Metal–Metal Interactions in One Dimension. 3.[1] Segregated Canted Stacks of Tetrakis(dithioacetato)diplatinum(II)

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Received May 20, 1980

The title compound has been synthesized by heterogeneous reaction between K_2PtCl_4 and CH_3CSSH in toluene. The X-ray structure consists of dimeric units stacking in columns along the crystallographic *c* axis (monoclinic space group $P2_1/n$). The Pt–Pt axis of each dimer is inclined with respect to the [001] direction by about 28°. The intra- and intermolecular Pt–Pt distances are 2.767 (1) and ~3.8 Å. The physical and chemical properties of the platinum compound are compared with those of the known palladium(II) analogues.

Introduction

The important features necessary for inorganic one-dimensional systems have been reviewed by several authors.[2] In any systematic search for new materials, columnar structures built up of planar repeat units stacking as closely as possible along the normal to their planes are highly desired.

A stumbling block facing strategies of synthesis based upon molecular stacking is that, besides the capacity of a molecule to give metal–metal interactions, unpredictable and as yet largely uncontrollable packing forces dictate whether linear stacks do form. In order to devise methods for better control of the interplay between electronic and packing factors, information on their relative role in new low-dimensional systems and how these factors are related to solid-state properties appears useful.

In a previous paper[3] it was shown that palladium(II) dithioacetate exists in several solid phases. The single-crystal X-ray determinations of two such forms reveal that they possess linear chains of directly interacting metal atoms, with short M–M contacts, as a result of a one-dimensional arrangement of either dimeric (structure B) or alternating monomeric and dimeric units (structure A). Theoretical work[1] indicates that the intermolecular M–M interactions along the stacks are of bonding character, in the order monomer–monomer < monomer–dimer < dimer–dimer, and that these interactions might play some role as determinants of structure.

This situation, coupled with the expected and well-documented increasing ability to give metal–metal interactions on going down the nickel triad, suggests that platinum(II) dithioacetate may be an appropriate candidate for observing segregated molecular stacks with direct M–M interactions. In the present paper, the synthesis, properties, and single-crystal X-ray determination of the dithioacetic acid derivative of platinum(II) are reported.

Experimental Section

Reagents. Dithioacetic acid was prepared according to known procedures.[4] K_2PtCl_4 was used as obtained from B.D.H. Chemicals Ltd.

Preparation of the Complex. K_2PtCl_4 (4.0 g, 9.6 mmol) was added to a solution of CH_3CSSH (3.55 g, 38.5 mmol) in 200 mL of toluene. The mixture was refluxed under nitrogen, for ~10 h, and then filtered. Upon cooling of the filtrate at room temperature, needles with a copper red luster, of composition $Pt(CH_3CSS)_2$, were obtained; 1.50 g, 41% yield, referred to original platinum. Anal. Calcd for $PtC_4H_6S_4$: C, 12.73; H, 1.59; S, 33.98; Pt, 51.70. Found: C, 12.53; H, 1.45; S, 33.79; Pt, 51.89 (mp 259–260 °C). Crystals of suitable size for X-ray analysis and single-crystal-polarized spectra were obtained upon slow evaporation of a toluene solution of the complex, at 50 °C, under nitrogen.

Chemical Analyses. These were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Mass Spectra. The mass spectra were recorded with an AEI MS-9 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. Fragments containing one or two platinum atoms were distinguished by comparing the observed and calculated[5] isotopic patterns.

Vibrational Spectra. These were recorded, in the region 5000–250 cm^{-1}, with a Perkin-Elmer 521 spectrophotometer. KBr pellets and Nujol mulls were used.

Visible–UV Spectra. Solution and Nujol mull spectra were recorded on a Cary 14 spectrophotometer. A Beckman DK-1A spectrophotometer was used for the reflectance spectra. Single-crystal-polarized spectra, between ~12 500 and ~25 000 cm^{-1}, were recorded on a Shimadzu MPS 50L microspectrophotometer, with a single Glan Thompson prism in the sample beam as a polarizer.

Differential Thermal Analysis. This was performed at 3°/min with a Du Pont 900 differential analyzer.

NMR Spectra. Proton chemical shifts were measured at 100 °C, in deuteriobenzene, with a Perkin-Elmer R 12, 60-MHz spectrometer. No signal could be detected at room temperature (~37 °C) because of the low solubility of the compound.

