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# Vibrational Study of Dithioacetate Complexes of Nickel, Palladium and Platinum

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## Abstract

Raman, resonance Raman and infrared spectra at *ca.* 80 K of the complexes $[M(dta)_2]_n$ (M = Ni, Pd or Pt; dta = $CH_3CS_2$; $n = 1$ or 2) and $Ni_2(dta)_4I$ are reported and assigned. Excitation profile studies have confirmed that the electronic bands at $\geqslant 18600$ $cm^{-1}$ involve metal(d)–ligand($\pi$) charge transfer. The assignment of the lower energy electronic bands as transitions to Frenkel exciton levels is discussed in the light of the Raman spectroscopic results.

## Introduction

Dithioacetic acid forms complexes with nickel, palladium and platinum of general formula $[M(dta)_2]_n$ (where M = Ni, Pd or Pt; dta = $CH_3CS_2$). The nickel and platinum dithioacetates are dimeric but palladium forms three distinct dithioacetates, one of which involves both monomers and dimers [1]. The crystal structures of the complexes are all different from one another, but all the complexes have a cage structure (Fig. 1a) with the sulphur atoms arranged

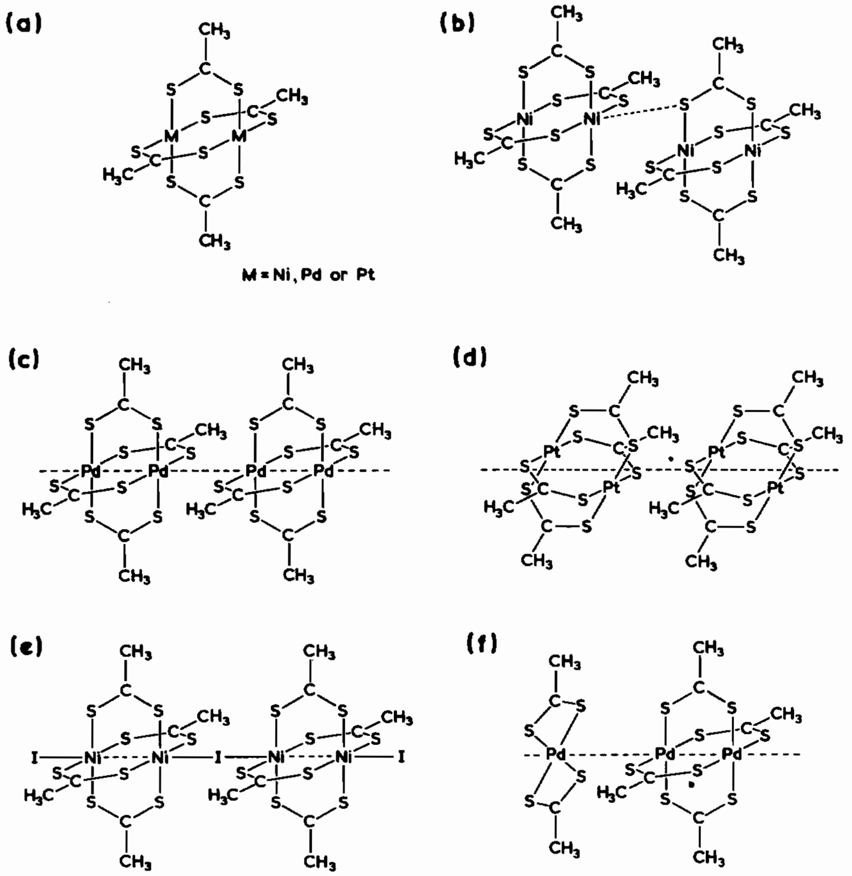

Fig. 1. Structure of the dimers and their crystal stacking. (a) Structure of the dimer unit. (b) Stacking of the dimers in $Ni_2(dta)_4$. (c) Stacking of the dimers in $Pd_2(dta)_4{\cdot}CS_2$. (d) Stacking of the dimers in $Pt_2(dta)_4$. (e) Stacking of the dimers in $Ni_2(dta)_4I$. (f) Stacking of the monomers and dimers in the $Pd(dta)_2$, A form.

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around the metal atoms in a roughly square-planar geometry.

In $Ni_2(dta)_4$ [2] (Fig. 1b), the dimeric units are in the 'slipped-stack' arrangement such that there is a Ni–S contact between two adjacent dimer units. In $Pd_2(dta)_4 \cdot CS_2$ [1] (Fig. 1c), where the $CS_2$ molecule is necessary for the stabilization of a structure which involves dimeric units only, the dimers stack in a linear metal chain affording short Pd–Pd contacts. The A form for $Pd(dta)_2$ [1] (Fig. 1f), which contains both monomeric and dimeric units, also has a columnar arrangement of palladium atoms. $Pt_2(dta)_4$ [3] (Fig. 1d) stacks with the Pt–Pt axis at an angle of about 28° to the stacking axis.

