}^{-1} \times 10^3$, log $\epsilon = 3.50$) clearly indicate the presence in solution of monomeric species.

The energies and the intensities of the absorptions of A, B, and C do not show any significant variation when solvents other than benzene are used, e.g., cyclohexane, toluene, dichloromethane, or chloroform. Even in carbon disulfide, which causes the precipitation of B, the spectra of A and C are unchanged (see also the NMR section). The solution spectra of all the three species remain unaltered for several weeks, at room temperature. At higher temperatures, e.g., 80–100 °C significant variations occur with time. As shown in Figure 6, the spectrum of B changes progressively into that of A and then into a final spectrum which differs from that of C only in a slightly increased intensity of the ~21 and ~22 $\text{cm}^{-1} \times 10^3$ bands. Accordingly, the A spectrum transforms into a C type spectrum, and solutions of C simply increase the intensity of their bands by a small factor, 1.05–1.1. Unfortunately, not yet understood catalytic effects appear to influence the rate of the transformations occurring in solution in an unpredictable

Table IX. Important Dimensions (Distances, Å; Angles, deg) of Monomeric and Dimeric Dithiocarboxylato Complexes of Palladium(II)

	form A		form B dimer	Pd ₂ (dtpa) ₄ ^a dimer	Pd(dtb) ₂ ^b monomer
	monomer	dimer			
Pd-Pd (intra)		2.754 (1)	2.738 (1)	2.715 (3)	
Pd-Pd (inter)	3.399 (1)		3.257 (1)	3.297 (3)	
Pd (inward dist)	0	0.07	0.06	0.06	0
Pd-S	2.331 (5)	2.317 (5)	2.327 (1)	2.332 (6)	2.328 (3)
S-C	1.68 (2)	1.69 (2)	1.677 (4)	1.67 (1)	1.70 (1)
C-C ^c	1.47 (2)	1.49 (5)	1.528 (7)	1.54 (2)	1.47 (1)
SPdS	73.6	89.95	90.0	89.4	74.5
PdSC	87.15	111.5	110.0	108.8	86.3
SCS	112.1	126.7	128.7	129.9	112.3
SCC	124.1	116.7	115.7	115.4	123.8
space group	C2/c		P4/ncc	Iba2	P2 ₁ /c

^a M. Bonamico, G. Dessy, and V. Fares, *J. Chem. Soc., Dalton Trans.*, 2315 (1977) (dtpa = C₆H₅CH₂CSS⁻). ^b M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *ibid.*, 2250 (1975) (dtb = C₆H₅CSS⁻). ^c Adjacent to C-S bonds.

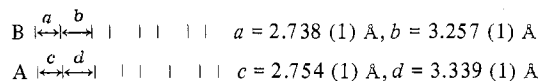
manner, and quantitative thermodynamic conclusions cannot be drawn from the temperature and time dependence of the spectra. Attempts are being made to overcome this difficulty, which is revealed also by the NMR spectra. Meanwhile, the following qualitative and partial conclusions can be anticipated.

(i) At increasing temperatures, the dimeric molecules become progressively unstable toward the monomeric species and another polynuclear species (see point ii).

(ii) In addition to the monomeric species, original solutions of C contain polynuclear species (different from the dimers of A and B) which partly transform into monomers upon increase in the temperature; this is shown by the fact that final solutions of B, A, and C, with no maximum or shoulder at 25 cm⁻¹ × 10³ show molar extinctions, for the bands at ~21 and ~22 cm⁻¹ × 10³, higher than those of an original solution of C. The same conclusion may be inferred from the presence of two peaks in the NMR spectra at 100 °C and from the molecular weight results.

Discussion

The capacity of the palladium(II)-dithioacetato system to give several solid phases and the attainment of two linear metal chains in forms A and B, i.e.



are remarkable. Polymorphism is practically unknown for transition metal dithiocarboxylates,⁵ and, moreover, d⁸ complexes involving 1,1- and 1,2-dithiolato ligands generally adopt²³ laterally displaced structures which do not allow short metal-metal contacts (exceptions being bis(phenyldithioacetato)nickel(II) and -palladium(II)¹⁷).

The stacking alternation between monomers and dimers in structure A has not been observed previously and provides a new type of M-M interaction in one dimension.

