

Dimer Formation in the Crystal Structure of (Dithiobenzoato)-(trithioperoxybenzoato)platinum(II)†

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(Dithiobenzoato)(trithioperoxybenzoato)platinum(II) was obtained through reactions of $[\text{Pt}_2(\text{S}_2\text{CEt})_4]$ and $\text{PhC}(\text{O})\text{SH}$ and of $\text{K}_2[\text{PtCl}_4]$, $\text{CF}_3\text{SO}_3\text{Ag}$ and $\text{PhC}(\text{O})\text{SH}$. It crystallizes in the monoclinic space group $C2/c$ with $a = 16.629(2)$, $b = 6.296(1)$, $c = 29.182(2)$ Å, $\beta = 91.85(1)^\circ$, and $Z = 8$. The complex has four- and five-membered chelate rings with a normal square-planar PtS_4 arrangement. The structure consists of dimers with a configuration in which the five-membered chelate ring of one molecule lies over the four-membered ring of the other. An extended-Hückel molecular orbital calculation suggests intradimer charge-transfer interaction as the driving force for the formation of the dimer. The diffuse reflectance spectrum of a powder sample of the complex gives new bands which are absent from the solution spectra.

Dithiocarboxylic acids produce dinuclear complexes upon reaction with nickel(II), palladium(II) or platinum(II) halides.¹⁻⁷ The reaction between acetic acid and platinum(II) halide together with a silver salt gave a tetraplatinum complex, $[\text{Pt}_4(\text{O}_2\text{CMe})_8]$.⁸ Various forms of $[\{\text{Pt}(\text{SOCPh})_2\}_n]$ have been reported to be obtained upon reaction of $\text{Na}_2[\text{PtCl}_4]$ and $\text{Na}[\text{SOCPh}]$.⁹ However, to our knowledge, no structural study of platinum(II) cluster complexes with monothiocarboxylate ligands has been reported, and hence we tried to prepare multinuclear platinum(II) complexes with this type of ligand.

In a trial using $\text{PhC}(\text{O})\text{SH}$ we obtained $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$ unexpectedly. This report describes the formation, crystal structure and characterization of this complex. The crystal structure differs from those of $[\text{Ni}(\text{S}_2\text{CC}_6\text{H}_4\text{Pr}^i\text{-}p)(\text{S}_3\text{CC}_6\text{H}_4\text{Pr}^i\text{-}p)]$ ¹⁰ and $[\text{Pt}(\text{S}_2\text{CBu}^t)(\text{S}_3\text{CBu}^t)]$ ¹¹ in that it is comprised of the dimer.

Experimental

Microanalyses were by the Microanalytical Center of Kyoto University. A Shimadzu MPS-2000 spectrophotometer was used to record both solution electronic and diffuse reflectance spectra of powder samples. The salt $\text{K}_2[\text{PtCl}_4]$ (Wako), $\text{PhC}(\text{O})\text{SH}$ and $\text{CF}_3\text{SO}_3\text{Ag}$ (Nacalai) were used without further purification. Toluene, hexane, diethyl ether and dichloromethane (Nacalai) were distilled from calcium hydride. The complex $[\text{Pt}_2(\text{S}_2\text{CEt})_4]$ was prepared similarly to $[\text{Pt}_2(\text{S}_2\text{CMe})_4]$ as described by Bellitto *et al.*⁴

(Dithiobenzoato)(trithioperoxybenzoato)platinum(II).—

Method A. The complex $[\text{Pt}_2(\text{S}_2\text{CEt})_4]$ (311 mg, 0.384 mmol) and $\text{PhC}(\text{O})\text{SH}$ (6.7 cm³, 7.8 g, 56 mmol) were refluxed in toluene (100 cm³) under an argon atmosphere for 52 h. After filtration of the mixture, the filtrate was evaporated to give a dark red oil. The oil was dissolved in hexane (50 cm³) and cooled in a freezer overnight, whereupon white and dark red solids were precipitated. The precipitate was filtered off and

washed three times with diethyl ether (15 cm³ each) to remove the white solid. The residual dark red solid was recrystallized from dichloromethane to give $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$ (yield 21.7 mg, 5.3%) (Found: C, 31.20; H, 1.85; S, 29.85. $\text{C}_{14}\text{H}_{10}\text{PtS}_5$ requires C, 31.50; H, 1.90; S, 30.05%), m.p. (in evacuated tube) 193–194 °C.