$Ni_2(dta)_4$ and $Pt_2(dta)_4$, but none of the isomers of $Pd(dta)_2$, undergo oxidative addition with iodine to form complexes of formula $M_2(dta)_4I$, which are linear-chain, iodine-bridged complexes with nearly symmetrical metal–iodine distances and shorter metal–metal separations than in the starting complexes. The iodine and nickel atoms stack along the twofold axis (Fig. 1e). $Pt_2(dta)_4$ also reacts further with halogens to form oxidised dimers of the type $Pt_2(dta)_4X_2$, where X = Cl, Br or I.

The short intramolecular metal–metal distances in the dimers (2.564 Å for $Ni_2(dta)_4$; 2.754 Å for $Pd_2(dta)_4 \cdot CS_2$; and 2.767 Å for $Pt_2(dta)_4$) together with the inward distortion of the metal atoms from the $S_4$ plane [1] are attributed to some form of metal–metal interaction although, as these are $d^8$–$d^8$ systems, no formal metal–metal bond is to be expected.

All the dithioacetates in the solid state show additional bands in their electronic spectra between ~15 000 and 18 000 $cm^{-1}$ which are not present in solution and are polarized in the stacking direction. There has been some discussion [4, 5] as to whether these are caused by intermolecular metal–metal interactions, especially in the case of the palladium complexes with their linear palladium chains, since $d^8$ complexes with sulphur-donor ligands generally adopt laterally displaced structures which do not allow short metal–metal contacts [6, 7].

$Ni_2(dta)_4I$ [1] and $Pt_2(dta)_4I$ [8] each show an asymmetric broad electronic band in the near infrared region, at 6000 $cm^{-1}$ for $Ni_2(dta)_2I$ and at 7800 $cm^{-1}$ for $Pt_2(dta)_4I$. This is attributed to a transition between the bands arising from the interaction of an $M^{III}$ dimer and an $M^{II}$ dimer through the halogen bridge.

A Raman study of these complexes was undertaken to attempt to elucidate the nature of the additional electronic bands and to investigate the differences in bonding on oxidation to the intervalence state. A summary of the properties of the complexes studied is given in Table I.

## Experimental

The complexes were prepared by literature methods [1–3]. Electronic spectra were recorded as pressed discs in KBr at *ca.* 80 K on a Varian 2390 spectrometer. Infrared spectra were recorded at *ca.* 80 K as wax (B.D.H., melting point 49 °C) or KBr discs on a Bruker IFS 113 V spectrometer. Raman spectra were recorded using a Spex 14018 (R6) spectrometer. Exciting radiation was provided by Coherent Radiation models CR12 argon-ion and 3000 K krypton-ion lasers. Samples were prepared as pressed discs in KBr or $K[NO_3]$ and held at liquid nitrogen temperature, except for $Pt_2(dta)_4$ which reacted with all common dispersing agents and so was prepared as a polyethylene disc. Owing to its air-sensitivity, $Pt_2(dta)_4$ was stored and handled in a glove box. Excitation profiles were measured relative to the $\nu_1(a_1)$ band of $K[NO_3]$ as standard, and corrected for the spectral response of the instrument.

## Results

### *Band Assignments*

The bands observed in the infrared and Raman spectra are listed in Tables II and III together with suggested assignments. The Raman spectrum of the ligand as its caesium salt is dominated by a band

TABLE I. Summary of Properties of Complexes Studied

| Complex | Colour (powder) | Electronic band maxima ($cm^{-1} \times 10^3$) KBr disc, 80 K$^a$ | Reacts with $I_2$ to form $M_2(dta)_4I$ | Reacts with $X_2$ to form $M_2(dta)_4X_2$ |
|---|---|---|---|---|
| $Ni_2(dta)_4$ | black | 15.3m, 16.0m, 21.1s | yes | no |
| $Pd(dta)_2$ A form | red | 17.7m, 18.6s, 19.7m | no | no |
| $Pd_2(dta)_4 \cdot CS_2$ | green | 15.2m, 18.8sh, 23.3s | no | no |
| $Pt_2(dta)_4$ | purple | 15.2, 19.0, 22.7s$^b$ | yes | yes, X = Cl, Br, I |
| $Ni_2(dta)_4I$ | black | 6.0m, 15.1m, 21.2s | – | yes, X = I |

$^a$sh = shoulder, m = medium, s = strong. $^b$Ref. 3, reflectance at 298 K diluted in MgO powder.

TABLE II. Wavenumbers ($\tilde{\nu}$ (cm$^{-1}$)) and Assignments of Bands Observed in the Infrared Spectra[a]