Crystal Data and Intensity Measurements. A needle-shaped crystal of dimensions 0.40 × 0.02 × 0.02 mm was selected and sealed in a glass capillary under nitrogen. Preliminary photographs showed Laue symmetry 2/*m*; *h0l* reflections were absent for $h + l \neq 2n$, and *0k0* reflections were absent for $k \neq 2n$, so that the space group is $P2_1/n$. The cell dimensions obtained by least-squares refinement of setting angles of 25 reflections measured on a Philips PW1100 four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) are *a* = 8.919 ± 0.003 Å, *b* = 16.628 ± 0.004 Å, *c* = 12.740 ± 0.003 Å, *β* = 110.40 ± 0.04°, and *V* = 1770.9 Å³. The formula weight is 377.4 ($PtC_4S_4H_6$); D_c = 2.83 g cm⁻³ for *Z* = 8, corresponding to 2 formula units (or a dimer) per asymmetric unit. The absorption coefficient for Mo Kα is 174.5 cm⁻¹. Intensity data were collected by the ω–2θ scan technique (scan width 1.2° (θ), scan speed 0.05° (θ) s⁻¹) in the range 3° ≤ θ ≤ 25°. The intensity of three reference reflections monitored after every 180 min did not show significant variations. A total of 2880 independent reflections were measured, 742 of which, having $I \leq 3\theta(I)$,[6] were considered as

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Table I. Fractional Atomic Coordinates and Thermal Parameters[a] for Nonhydrogen Atoms of $Pt_2(CH_3CSS)_4$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0.04706 (5)	−0.00839 (3)	0.15776 (4)	341 (3)	286 (3)	246 (3)	9 (2)	147 (2)	−26 (2)
Pt(2)	0.97723 (6)	0.02090 (3)	0.34956 (4)	426 (3)	286 (3)	251 (3)	33 (2)	174 (2)	−20 (2)
S(1)	0.9119 (4)	0.01072 (2)	0.0748 (3)	495 (20)	479 (23)	289 (18)	102 (16)	136 (15)	78 (16)
S(2)	0.2832 (4)	0.0638 (2)	0.2238 (3)	383 (18)	538 (25)	415 (20)	64 (16)	170 (15)	5 (18)
S(3)	0.8181 (4)	−0.0843 (2)	0.0796 (3)	481 (20)	540 (25)	437 (21)	−160 (17)	223 (17)	−194 (19)
S(4)	0.1886 (4)	−0.1247 (2)	0.2308 (3)	578 (21)	369 (24)	570 (24)	111 (17)	331 (18)	−9 (19)
S(5)	0.2413 (4)	0.0555 (2)	0.4501 (3)	570 (21)	472 (24)	335 (19)	93 (17)	129 (16)	−62 (17)
S(6)	0.0303 (4)	−0.1113 (2)	0.4059 (3)	596 (21)	339 (21)	377 (19)	22 (16)	247 (17)	67 (16)
S(7)	0.7107 (4)	−0.0102 (3)	0.2596 (3)	392 (18)	700 (29)	441 (21)	67 (17)	206 (15)	−31 (20)
S(8)	0.9232 (5)	0.1562 (2)	0.3073 (3)	862 (28)	348 (22)	478 (24)	174 (20)	289 (20)	3 (18)
C(1)	0.8856 (14)	0.1706 (8)	0.1688 (12)	437 (73)	276 (76)	498 (88)	85 (57)	141 (65)	136 (64)
C(2)	0.8241 (20)	0.2531 (10)	0.1270 (16)	821 (107)	436 (100)	960 (135)	296 (78)	356 (97)	221 (95)
C(3)	0.6842 (15)	−0.0652 (9)	0.1436 (12)	419 (73)	456 (94)	537 (87)	2 (62)	188 (63)	46 (73)
C(4)	0.5182 (16)	−0.1003 (11)	0.0891 (14)	368 (79)	741 (125)	715 (113)	−227 (70)	151 (76)	−53 (94)
C(5)	0.1344 (13)	−0.1564 (7)	0.3381 (10)	355 (65)	275 (72)	292 (69)	−14 (53)	84 (54)	−71 (57)
C(6)	0.1893 (18)	−0.2420 (9)	0.3797 (13)	726 (99)	311 (86)	571 (101)	84 (72)	192 (82)	18 (77)
C(7)	0.3374 (14)	0.0791 (8)	0.3621 (11)	432 (70)	254 (73)	424 (74)	−23 (54)	146 (58)	−105 (60)
C(8)	0.4983 (16)	0.1231 (10)	0.4161 (14)	581 (95)	632 (110)	636 (108)	−130 (71)	183 (83)	−88 (85)

[a] The esd's in parentheses refer to the last digit. Anisotropic thermal factors are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})10^{-4}]$.