Method B. Finely pulverized $\text{K}_2[\text{PtCl}_4]$ (525 mg, 1.26 mmol) and $\text{PhC}(\text{O})\text{SH}$ (14.5 g, 105 mmol) were mixed in toluene (50 cm³) under an argon atmosphere. When $\text{CF}_3\text{SO}_3\text{Ag}$ (1.62 g, 6.30 mmol) was added to the mixture the colour immediately turned black. The mixture was refluxed for 3 h and filtered. The filtrate was evaporated to dryness, yielding dark red crystals together with a black oil. Both the crystals and the oil were dissolved in dichloromethane (90 cm³). After filtration, the filtrate was charged on a 32 × 300 mm column packed with Merck silica gel 60, and eluted with dichloromethane–hexane (1:1, v/v). The first red band was collected to give a red powder after evaporation of the eluate. The red powder was recrystallized from dichloromethane to give $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$ (yield 0.108 g, 16%) (Found: C, 31.50; H, 1.95; S, 29.90%), m.p. (in evacuated tube) 191–193 °C. The crystal for X-ray analysis was obtained by slow evaporation of a solution of the complex in hexane–dichloromethane.

Crystal Structure Determination of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$.—

Crystal data. $\text{C}_{14}\text{H}_{10}\text{PtS}_5$, $M = 533.64$, monoclinic, space group $C2/c$ (see below), $a = 16.629(2)$, $b = 6.296(1)$, $c = 29.182(2)$ Å, $\beta = 91.85(1)^\circ$, $U = 3053.7$ Å³ (least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), $Z = 8$, $D_c = 2.32$ g cm⁻³. Dark red tablets, crystal dimensions 0.13 × 0.14 × 0.18 mm; $\mu(\text{Mo-K}\alpha) = 99.28$ cm⁻¹, $F(000) = 2016.0$.

Data collection and processing. Enraf-Nonius CAD-4 diffractometer, room temperature, ω - 2θ scan mode with ω scan width = $0.8 + 0.35\tan\theta$ and ω scan speed 0.87–4.12° min⁻¹, graphite-monochromated Mo-K α radiation. 3972 Reflections were measured in the range 2θ 2–60°; $\pm h$, $+k$, $+l$. All reflections were corrected for Lorentz and polarization effects and empirical absorption corrections based on the ψ -scanning method (transmission 99.8–81.1%) were applied,¹² but not for extinction. 1369 Unique reflections with $F_o > 3\sigma(F_o)$ were used for the structure determination.

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

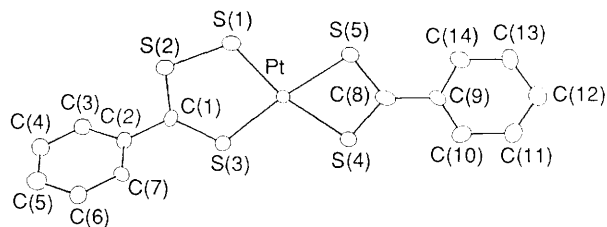
Non-SI unit employed: eV $\approx 1.60 \times 10^{-19}$ J.

Table 1 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Pt	8 383(1)	1 843(1)	340(1)
S(1)	8 415(3)	5 037(9)	687(2)
S(2)	7 803(3)	4 705(9)	1 271(2)
S(3)	7 628(3)	341(8)	884(2)
S(4)	8 547(3)	-1 109(8)	-125(2)
S(5)	9 215(3)	2 901(9)	-240(2)
C(1)	7 467(12)	2 183(25)	1 280(6)
C(2)	7 023(11)	1 672(32)	1 708(6)
C(3)	6 484(13)	3 158(35)	1 898(7)
C(4)	6 143(18)	2 684(40)	2 295(11)
C(5)	6 244(13)	736(41)	2 515(9)
C(6)	6 762(13)	-717(39)	2 324(8)
C(7)	7 175(12)	-310(36)	1 897(7)
C(8)	9 147(9)	405(29)	-449(7)
C(9)	9 565(13)	-302(34)	-875(7)
C(10)	9 406(13)	-2 261(30)	-1 053(7)
C(11)	9 801(11)	-2 899(35)	-1 421(8)
C(12)	10 310(12)	-1 575(39)	-1 644(7)
C(13)	10 466(11)	503(36)	-1 459(7)
C(14)	10 084(14)	1 078(34)	-1 088(7)