| Cs(dta) | $Ni_2(dta)_4$ | $Ni_2(dta)_4I$ | $Pd(dta)_2$ A form | $Pd_2(dta)_4 \cdot CS_2$ | $Pt_2(dta)_4$[b] | Assignment |
|---|---|---|---|---|---|---|
| | | 86.0vs | | | | $\nu$(NiNi) |
| 240.6w | 243.3sh | | | | | |
| | 245.7s | 247.8w | 253.4s | 248.8s | 261.5s | $\nu$(MS) dimer |
| | | 290.0w | 284.0s | 284.0s | 266.6sh | |
| | | | 292.9m | | | |
| 335.6sh | 319.9w | 317.2w | 316.3w | | 338.9w | |
| 337.8s | | | | | | $\nu$(MS) monomer |
| 340.2m | | | | | | |
| | | | 348.6vs | | | |
| 366.9m | 388.9m | 378.9m | 393.9w | 394.4m | 366.9w | |
| | 399.0m | 384.1m | 397.3m | 402.4s[c] | | |
| | | 403.6ms | 434.2w | | | |
| 439.7bd | 438.3s | 441.1m | 449.4s | 447.9s | 448.4s | $\delta$(SCS) |
| 475.7w | | 444.7m | | | | |
| 480.0m | | 447.5m | | | | |
| 610.9w | | | 603.2w | 603.0vw | | |
| | | | 835.9s | | | $\nu$(CS) monomer |
| | | 879.9m | 892.0sh | | | |
| | 878.3sh | | | | | |
| 872s | 898.5s | 896.4m | 903.1s | 900.0s | | $\nu$(CS) dimer |
| 924.8w | 1105.9m | 1103.2w | | 1088.8m | | |
| 1018.6w | | | 1138.5w | 1135.5w | | |
| 1097.7 | | | 1156.6sh | | | |
| 1131.4s | 1168.3s | 1160.1m | 1174.8vs | 1161.1s | | $\nu$(C=S) |
| | | | 1186.4s | | | |
| | 1260.4w | 1261.9w | 1343.1w | | | |
| 1343.8m | 1352.5w | 1355.6w | 1356.5w | 1354.7w | | |
| 1408.2s | 1423vw | 1412.8m | | 1419w | | |
| | | 1444.8w | | | | |
| | | | | 1504.4s | | |
| 1566.6s | | 1514vw | | | | $CS_2$ mode |
| 1658.9vw | | | | | | |

[a] s = strong, v = very, w = weak, bd = broad, sh = shoulder. [b] Not recorded at >600 cm$^{-1}$. [c] Mode of $CS_2$.

at 612 cm$^{-1}$, and a strong feature is observed in the Raman spectra of all of the complexes at 606–620 cm$^{-1}$ (Figs. 2–6). This is assigned to $\nu_s$(CS) (supporting assignments: $K_2[Pt_2(S_2C_2O_2)_2]$, $\nu$(CS) = 573 cm$^{-1}$ [9]; $Pt_2(S_2CNH_2)_3$, $\nu$(CS) = 622 cm$^{-1}$ [10]).

For the dithioacetate complexes of nickel, palladium and platinum, $\nu$(CS) is split into two components of which the one at a lower wavenumber is the more intense (except in the case of the A form of $Pd(dta)_2$) and is enhanced at resonance. Accordingly, this is probably best assigned to the totally symmetric mode. In the case of $Ni_2(dta)_4I$, there is no splitting of $\nu$(CS).

There is no corresponding infrared mode in this region. However, a strong $\nu$(CS) band is observed in the infrared spectrum at ~890 cm$^{-1}$ with a corresponding weak band in the Raman spectrum between 830 and 890 cm$^{-1}$. The $\nu$(C=S) band occurs between 1120 and 1190 cm$^{-1}$ in the Raman spectrum and is also weak, while the corresponding infrared band between 1160 and 1190 cm$^{-1}$ is strong.

For the A form of $Pd(dta)_2$ only, a strong Raman band is observed at 398 cm$^{-1}$ which is in the region where $\nu$(MS) would be predicted for a square-planar system [11–13] and so this band is assigned to the $\nu$(PdS) stretch of the monomer unit. The infrared-active $\nu$(Pd–S) occurs at 348.6 cm$^{-1}$.

All five complexes studied show a strong Raman feature around 250 cm$^{-1}$, the wavenumber of which depends on the metal atom, increasing from 244 cm$^{-1}$ for $Ni_2(dta)_4$ to 254 cm$^{-1}$ for $Pd_2(dta)_4 \cdot CS_2$ and to 277 cm$^{-1}$ for $Pt_2(dta)_4$. The band wavenumber differs by 1 cm$^{-1}$ for $Ni_2(dta)_4$ and $Ni_2(dta)_4I$, whereas for the two forms of $Pd(dta)_2$ the band position differs by only 2 cm$^{-1}$. From its variation with coordinated metal ion, this band may be unambiguously assigned to the symmetric stretch, $\nu$(MS), of the dimers. This increase in wavenumber on going from nickel to palladium to platinum is also observed, although to a lesser extent, for the infrared-active $\nu$(MS) (*i.e.* $Ni_2(dta)_4$, 246; $Pd_2(dta)_4 \cdot CS_2$, 249; $Pt_2(dta)_4$, 262 cm$^{-1}$). This reflects the