"unobserved". Data were corrected for the usual Lorentz–polarization factors. An absorption correction following the semiempirical method of North et al.[7] was applied.

Structure Solution and Refinement. The structure was solved by the automatic centrosymmetric routine of SHELX[8] in which an E map yielded the positions of the Pt atoms. The remaining nonhydrogen atoms were found by heavy-atom methods. All atoms were assumed to be uncharged; the scattering factors[9] for Pt and those of the SHELX system for S and C were used. Correction for anomalous dispersion was included. Isotropic full-matrix least-squares refinement led to an R of 0.08. Introduction of anisotropic temperature factors lowered the value of R to the final value 0.034 for the 2138 observed reflections ($R_w = 0.036$). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with the final weighting scheme $w = 1.1376/[(\sigma(F_o)^2 + 0.000422F_o^2]$.

Results

Platinum(II) dithioacetate remains unaltered for several months in inert atmosphere but decomposes upon exposure to air. Although the decomposition process takes several days to become visible, considerable changes occur in the X-ray diffraction patterns within ∼5 min. Care was taken, therefore, to perform physical measurements in a dry nitrogen atmosphere and employ carefully dried and deoxygenated solvents. Differential thermal analysis of the compound does not indicate any phase transition below the melting point. Completely insoluble in polar solvents, the complex is also sparingly soluble (∼5 × 10⁻⁴ M) in benzene, toluene, dichloromethane, etc. The solutions are quite stable, both at room temperature and at ∼100 °C (vide infra). The solute, unlike the palladium(II) analogues,[3] is recovered unaltered from the solutions regardless of the nature of the solvent.

The ¹H NMR spectrum in C_6D_6, at 100 °C, consists of a 1:2:1 triplet, centered at $\tau = 7.76$ ppm from Me_4Si. This pattern indicates coupling of the methyl protons with two equivalent ¹⁹⁵Pt isotopes (natural abundance 37%, $I = \frac{1}{2}$); i.e., bridging ligands are present. That $Pt(CH_3CSS)_2$ has a multinuclear, completely bridged structure is also suggested by its vibrational spectrum. Only two C–S stretching frequencies are observed ($\bar{\nu}_{as}(CSS) = 1170$ cm⁻¹, $\bar{\nu}_s(CSS) = 895$

Table II. Main Interatomic Distances (Å) in $Pt_2(CH_3CSS)_4$[a]

Pt(1)–Pt(2)	2.767 (1)	S(4)–C(15)	1.684 (12)
Pt(1)–S(1)	2.318 (4)	S(6)–C(5)	1.651 (12)
Pt(1)–S(2)	2.313 (3)	S(2)–C(7)	1.676 (13)
Pt(1)–S(3)	2.311 (3)	S(5)–C(7)	1.678 (13)
Pt(1)–S(4)	2.321 (4)	C(1)–C(2)	1.504 (21)
Pt(2)–S(5)	2.328 (3)	C(3)–C(4)	1.516 (19)
Pt(2)–S(6)	2.310 (4)	C(5)–C(6)	1.539 (19)
Pt(2)–S(7)	2.309 (3)	C(7)–C(8)	1.543 (18)
Pt(2)–S(8)	2.324 (4)	S(8)–S(1)	3.040 (8)
S(1)–C(1)	1.672 (14)	S(5)–S(2)	3.037 (8)
S(8)–C(1)	1.695 (15)	S(7)–S(3)	3.038 (8)
S(3)–C(3)	1.694 (14)	S(6)–S(4)	3.034 (8)
S(7)–C(3)	1.683 (15)		

[a] The esd's in parentheses refer to the last digit.

