Synthesis, *X*-Ray Crystal Structures and Spectroscopic Properties of Two Binuclear Platinum(III) Dithiocarboxylate Complexes†

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Two binuclear platinum(III) dithiocarboxylato-derivatives $[\mathrm{Pt_2(RCS_2)_4I_2}]$ [R = $\mathrm{PhCH_2}$ (**1**), $\mathrm{Me_2CH}$ (**2**)] have been synthesized and characterized. The complex (**2**) crystallizes in two forms, one of which, (**2a**), includes molecular iodine in the unit cell. The crystal structures of compounds (**1**) and (**2a**) have been determined and their main feature is that the molecular units are dimeric, with Pt–Pt distances of 2.598(2) Å for compound (**1**) and 2.578(1) Å for compound (**2a**); the Pt–I distances were 2.753(3) and 2.763 Å (mean) for compounds (**1**) and (**2a**), respectively. Both Pt–Pt distances are shorter than those found in the corresponding unoxidized starting compounds. This is in agreement with an electronic configuration $(d_\sigma)^2$. The relationship between the metal–metal distance and oxidation state is discussed.

In a previous paper[1] we described the synthesis and the physical properties of some linear-chain $\mathrm{Pt^{II}}$ derivatives of dithiocarboxylic acids. These compounds react with halogens to give complexes of general formula $[\mathrm{Pt_2(RCS_2)_4X_2}]$ (R = $\mathrm{PhCH_2}$ or $\mathrm{Me_2CH}$; X = Cl, Br, or I) and are of interest because the platinum atoms display the unusual oxidation state of +3.[2–12] In the case of the dithioacetatoplatinum derivative we isolated two compounds, one of which is a linear-chain mixed-valence semiconducting material,[2] while with the substituted ligands only platinum(III) complexes have been obtained.

Here we describe the synthesis, characterization, and *X*-ray crystal structures of tetrakis(dithiophenylacetato)di-iododiplatinum(III), $[\mathrm{Pt_2(PhCH_2CS_2)_4I_2}]$ (**1**), and tetrakis(dithioisobutanoato)di-iododiplatinum(III) di-iodine, $[\mathrm{Pt_2(Me_2CHCS_2)_4I_2}]\cdot\mathrm{I_2}$ (**2a**). Complex (**2**) also exists in a second crystalline form corresponding simply to $[\mathrm{Pt_2(Me_2CHCS_2)_4I_2}]$ (**2b**).

The relationship between the metal–metal distance and the oxidation state is discussed.

Experimental

Elemental analyses were performed by Alfred Bernhardt Mikroanalytische Laboratorium, Elbach, West Germany.

Synthesis.—Ligands. Dithioisobutanoic acid, $\mathrm{Me_2CHCS_2H}$, and dithiophenylacetic acid, $\mathrm{PhCH_2CS_2H}$, were prepared according to known procedures.[13] $\mathrm{K_2[PtCl_4]}$ was used as obtained from B.D.H. Chemicals Ltd. $[\mathrm{Pt_2(Me_2CHCS_2)_4}]$ and $[\mathrm{Pt_2(PhCH_2CS_2)_4}]$ were prepared as reported previously,[1,14] and the purity checked by elemental analyses and i.r. spectroscopy. Iodine was used as obtained commercially from Carlo Erba Ltd.

$[\mathrm{Pt_2(PhCH_2CS_2)_4I_2}]$ (**1**). Tetrakis(dithiophenylacetato)diplatinum(II) (0.370 g, 0.35 mmol) was dissolved in hot toluene (120 $\mathrm{cm^3}$) until a clear red-orange solution was obtained. Iodine (0.136 g, 1.07 mmol), dissolved in toluene (30 $\mathrm{cm^3}$) was added. On cooling, dark violet crystals separated from the resulting deep violet solution (yield *ca.*61%) (Found: C, 30.8; H, 2.40; I, 19.6; Pt, 29.8; S, 18.4. Calc. for $\mathrm{C_{32}H_{28}I_2Pt_2S_8}$: C, 29.3; H, 2.15; I, 19.35; Pt, 29.7; S, 19.55%).

$[\mathrm{Pt_2(Me_2CHCS_2)_4I_2}]$ (**2b**). This compound was synthesized following the same procedure as that described above (yield *ca.* 50%) (Found: C, 17.1; H, 2.45; I, 22.8; Pt, 34.75; S, 22.7. Calc. for $\mathrm{C_{16}H_{28}I_2Pt_2S_8}$: C, 17.15; H, 2.50; I, 22.7; Pt, 34.8; S, 22.9%).

$[\mathrm{Pt_2(Me_2CHCS_2)_4I_2}]\cdot\mathrm{I_2}$ (**2a**). This complex was obtained by slow evaporation to dryness of the deep violet solution obtained by reaction of the starting material with an excess of iodine. The compound was characterized by *X*-ray crystal structure analysis (see below).