TABLE III. Wavenumbers ($\tilde{\nu}$ (cm$^{-1}$) and Assignments of Bands Observed in the Raman Spectrum of M(dta)$_2$, Ni$_2$(dta)$_4$I, and Cs(dta)$^a$

| Cs(dta) | Ni$_2$(dta)$_4$ | Ni$_2$(dta)$_4$I | Pd(dta)$_2$ A form | Pd$_2$(dta)$_4$·CS$_2$ | Pt$_2$(dta)$_4$ | Assignment |
|---|---|---|---|---|---|---|
| 94 | 48.5 | | | | 82 | |
| | | | | 88.4 | 91.5 | ring deformation |
| | | 94.5 | | | | $\nu_s$(NiNi) |
| | | 99.5 | | | | |
| 102 | 121 | 120 | 118.5 | | 140.5 | |
| 148 | 159 | | 135 | 143 | 143 | δ(SMS) |
| | | | 173 | | | |
| | | | | 179 | | |
| | | 184 | | | | ν(NiI) |
| | 196 | 194 | 213.5 | | | |
| | 219 | 213 | 230 | 228.5 | | ν(MS), δ(MSC) |
| | 233 | 233 | 238 | 238 | | |
| | 244 | 245 | 252 | 254 | 277 | ν(MS) dimer |
| | 287 | 305 | | 280 | | |
| | | | 340 | | | |
| | | | 348 | | | 2 × 173 |
| | | | 398.4 | | | ν(MS) monomer |
| 369 | 400 | | | 400 | 398 | δ(SCS) |
| | 418.5 | 421 | 410 | 425.5 | | |
| | 442.5 | 424 | 424.5 | | 442.5 | |
| | | | | | 453 | |
| | 454 | | | 499 | | |
| | 509 | | 508 | 506 | | |
| 612 | 606 | 611 | 608 | 608 | 606 | ν(CS) |
| 620sh | | | 619.4 | 620 | 618.5 | |
| | | 707 | | | | 611 + 94.5 |
| | | | 799 | | | 2 × 398.4 |
| 832 | 838 | | | 815 | | ν(CS) |
| 876 | 890 | 893 | 869 | 871 | | |
| 883 | | | 1019 | | 1013 | ν(MS) monomer + ν(CS) |
| 1101 | 1109 | 1109.5 | | 1100 | 1096 | |
| | 1130 | 1123 | | 1124 | | |
| | 1187 | | 1188 | | | ν(C=S) |
| | | 1240 | 1238 | | 1231 | 2 × ν(CS) |
| | 1351 | 1348 | 1342 | 1391 | | |
| | 1388 | | | | | |
| | | | 1807 | | | 3 × ν(CS) |

$^a$dta = dithioacetate.

increase in metal(d)–ligand(π) overlap on going down a group in the periodic table (*cf.* the complexes of [C$_2$S$_2$(CN)$_2$]$^{2-}$ with nickel(II), palladium(II), and platinum(II) [14]).

The assignment of the bridging modes is less clear cut. However, ligand modes can be identified since they occur at approximately the same wavenumber for all the complexes and correspond to observed features in the spectrum of Cs(dta). So, the weak band at about 400 cm$^{-1}$ (369 cm$^{-1}$ for Cs(dta)) is assigned to δ(SCS) (the analogous infrared-active mode occurs at 438–449 cm$^{-1}$). There are no bands in the Raman spectrum of Cs(dta) between 148 and 369 cm$^{-1}$ so, on the basis of previous assignments of δ(MSC) [13] (*ca.* 220 cm$^{-1}$), it is proposed that δ(MSC) occurs between 200 and 240 cm$^{-1}$, and that the bands between 150 and 200 cm$^{-1}$ are assigned to δ(SMS) [12].

The assignments of the strong Raman bands at 88 cm$^{-1}$ for Pd$_2$(dta)$_4$·CS$_2$ and at 91.5 and 82 cm$^{-1}$ for Pt$_2$(dta)$_4$ are problematic. However, from the excitation profile of the 88 cm$^{-1}$ band and by comparison with the 94.5 cm$^{-1}$ band in Ni$_2$(dta)$_4$I, it is possible that this mode could be associated with an axial cage deformation along the stacking axis, associated with the partial metal–metal bond. The Pd–Pd overlap population in the dimer has been calculated as 0.026 of an electron [15].

It is similarly not clear why the band at 173 cm$^{-1}$ in the Raman spectrum of the A form of Pd(dta)$_2$ should be so strong, but, from the absence of a strong feature in this region for any of the purely

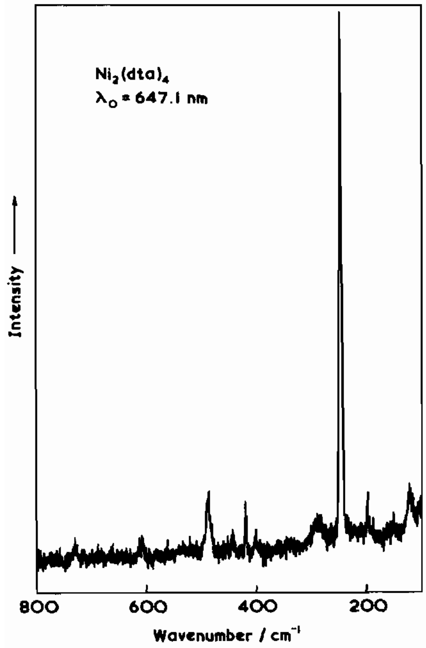

Fig. 2. Resonance Raman spectrum of $Ni_2(dta)_4$, with $\lambda_0 = 647.1$ nm.