The structural differences between phases A and B arise primarily from poorly understood packing forces associated with the presence (or absence) of carbon disulfide molecules: B can be obtained only from solutions containing carbon disulfide and it transforms into a red phase (different from A) when the solvent is eliminated from the structure upon either standing in the air or heating. Solutions of B, however, contain dimers only but separate A in the absence of carbon disulfide. Apparently, the columns of dimers cannot attain the densest honeycomb packing of rods²⁶ observed in structure A (Figure 3). On the other hand, the M-M interactions along the columns of A are weaker than those along the columns of dimers, as shown by the longer intra- and intermolecular Pd-Pd contacts and by the different periodicity.²⁴ These observations suggest that structure A is determined primarily by the more favorable interactions among the columns which

are allowed by the stacking alternation between monomers and dimers, relative to the dimer-dimer pattern.

A point which deserves attention is the coexistence of the monomeric and dimeric molecules not only in the solid state but also in solution and in the vapor. Species such as Ni₂(C₆H₅CH₂CS₂)₄²⁷ and Pt₂(S₂C₂H₂)₄,¹⁵ despite the stable dimeric structure in the solid state, with M-M distances of 2.551 (3) and 2.748 (2) Å, respectively, dissociate completely into monomers upon dissolution in such nonpolar solvents as benzene, chloroform, etc. This behavior is commonly assumed to be indicative of the weakness of the M-M interactions, leading to the rather intriguing prospect of a weak M-M bonding associated with a short M-M bond distance. Clearly, the discrepancy arises from the wrong assumption that the M-M interactions alone, and not the total energy of the system, are responsible for the stability of the dimeric structure. A comparison between the molecular structures of Pd(dta)₂ and Pd₂(dta)₄, and between their electronic spectra, shows that the mixing of the electronic structures of the metal ions and of the chelating ligands in the dimer cannot be described easily in terms of additive and/or transferable parameters referring to the monomeric molecule. As compared with the monomeric case, the total energy of the dimeric molecule appears to be a compromise between several conflicting drives. Unfavorable factors such as the increased repulsive core-core interactions, the noncoplanarity of the palladium and sulfur atoms, etc. oppose the attractive M-M interactions, a more favorable SPdS angle (90°), etc. The role of the M-M interactions can then be interpreted as providing such an energy balance as to make the total energy of the Pd₂(dta)₄ molecule just twice that of the Pd(dta)₂ molecule. The importance of energy terms related to the spatial array of the ligands and to the ligand geometry is indicated by the almost constant set of angles which distinguishes a terminal from a bridging ligand, as shown in Table IX, and by the very similar coordination geometries observed for the structurally determined monomeric and dimeric planar dithiocarboxylato derivatives, irrespective of the substituent attached to the CS₂ group and of the central metal ion.^{16,17,28} In solution, slight modifications of the spatial array of ligands might render the M-M energy contribution insufficient to stabilize the dimeric molecule. The dimer-monomer transformation of Ni₂(C₆H₅-CH₂-CSS)₄, in solution, at room temperature and of Pd₂(dta)₄ at higher temperatures might then be explained without the assumption of a weak M-M interaction.

A last remark concerns the structure of C, which remains an unresolved problem. The Debye-Scherrer diagrams of C show the lines of A and three additional lines, of medium intensity; this would seem to indicate that C contains, in addition to large amounts of the known A monoclinic modification, small amounts of another modification. The electronic spectral results, however, rule out the hypothesis of a

C structure mainly based on that of A. The solution spectra of C show the characteristic transitions of the D_{2h} monomeric molecule (and with higher intensity than solutions of A, indicating that there is a larger fraction of monomers in C than in A), but they do not exhibit any discernible transition at $25 \text{ cm}^{-1} \times 10^3$. Thus the D_{2d} dimer contained in structures A and B should not contribute to structure C to any appreciable extent. There is no apparent reason that the isolated dimers with four bridging ligands should be stable or unstable according to whether they are produced by the A or C lattice, respectively. As pointed out before, that polynuclear species are present in C, in addition to the monomeric ones, is clearly indicated by the molecular weight data, the NMR spectral patterns, the infrared spectra, showing the bands of the bridging and terminal ligands both in the solid state and in solution, and also the ϵ_M values of the monomer transitions in C solutions, higher than those of A but less than the 3 times greater values expected were monomers only present. Detailed structural assignments for the polynuclear species would be inappropriate on the basis of the present experimental results.

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Registry No. Pd(CH₃CS₂)₂, 70072-39-8; Pd(CH₃CS₂)₂^{1/2}CS₂, 70072-41-2; Pd(CH₃CS₂)₂ (salt form), 63882-63-3.

Supplementary Material Available: Listings of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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