Physical Measurements.—Routine i.r. spectra were recorded with a Perkin-Elmer 621 spectrophotometer on KBr pellets. The solution electronic spectra were recorded on a Cary 14 spectrophotometer. Diffuse-reflectance spectra were recorded with a Beckmann DK-2A spectrophotometer on MgO-diluted samples. Molecular weight measurements were carried out with an apparatus described in the literature,[15] based on a cryoscopic method. Differential scanning calorimetry (d.s.c.) and thermal gravimetric analyses (t.g.a.) were performed with a Stanton Redcroft STA-780 apparatus under $\mathrm{N_2}$ (scanning rate 5 °C $\mathrm{min^{-1}}$). *X*-Ray photoelectron spectra were recorded on a VG ESCA 3 MK II instrument at the Servizio ESCA of the Area della Ricerca di Roma, C.N.R., using Al-K_α radiation (1 486.6 eV). No loss of iodine from the compounds in the high-vacuum chamber of the spectrometer was detected. Samples were dusted on double-sided adhesive tape. Binding energies reported are relative to the C 1*s* peak (285.0 eV) from the tape used as reference. N.m.r. spectra were obtained with a Bruker WP-200 spectrometer of the Servizio NMR of the Area della Ricerca di Roma, C.N.R., operating at 4.7 T; the solvent was used for reference and field-frequency lock.

Crystal Structure Determinations.—Crystal data for $[\mathrm{Pt_2(PhCH_2CS_2)_4I_2}]$ (**1**). $\mathrm{C_{32}H_{28}I_2Pt_2S_8}$, M = 1 313.08, orthorhombic, space group *Pbcn*, a = 20.560(5), b = 17.561(4), c = 11.699(3) Å, U = 4 224 Å^3, Z = 4, D_c = 2.07 g cm^{-3}, $F(000)$ = 2 439.64, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 88.4 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°. 1 691 Unique reflections with $I > 2.5\sigma(I)$ were used for structure determination. Lorentz-polarization and semi-empirical absorption corrections, based on a 360° ψ-scan around the scattering vector of selected reflections were applied.

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† *Supplementary data available* (No. SUP 56381, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

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, for $[Pt_2(PhCH_2CS_2)_4I_2]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	−13(0)	1 586(0)	1 390(1)	C(6)	2 964(7)	−392(10)	−209(12)
I	−64(1)	1 617(1)	−961(2)	C(7)	2 416(7)	−861(10)	−222(12)
S(1)	937(3)	870(4)	1 248(5)	C(8)	1 943(7)	−787(10)	627(12)
S(2)	625(3)	477(3)	3 673(5)	C(9)	1 049(14)	2 799(13)	2 476(25)
S(3)	616(3)	2 691(3)	1 279(6)	C(10)	1 587(14)	3 360(14)	2 430(25)
S(4)	966(3)	2 301(4)	3 698(6)	C(11)	2 226(7)	3 016(9)	2 693(18)
C(1)	1 038(10)	355(13)	2 449(20)	C(12)	2 593(7)	3 177(9)	3 666(18)
C(2)	1 539(10)	−291(13)	2 457(23)	C(13)	3 213(7)	2 865(9)	3 790(18)
C(3)	2 018(7)	−244(10)	1 487(12)	C(14)	3 466(7)	2 392(9)	2 942(18)
C(4)	2 566(7)	225(10)	1 500(12)	C(15)	3 099(7)	2 231(9)	1 969(18)
C(5)	3 039(7)	151(10)	652(12)	C(16)	2 479(7)	2 543(9)	1 844(18)

Table 2. Fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses, for $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$ (**2a**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	984(1)	3 350(1)	3 286(1)	C(3), C(4) a	155(71)	2 814(50)	6 627(36)
Pt(2)	−950(1)	1 419(1)	2 076(1)	b	−1 955(62)	1 611(48)	5 467(42)
I(1)	3 050(2)	5 424(1)	4 584(1)	c	−1 401(87)	2 514(55)	5 999(45)
I(2)	−3 019(2)	−657(1)	798(1)	d	161(82)	951(38)	5 752(55)
I(3)	4 439(2)	6 653(1)	3 118(1)	e	672(54)	1 988(50)	6 450(41)
I(4)	5 615(2)	7 852(1)	2 135(1)	C(5)	−2 264(18)	3 562(13)	2 390(13)
S(1)	1 200(6)	3 043(4)	4 852(4)	C(6)	−3 330(20)	4 216(13)	2 243(15)
S(2)	−709(5)	4 266(3)	3 475(4)	C(7)	−3 325(35)	4 572(23)	1 253(24)
S(3)	928(5)	3 822(3)	1 817(3)	C(8)	−4 784(21)	3 601(17)	2 071(21)
S(4)	2 854(6)	2 603(5)	3 198(4)	C(9)	305(18)	2 632(12)	695(12)
S(5)	−1 718(6)	1 380(4)	3 451(4)	C(10)	336(21)	2 759(13)	−321(13)
S(6)	−2 678(5)	2 252(3)	1 479(4)	C(11)	−967(25)	3 112(18)	−799(16)
S(7)	−359(6)	1 321(3)	588(3)	C(12)	1 738(24)	3 561(18)	−164(18)
S(8)	621(6)	422(4)	255(4)	C(13)	2 310(23)	1 227(17)	2 916(15)
C(1)	−345(20)	2 139(14)	4 640(14)	C(14)	3 475(27)	601(22)	2 968(49)
C(2)	−517(32)	2 060(24)	5 657(18)	C(15)	3 970(29)	486(20)	2 117(22)
				C(16)	4 223(37)	682(31)	4 066(24)

* Positions of C(3), C(4) represented by a—e (each with occupancy 0.40).

The structure was solved and refined by Patterson and Fourier methods. The refinement was accomplished by a least-squares method, using anisotropic thermal parameters for non-hydrogen atoms. The carbon atoms of the phenyl rings were refined as rigid groups and the hydrogen atoms were introduced in calculated positions with $B = 4$ Å^2. The quantity minimized was $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$) with weight $w^{-1} = \sigma^2(F_o) + 0.011\,962\ F_o^2$. Final values for R ($= \Sigma|\Delta|/\Sigma|F_o|$) and R' [$= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$] were 0.0515 and 0.0630, respectively. Neutral scattering factors (f' and f'' values) were used for non-hydrogen atoms.[16] Computations were performed on a IBM 3330/168 computer using the SHELX program system and on a HP-21-MX computer with a set of programs written by Cerrini and Spagna.[17] Final positional parameters are given in Table 1.