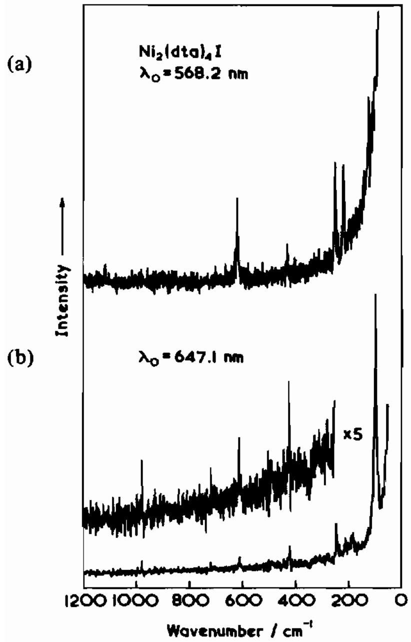

Fig. 3. (a) Off-resonance Raman spectrum of $Ni_2(dta)_4I$, with $\lambda_0 = 568.2$ nm. (b) On-resonance Raman spectrum of $Ni_2(dta)_4I$, with $\lambda_0 = 647.1$ nm.

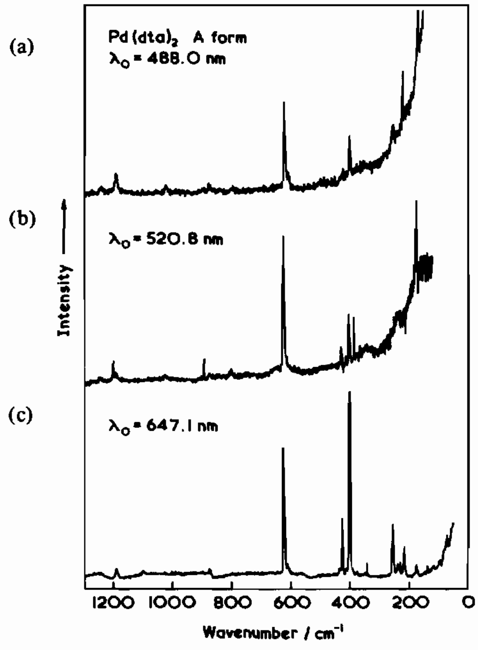

Fig. 4. Resonance Raman spectra of $Pd(dta)_2$, A form. (a) $\lambda_0 = 488.0$ nm, (b) $\lambda_0 = 520.8$ nm, (c) $\lambda_0 = 647.1$ nm.

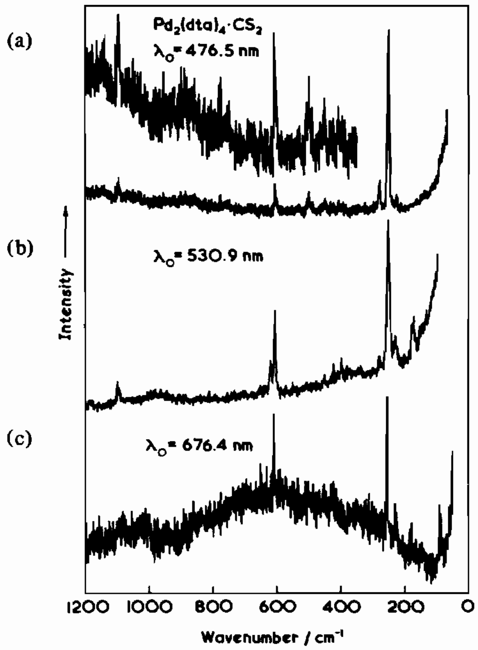

Fig. 5. Resonance Raman spectra of $Pd_2(dta)_4 \cdot CS_2$. (a) $\lambda_0 = 476.5$ nm (X5), (b) $\lambda_0 = 530.9$ nm, (c) $\lambda_0 = 676.4$ nm.

dimeric complexes, this mode should be associated with a bending mode of the square planar unit, probably δ(SPdS).

In addition to the bands already assigned, $Ni_2(dta)_4I$ also has a strong Raman band at 94.5 $cm^{-1}$ and a weaker band at 184 $cm^{-1}$. It is expected that the strongest band will be that attributed to ν(NiNi) and that ν(NiI) will be weaker and lie to higher wavenumber, *cf.* spectroscopic results on structurally related systems such as $K_4[Pt_2(pop)_4I] \cdot nH_2O$ [16] (pop = $P_2O_5H_2$) for which ν(PtPt) is at 100 (strong) and ν(PtI) is at 185 $cm^{-1}$ (weak). Accordingly, the band at 94.5 $cm^{-1}$ is assigned to ν(NiNi) and the

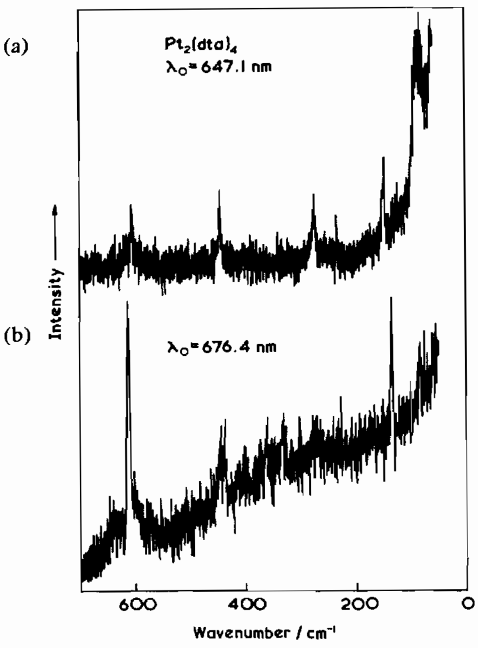

Fig. 6. Resonance Raman spectra of $Pt_2(dta)_4$.

