Two Polymorphic Forms of the Tetrakis(dithioisobutanoato)diplatinum(II) Complex: *X*-Ray Crystal Structure and Spectroscopic Evidence of Intermolecular Interactions in the Solid State

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Summary Two polymorphic forms (A and B) of $Pt_2(Me_2CHCS_2)_4$ have been isolated and preliminary optical data and the *X*-ray crystal structure of the A form are reported; the low-energy absorption band, in the solid state, present in both forms and in tetrakis(dithioacetato)-diplatinum(II), can be explained as neutral Frenkel excitons, propagating along the stacks of dimers.

During the past decade there has been considerable interest in the electronic properties of metal-chain compounds, and in particular in the so-called 'mixed-valence' platinum compounds, because they are highly conducting materials.[1] However, several square-planar complexes of platinum(II), having the d^8 configuration, are of interest because they form stacks with an intermolecular distance short enough to produce 'unusual' optical properties in the solid state.[2] Recently, we synthesised tetrakis(dithioacetato)diplatinum(II),[3] which exists as deep purple needles with a metallic lustre, and is strongly dichroic in plane-polarized light. The most striking feature of this compound is its diffuse reflectance spectrum, which shows a low-energy band below 18000 cm^{-1}, absent in solution. The crystal structure of this complex consists of canted binuclear units stacked along the *c* axis of the unit cell.[3]

With the aim of clarifying the relationship between the structure and the low-energy band present in the solid state, we have extended the work to the synthesis of new complexes of platinum(II) with dithioisobutanoic acid. The A form was isolated following reaction of K_2PtCl_4 with the free acid in refluxing toluene, under an inert atmosphere, for 3 days. On cooling, the solution gave deep purple needle-like crystals. As for the dithioacetatoplatinum(II) complex, the crystals are strongly dichroic in plane-polarized light. In an attempt to grow single crystals suitable for optical measurements, by evaporation of a toluene solution to dryness, we isolated green crystals (form B) having the same composition ML_2 (L = dithioisobutanoato) as form A. Dissolution of form B in toluene gives the same solute species as does form A. Thus, on cooling (0 °C), a toluene solution of form B gives crystals of form A; further, form B can be obtained by heating form A at 155 °C. A differential scanning calorimetry trace of the purple A form shows an exothermic transition to the B form at 155 °C.

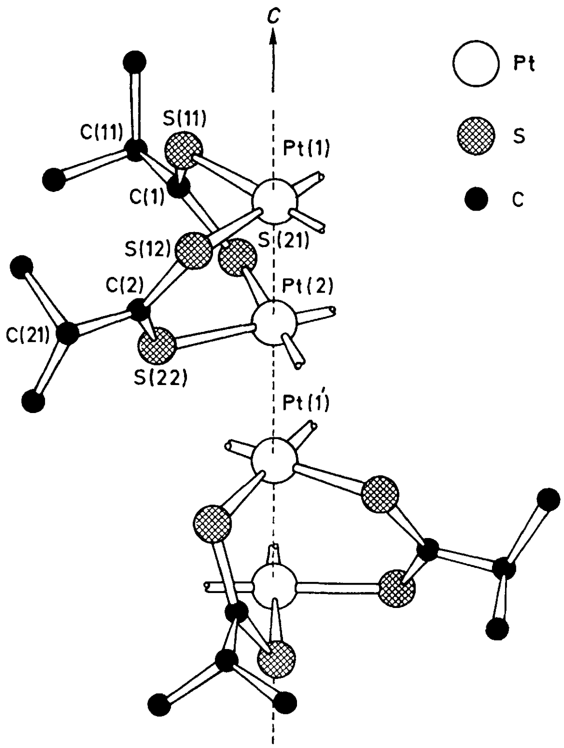

FIGURE 1. A view of a part of crystal structure of the A form of $Pt_2[Me_2CHCS_2]_4$, showing two adjacent dimeric units. Bond lengths (Å): Pt(1)–Pt(2) 2·795(2), Pt(2)–Pt(1′) 3·081(2), Pt(1)–S(11) 2·306(6), Pt(1)–S(12) 2·326(7), Pt(2)–S(21) 2·311(8), Pt(2)–S(22) 2·305(9), S(11)–C(1) 1·700(3), S(12)–C(2) 1·680(3), S(21)–C(1) 1·700(3), S(22)–C(2) 1·740(3), C(1)–C(11) 1·55(4), and C(2)–C(21) 1·54(4).

Crystal data: $C_{16}H_{28}Pt_2S_8$ (form A), orthorhombic, space group *Pccn*, $a = 9{\cdot}947(4)$, $b = 22{\cdot}379(9)$, $c = 11{\cdot}752(2)$ Å, $Z = 4$, $U = 2616$ Å^3. The structure was refined to $R = 0{\cdot}06$ for 1190 significant reflections [$I \geqslant 3\sigma(I)$], collected on a Syntex $P2_1$ automated diffractometer, by the θ–2θ scan technique, with Cu-K_α radiation.† The platinum atoms lie on two-fold axes (*c* direction) in a columnar arrangement. As shown in Figure 1, dimeric units are formed between two adjacent independent atoms in a bridged cage structure. Two different short Pt–Pt distances are present along the two-fold axis: Pt(1)–Pt(2), in the dimer, is 2·795 Å, while Pt(2)–Pt(1′) between adjacent dimers is 3·081 Å. Each platinum atom is surrounded by pairs of sulphur atoms in a square-planar arrangement, at an average Pt–S distance of 2·31 Å. The two $[PtS_4]$ units are rotated by *ca.* 45° from the eclipsed structure. The green form B crystallises in the tetragonal space group *I*4/*m* and contains linear chains of dimers with interdimer and intradimer Pt–Pt distances of 3·40 and 2·85 Å, respectively. The full structural elucidation is in progress.

