Linear-chain Platinum(II) Dithiocarboxylates: Crystal Structure of Tetrakis(phenyldithioacetato)diplatinum(II)†

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The crystal structure of the linear-chain compound tetrakis(phenyldithioacetato)diplatinum(II) has been determined. It crystallizes in the orthorhombic space group *Iba*2, with unit-cell dimensions $a = 9.345(4)$, $b = 29.563(5)$, $c = 12.005(2)$ Å, and $Z = 4$. The crystal structure consists of Pt_2S_8 dimeric units, with a bridging acetate cage structure, in which the Pt–Pt distance is 2.764(1) Å. The two PtS_4 squares are rotated by 25° from the eclipsed structure. The dimers are stacked along the two-fold *c* axis with inter-dimer Pt–Pt distances of 3.238(1) Å. The structure has been examined in the light of three other linear-chain platinum(II) dithiocarboxylate compounds. All these complexes are characterized by having high anisotropic optical and electrical properties. Only $[Pt_2(Pr^iCS_2)_4]$, form A, shows appreciable electrical conductivity ($\sigma = 2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$) and this is related to the unusual short inter-dimer Pt–Pt distance, 3.081 Å. Polarized single-crystal absorption spectra are also reported and discussed.

Compounds of the type $[M_2(RCS_2)_4]$ (M = Pt^{II}, Pd^{II}, or Ni^{II}; R = aliphatic group) have been prepared and some of them structurally characterized during the last few years in this laboratory.[1–5] These complexes are interesting since they show anisotropic physical properties arising from their columnar structures. The platinum complexes readily undergo oxidative addition with halogens (X), giving compounds of formula $[Pt_2(RCS_2)_4X_2]$, which contain Pt in the unusual formal oxidation state of +3.[6] In the case of dithioacetic derivatives of Pt and Ni, linear-chain mixed-valence compounds could be isolated.[7,8] In a preliminary communication[5] we reported that tetrakis(dithioisobutanoato)diplatinum(II) crystallizes in two polymorphic forms, both having a columnar structure, characterized by a low-energy band (<18 000 cm^{-1}) in the visible diffuse reflectance spectrum absent in solution.[5] With the aim of studying the unusual optical properties of this class of compounds in the solid state, we have synthesized new Pt^{2+} dithiocarboxylates in an attempt to vary the intra-columnar distance *R* and observe possible relationships between this parameter and the optical properties. In this context we have investigated the crystal structure of the linear-chain complex tetrakis(phenyldithioacetato)diplatinum(II) and the optical and electrical properties of these tetrakis(dithiocarboxylato)-diplatinum(II) complexes.

Experimental

Elemental analyses were performed by Alfred Bernhardt Mikroanalytische Laboratorium, Elbach, West Germany, and by Servizio Microanalisi del C.N.R., Area della Ricerca di Roma, Montelibbretti, Italy.

Reagents.—The dithiocarboxylic acids Pr^iCS_2H, $PhCH_2CS_2H$, and *p*-$Pr^iC_6H_4CS_2H$ were prepared according to known procedures.[9,10] $K_2[PtCl_4]$ was used as obtained (BDH).

Synthesis of the Complexes.—$[Pt_2(MeCS_2)_4]$ and $[Pt_2(p\text{-}Pr^iC_6H_4CS_2)_4]$ were prepared as reported previously[4,11] and the purity was checked by normal physico-chemical methods. $[Pt_2(PhCH_2CS_2)_4]$ was prepared according to the procedure reported by Furlani and Luciani.[12] The crude dark green product was extracted with toluene by using a Soxhlet apparatus. The resulting red-brown solution gave needle-like crystals with a copper lustre, on cooling.

$[Pt_2(Pr^iCS_2)_4]$, *form* A. $K_2[PtCl_4]$ (1 g, 2.4 mmol) was added to a solution of Pr^iCS_2H (1.15 g, 9.6 mmol) in toluene (50 cm^3). The mixture was stirred under reflux in an inert atmosphere for 3 d and then filtered. Upon cooling of the filtrate needle-like crystals having a copper lustre separated, yield 30% (Found: C, 22.35; H, 3.20; Pt, 44.95; S, 29.50. Calc. for $C_{16}H_{28}Pt_2S_8$: C, 22.15; H, 3.25; Pt, 45.00; S, 29.60%). Crystals suitable for *X*-ray analysis and single-crystal polarized spectra were obtained by slow cooling of a toluene solution of the complex.