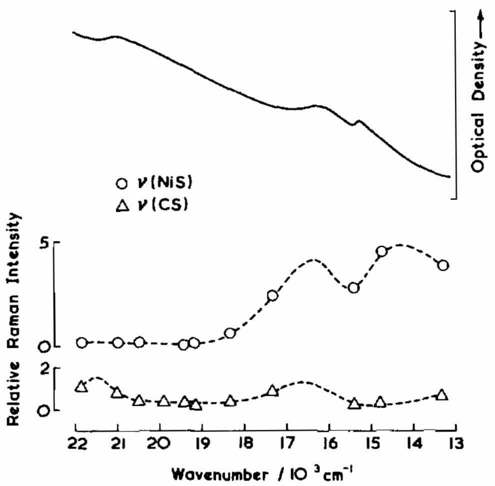

Fig. 7. Electronic spectrum (KBr disc, *ca.* 80 K) of $Ni_2(dta)_4$, together with excitation profiles of its 244 and 606 $cm^{-1}$ bands, $\nu$(NiS) and $\nu$(CS), respectively.

band at 184 $cm^{-1}$ to $\nu$(NiI), although there is likely to be some mixing of the relevant symmetry coordinates.

*Excitation Profiles* (Figs. 7–10)

*$Ni_2(dta)_4$*

The Raman spectra of this complex (Fig. 2) vary greatly with exciting line. At resonance with the 21 100 $cm^{-1}$ band, the most intense band in the spectrum is that assigned to $\nu_s$(CS). On the other hand, at resonance with the 16 000 and 15 300 $cm^{-1}$ bands, the spectrum is dominated by the band

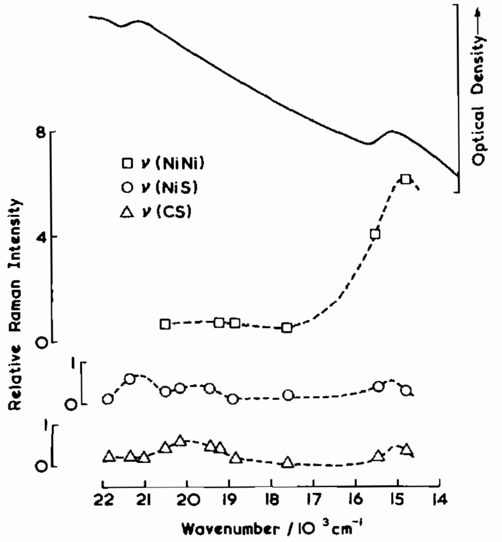

Fig. 8. Electronic spectrum (KBr disc, *ca.* 80 K) of $Ni_2(dta)_4I$, together with the excitation profiles of its 94.5, 245, and 611 $cm^{-1}$ bands, $\nu$(NiNi), $\nu$(NiS), and $\nu$(CS), respectively.

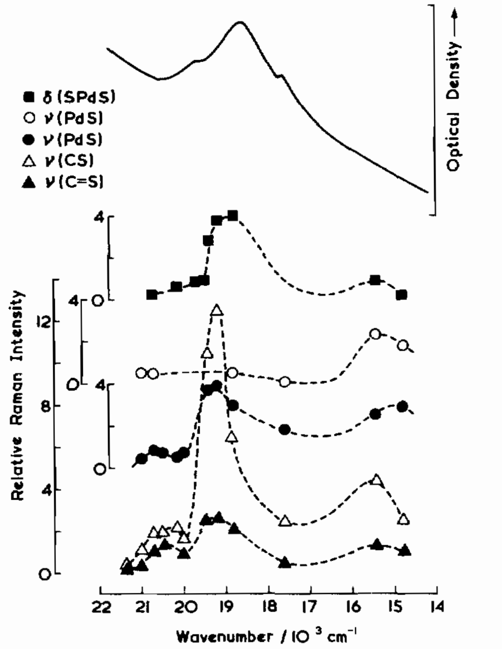

Fig. 9. Electronic spectrum (KBr disc, *ca.* 80 K) of $Pd(dta)_2$, A form, together with the excitation profiles of the 173, 238, 398, 619, and 1188 $cm^{-1}$ bands, $\delta$(SPdS), $\nu(PdS)_{dimer}$, $\nu(PdS)_{monomer}$, $\nu$(CS), and $\nu$(C=S), respectively.

assigned to $\nu_s$(NiS), and it also shows evidence of the first overtone of $\nu_s$(NiS).