Crystal data for $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$ (**2a**). $C_{16}H_{28}I_4Pt_2S_8$, $M = 1\,374.71$, triclinic, space group $P\bar{1}$, $a = 10.350(5)$, $b = 13.117(2)$, $c = 14.210(3)$ Å, $\alpha = 108.22(2)$, $\beta = 107.91(3)$, $\gamma = 100.77(2)$°, $U = 1\,656$ Å^3, $Z = 2$, $D_c = 2.76$ g cm^{-3}, $F(000) = 1\,240$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 131.6$ cm^{-1}.

3 729 Unique reflections with $I > 2\sigma(I)$ were used for the structure determination. Difference Fourier syntheses revealed positional disorder for the two methyl groups linked to the carbon atom C(2); five peaks correspond to different orientations of these groups. Experimental data did not permit refinement of the occupancy of the carbon atoms involved, *i.e.* C(3) and C(4), and therefore an occupancy of 0.40 was used in structure factor calculations. The final R and R' values were 0.057 and 0.056, respectively. Details of the procedure are as given above for complex (**1**). Final positional parameters are given in Table 2.

Crystal data for $[Pt_2(Me_2CHCS_2)_4I_2]$ (**2b**). $C_{16}H_{28}I_2Pt_2S_8$, $M = 1\,129.62$, monoclinic, space group $P2_1/c$, $a = 8.043(2)$, $b = 16.858(5)$, $c = 10.993(2)$ Å, $\beta = 94.97(2)$°, $U = 1\,485$ Å^3, $Z = 2$, $D_c = 2.51$ g cm^{-3}.

Results

The chemical oxidation of the tetrakis(dithiocarboxylato)-diplatinum(II) complexes with an excess of iodine yielded deep violet compounds of general formula $[Pt_2(RCS_2)_4I_2]$ (R = Me_2CH or $PhCH_2$). The platinum atoms are in the unusual oxidation state of +3. They are dimeric, single-valence compounds and have been characterized by elemental analysis, i.r. spectra, and *X*-ray crystal diffraction (see below). They are very soluble in non-polar or weakly polar organic solvents such as toluene, chloroform, or dichloromethane and solutions in these solvents are quite stable at room temperature and to the air. Molecular weight data for the dithioisobutanoato-derivative indicate that in benzene solution this complex contains only dimeric species. Differential thermal analyses, d.s.c., and t.g.a. were useful in determining the difference between the two crystalline forms of the dithioisobutanoato-derivative and unequivocally showed that molecular iodine was lost at 145 °C from crystals obtained by the slow evaporation of a solution of the compound to dryness. Both forms melt at the same temperature.

A preliminary *X*-ray investigation has been carried out on all

Table 3. Main interatomic distances (Å) and angles (°), with e.s.d.s in parentheses, for $[Pt_2(PhCH_2CS_2)_4I_2]$ (**1**)

Pt–Pt′	2.598(2)	Pt–S(3)	2.334(6)	S(3)–C(9)	1.67(3)	C(2)–C(3)	1.51(3)
Pt–I	2.753(3)	Pt′–S(4)	2.330(6)	S(4)–C(9)	1.69(3)	C(9)–C(10)	1.48(3)
Pt–S(1)	2.329(5)	S(1)–C(1)	1.68(2)	C(1)–C(2)	1.53(3)	C(10)–C(11)	1.48(3)
Pt′–S(2)	2.321(6)	S(2)–C(1)	1.68(2)				

Pt′–Pt–S(1)	93.1(2)	I–Pt–S(3)	87.1(2)	S(3)–Pt–S(4′)	90.9(2)
Pt′–Pt–S(2′)	92.5(2)	I–Pt–S(4′)	85.0(2)	Pt–S(1)–C(1)	109.5(3)
Pt′–Pt–S(3)	92.5(2)	S(1)–Pt–S(3)	88.9(2)	Pt–S(2′)–C(1′)	110.8(2)
Pt′–Pt–S(4′)	93.5(2)	S(1)–Pt–S(4′)	173.4(2)	Pt–S(3)–C(9)	110.1(3)
I–Pt–Pt′	178.5(2)	S(1)–Pt–S(2′)	90.0(3)	Pt–S(4′)–C(9′)	109.1(2)
I–Pt–S(1)	88.4(2)	S(2′)–Pt–S(3)	174.9(2)	S(1)–C(1)–S(2)	126(1)
I–Pt–S(2′)	87.9(2)	S(2′)–Pt–S(4′)	89.7(2)	S(3)–C(9)–S(4)	127(2)

Symmetry code for primed atoms $\bar{x}, y, \bar{z}$.