$[Pt_2(Pr^iCS_2)_4]$, *form* B. Form A of the complex was dissolved in hot toluene, and evaporated to dryness under nitrogen. Green crystals were isolated.

Physical Measurements.—Routine i.r. spectra were recorded on a Perkin-Elmer 621 spectrophotometer on KBr pellets. Solution electronic spectra were recorded on a Cary 14 spectrophotometer. A Beckmann DK2A instrument was used to record diffuse reflectance spectra on MgO-diluted samples. Room-temperature single-crystal polarized absorption spectra (12 500—25 000 cm^{-1}) were recorded on a Shimadzu MPS 50L microspectrophotometer, with a single Glan-Thompson prism in the sample beam as polarizer. Single-crystal polarized spectra at room temperature (r.t.) and liquid N_2 temperature (l.n.t.) were registered with a microspectrophotometer described in ref. 13 (Department of Theoretical Chemistry, University of Regensburg, West Germany). *X*-Ray photoelectron spectra were recorded on a VG ESCA 3 MK_α II instrument, using Al-K_α (1 486.6 eV) radiation (Servizio ESCA, Area di Ricerca di Roma). Electrical conductivity measurements were performed on polycrystalline samples using the van der Paw method;[14] the apparatus used has been described previously.[7] *X*-Band e.s.r. spectra were obtained at r.t. and at 110 K with a Varian E9 spectrometer, equipped with a standard variable-temperature accessory.

Crystal Structure Determinations.—*Crystal data for* $[Pt_2(PhCH_2CS_2)_4]$. $C_{32}H_{28}Pt_2S_8$, $M = 1\,059.27$, orthorhombic, space group *Iba*2, $a = 9.345(4)$, $b = 29.563(5)$, $c = 12.005(2)$ Å,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

Table 1. Fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	0	0	0	C(6)	4 761(15)	1 715(4)	3 593(12)
Pt(2)	0	0	2 303(1)	C(7)	5 690(15)	1 345(4)	3 619(12)
S(1)	2 021(5)	456(2)	−28(6)	C(8)	5 540(15)	997(4)	2 843(12)
S(2)	2 421(6)	152(2)	2 361(7)	C(9)	−1 198(24)	940(6)	1 137(27)
S(3)	−1 437(6)	633(2)	−53(7)	C(10)	−1 679(21)	1 426(7)	1 081(25)
S(4)	−440(6)	776(2)	2 343(7)	C(11)	−471(16)	1 744(5)	768(16)
C(1)	2 928(19)	413(5)	1 140(21)	C(12)	−113(16)	2 084(5)	1 525(16)
C(2)	4 369(23)	637(7)	1 138(28)	C(13)	986(16)	2 387(5)	1 277(16)
C(3)	4 461(15)	1 018(4)	2 042(12)	C(14)	1 726(16)	2 350(5)	272(16)
C(4)	3 531(15)	1 387(4)	2 016(12)	C(15)	1 368(16)	2 011(5)	−485(16)
C(5)	3 681(15)	1 736(4)	2 792(12)	C(16)	270(16)	1 707(5)	−236(16)

Table 2. Interatomic distances (Å) and angles (°) with e.s.d.s in parentheses*

Pt(1)–Pt(2)	2.764(1)	S(2)–C(1)	1.72(2)
Pt(1^I)–Pt(2)	3.238(1)	S(3)–C(9)	1.71(3)
Pt(1)–S(1)	2.321(5)	S(4)–C(9)	1.68(3)
Pt(1)–S(3)	2.305(5)	C(1)–C(2)	1.50(3)
Pt(2)–S(2)	2.308(5)	C(2)–C(3)	1.57(3)
Pt(2)–S(4)	2.330(5)	C(9)–C(10)	1.51(3)
S(1)–C(1)	1.64(3)	C(10)–C(11)	1.52(2)

Pt(2)–Pt(1)–S(1)	90.8(2)	S(2)–Pt(2)–S(4^{II})	91.0(2)
Pt(2)–Pt(1)–S(3)	91.6(2)	S(4)–Pt(2)–S(4^{II})	177.6(2)
Pt(1)–Pt(2)–S(2)	91.7(2)	Pt(1)–S(1)–C(1)	111.2(6)
Pt(1)–Pt(2)–S(4)	91.2(2)	Pt(2)–S(2)–C(1)	109.3(7)
S(1)–Pt(1)–S(1^{II})	178.3(2)	Pt(1)–S(3)–C(9)	109.4(8)
S(1)–Pt(1)–S(3)	90.1(2)	Pt(2)–S(4)–C(9)	109.9(8)
S(1)–Pt(1)–S(3^{II})	89.8(2)	S(1)–C(1)–S(2)	128.3(11)
S(3)–Pt(1)–S(3^{II})	176.9(2)	S(3)–C(9)–S(4)	128.5(11)
S(2)–Pt(2)–S(2^{II})	176.5(2)	C(1)–C(2)–C(3)	109(2)
S(2)–Pt(2)–S(4)	88.9(2)	C(9)–C(10)–C(11)	112(2)