The crystals of both forms are strongly dichroic when viewed under a polarizing microscope and appear to have the low-energy bands polarized along the chain axis. The diffuse reflectance spectra of both forms of the tetrakis-(dithioisobutanoato)diplatinum complexes and the tetrakis-(dithioacetato)diplatinum(II), all diluted in MgO, are shown in Figure 2. All three compounds contain stacked columnar dimers, with four bridging ligands, at very short interdimeric distances. This is analogous to the tetracyanoplatinate(II) salts,[4] where $Pt(CN)_4{}^{2-}$ units are stacked at very short distances (3·10—3·70 Å). In this series it has been found that the lowest energy bands are neutral Frenkel excitons propagating along the stacks, arising either from a ligand-field $5d_{z^2} \rightarrow 6p_z$ or a metal-to-ligand charge-transfer transition $5d_{z^2} \rightarrow \pi_L^*$.[5]

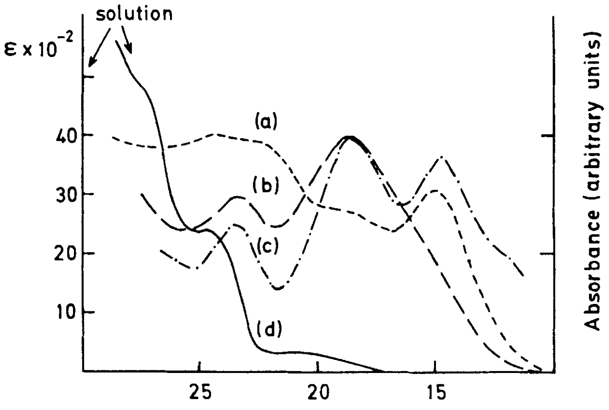

FIGURE 2. Diffuse reflectance spectra of $Pt_2(MeCS_2)_4$ (a), $Pt_2[Me_2CHCS_2]_4$ B form (b), $Pt_2[Me_2CHCS_2]_4$, A form (c), and spectra of a toluene solution of $Pt_2[Me_2CHCS_2]_4$ (d).

The most remarkable difference between our compounds and the tetracyanoplatinate(II) salts is that our compounds are dimers instead of monomers; nevertheless they seem to have the same optical behaviour, below 18000 cm^{-1}, in the solid state. In fact, in this region, we note absorption bands which are absent in solution, probably arising from intermolecular interactions between dimers. A schematic representation of the three linear chains present in our compounds, together with the distance R_C between the centres of adjacent dimers, is given in Figure 3. The

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

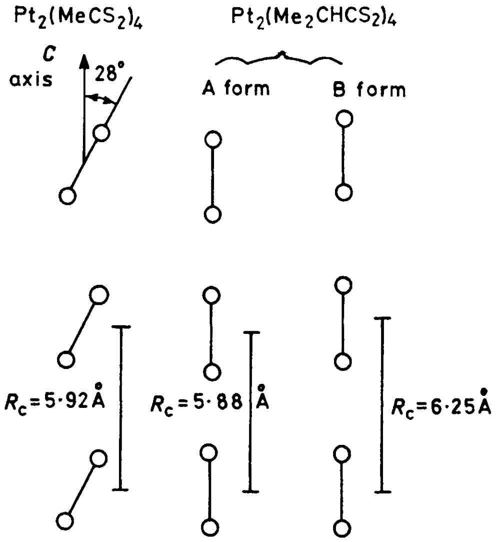

FIGURE 3. Schematic representation of the three linear chains of dimers. R_c = distance between centres of adjacent dimers.

parameter R_c has similar values in the dithioacetatoplatinum compound and in the A form of the title platinum complex, whereas it is longer in the B form. From the above considerations we tentatively ascribe the 14800 cm^{-1} band of the A form, and that at 15200 cm^{-1} for the dithioacetatoplatinum complex, to $5d_{z^2} \rightarrow 6p_z$ (or to π_L^*) transitions in the dimer, or more likely to an admixture of both, which are red-shifted because of the intermolecular interactions, occurring *via* a neutral Frenkel exciton mechanism. Owing to the higher value of R_c, and, probably, to the higher site symmetry in the green form, this band is less intense and should fall at higher energy. The reflectance spectrum indeed shows an ill-defined shoulder above 15000 cm^{-1}, difficult to localize exactly because it is obscured by the intense band at 18000 cm^{-1}. The shoulder at 12000 cm^{-1} in the A form is possibly a spin-forbidden transition to a triplet state. Further work is in progress to verify this assignment, and will be reported later.

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[1] See for example: 'Chemistry and Physics of 1D Metals,' ed. H. J. Keller, NATO Adv. Study Inst., B **25**, Plenum Press, New York, 1977; J. S. Miller, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 25.

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