Table 2 Interatomic distances (Å) and interbond angles ($^\circ$) with e.s.d.s in parentheses

Pt-S(1)	2.251(6)	Pt-S(3)	2.263(6)
Pt-S(4)	2.322(5)	Pt-S(5)	2.318(6)
S(1)-S(2)	2.024(8)	S(2)-C(1)	1.684(17)
S(3)-C(1)	1.665(18)	S(4)-C(8)	1.691(19)
S(5)-C(8)	1.688(19)		
S(1)-Pt-S(3)	93.6(2)	S(1)-Pt-S(4)	167.4(2)
S(1)-Pt-S(5)	93.8(2)	S(3)-Pt-S(4)	98.8(2)
S(3)-Pt-S(5)	172.0(2)	S(4)-Pt-S(5)	73.7(2)
Pt-S(1)-S(2)	106.3(3)	S(1)-S(2)-C(1)	106.7(7)
Pt-S(3)-C(1)	107.5(7)	Pt-S(4)-C(8)	87.6(7)
Pt-S(5)-C(8)	87.8(7)	S(2)-C(1)-S(3)	125.8(11)
S(2)-C(1)-C(2)	112.7(13)	S(3)-C(1)-C(2)	121.4(13)
S(4)-C(8)-S(5)	110.9(11)	S(4)-C(8)-C(9)	126.1(14)
S(5)-C(8)-C(9)	123.0(14)		
Selected intradimer non-bonded distances			
Pt...Pt'	3.587(1)	S(1)...S(4')	3.667(7)
S(3)...S(5')	3.712(7)	S(2)...C(8')	3.971(18)
C(1)...C(8')	3.869(25)		

**Fig. 1** Molecular structure (30% probability ellipsoids) and atom-labelling scheme for $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$

Structure analysis and refinement. Systematic absences revealed two possible space groups, $C2/c$ and Cc . Structure analyses were performed on the basis of each group using atom scattering factors (f' and f'' values) taken from ref. 13. The direct method followed by normal heavy-atom procedures revealed the approximate structure. The refinement was accomplished by the block-diagonal least-squares method, using anisotropic thermal parameters for non-hydrogen atoms. At this stage an abnormal molecular geometry and abnormal thermal parameters for some light atoms were obtained from the analysis based on space group Cc . We concluded that the crystal belongs to the space group $C2/c$. The final refinement

was performed by using the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions (C-H 1.00 Å) but not refined. The final R values are $R = 0.062$ and $R' = 0.048$. The weighting scheme $w = 1/\sigma^2$ with σ from counting statistics was employed. The residual density in the final Fourier difference map was $0.5 \text{ e } \text{Å}^{-3}$. All calculations were performed on a FACOM M760/6 computer at the Data Processing Center of Gifu University by using the program system KPPXRAY.¹⁴ Final fractional atomic coordinates of the non-hydrogen atoms are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

EHMO Calculations.—Extended-Hückel molecular orbital (EHMO) calculations^{15,16} were performed by using the program coded by Kobayashi and distributed through Shokubai-gakkai.¹⁷ The atomic orbital parameters are the same as those adopted by Hoffmann and co-workers^{18,19} for calculations of platinum complexes with sulphur-containing ligands. The calculations were performed for the geometry obtained from the X-ray diffraction study.

Results

(Dithiobenzoato)(trithioperoxybenzoato)platinum(II) was obtained from reactions of $[\text{Pt}_2(\text{S}_2\text{CET})_4]$ and an excess of $\text{PhC}(\text{O})\text{SH}$ and of $\text{K}_2[\text{PtCl}_4]$, $\text{CF}_3\text{SO}_3\text{Ag}$ and an excess of $\text{PhC}(\text{O})\text{SH}$, both in refluxing toluene. Since monothiobenzoic acid gives dithiobenzoic acid and elemental sulphur at higher temperatures ($> ca. 50^\circ\text{C}$), albeit in low yield,²⁰ these degradation products would be the source of the trithioperoxybenzoate and dithiobenzoate ligands of the final product.