* Symmetry codes: I $-x, y, \frac{1}{2}+z$; II, $-x, -y, z$. The carbon atoms C(3)—C(8) and C(11)—C(16) belonging to the phenyl rings were refined as rigid bodies with C–C 1.395 Å.

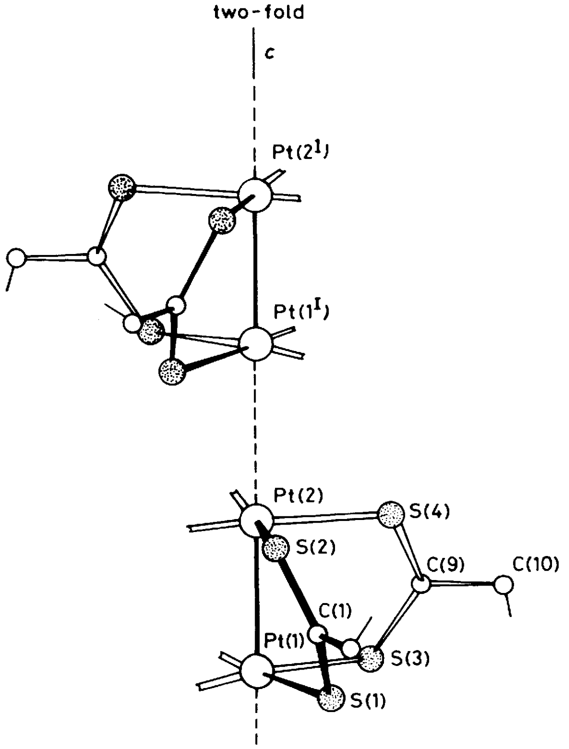


Figure 1. A view of a part of the crystal structure of $[Pt_2(PhCH_2CS_2)_4]$, showing the stacking of dimers along the two-fold axis. Only the first carbon atoms belonging to the $PhCH_2$ are shown

$U = 3\,317$ Å^3, $Z = 4$, $D_c = 2.12$ g cm^{-3}, $F(000) = 2\,016$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 93.3 cm^{-1}.

Intensity data were recorded at room temperature on a Syntex $P2_1$ diffractometer in θ—2θ scan mode with a range of 2θ = 3—60°. 1 630 Unique reflections with $I > 2\sigma(I)$ were used for structure determination. Lorentz-polarization and semi-empirical absorption corrections, based on a 360° ψ-scan around the scanning vector of selected reflections were applied. As the complex is isomorphous with the corresponding Ni and Pd complexes,[2] the atomic co-ordinates of these compounds were used for the first stage and then refined by a least-squares method with all non-hydrogen atoms anisotropic. The carbon atoms of the phenyl rings were refined as rigid groups and the hydrogen atoms in calculated positions (B = 4.5 Å^2). The quantity minimized was $\Sigma w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$]. Final values for R (= $\Sigma|\Delta|/\Sigma|F_o|$) and R' = $(\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ are 0.0374 and 0.0461, respectively. Neutral scattering factors (f' and f'') were used for non-hydrogen atoms.[15] Computations were performed on an IBM 4361 computer using the SHELX program system.[16] Final positional parameters are given in Table 1.

Crystal data for $[Pt_2(Pr^iCS_2)_4]$, *form* B. $C_{16}H_{28}Pt_2S_8$, M = 867.09, dark green tetragonal needles, space group $I4/m$, $a = b$ = 14.477(4), c = 6.247(1) Å, U = 1 309.3(5) Å^3, D_m = 2.18(1) g cm^{-3} (by flotation), Z = 2, D_c = 2.200 g cm^{-3}, $F(000)$ = 816, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 53.82 cm^{-1}.