*$Ni_2(dta)_4I$*

The wavenumbers of most of the bands in the Raman spectrum of $Ni_2(dta)_4I$ (Fig. 3) are unshifted

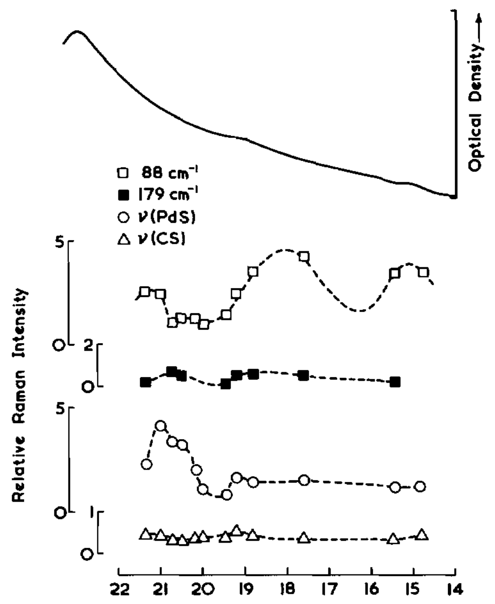

Fig. 10. Electronic spectrum (KBr disc, *ca.* 80 K) of $Pd_2$-$(dta)_4 \cdot CS_2$, together with the excitation profiles of the 88, 179, 254 [$\nu$(PdS)], and 608 [$\nu$(CS)] $cm^{-1}$ bands.

from their values for $Ni_2(dta)_4$, the main difference being the additional bands attributed to $\nu$(NiNi) and $\nu$(NiI) for the former. At resonance with the 15 100 $cm^{-1}$ band, the $\nu$(NiNi) band dominates the spectrum and the $\nu$(NiS) and $\nu$(CS) bands are also somewhat enhanced. At resonance with the 21 200 $cm^{-1}$ band, the $\nu$(NiS) band alone is enhanced but the $\nu$(NiNi) band remains the strongest band in the spectrum.

### *Pd(dta)₂ A form*

As for $Ni_2(dta)_4$, the Raman spectrum of $Pd(dta)_2$ (Fig. 4) depends on the exciting line. At resonance with the 18 600 $cm^{-1}$ band, the band due to $\nu_s$(CS) dominates the spectrum, whilst those due to $\nu_s(PdS)_{monomer}$, $\nu$(C=S) and $\delta$(SPdS), but not $\nu_s(PdS)_{dimer}$, also show enhancement. Bands attributable to overtones of $\delta$(SPdS), $\nu_s(PdS)_{monomer}$ and $\nu_s$(CS) are observed. Some enhancement of these bands is also observed at resonance with the 19 700 $cm^{-1}$ band, although the excitation profiles maximise somewhat (~750 $cm^{-1}$) to a higher wavenumber.

At resonance with the 17 700 $cm^{-1}$ band all the Raman bands are enhanced and most show overtones. Raman bands attributed to $\nu_s(PdS)_{monomer}$ and $\nu_s(PdS)_{dimer}$ are of comparable intensities with $\nu_s$(CS) giving rise to the most intense band in the spectrum. The excitation profile (Fig. 9) maximises around 15 500 $cm^{-1}$, a significant red shift, probably caused by interference with the more intense 18 600 $cm^{-1}$ band (*cf.* $[WS_4]^{2-}$ [17]).

### *Pd₂(dta)₄·CS₂*

The Raman spectrum of $Pd_2(dta)_4 \cdot CS_2$ (Fig. 5) is essentially the same as that of the A form with the bands attributed to the monomer being missing. The sample could not be exposed to the laser beam for longer than 2 to 3 h, otherwise it started to decompose to the A form by losing carbon disulphide.

Similar to the situation for $Ni_2(dta)_4$, the band attributed to $\nu_s$(CS) is not subject to resonance enhancement. That attributed to $\nu_s$(PdS) and the 88 $cm^{-1}$ band are enhanced at resonance with the 23 300 $cm^{-1}$ band but the excitation profiles are red shifted to peak at about 21 500 $cm^{-1}$ (Fig. 10). Only the 88 $cm^{-1}$ band is enhanced with exciting lines of wavenumber <21 500 $cm^{-1}$ and the excitation profile peaks under the 15 200 $cm^{-1}$ band and at about 18 200 $cm^{-1}$ (red shifted from the 18 800 $cm^{-1}$ band). The 179 $cm^{-1}$ band shows no significant enhancement with any of the exciting lines used.

### *Pt₂(dta)₄*

As $Pt_2(dta)_4$ was found to react on grinding with all alkali halides and internal reference materials, its Raman spectrum (Fig. 6) was recorded as a polyethylene disc and no excitation profiles were obtainable. With 647.1 nm excitation (resonant with the 15 200 $cm^{-1}$ band) the 91.5 $cm^{-1}$ and $\nu_s$(CS) bands are both strong whereas with 676.4 nm excitation, $\nu_s$(CS) gives rise to the stronger Raman band. This implies that it is the 91.5 $cm^{-1}$ band which is the more enhanced at resonance with the 15 200 $cm^{-1}$ electronic band.