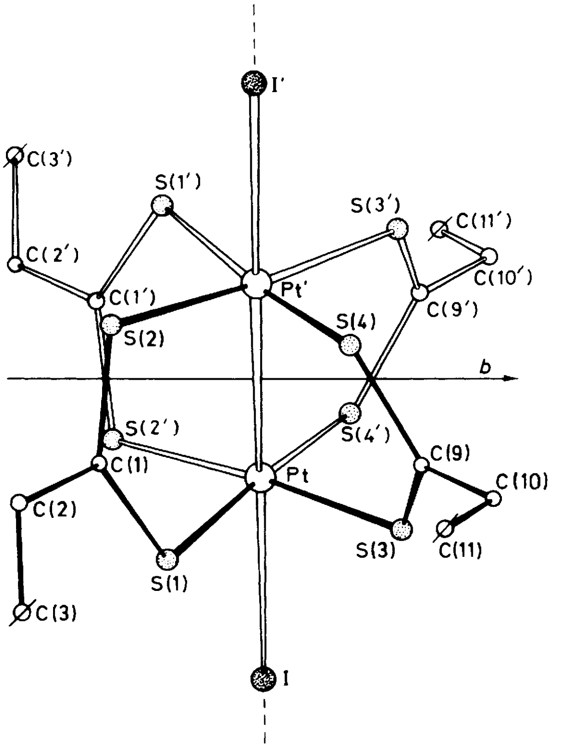

Figure 1. View of the $[Pt_2(PhCH_2CS_2)_4I_2]$ dimeric unit with the two-fold axis in the plane of the page. Only the first carbon atoms belonging to the phenyl groups are shown (with diagonal line)

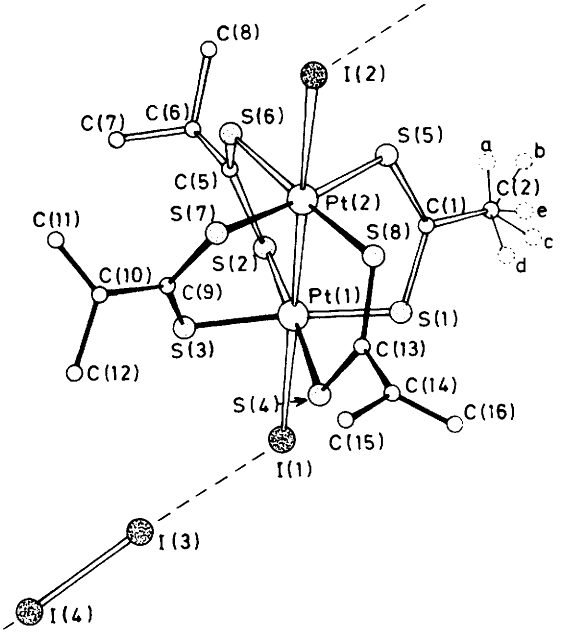

Figure 2. Perspective view of the $[Pt_2(Me_2CHCS_2)_4I_2]$ dimeric unit linked with the iodine molecule

three complexes and the unit-cell parameters are reported above. The full *X*-ray crystal structure was completed for the dithiophenylacetato derivative (**1**) and for the dithioisobutanoato-complex containing molecular iodine (**2a**), for comparison.

Crystal Structure of $[Pt_2(PhCH_2CS_2)_4I_2]$ (**1**).—Structural information for compound (**1**) is reported in Table 3 and Figure 1. The crystal structure consists of binuclear units, stacking in columns along the *c* axis, with an interdimer iodine–iodine distance of 3.611(3) Å. These dimers are formed by a two-fold axis parallel to the *b* axis and involve four bridging ligands to give a cage structure with the iodine atoms in the apical positions. In the dimer, the platinum atoms have six neighbours in a tetragonally distorted octahedral geometry, being surrounded by four sulphur atoms in a square-planar arrangement and by iodine and a further platinum atom in apical positions. Adjacent S_4 planes along the columns are essentially normal to the *c* axis, and the S_4 squares are twisted by 25° from the eclipsed structure. The Pt–Pt distance is 2.598(2) Å, 0.22 Å shorter than the separation between the S_4 planes. The I–Pt–Pt angle is close to 180°, so that the I–Pt–Pt–I sequence is linear. The mean Pt–S distance is 2.329(6) Å and the average Pt–Pt–S angle is 92.9°. The Pt–I bond length is 2.753(3) Å. In the ligand the C–S distances are in the range 1.67—1.69 Å (mean 1.68 Å), the S–C–S angles average 126°, and the average Pt–S–C angle is 109.9°.

Crystal Structure of $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$ (**2a**).—Structural information on this complex is reported in Table 4 and Figures 2—4. The crystal structure consists of binuclear molecules, $Pt_2(Me_2CHCS_2)_4I_2$, involving four bridging ligands linked by iodine molecules to give infinite zigzag chains lying in the $(2\bar{2}0)$ planes (see Figures 3 and 4). In the dimeric unit (see Figure 2) each platinum atom is six-co-ordinated in a tetragonally distorted octahedral geometry, being surrounded by four sulphur atoms in an approximately square-planar arrange-

Table 4. Main interatomic distances (Å) and angles (°), with e.s.d.s in parentheses, for $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$ (**2a**)

Pt(1)–Pt(2)	2.578(1)	Pt(2)–S(5)	2.335(5)	S(1)–C(1)	1.68(3)	S(7)–C(9)	1.67(2)
Pt(1)–I(1)	2.764(2)	Pt(2)–S(6)	2.343(5)	S(2)–C(5)	1.69(3)	S(8)–C(13)	1.69(3)
Pt(2)–I(2)	2.763(2)	Pt(2)–S(7)	2.348(5)	S(3)–C(9)	1.68(2)	C(1)–C(2)	1.54(3)
Pt(1)–S(1)	2.336(5)	Pt(2)–S(8)	2.339(6)	S(4)–C(13)	1.66(3)	C(5)–C(6)	1.52(2)
Pt(1)–S(2)	2.337(5)	I(1)–I(3)	3.476(2)	S(5)–C(1)	1.67(3)	C(9)–C(10)	1.51(2)
Pt(1)–S(3)	2.342(4)	I(2)–I(4)	3.518(2)	S(6)–C(5)	1.67(2)	C(13)–C(14)	1.57(3)
Pt(1)–S(4)	2.345(6)	I(3)–I(4)	2.759(2)				