Oscillation photographs show that only the $l = 2n$ layers are strong; this clearly indicates the existence of platinum chains with the Pt atoms stacked along the four-fold axis at $\sim c/2$. Owing to the quality of the crystals a total of only 302 independent reflections with intensity $I \geqslant 3\sigma(I)$ could be collected and corrected for background Lorentz and polarization effects and for absorption. Several attempts to refine the crystal structure did not give satisfactory results, owing to the statistical disorder of sulphur and carbon atoms. The Pt–Pt distance inside the dimer has been estimated from a Patterson map to be 2.76(1) Å. Consequently, this gives an inter-dimeric Pt–Pt distance of 3.49(1) Å.

Results

Tetrakis(dithioisobutanoato)diplatinum(II) has been isolated in two forms: the crystal structure of the first, A, crystallizing in the orthorhombic space group *Pccn* previously reported.[5] The second, form B, is tetragonal, space group $I4/m$ (see above). A differential scanning calorimetry (d.s.c.) trace of form A shows

Table 3. Electronic spectra (10^3 cm^{-1}) of tetrakis(dithiocarboxylato)diplatinum(II) complexes[a]

Compound	Diffuse reflectance	Single-crystal absorption (r.t.) $\vec{E}\parallel c$	$\vec{E}\perp c$	Solution[b]	Ref.
$[Pt_2(Pr^iCS_2)_4]$, form A	11.20[c]	11			This work
	14.80	14.8			
	18.50	18.5		20.4 (2.4)	
	23.50	n.m.		24.8 (3.24)	
	n.m.			28.6[c] (3.40)	
				32.8 (4.30)	
$[Pt_2(Pr^iCS_2)_4]$, form B	~15.0[c]	15.0		35.2[c] (4.20)	This work
	18.8	18.2	18.2		
	23.5	n.m.	n.m.		
	n.m.				
$[Pt_2(PhCH_2CS_2)_4]$	~12.8[c]	12.5			This work
	15.3	15.3			
	23.8	23.8	23.8	24.4[d]	
	n.m.	n.m.	n.m.	27.8[c]	
				32.00	
$[Pt_2(MeCS_2)_4]$	15.2	15.2			This work, ref. 4
	19.0	19.0			
	22.7	22.7		22.8[c] (2.9)	
	24.4	n.m.	n.m.	24.6 (3.10)	
	n.m.			28.9[c] (3.2)	
				32.8 (4.20)	
				34.5[c] (4.1)	

[a] n.m. = Not measured beyond highest wavenumber indicated. [b] Dichloromethane or toluene; values in parentheses are log (ε/dm^3 mol^{-1} cm^{-1}). [c] Shoulder. [d] Unknown concentration due to the very low solubility (see text).

an exothermic transition to form B at 155 °C. They are insoluble in polar solvents such as water or methanol and slightly soluble in non-polar organic solvents such as toluene, dichloromethane, and chloroform. Both forms in toluene solution give the same visible spectrum, indicating that the same molecular species exists in solution. Form B, dissolved in hot toluene, gives form A on cooling. The i.r. spectra (KBr region) of both forms A and B are superimposable suggesting the same molecular unit in the solid state. The mass spectrum of sublimed form B shows the highest *m/e* ratio peak at 866, corresponding to the dimeric ion $[Pt_2(Pr^iCS_2)_4]^+$.

The synthesis of a platinum(II) phenyldithioacetate complex has been reported previously.[12] D.s.c. does not show any phase transition below the melting point at 242 °C; this value is slightly lower than that reported previously.[12] The compound is slightly soluble in toluene and crystals for *X*-ray investigations were obtained by slow cooling of hot toluene solution. The i.r. spectrum is similar to the corresponding Ni and Pd derivatives, whose crystal structures have been solved,[2] and these results are in agreement with the *X*-ray crystal structure (see below).

Description of the Crystal Structure of $[Pt_2(PhCH_2CS_2)_4]$.—Results are reported in Table 2 and Figure 1. The crystal structure consists of binuclear units stacking in columns along the two-fold *c* axis, with interdimer Pt–Pt distances of 3.238(1) Å. Each platinum in the dimer has five neighbours: four sulphur atoms, which form a square-planar arrangement, and the other platinum atom at a distance of 2.764(1) Å. Each of the two Pt atoms is displaced, towards the other, by approximately 0.05 Å from the plane made by four co-ordinating sulphur atoms; the distance between the two planes made by the sulphur atoms is 2.86 Å. This displacement is similar to that observed in the Pd analogue and suggests that Pt–Pt interaction is stronger than in the Ni analogue [Ni–Ni 2.551(3) Å], taking into account the larger covalent radius of Pt. The two PtS_4 units are rotated by *ca.* 25° from the eclipsed structure. The Pt–S distances are in the range 2.305—2.330 Å and the average Pt–Pt–S angle is 91.3°. In the ligand the C–S distances are in the range 1.64—1.72 Å, the S–C–S angle average is 128.4° and the Pt–S–C angle average is 110.0°.