## Discussion

The results are consistent with the electronic transitions at ⩾18 600 $cm^{-1}$ being associated with metal ($d_{z^2}$)-to-ligand($\pi$) charge transfer, as predicted from molecular orbital calculations on the palladium system [15].

In the case of $Ni_2(dta)_4$, only the band attributed to $\nu_s$(CS) is enhanced at resonance with the 21 500 $cm^{-1}$ transition and not to a great extent, indicating that the bond length changes on excitation are small and spread out over the whole molecule, but with a greater change in the carbon–sulphur than the metal–sulphur interaction. On the other hand, for $Ni_2(dta)_4I$ it is the band attributed to $\nu_s$(NiS) which shows enhancement under this absorption band, although to an even smaller extent than for $Ni_2$-$(dta)_4$.

The Raman spectrum of $Pd_2(dta)_4 \cdot CS_2$ shows substantial enhancement of the band attributed to $\nu_s$(PdS) and also to the 88 $cm^{-1}$ band at resonance with the 18 800 $cm^{-1}$ band, indicating a significant increase in PdS bond length on excitation. A similar effect may be inferred from the $Pt_2(dta)_4$ spectra.

The A form of $Pd(dta)_2$, however, shows preferential and very substantial enhancement of the $\nu_s$(CS) band; those due to $\nu_s(PdS)_{monomer}$, $\delta$(SPdS) and $\nu$(C=S) are also enhanced at resonance with the 18600 and 19700 cm$^{-1}$ bands, indicating that the transition is localised on the monomers and that there are large bond length changes on excitation involving mainly the CS bond.

The situation at resonance with the electronic bands of wavenumber <18600 cm$^{-1}$ is more complicated than that discussed above since the origin of these bands has not been established unambiguously. It has been suggested [18, 19] that the low energy bands characteristic of 'stacked' systems and which are polarised parallel to the metal chain arise from transitions to neutral Frenkel exciton levels formed from simple molecular levels. Such transitions could arise from either a metal $d_{z^2} \rightarrow p_z$ transition, a metal($d_{z^2}$) → ligand($\pi$) charge transfer, or a mixture of both.

On the basis of this model, the observed enhancement of the $\nu_s$(NiS) band for $Ni_2(dta)_4$ would indicate that the resonant transition is of a charge-transfer type whereas the observed enhancement of bands attributed to the metal–metal interaction but not to $\nu$(MS) for $Pd_2(dta)_4 \cdot CS_2$ and $Pt_2(dta)_4$ would suggest that the resonant transition has, in these cases, $d_{z^2} \rightarrow p_z$ character. As expected, owing to the greater degree of metal–metal interaction in $Ni_2(dta)_4I$, the band attributed to $\nu$(NiNi) alone is enhanced, and substantially so, at resonance with the 15100 cm$^{-1}$ band, *i.e.* the resonant transition is of the metal $d_{z^2} \rightarrow p_z$ type.

The A form of $Pd(dta)_2$ behaves quite differently from the other complexes studied. All the modes are enhanced at resonance with the 15200 cm$^{-1}$ band, but not to the same extent as at resonance with the 18600 cm$^{-1}$ band. The 15200 cm$^{-1}$ band is interpreted as arising from a charge-transfer transition involving both the monomeric and dimeric units, this interpretation implying an excited-state geometry with only small changes to all bond lengths from those for the ground state.

Such a changeover in interaction from charge-transfer type for $Ni_2(dta)_4$ to metal $d_{z^2} \rightarrow p_z$ character for the palladium and platinum complexes agrees with the prediction that, for $Ni_2(dta)_4$, the highest occupied molecular orbital is of sulphur $3p_z$ type [20] whilst for the two forms of $Pd(dta)_2$, it is of metal $5p_z$ type [15]. This may also be reflected in the crystal structures adopted, $Ni_2(dta)_4$ having a slipped stack arrangement with the closest intermolecular contacts being nickel–sulphur, whereas for the palladium complexes the closest intermolecular contacts are palladium–palladium. However, the dominant energy term determining the structure is likely to be that associated with the packing of the units.

The observation of Raman bands at 88 cm$^{-1}$ for $Pd_2(dta)_4 \cdot CS_2$ and 91.5 cm$^{-1}$ for $Pt_2(dta)_4$ associated with some form of metal–metal interaction, but no corresponding band for $Ni_2(dta)_4$, agrees with the proposed increase in metal–metal interaction as the $n$d–($n$ + 1)p separation decreases on going down a group [3, 21]. It would be attractive to tie this in with a changeover in exciton level from charge-transfer to $d_{z^2} \rightarrow p_z$ type on going from nickel to palladium to platinum, as the wavenumber of the $d_{z^2} \rightarrow p_z$ transition of the metal decreases.

An alternative explanation for the electronic bands is that they might arise from levels caused by trace impurities in the solid but such bands would be unlikely to give the resonance enhancement observed. Thus the Raman spectroscopic evidence agrees with the assignment of the 'anomalous' electronic bands as arising from transitions to exciton levels.

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