Table III. Main Interatomic Angles (Deg) in $Pt_2(CH_3CSS)_4$[a]

S(1)–Pt(1)–S(2)	89.9 (1)	Pt(1)–S(1)–C(1)	112.1 (5)
S(1)–Pt(1)–S(3)	90.9 (1)	Pt(1)–S(2)–C(7)	110.7 (5)
S(1)–Pt(1)–S(4)	176.2 (1)	Pt(1)–S(3)–C(3)	110.8 (5)
S(1)–Pt(1)–Pt(2)	90.9 (1)	Pt(1)–S(4)–C(5)	108.4 (4)
S(2)–Pt(1)–S(3)	175.1 (1)	Pt(2)–S(5)–C(7)	110.2 (4)
S(2)–Pt(1)–S(4)	89.3 (1)	Pt(2)–S(6)–C(5)	111.2 (5)
S(2)–Pt(1)–Pt(2)	92.5 (1)	Pt(2)–S(7)–C(3)	111.3 (5)
S(3)–Pt(1)–S(4)	89.6 (1)	Pt(2)–S(8)–C(1)	109.1 (5)
S(3)–Pt(1)–Pt(2)	92.3 (1)	S(1)–C(1)–S(8)	129.0 (8)
S(4)–Pt(1)–Pt(2)	92.9 (1)	S(1)–C(1)–C(2)	116.6 (12)
S(5)–Pt(2)–S(6)	90.4 (1)	S(8)–C(1)–C(2)	114.4 (11)
S(5)–Pt(2)–S(7)	176.2 (1)	S(3)–C(3)–S(7)	128.2 (8)
S(5)–Pt(2)–S(8)	88.6 (1)	S(3)–C(3)–C(4)	116.6 (11)
S(5)–Pt(2)–Pt(1)	91.9 (1)	S(7)–C(3)–C(4)	115.3 (10)
S(6)–Pt(2)–S(7)	90.3 (1)	S(4)–C(5)–S(6)	130.9 (8)
S(6)–Pt(2)–S(8)	175.3 (5)	S(4)–C(5)–C(6)	114.9 (10)
S(6)–Pt(2)–Pt(1)	91.2 (1)	S(6)–C(5)–C(6)	114.2 (10)
S(7)–Pt(2)–S(8)	90.4 (1)	S(2)–C(7)–S(5)	129.8 (8)
S(7)–Pt(2)–Pt(1)	91.8 (1)	S(2)–C(7)–C(8)	115.1 (10)
S(8)–Pt(2)–Pt(1)	93.3 (1)	S(5)–C(7)–C(8)	115.2 (10)

[a] The esd's in parentheses refer to the last digit.

cm⁻¹), and these are almost superimposable on those of $Pd_2(CH_3CSS)_4$.[3] Different frequencies are shown by the terminal ligands of monomeric $Pd(CH_3CSS)_2$.[3]

No well-defined Pt–S bands could be observed. It has been suggested[10] that Pt–Pt interaction may shift the Pt–S frequency below 200 cm⁻¹ or, otherwise, drastically reduce its intensity.

Description of the Structure. Structural information on platinum dithioacetate is reported in Tables I–III and Figures

(6) Standard deviations on intensities were computed as $\sigma(I) = [P + 0.25(T_p/T_B)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, where P is the total peak count in a scan of time T_p, B_1 and B_2 are the backgrounds counts, each in a time T_B, and I is the intensity, equal to $P - 0.5(T_p/T_B)(B_1 + B_2)$.

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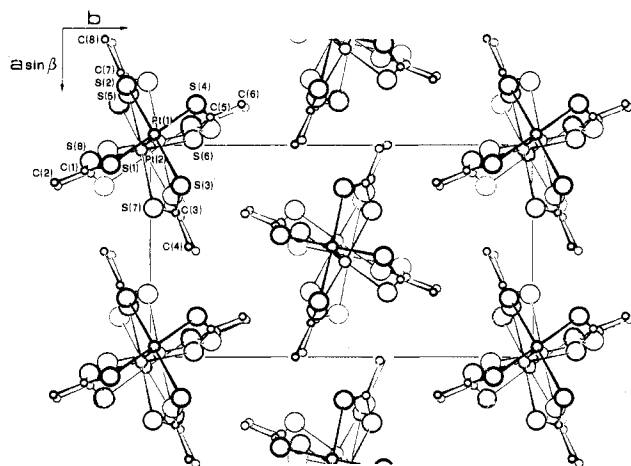(9) "International Tables for X-ray Crystallography"; Vol. IV, Kynoch Press: Birmingham, 1974.