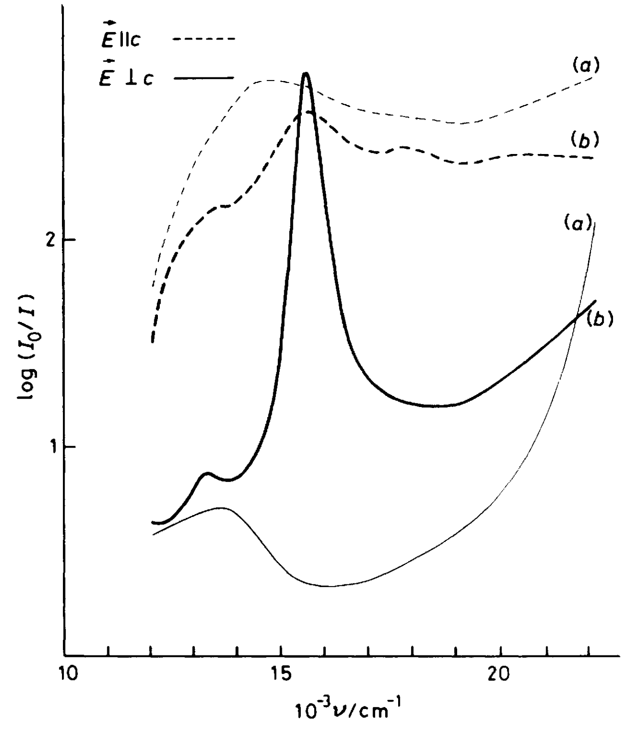


Figure 2. Polarized absorption spectra of $[Pt_2(Pr^iCS_2)_4]$, form A, at (*a*) r.t. (295 K) and (*b*) l.n.t. (77 K)

Electronic Spectra.—Due to the high lustre of these compounds, the diffuse reflectance spectra were recorded on

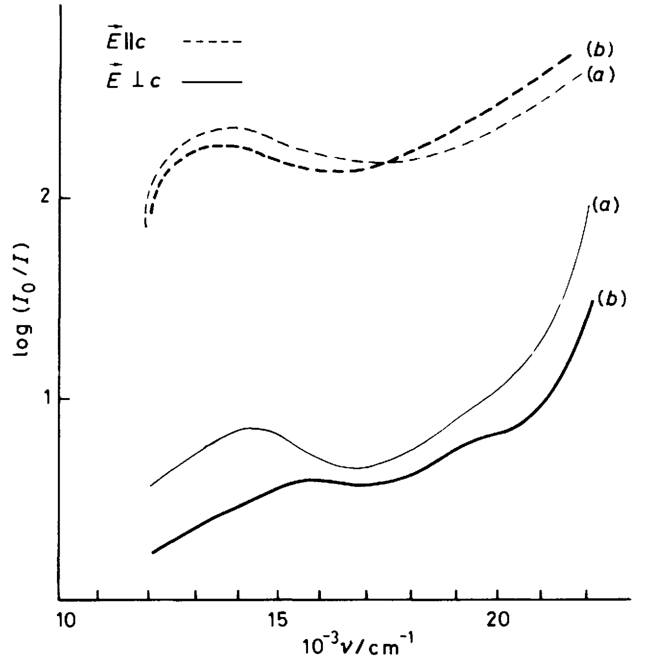


Figure 3. Polarized absorption spectra of $[Pt_2(MeCS_2)_4]$ at (*a*) r.t. (295 K) and (*b*) l.n.t. (77 K)

samples diluted in MgO. We were also able to record single-crystal absorption spectra of extremely thin crystals (10—30 μm) of $[Pt_2(Pr^iCS_2)_4]$, forms A and B, and $[Pt_2(MeCS_2)_4]$. The electronic spectral data are reported in Table 3; for completeness the solution spectra of these complexes are reported also. The first observation to be made in the single-crystal absorption spectra is that the high-intensity absorption dominates the visible region, with complete polarization of the absorption bands below 20 000 cm^{-1} (along the stacking direction).