Structure of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$.—Fig. 1 presents the structure of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$. Selected bond lengths and the valence angles of the complex are shown in Table 2. The platinum atom is surrounded by four sulphur atoms in an approximately square-planar arrangement. The trithioperoxybenzoate and the dithiobenzoate ligands form five- and four-membered chelate rings, respectively. The Pt-S(1) and Pt-S(3) distances in the five-membered ring are 2.251(6) and 2.263(6) Å, respectively. The Pt-S(4) and Pt-S(5) distances in the four-membered ring are 2.322(5) and 2.318(6) Å, respectively, *ca.* 0.06 Å longer than the former distances. The S(1)-Pt-S(3) angle is $93.6(2)^\circ$ and S(4)-Pt-S(5) is $73.7(2)^\circ$.

The packing of this complex in the unit cell is given in Fig. 2. The crystal consists of dimers of the complex. The structure of the dimer is shown in Fig. 3. There exists a crystallographic inversion centre at the midpoint of the two platinum atoms of the dimer, and both of the PtS_4 planes in the dimer are parallel to each other. The five-membered ring of the molecule is located over the four-membered ring of the other molecule. The intradimer distance of the best planes of the four co-ordinating sulphur atoms around each of the platinum atoms is 3.67(2) Å. The intradimer Pt...Pt' distance is 3.587(1) Å. Each of the platinum atoms is shifted 0.04 Å inward from the best plane of the four co-ordinating sulphur atoms to the centre of the dimer. Some nearest intradimer distances are given in Table 2.

Electronic Spectra.—Fig. 4 shows the electronic absorption spectrum of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$ in CH_2Cl_2 and the diffuse reflectance spectrum of the powdered complex diluted with MgO powder. The absorption peak maxima (and their molar absorption coefficients) in CH_2Cl_2 solution were 257 (3.35×10^4), 317 (2.88×10^4) and 475 nm ($1.69 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The diffuse reflectance spectrum shows broad bands at 256, 336, 418, 504, 618(sh) and 672(sh) nm. The last four of