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Figure 1. Atomic arrangement in the structure of $Pt_2(CH_3CSS)_4$, projected along the *c* axis.
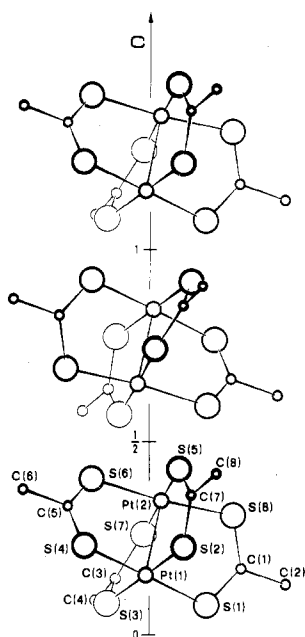
Figure 2. Stacking of the $Pt_2(CH_3CSS)_4$ units along the *c* axis.

Table IV. Platinum-Containing Ions in the Mass Spectra of $Pt_2(CH_3CSS)_4$

ion	m/e	RI
PtS^+	227	1.85
$PtCS^+$	240	1.85
$PtCH_3CS^+$	253	3.70
PtS_2^+	259	3.70
$PtCH_3CSS^+$	285	7.40
$Pt(CH_3CSS)S^+$	318	7.40
$Pt(CH_3CSS)CH_3CS^+$	343	7.40
$Pt(CH_3CSS)_2^+$	377	100
$Pt(CH_3CSS)_2S^+$	409	9.25
$Pt(CH_3CSS)_2CS_2^+$	454	1.85
$Pt(CH_3CSS)_3CS^+$	512	5.55
$Pt_2(CH_3CSS)_2^+$	571	7.40
$Pt_2(CH_3CSS)_3^+$	663	1.85
$Pt_2(CH_3CSS)_4^+$	755	29.63

Table V. Electronic Spectra of Dithioacetato Complexes of Platinum(II) and Palladium(II)[a]

compd	solution[c]	reflec-tance	Nujol mull	single crystal	polari-zation
$Pt_2(CH_3CSS)_4$		15.2	14.8	15.2	$\|c$
		19.0	18.5	19.0	$\|c$
	22.8[b] (~2.9)	22.7	21.6[b]	>22	
	24.6 (3.10)	24.4	24.1		
	28.9[b] (~3.2)	nm[f]	29.4[b]		
	32.8 (4.20)		32.3[b]		
	~34.5[b] (~4.1)		>33		
	~37.7[b] (~4.0)				
	>38				
form B (Pd)		16.3	16.5[b]	16.3	$\|c^d$
		22.2	21.7[b]	>22	
	25.0 (3.37)	25.0	25.6[b]		
	30.8 (3.76)	nm	29.2		
	33.9 (4.27)		33.9		
	35.7 (4.27)		34.4[b]		
	40.8 (4.19)		40.7		
	43.5 (4.23)		44.2		
form A (Pd)	17.5[b]	17.5[b]	18.3[b]	$\|a^e$	
	20.8 (3.04)	19.6	20.4[b]	20.2	$\|a$
	22.0 (3.10)	22.2[b]	~22[b]	22.0	$\perp a$
	25.0[b]	24.4	24.4[b]		
	26.0[b]	nm	30.5		
	30.8 (3.78)		33.6		
	33.9 (4.40)		34.8[b]		
	35.5[b]		40.5		
	37.7[b]		43.5		
	40.5 (4.16)				
	43.5 (4.10)				

[a] Energies in 10^3 cm^{-1} (log ϵ in parentheses). [b] Shoulder. [c] In benzene or dichloromethane for $Pt_2(CH_3CSS)_4$, in cyclohexane for the palladium compounds. [d] Tetragonal $P4/ncc$ space group. [e] Monoclinic $C2/c$ space group. [f] nm = not measured beyond this frequency.

1 and 2. A list of structure factors is available as supplementary material. The crystal structure consists of binuclear units with four bridging ligands. Each Pt atom is surrounded by four sulfur atoms in an approximately square-planar arrangement. The mean Pt–S distance is 2.317 Å. The Pt–Pt separation in the dimer is 2.767 (1) Å, about 0.17 Å shorter than the distance between the centers of the S_4 planes. The average Pt–Pt–S angle is 92.1°. The two PtS_4 squares are reciprocally twisted by about 20° from the eclipsed D_{4h} structure.