Polarized Absorption Spectra.—$[Pt_2(Pr^iCS_2)_4]$, *form* A. Figure 2 shows the single-crystal polarized absorption spectra at r.t. and l.n.t. The spectra were recorded with the electric field vector $\vec{E}$ parallel and perpendicular to the columnar axis c ($\vec{E}\|c$ and $\vec{E}\perp c$ respectively). Whereas the $\vec{E}\perp c$ absorption is relatively weak, for $\vec{E}\|c$ polarization we can only observe the strongly increasing slope at the long-wavelength side. At l.n.t. for $\vec{E}\perp c$ a new band appears at 15 600 cm^{-1} and a small red shift of that at 13 600 cm^{-1} is observed.

$[Pt_2(MeCS_2)_4]$. The single-crystal polarized absorption spectrum is shown in Figure 3. The main feature is that, when $\vec{E}\|c$, a complete absorption between 10 000 and 20 000 cm^{-1} is observed. The $\vec{E}\perp c$ spectrum is characterized by no absorption band in this region. This behaviour is independent of the temperature down to l.n.t.

$[Pt_2(Pr^iCS_2)_4]$, *form* B. The single-crystal polarized absorption spectra at r.t. and l.n.t. are reported in Figure 4. The $\vec{E}\perp c$ absorption spectrum at r.t. is characterized by a maximum at 18 210 cm^{-1} which disappears at low temperature. Two new weak bands at 15 520 cm^{-1} and 17 050 cm^{-1} are present at l.n.t. The $\vec{E}\|c$ absorption spectrum is characterized by a strong absorption starting at 13 000 cm^{-1} with a maximum at 18 000 cm^{-1}. At l.n.t. the maximum disappears and two new bands, at the same frequency as the $\vec{E}\perp c$ spectrum at the same temperature, appear but with higher intensity.

$[Pt_2(PhCH_2CS_2)_4]$. Only the single-crystal polarized spectrum at r.t. of this complex has been recorded. A complete polarization of the absorption is observed when $\vec{E}\|c$. No absorption is observed when $\vec{E}\perp c$ is between 10 000 and 24 000 cm^{-1}.

Table 4. Comparison of geometric properties and r.t. d.c. electrical conductivity of various platinum(II) dithiocarboxylate complexes

Compound	M–M (intra)/ Å	M–M (inter)/ Å	σ/ Ω^{-1} cm^{-1}	Ref.
$[Pt_2(Pr^iCS_2)_4]$, form A	2.795(2)	3.081(2)	2 × 10^{-5}	This work, ref. 5
$[Pt_2(PhCH_2CS_2)_4]$	2.764(1)	3.238(1)	1 × 10^{-6}	This work
$[Pt_2(Pr^iCS_2)_4]$, form B	2.76(1)	3.49(1)	Insulator*	This work
$[Pt_2(MeCS_2)_4]$	2.767(1)	3.819(1)	Insulator*	Ref. 4

* $\sigma < 10^{-8}$ Ω^{-1} cm^{-1}.

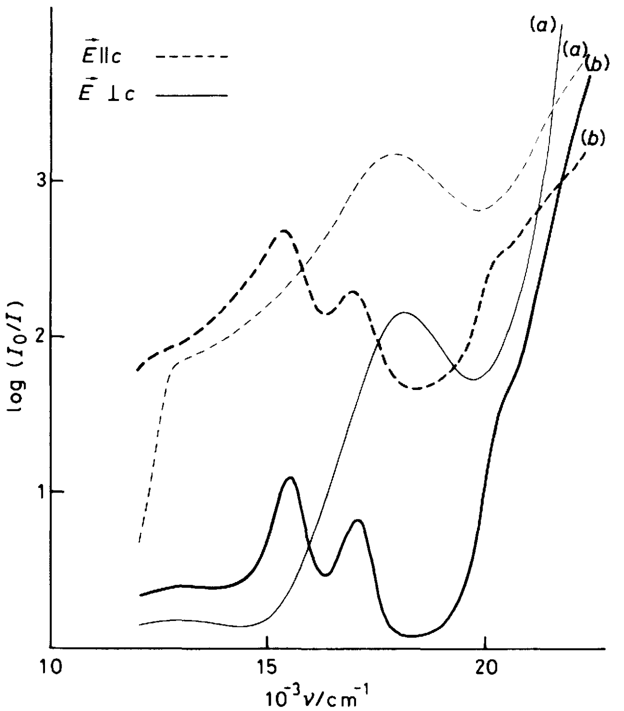
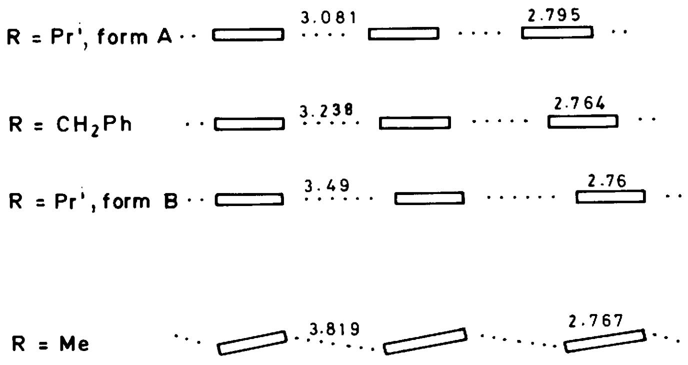