I(1)–Pt(1)–Pt(2)	179.75(4)	I(2)–Pt(2)–S(8)	87.0(2)	Pt(2)–S(5)–C(1)	108.8(7)
I(1)–Pt(1)–S(1)	87.5(2)	S(1)–Pt(1)–S(2)	90.8(2)	Pt(2)–S(6)–C(5)	109.9(8)
I(1)–Pt(1)–S(2)	87.2(2)	S(1)–Pt(1)–S(3)	174.7(3)	Pt(2)–S(7)–C(9)	109.4(5)
I(1)–Pt(1)–S(3)	87.2(2)	S(1)–Pt(1)–S(4)	89.0(2)	Pt(2)–S(8)–C(13)	109.1(9)
I(1)–Pt(1)–S(4)	87.3(2)	S(2)–Pt(1)–S(3)	88.8(2)	S(1)–C(1)–S(5)	126.2(12)
Pt(2)–Pt(1)–S(1)	92.5(2)	S(2)–Pt(1)–S(4)	174.4(3)	S(2)–C(5)–S(6)	125.4(10)
Pt(2)–Pt(1)–S(2)	92.7(2)	S(3)–Pt(1)–S(4)	90.8(2)	S(3)–C(9)–S(7)	126.3(10)
Pt(2)–Pt(1)–S(3)	92.9(2)	S(5)–Pt(2)–S(6)	89.6(2)	S(4)–C(13)–S(8)	126.4(14)
Pt(2)–Pt(1)–S(4)	92.8(2)	S(5)–Pt(2)–S(7)	174.9(3)	S(1)–C(1)–C(2)	116.0(2)
Pt(1)–Pt(2)–I(2)	179.38(5)	S(5)–Pt(2)–S(8)	91.4(2)	S(2)–C(5)–C(6)	115.0(2)
Pt(1)–Pt(2)–S(5)	92.6(2)	S(6)–Pt(2)–S(7)	89.3(2)	S(3)–C(9)–C(10)	117.0(1)
Pt(1)–Pt(2)–S(6)	92.7(2)	S(6)–Pt(2)–S(8)	174.6(3)	S(4)–C(13)–C(14)	117.0(2)
Pt(1)–Pt(2)–S(7)	92.4(2)	S(7)–Pt(2)–S(8)	89.7(2)	S(5)–C(1)–C(2)	118.0(2)
Pt(1)–Pt(2)–S(8)	92.7(2)	Pt(1)–S(1)–C(1)	109.1(9)	S(6)–C(5)–C(6)	119.0(2)
I(2)–Pt(2)–S(5)	86.9(2)	Pt(1)–S(2)–C(5)	109.4(6)	S(7)–C(9)–C(10)	117.0(2)
I(2)–Pt(2)–S(6)	87.7(2)	Pt(1)–S(3)–C(9)	109.3(5)	S(8)–C(13)–C(14)	116.0(2)
I(2)–Pt(2)–S(7)	88.2(2)	Pt(1)–S(4)–C(13)	109.5(9)		

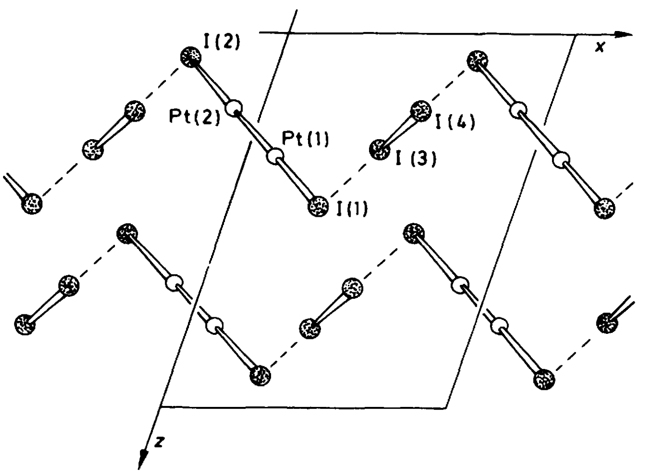

Figure 3. Two-dimensional network of iodine and platinum atoms in $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$ projected along (010)

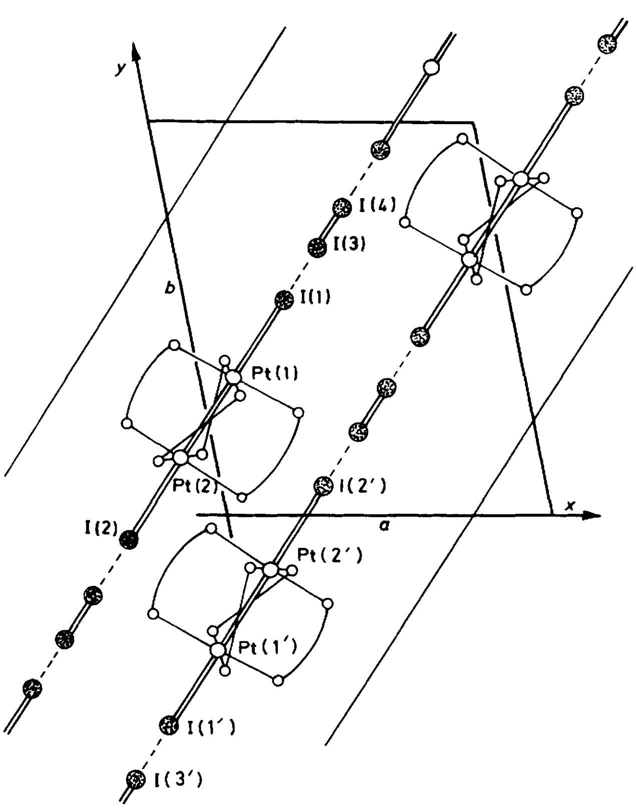

Figure 4. Two-dimensional network in $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$ lying in the $(2\bar{2}0)$ planes, projected along (001)