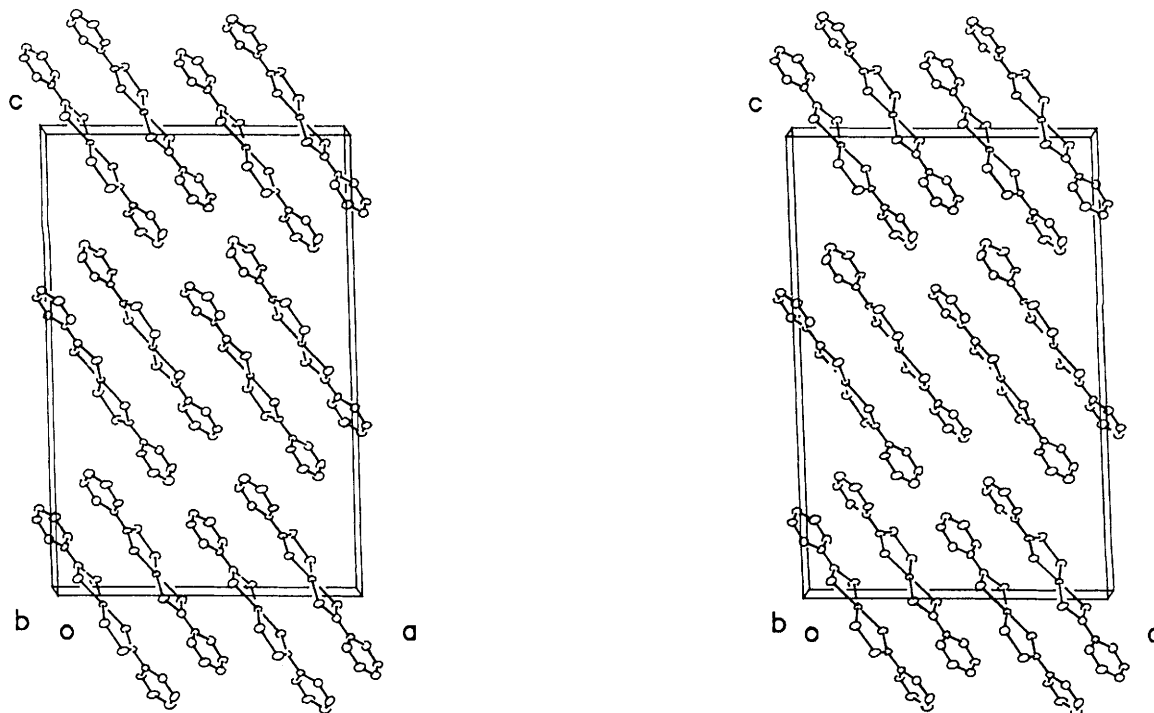


Fig. 2 Stereoview of the unit cell of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$

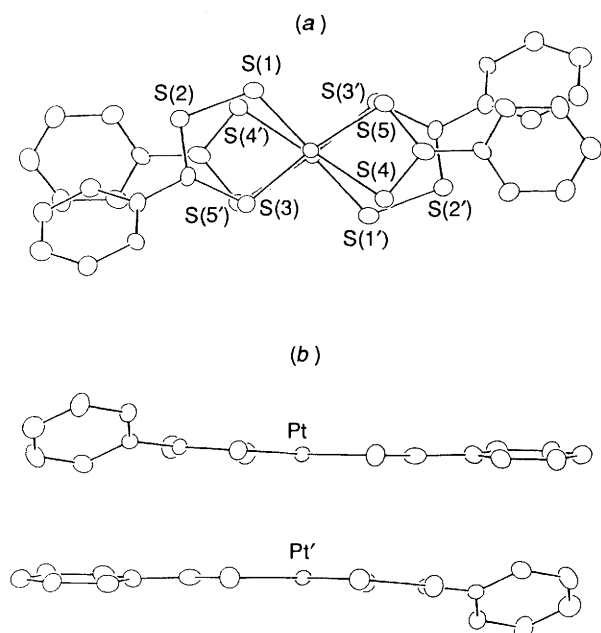


Fig. 3 Geometry (30% probability ellipsoids) of the dimer in the crystal of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$: (a) top view, (b) side view

these bands do not have corresponding absorption bands in the solution spectrum.

To examine the possibility of the formation of dimers in solution, we recorded the absorption spectra of a concentrated CH_2Cl_2 solution of the complex ($3 \times 10^{-3} \text{ mol dm}^{-3}$) at low temperatures (-20 to -70°C), but found no new bands.

Discussion

Several metal complexes with chelating trithioperoxy-carboxylate and dithiocarboxylate ligands have been reported.^{10,11,21,22} X-Ray crystal-structure analyses have established the molecular structures and packing geometries of (*p*-isopropyl-dithiobenzoato)(*p*-isopropyltrithioperoxybenzoato)nickel(II)¹⁰ and (dithiopivalato)(trithioperoxypivalato)platinum(II).¹¹ The

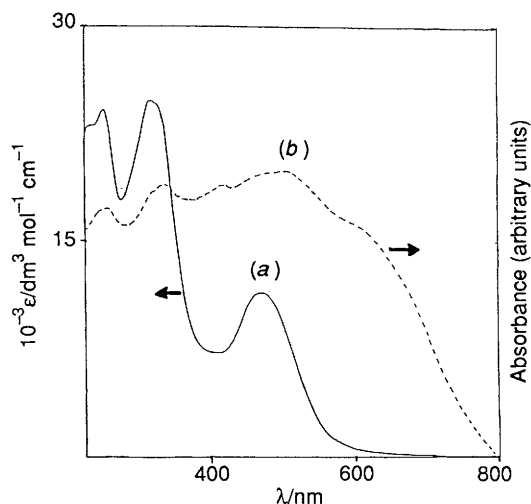


Fig. 4 Electronic spectra of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]$: (a) Absorption spectrum of a CH_2Cl_2 solution; (b) Diffuse reflectance spectrum of the powder diluted with MgO powder

present platinum complex has a co-ordination geometry and intramolecular bond distances and angles similar to those of the reported nickel and platinum complexes. However, the packing in the crystal is quite different. In the crystals of the latter two complexes the nearest intermolecular metal-metal distances are 4.01^{10} and 6.20 \AA^{11} respectively, and there is no indication of metal-metal interactions. In contrast, the present structure consists of dimers as shown in Fig. 2. The intradimer $\text{Pt} \cdots \text{Pt}'$ distance of $3.587(1) \text{ \AA}$ is comparable to intermolecular $\text{Pt} \cdots \text{Pt}$ distances (3.08 – 3.82 \AA) in the crystals of tetrakis(dithiocarboxylato)diplatinum(II) complexes^{4–7} which have extended linear chains of platinum atoms.