For the dithioacetate ligand, the C–S distances are in the range 1.65–1.70 Å (mean value 1.68 Å). The S–C–S angles average 129.5°. The molecules are stacked in columns along the crystallographic *c* axis, the Pt–Pt axis of each dimer being inclined with respect to the direction [001] by about 28°. Adjacent dimers are related by crystallographic inversion centers. The separations between Pt atoms of adjacent units are 3.819 (1) and 3.776 (1) Å. Because of the inclination of the pseudo-fourfold axis of the molecules, the separations between the platinum atoms of one dimer and sulfur atoms of the PtS_4 squares of adjacent dimers are shorter. Distances of 3.482 (4) and 3.517 (4) Å occur between Pt(1) and S(1)' and Pt(2) and S(6)', respectively. All other intermolecular

distances are considerably longer than the sum of van der Waals radii. The columns of dimers are arranged according to a compact hexagonal packing of rods, similar to that found in the A form of palladium dithioacetate.[3]

Mass Spectra. The observed platinum-containing ions are listed in Table IV. The reported m/e ratios are based on the most intense peak, and intensities are given relative to a platinum-containing base peak of 100 units. The principal species in the vapor is the monomer, the $Pt(CH_3CSS)_2^+$ ion being the basic peak. The next strongest peak, at m/e 755, is $Pt_2(CH_3CSS)_4^+$. No more highly associated molecules are present in the vapor, unlike the case of the corresponding palladium complexes.[3]

Electronic Spectra. Electronic spectral information on $Pt_2(CH_3CSS)_4$ is summarized in Figure 3 and Table V which also reports, for comparison, the spectra of the related palladium compounds, only partially described previously. The observed single-molecule bands (solvent and time independent)

Table VI. Average Distances (Å) and Angles (Deg) in Platinum and Palladium Dithioacetato Complexes

compd	M–M	M–S	C–S	C–C	SCS	MSC
Pt$_2$(CH$_3$CSS)$_4$	2.767 (1)	2.317 (4)	1.679 (15)	1.526 (21)	129.5 (8)	110.5 (5)
Pd$_2$(CH$_3$CSS)$_4{}^a$	2.738 (1)	2.327 (1)	1.677 (4)	1.515 (7)	128.7 (2)	109.9 (1)
Pd$_2$(CH$_3$CSS)$_4{}^b$	2.754 (1)	2.317 (6)	1.69 (2)	1.49 (5)	126.7 (11)	111.5 (8)
Pd(CH$_3$CSS)$_2{}^b$		2.331 (5)	1.69 (2)	1.47 (2)	112.1 (10)	87.15 (7)
CH$_3$CSSK^c			1.67 (1)	1.40 (5)	123.5 (6)	

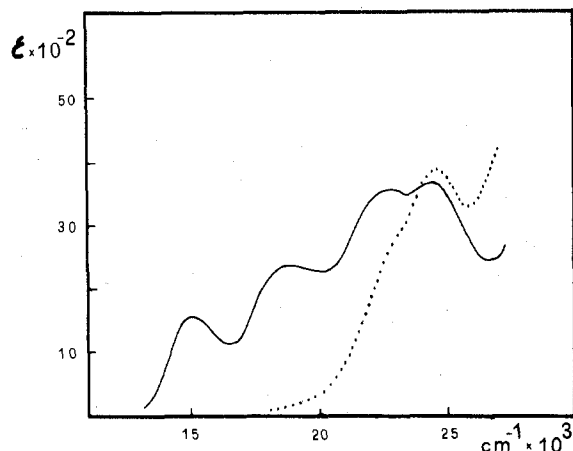^{a} Form B.[3] ^{b} Form A.[3] ^{c} Reference 13.

Figure 3. Low-energy electronic spectrum of Pt$_2$(CH$_3$CSS)$_4$: ···, in toluene; —, reflectance spectrum of a sample diluted in MgO. The intensity of the reflectance spectrum is in arbitrary units.

undergo only little shifts on solid formation, which is a strong indication that the molecular geometries revealed by the X-ray analyses are retained in solution. Unlike those of Pd$_2$(CH$_3$-CSS)$_4$, the frequencies and intensities of the platinum dimer do not vary upon increasing the temperature of the solutions to 80–100 °C.

Single-crystal, diffuse reflectance, and Nujol mull spectra are quite similar and display reproducible bands, between ~15000 and ~22000 cm^{-1}, which are not present in solution.