ment and by an iodine atom and the other platinum atom in the apical positions. The two S_4 squares are twisted by about 27° from the eclipsed structure. The Pt–Pt distance is 2.578(1) Å, about 0.22 Å shorter than the separation between the S_4 planes. The I–Pt–Pt angles are very close to 180°, so that the I(1)–Pt(1)–Pt(2)–I(2) sequence is linear. The mean Pt–S distance is 2.341(5) Å and the average Pt–Pt–S angle is 92.7°. The two Pt–I distances are not significantly different, *i.e.* 2.763(2) and 2.764(2) Å. The C–S distances in the ligand are in the range 1.66—1.69 Å (mean 1.677 Å), the S–C–S angles average 126°, and the average Pt–S–C angle is 109.3°. The I–I bond length in the molecular iodine is 2.759(2) Å; the distance between the co-ordinated iodine atom and the neighbouring iodine atoms in the iodine molecule is 3.476(2) Å for I(1) ··· I(3) and 3.518(2) Å for I(2) ··· I(4). Figures 3 and 4 show the two-dimensional network resulting from the linear chain I ··· I–I ··· I and the sequence I–Pt–Pt–I. The shortest contacts between adjacent molecules are 3.6—3.8 Å and mostly involve the five positions occupied by the disordered methyl C(3) and C(4) atoms of one of the four ligands.

X-Ray Photoelectron Spectra.—The electron binding energies of various platinum dithiocarboxylato-derivatives are reported

Table 5. Electron binding energies (eV) of various platinum dithiocarboxylato-derivatives[a]

	Pt		I		S^b	C	
Compound	$4f_{\frac{7}{2}}$	$4f_{\frac{5}{2}}$			(2*p*)	(1*s*)	Ref.
$[Pt_2(MeCS_2)_4]$	72.50 (1.8)	75.80 (1.8)					2
$[Pt_2(MeCS_2)_4I]$	73.20 (2.1)	76.50 (2.0)	619.2	630.8	163.50		2
$[Pt_2(MeCS_2)_4I_2]$	74.35 (2.0)	77.70 (2.0)	619.6	630.6	162.70		2
$[Pt_2(PhCH_2CS_2)_4]$	73.00 (1.9)	76.65 (1.9)			163.7	285.1	*c*
$[Pt_2(PhCH_2CS_2)_4I_2]$	74.60 (1.9)	78.10 (1.9)	619.10	630.9	164.1		*c*
$[Pt_2(Me_2CHCS_2)_4]$	72.90 (2.0)	76.30 (2.0)			163.2		*c*
$[Pt_2(Me_2CHCS_2)_4I_2]$	74.35 (2.1)	77.65 (2.0)	619.1	630.9	163.75		*c*

[a] Full-widths at half-maximum are given in parentheses. [b] Broad peaks. [c] This work.

in Table 5. A charging effect was observed and the values reported are corrected to the C 1*s* band (285 eV). The full-width at half-maximum, f.w.h.m. ~2 eV, is the same for all the compounds and comparable to that found for $K_2[PtCl_4]$ (used as the standard) suggesting that all the platinum atoms in the dimer are equivalent. The observed shifts (>1.5 eV) in the $4f_{\frac{7}{2},\frac{5}{2}}$ Pt binding energies of the platinum(III) complexes compared to those of platinum(II) can be related to the change of the oxidation state of the metal. A further indication that the metal has been oxidized comes from the sulphur 2*p* binding energy, which is constant throughout the series.

Electronic Spectra.—The electronic spectra of $[Pt_2(MeCS_2)_4]$ and $[Pt_2(MeCS_2)_4I_2]$ have been reported previously.[2] The oxidation by iodine introduces several changes. The most remarkable feature is the appearance of a new absorbance band at 17.7 × 10^3 cm^{-1}, see Figure 5, which has been assigned as a ligand to metal charge-transfer band.[2] The other remarkable spectral feature is the disappearance of the 'solid-state effects,' shown by $[Pt_2(RCS_2)_4]$ compounds.[1] Both oxidized complexes show the same optical spectrum in solution and in the solid state.