The geometry of the dimer in Fig. 3 suggests the driving force for its formation is the intermolecular charge-transfer interaction between the four- and the five-membered chelate rings. The CS_3^- moiety in the trithioperoxybenzoate anion has six π electrons and the CS_2^- in the dithiobenzoate anion has four π electrons. Consequently, the phase relation of the frontier orbitals of this $4\pi + 6\pi$ dimer system is expected to be suitable

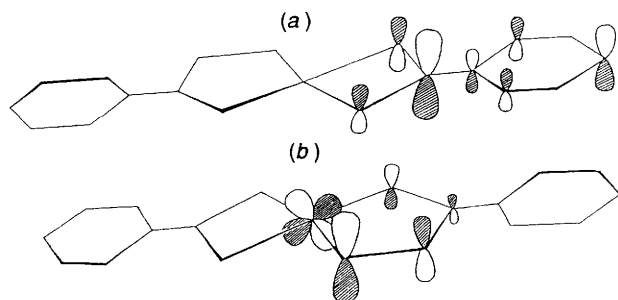


Fig. 5 (a) The LUMO and (b) the HOMO of $[\text{Pt}(\text{S}_2\text{CPh})(\text{S}_3\text{CPh})]_2$ as obtained with an extended-Hückel calculation

for intermolecular charge-transfer interaction,²³ if the π systems of both ligands are not extensively mixed through the Pt atom.* This is supported by extended-Hückel molecular orbital calculations. The HOMO of the complex is calculated to be a π orbital localized predominantly on the trithioperoxybenzoato CS_3 group and the Pt atom (CS_3 , 55; Pt, 33; dithiobenzoato, 4%). The LUMO is obtained as a π orbital localized on the dithiobenzoato CS_2 group (CS_2 , 52; Pt, 2; trithioperoxybenzoato, 0%). The HOMO and the LUMO are depicted in Fig. 5. These orbitals overlap each other in phase in the dimer with the geometry given in Fig. 3. We propose electron delocalization from the five-membered chelate ring of one molecule onto the four-membered chelate ring of the other molecule as the dominant interaction for the formation of the dimer.

The present molecular orbital calculation shows as expected that the Pt $5d(z^2)$ atomic orbital is distributed predominantly in high-lying (ca. 0.8 eV below the HOMO) doubly occupied molecular orbitals and the Pt $6p(z)$ atomic orbital in low-lying (ca. 5.0 eV above the LUMO) unoccupied molecular orbitals, where the z axis is parallel to the intradimer Pt \cdots Pt' direction. We suppose that intermolecular electron delocalization from the Pt $5d(z^2)$ orbital to the Pt $6p(z)$ orbital is a driving force for the inward shifts of the platinum atoms from the planes of the co-ordinating sulphur atoms.

The existence of intermolecular electronic interaction in the dimer is confirmed through a comparison of the solution and powder electronic spectra of the complex. The reflectance spectrum exhibits extra bands at 418, 504, 618(sh) and 672(sh) nm. We suppose that the lowest-energy band in the reflectance spectrum is the intermolecular charge-transfer band arising from the dimer structure of the crystal.

The absence of the formation of dimers in the crystal of (dithiopicvalato)(trithioperoxyvalato)platinum(II)¹¹ would be

* Note that the lowest unoccupied molecular orbital (LUMO) of a linear four- π -electron system and the highest occupied molecular orbital (HOMO) of a linear six- π -electron system are essentially the same orbital with respect to their nodal properties (i.e. phase relation).

due to the bulkiness of the Bu^t group in the ligands which prevents close approach of the ligand π systems.

Acknowledgements

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