Due to the high luster of Pt$_2$(CH$_3$CSS)$_4$, it was necessary to dilute it in MgO powder in order to obtain well-resolved reflectance spectra. Otherwise, a uniform high intensity dominates all the visible region, and no distinct maximum is discernible. For each compound, the low-energy solid-state bands are largely polarized in the stack direction. Because of the high intensities, crystals so thin had to be used for the single-crystal-polarized spectra that reliable intensity estimates could not be made. It seems, however, that the intensities of these bands are of the same order of magnitude as those corresponding to the lowest energy bands in solution.

Discussion

The molecular geometries of the platinum and palladium dithioacetato dimers are very similar. The corresponding average distances and angles are shown in Table VI.

The intramolecular M–M distance is slightly longer in the platinum than in the palladium structures. However, a comparison with the covalent radii (Pt, 1.30 Å; Pd, 1.28 Å) and intermetallic separations in the metallic state of the elements (Pt, 2.775 Å; Pd, 2.751 Å) shows that the M–M interaction is indeed stronger in the platinum dimer. The fact that the Pt–Pt separation is shorter than the distance between the centers of the S$_4$ planes by 0.17 Å, in comparison with 0.14 and 0.13 Å for the palladium dimers, further strengthens this conclusion.

Upon consideration of the larger covalent radius of platinum with respect to palladium, the Pt–S bonds appear to be stronger, despite the unfavorable larger displacement of the platinum atoms from the S$_4$ planes.

The average C–S distance in Pt$_2$(CH$_3$CSS)$_4$, 1.69 Å, is essentially the same as that in the structures of the palladium complexes and the free ligand.[13]

Possible differences between the C–C bond lengths in the platinum and palladium dimers are masked by the inaccuracy of the structural parameters. A difference which is not masked, however, is the longer C–C distance in the platinum complex than in the potassium salt of the free ligand and in the monomeric Pd(CH$_3$CSS)$_2$ molecule.

These patterns are not unexpected. A recent MO investigation[1] of Pd(CH$_3$CSS)$_2$ and Pd$_2$(CH$_3$CSS)$_4$ has indicated that on going from the former to the latter species one should have stronger Pd–S and weaker C–C bonds, as a result of an electron density shift from nonmethyl carbon to palladium determined primarily by the higher and lower energies of the nonmethyl carbon and palladium atomic levels, respectively, in the dimer. The lowering of the absolute levels and the increasing diffuseness of the valence orbitals on going from palladium to platinum should enhance this effect. The short Pd–Pd distance in Pd$_2$(CH$_3$CSS)$_4$ was accounted for by a positive Pd–Pd overlap population (0.026 electron) mainly due to the 5s, 5p$_z$ and 4d$_{z^2}$ orbitals. A higher overlap population is reasonably anticipated for the Pt dimer on account of the smaller nd–$(n + 1)$p separation in the third transition series.[11]

The foregoing evidence for a more stable platinum dimeric structure in the solid state parallels the indications that, unlike the case of Pd$_2$(CH$_3$CSS)$_4$, virtually no dissociation occurs in solution at temperatures ≤100 °C and that the second strongest peak in the mass spectra corresponds to a dimer. No peaks were observed near an m/e corresponding to a dimer for the palladium compounds under the same experimental conditions.[3]

As shown in Figures 1 and 2, the Pt$_2$(CH$_3$CSS)$_4$ units are stacked in columns along the crystallographic c axis. The type of stacking appears to be completely dependent on packing considerations. A key observation is that adjacent sulfur planes of successive molecules are only ~2.7 Å apart, i.e., less than the interplanar distance, 2.937 Å, within a single unit. Such an efficient occupancy of space would be very unlikely in a linear chain structure, with the S$_4$ planes orthogonal to the [001] direction. In the latter case, an interplanar spacing of 2.7 Å would involve intermolecular S–S contacts of 3.14 Å (for a staggerd configuration) which, if compared with the van der Waals contact of 3.45 Å for two sulfur atoms,[12] would imply severe interligand repulsion.

On the other hand, the observed intermolecular Pt–Pt (~3.8 Å), Pt–S (~3.5 Å), and S–S (≫3.45 Å) contacts and the relative arrangement of adjacent molecules do not suggest any significant stabilization of the stack by either metal–metal,[14]

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metal–ligand, or intermolecular HOMO–LUMO[15] back-bonding interactions.