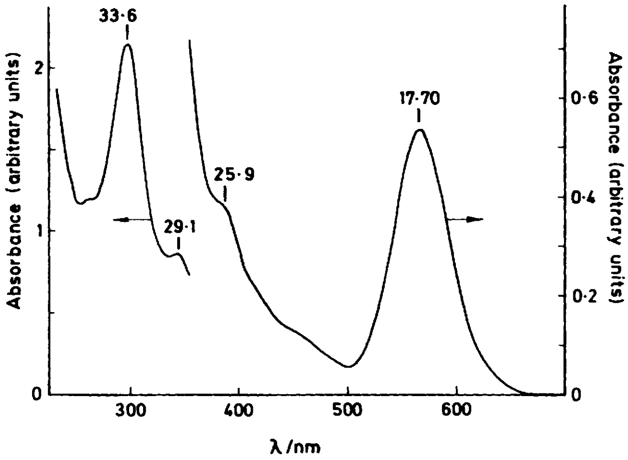

Figure 5. Solution spectrum of $[Pt_2(PhCH_2CS_2)_4I_2]$ in CH_2Cl_2 (values indicated in 10^3 cm^{-1})

N.M.R. Spectra.—The ^1H n.m.r. spectra of toluene solutions of complex (**2**) exhibit a well resolved –CH septet (δ 2.87, ^3J 6.80 Hz) and a doublet corresponding to the $-CH_3$ group (δ 1.21, ^3J 6.80 Hz), suggesting that all the four ligands are equivalent. The ^1H n.m.r. spectra of the unoxidized material, $[Pt_2(Me_2CHCS_2)_4]$ (in the same solvent), show the same behaviour except for the fact that the –CH septet and a $-CH_3$ doublet appear at different chemical shifts (δ 3.38, ^3J 6.80 Hz; δ 1.37, ^3J 6.80 Hz). In previous work[18] we showed that the starting material retains the dimeric structure in solution and therefore this is further evidence that complex (**2**) is dimeric in solution. The ^{13}C-$\{^1H\}$ n.m.r. spectra of both compounds were also recorded and they show a similar pattern except for the chemical shift, which is different. All these data confirm that the oxidized complex is dimeric in solution, as is the starting material. Finally, another interesting feature is the presence of two satellite lines from the –CH group, arising from ^{195}Pt–^{13}C coupling, in the ^{195}Pt–Pt ($I = 0$) molecules. The satellites from the ^{195}Pt–^{195}Pt molecules (which are expected to be 11% of the total) could not be detected due to the low signal:noise ratio.

Discussion

Dithiocarboxylato-bridged, metal–metal bonded, diplatinum(III) complexes, of general formula $[Pt_2(RCS_2)_4I_2]$ ($R = PhCH_2$ or Me_2CH), have been synthesized from the corresponding platinum(II) dithiocarboxylato-complexes by oxidation with an excess of iodine in toluene. The same reaction using CH_3I, instead of iodine, gave the same product. The formula $[Pt_2(RCS_2)_4I_2]$ is based on elemental analysis, molecular weight measurements, and i.r. spectra. The i.r. spectra of the starting materials and those of the oxidized ones are superimposable. The reaction, carried out with different Pt:I ratios, always gave the same compound in both cases, in contrast with the case of dithioacetato-derivatives, where a mixed-valence linear-chain complex $[Pt_2(MeCS_2)_4I]$ has been isolated.[2] Differential thermal analysis, d.s.c., and t.g.a. measurements for the dithiophenylacetato derivative show no phase transition below 300 °C. In the case of the two derivatives of dithioisobutanoate, compound (**2b**) shows no weight loss below 280 °C, in agreement with the elemental analysis. Conversely, the product obtained by evaporation of the solvent to dryness shows a weight loss of 9% at 145 °C, which does not correspond to the complete loss of molecular iodine per molecule of complex (**2a**); it therefore appears to be a mixture of

Table 6. Comparison of geometric properties of various platinum dithiocarboxylato-derivatives

Compound[a]	M–M (Å)	M–S (Å)	Pt–I (Å)	Metal oxidation state	Ref.
$[Pt_2(Me_2CHCS_2)_4]$ (form **A**)	2.795(2)	2.306(6)		II	1
$[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$	2.578(1)	2.34	2.763	III	*b*
$[Pt_2(PhCH_2CS_2)_4]$	2.761(2)	2.316(5)		II	1
$[Pt_2(PhCH_2CS_2)_4I_2]$	2.598(2)	2.329(6)	2.753(3)	III	*b*
$[Pt_2(MeCS_2)_4]$	2.767(1)	2.317(4)		II	18
$[Pt_2(MeCS_2)_4I]$	2.667(2)	2.324(6)	2.981	II–III	2
$[Mo_2(MeCS_2)_4]\cdot 2thf$	2.141(2)	2.468(5)		II–II	25
$[Mo_2(PhCS_2)_4]\cdot 2thf$	2.139(2)	2.456(5)		II–II	25

[a] thf = Tetrahydrofuran. [b] This work.

the two compounds (**2a**) and (**2b**). At 305 °C both materials melt with decomposition. The molecular structures of the compounds (**1**) and (**2a**) have very similar geometry, bond angles, and bond distances (see Results section). The only small but significant difference concerns the intramolecular Pt–Pt distance: 2.598(2) Å in compound (**1**) and 2.578(1) Å in compound (**2a**). The shorter Pt–Pt found in compound (**2a**) might be due to the polarization effects arising from the zigzag chain structure, which induces a greater positive charge on the Pt atoms. A similar interdimer interaction system due to I_2 molecules as shown in compound (**2**) has been observed previously in a few examples only.[19]

The I–I bond length is longer in compound (**2a**) [2.759(2) Å] than that found in crystalline iodine [2.715(6) Å].[20] The Pt–I distances, 2.753(3) Å for compound (**1**) and 2.764(2) Å for (**2a**), are almost the same and are longer than those found in Pt^{IV} complexes[21] and shorter than that found in the mixed-valence Pt dithioacetato derivative $[Pt_2(MeCS)_4I]$ [2.981(3) Å];[2] this is in agreement with the oxidation state of the metal.