Figure 4. Polarized absorption spectra of $[Pt_2(Pr^iCS_2)_4]$, form B, at (*a*) r.t. (295 K) and (*b*) l.n.t. (77 K); thickness of the crystal 16 μm

Electrical Conductivity Measurements.—The electrical conduction properties of the compounds have been investigated on powdered pressed samples. Table 4 reports the electrical behaviour of the platinum(II) dithiocarboxylate derivatives. The only compound which does show appreciable electrical conductivity at r.t. is $[Pt_2(Pr^iCS_2)_4]$, form A ($\sigma = 2 \times 10^{-5}$ Ω^{-1} cm^{-1}). Variable-temperature measurements of electrical conductivity were carried out for two different samples and for several pellets, and thermally activated charge-transport was observed in the range 200—285 K. The apparent activation parameter E_a, found by fitting the relation $\sigma = \sigma_0 \exp(-E_a/kT)$, was 0.15 eV.

E.S.R. Measurements.—At l.n.t. the e.s.r. spectra of powdered $[Pt_2(Pr^iCS_2)_4]$, form A, and $[Pt_2(PhCH_2CS_2)_4]$ are characterized by a weak single axial signal: $g_\perp = 2.268$, $g_\| = 1.970$. The spectra are similar to that reported previously for Pt^{IV}-doped Magnus green salts $\{[Pt(NH_3)_4][PtCl_4]\}$.[17] No hyperfine interactions are observed; the signal intensity is different for each compound. No e.s.r. signal was detected for $[Pt_2(MeCS_2)_4]$.



Scheme. Linear-chain $[Pt_2(RCS_2)_4]$ complexes; distances are in Å

Discussion

The molecular geometries for the reported platinum(II) dithiocarboxylate complexes are similar. They all contain dimeric units and the Pt–Pt distances are reported in Table 4. The platinum oxidation state is +2 and this is supported by analytical results and by ESCA experiments.[6] The intra-dimer Pt–Pt distance in the series varies from 2.76 to 2.80 Å, this can be related to the hindrance of the substituent in the ligand. We have previously observed a more pronounced shortening of the Pt–Pt intra-dimer distance when a single metal–metal bond is present as in the corresponding Pt^{III}–Pt^{III} compounds.[6] There are now several examples in the literature which suggest that a short metal–metal distance does not necessarily imply a direct metal–metal bond.[18–20]

The observed geometry arises as a result of a combination of the electronic and steric effects of the ligand and, of course, of the degree of direct metal–metal bond. The Pt–Pt distance inside the dimer is shorter than the distance between the centres of the sulphur planes, but this inward displacement varies from 0.17 Å to 0.10 Å. The lower observed value may be related to a better overlap between platinum atoms of adjacent dimers as is the case with $[Pt_2(Pr^iCS_2)_4]$, form A. Except for $[Pt_2(p\text{-}Pr^iC_6H_4CS_2)_4]$,[11] all the reported tetrakis(dithiocarboxylato)diplatinum(II) compounds crystallize in a columnar structure. The most striking feature is the short interdimeric Pt–Pt distance. This distance varies from 3.081 Å in $[Pt_2(Pr^iCS_2)_4]$, form A, to 3.49 Å, estimated for form B (see Table 4). These are therefore four linear-chain compounds having different intra-chain distances *R* (see Scheme). Several single-valence platinum(II) chain compounds are known, the most investigated being the tetracyanoplatinate(II) complexes;[21,22] all are characterized by having simple, square-planar $[Pt^{II}(CN)_4]^{2-}$ units. In the present case, the building unit is represented by a dimer, the Pt_2S_8 chromophore, and the intra-chain distance *R* is modulated by the substituent in the dithiocarboxylate ligand. Further in $[Pt_2(MeCS_2)_4]$,[4] the stacking is not collinear, the dimers being inclined with respect to the [001] direction by 28°, while the other examples show a columnar structure. Also, if the substituent is the $p\text{-}Pr^iC_6H_4$ group, the corresponding Pt^{II} complex is still dimeric, but the molecular units, with two bridging and two terminal dithiolate ligands, are not stacked in the unit cell. We therefore conclude that packing forces are mainly responsible for the stacking in these compounds.