In the palladium B structure the dimeric units stack in columns with collinear metal atoms, and the columns are arranged according to a square packing of rods. This structure is obtained only if carbon disulfide molecules are incorporated between different columns. Since the platinum and palladium dimers possess much the same molecular geometry and overall dimensions, one might guess the possibility that the platinum dimers attain a linear metal chain structure upon incorporation of carbon disulfide. All attempts to obtain such a structure have been unsuccessful.

Electronic Spectra. The single-molecule spectra of $Pt_2(C-H_3CSS)_4$ and $Pd_2(CH_3CSS)_4$ appear to be shifted with respect to each other. This suggests a similar electronic structure for both of these D_4 symmetry molecules. The high intensity of all the absorptions seems to indicate that the interactions of the metal orbitals with the ligands do not follow a crystal field scheme. The results of an LCAO–MO–SCF investigation[1] of the electronic structure of the palladium dimer are in agreement with this view. There is an efficient mixing of metal and ligand orbitals, and, further, distinct sequences of mainly metal MO's are not discernible. Attempts to assign the electronic transitions in terms of generalized MO's were not successful[16] and will not be repeated here for the platinum dimer.

Despite this shortcoming and the fact that the solid-state spectra are at best qualitative in nature, a comparison between solution and solid-state spectra of platinum(II) and palladium(II) dithioacetates, with the aim of reaching some preliminary conclusions about the nature of the solid-state effects, is of interest. As we said before, all of these solids display low-energy bands ($\sim 3000-4000$ cm^{-1} below the first solution band) which are not present in the single-molecule spectra and are largely polarized along the stack directions. There has been discussion in the literature[17-20] about the origin of the "unusual" solid-state absorption bands which divalent metal-atom chain compounds commonly display relative to their solution spectra, particularly as to whether such bands might be indicative of some form of M–M bonding.

The fact that both crystalline $Pt_2(CH_3CSS)_4$, in which there should be only van der Waals interactions between the molecules,[14] and the A and B palladium forms, in which direct M–M interactions can be reasonably assumed, exhibit similar spectral patterns provides further support for the view that no form of intermetallic interaction needs be invoked to account for the low-energy solid-state bands.

In light of these observations, it seems probable that the lowest crystal excited states of the dithioacetates should be neutral Frenkel excitons[21] and that the appearance of the low-energy crystal bands should be accounted for by crystal shifts of z-polarized single-molecule transitions in the higher parts of the spectra. Indeed, the similarity of solid-state band energies (above ~ 20000 cm^{-1}) to those of the solution peaks seems to indicate that the single-molecule transitions suffering the shifts should be located beyond the range of measurements. Such large shifts, however, would not be anticipated in current interpretations of the crystal spectra of metal chain compounds formed by simple square-planar units. For a variety of such materials, Davydov shifts have been successfully calculated[22-28] by using an extremely simplified model,[29] according to which a dipole-allowed single-molecule transition would be shifted in the crystal by approximately

$$I_{nm} = e^2 R^{-3}(x_n' x_m' + y_n' y_m' - 2z_n' z_m')$$

where R is the separation between the nth and mth molecules and (with a set of axes in each molecule which places the z axis between centers and common x and y axes orthogonal to z) x_n' is the x component of the transition dipole moment for the nth molecule etc.

Thus, for a 1.0-Å z transition moment centered on the metal atoms, we would anticipate shifts of about -12000 and -7000 cm^{-1}, for $Pd_2(CH_3CSS)_4$ (form B) and $Pt_2(CH_3CSS)_4$, respectively. These figures decrease to -4700 and -1400 cm^{-1}, respectively, if the strong admixture of metal and ligand characters in the ground and excited states of the molecules is taken into account and the transition moments are located at the centers of the dimers. In palladium form A there are two different molecular species in the stack, and an extended treatment, including second-order effects, would be required, but similar values would be expected.

The present experimental material is insufficient, particularly from the intensity viewpoint, to decide whether a point–multipole expansion approach to the crystal shifts of the dithioacetates is inadequate or the low-energy solid-state bands might have a different origin. Further work is planned in order to elucidate this point.

Registry No. $Pt_2(CH_3CSS)_4$ (coordination form), 74868-86-3; $Pt(CH_3CSS)_2$ (salt form), 74854-48-1; $Pd(CH_3CSS)_2$ (coordination form B), 63890-11-9; $Pd(CH_3CSS)_2$ (coordination form A), 63890-12-0; $Pd(CH_3CSS)_2$ (salt form), 63882-63-3; K_2PtCl_4, 10025-99-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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