The intradimer Pt–Pt distances in compounds (**1**) and (**2a**) are 0.2 Å shorter than those in the corresponding unoxidized derivatives; this behaviour has been observed in other Pt^{III} complexes.[2–12] All three compounds are diamagnetic and the formation of a single metal–metal bond stabilizes the dimer. A simple theory[7] predicts that two d_{σ^*} electrons are transferred to the halogen donor atoms moving from the Pt^{II}–Pt^{II} $[(d_\sigma)^2(d_{\sigma^*})^2]$ configuration to the Pt^{III}–Pt^{III} $[(d_\sigma)^2]$ configuration; consequently the Pt–Pt bond distance is shortened. To reinforce this view, only one example of a mononuclear Pt^{III} complex has been isolated and characterized to date: $[NBu_4][Pt(C_6Cl_5)_4]$[22] (the steric constraints of the ligands may in this case be responsible for the absence of dimerization). A general systematic variation of the bond distances with oxidation number has not been found in this class of compounds because it depends on several parameters, the most important being (*i*) the type of ligand, (*ii*) the ionic radius of the metal ion, and (*iii*) the axial ligand involved. In our case two of these conditions remain constant; in Table 6 is reported a series of dithiocarboxylato-complexes, having the same cage structure, with different metal ion but comparable ionic radii.

Some years ago, Pauling[23] showed that the expression (1),

$$D_{n'} = D_1 - a'\log n' \qquad (1)$$

where n' is defined as the bond order ($n' > 0$), predicts metal–metal distances $D_{n'}$ for a wide range of metals and alloys. Quite recently this relationship has been applied to one-dimensional platinum metal complexes.[24] In our case, the equation predicts the metal–metal distance in the Mo derivatives[25] quite well but it is unable to reproduce the value found in the mixed-valence Pt dithiocarboxylate.[2] A possible explanation resides in the choice of the a' coefficient which (of course) must be different for infinite chains compared to isolated molecules or clusters. The significantly longer Pt–S distance observed in the oxidized compound should be related to the stronger Pt–Pt bond inside the dimer.

If the comparison is made with the unoxidized Pt^{II} compounds (see Table 6) a simple linear relationship can be found if the intradimer Pt–Pt distance is plotted *versus* the oxidation state. Finally, the complexes retain the dimeric molecular structure in solution and this is confirmed by molecular weight measurements, n.m.r. and electronic spectra providing further evidence of the stability of Pt^{III} dimers.

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References

1 C. Bellitto, G. Dessy, V. Fares, and A. Flamini, *J. Chem. Soc., Chem. Commun.*, 1981, 409; C. Bellitto, M. Bonamico, G. Dessy, V. Fares, and A. Flamini, unpublished work.

2 C. Bellitto, A. Flamini, L. Gastaldi, and L. Scaramuzza, *Inorg. Chem.*, 1983, **22**, 444.

3 G. S. Muraveiskaya, G. A. Kukina, V. S. Orlova, O. N. Evstrafeva, and M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, 1976, **226**, 76.

4 F. A. Cotton, L. R. Falvello, and S. Han, *Inorg. Chem.*, 1982, **21**, 1709.

5 F. A. Cotton, L. R. Falvello, and S. Han, *Inorg. Chem.*, 1982, **21**, 2889.

6 H. L. Conder, F. A. Cotton, L. R. Falvello, S. Han, and R. A. Walton, *Inorg. Chem.*, 1983, **22**, 1887.

7 Che Chi-Ming, W. P. Schaefer, H. B. Gray, M. K. Dickson, P. B. Stein, and P. M. Roundhill, *J. Am. Chem. Soc.*, 1982, **104**, 4253.

8 Che Chi-Ming, F. H. Herbstein, W. P. Schaefer, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 4604.

9 J. D. Schagen, A. R. Overback, and H. Schenk, *Inorg. Chem.*, 1978, **17**, 1938.

10 L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 6761.

11 L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, 1982, **21**, 2116.

12 L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 2605.

13 (*a*) J. Houben and H. Pohl, *Chem. Ber.*, 1907, **40**, 1907; J. M. Beiner and A. Thuillier, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1972, **274**, 642.

14 C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586.

15 D. F. Shriver, 'The Manipulation of Air-sensitive Compounds,' McGraw-Hill, New York, 1969, p. 159.

16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

17 G. M. Sheldrick, SHELX Program System, University Chemical Laboratory, Cambridge, 1976; S. Cerrini and R. Spagna, abstracts of 4th European Crystallographic Meeting, Oxford, 1977, p. 7.

18 C. Bellitto, A. Flamini, O. Piovesana, and P. F. Zanazzi, *Inorg. Chem.*, 1980, **19**, 3632.

19 M. Ferrari Belicchi, G. Gasparri Fava, and C. Pelizzi, *Acta Crystallogr., Sect. B*, 1981, **37**, 924 and refs. therein.

20 F. Van Bolhuis, P. B. Koster, and T. Migchelse, *Acta Crystallogr.*, 1967, **23**, 90.

21 V. B. Freckmann and K. F. Tebbe, *Acta Crystallogr., Sect. B*, 1981, **37**, 1520.

22 R. Uson, J. Fornier, M. Tomas, B. Menjon, K. Smikel, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 1984, 751.

23 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, pp. 239—256.

24 A. H. Reis, jun., and S. W. Peterson, *Inorg. Chem.*, 1976, **15**, 3186; J. M. Williams, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 651.

25 F. A. Cotton, P. E. Fauwick, R. H. Niswander, and J. W. Setukoski, *Acta Chem. Scand., Ser. A*, 1978, **32**, 663.

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