The anisotropic optical and electrical properties are related to the chain structure present. The solid-state spectra above 20 000 cm^{-1} are quite similar to the solution spectra and seem to be independent of the type of substituent, so they are single-molecule transitions.[7] From Table 3 we observe that the absorption bands below 20 000 cm^{-1} are absent in solution and completely polarized along the stacking direction. The nature of the excited states giving these intense absorptions can be rationalized on the basis of an energy band approach, based on a molecular orbital treatment.[23]

Assuming that $[Pt_2(Pr^iCS_2)_4]$, form A, has approximate D_{4h} symmetry, the highest occupied molecular orbital is the $d\sigma^*$ antibonding orbital, $1a_{2u}$, and the lowest unoccupied orbital is the $p\sigma$ bonding orbital $2a_{1g}$. Because the Pt–Pt distance between adjacent dimers is 3.08 Å, the interaction of σ^* and $p\sigma$ ($6p_z$ in origin) orbitals of adjacent molecules within the stack make possible the formation of the band system along the stack direction, the σ^* band being fully occupied. Qualitatively, the lowest energy band polarized along the chain direction at 14 800 cm^{-1} (1.83 eV) could be assigned as $\sigma^*(1a_{2u})\rightarrow p\sigma(2a_{1g})$ or π_L (L = ligand) inter-band transitions.

The r.t. electrical conductivity varies systematically with the inter-dimeric Pt–Pt distance and the observed appreciable r.t. electrical conductivity in $[Pt_2(Pr^iCS_2)_4]$, form A, can be related to the unusual short intra-chain Pt–Pt contact (3.08 Å). A previous investigation of the electrical conduction properties of the salts $M_x[Pt(CN)_4]\cdot nH_2O$ (M = cation or dication) showed that the r.t. d.c. conductivity is strongly dependent on the metal–metal distance.[24] Further, the d.c. electrical conductivity at r.t. of our compound is comparable in order of magnitude to that found in $Li_2[Pt(CN)_4]\cdot 3H_2O$, where the Pt–Pt distance is 3.18 Å and in bis(1,2-benzoquinonedioximato)diplatinum(II), where the Pt–Pt distance is 3.17 Å.[25,26] Variable-temperature conductivity measurements give an activation parameter E_a lower than the value of the lower-energy absorption band in the optical spectrum. The energy gap is too large to allow significant carrier formation by promotion of electrons across the gap. This may therefore be associated with an indirect (phonon-assisted) thermal activation process or it may be extrinsic and due to the presence of impurities, which act as acceptors for electrons promoted from the top of the σ^* valence band.

From the e.s.r. measurements the *g* values suggest the presence of Pt^{III} impurities, since similar values have been observed in several Pt-doped salts such as irradiated crystals of $K_2[PtCl_4]$[27] and also in $[Pt(CN)_4]^{2-}$ salts.[24]

Perpendicular to the stacking direction an absorption band at 13 600 cm^{-1} is observed and this can be assigned as a spin-forbidden transition to the triplet state. On lowering the temperature, two bands are observed at 13 400 and 15 600 cm^{-1}, the latter being narrow and unusually intense. Spin–orbit coupling is effective in these heavier metal complexes and therefore must be considered. These bands are also observed in the optical spectrum of $[Pt_2(Pr^iCS_2)_4]$, form B, at l.n.t., although they lie at higher energies, *i.e.* at 15 500 and 17 050 cm^{-1}, and this may be related to the longer inter-dimeric distance.[28] These absorption bands are not observed in $[Pt_2(MeCS_2)_4]$, even at l.n.t. In the latter case the canted structure does not allow a direct overlap of the appropriate Pt orbitals, therefore the neutral Frenkel exciton model would be more appropriate.[29] The band at 15 200 cm^{-1} can be ascribed to the $\sigma^* \rightarrow 6p\sigma$ or π_L transition in the dimer or to an admixture of both, which are red-shifted because of the intermolecular interactions.

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