

# Piezochromism and Related Phenomena Exhibited by Palladium Complexes

By Hideo D. Takagi\*, Kyoko Noda and Sumitaka Itoh

Research Center for Materials Science, Nagoya University, Furocho, Chikusa, Nagoya 464-8602, Japan

\*E-mail: htakagi@chem.nagoya-u.ac.jp

and Satoshi Iwatsuki

Department of Chemistry, Waseda University, Okubo, Shinjuku, Tokyo 169-8555, Japan

*Piezochromic phenomena are explained by pressure perturbation to the HOMO and/or LUMO energy levels of the related electronic transition. The piezochromism of solid inorganic and organic materials has been investigated by examination of the phase transition phenomena. Specific electronic properties of the solids, acquired by tuning the external pressure, may be used as electronic devices and as pressure sensors. The effects of pressure perturbations on the absorption and emission spectra exhibited by solid palladium complexes are reviewed here. Related phenomena exhibited by platinum complexes and other metal complexes are included for comparison.*

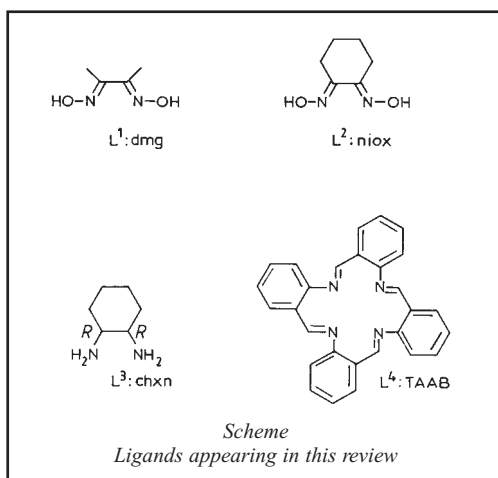
Piezochromic phenomena – colour changes in solid specimens or solution samples induced by external pressures – are explained by pressure perturbation to the HOMO and/or LUMO (highest occupied molecular orbital and/or lowest unoccupied molecular orbital) energy levels of the related electronic transition. The piezochromism of solid inorganic and organic materials has been investigated by examining phase transition phenomena. Specific electronic properties of the solids, acquired by tuning the external pressure, may be used as electronic devices and as pressure sensors.

Changes in the absorption and emission spectra of metal complexes in solution are related to changes in solvent polarity at each pressure: a gradual increase of the dielectric constant of the solvent with pressure affects the energies of the HOMO and LUMO levels involved in the electronic transitions within the metal complexes, and a corresponding colour change may be observed. However, such a pressure perturbation to the dielectric constant of solvents is usually small (1) and the piezochromic effect of samples in solution is rather ambiguous – partly because of the narrow range of applied pressures (< 5000 bar).

It is known that the compressibility of solids is

much smaller (< 0.001%) than that of liquids. This small compressibility is explained by the difficulty of intermolecular and/or interionic compression in the crystals that comprise the solid and by the difficulty of compression along the bond axis in the molecules or complex ions. For example, lateral compression between the chains takes place for alkylsilicon and alkylgermanium polymers at relatively low pressures (ca. 10,000 bar), followed by compression along the Si–Si and Ge–Ge axes at higher pressures (> 20,000 bar) (2–7). Moreover, deformation of compounds by the external pressure does not take place in a free way: there is a quantum mechanical restriction – “symmetry rules” (8, 9) – that governs the direction of deformation. Specific interactions, such as hydrogen bonding and ion-pair interactions, also perturb the structures at elevated pressures (10). In addition to knowing the “symmetry rules,” it is essential to comprehend the “theories of electronic transitions” and “molecular symmetry and vibrations” for a proper understanding of piezochromic effects (11).

In this short review the effects of pressure perturbations on the absorption and emission spectra that are exhibited by solid palladium complexes are



summarised. Related phenomena exhibited by platinum complexes and other metal complexes are included for comparison.

### Square-Planar Pd(II) Complexes

Probably the most classical studies of the piezochromism of metal complexes concern Ni(II), Pd(II) and Pt(II) complexes with dimethylglyoximate,  $L^1$ : dmg<sup>-</sup>. (Ligands appearing in this review and other related ligands are summarised in the Scheme.) These complexes all have square-planar,  $D_{4h}$ , symmetry, and the absorption spectra for each complex in solution and solid form are very different. The crystal structure of  $[\text{Ni}(\text{dmg})_2]$  was reported by Godychi and Rundle (12). The planar  $[\text{Ni}(\text{dmg})_2]$  units are stacked one upon another with a rotation of  $90^\circ$  for each alternate layer. The Ni(II) ions line up with an average Ni---Ni distance of 3.233 Å. The Pd(II) and Pt(II) complexes exhibit similar structures with the Pd---Pd and Pt---Pt distances being 3.253 and 3.25 Å, respectively (13, 14). As the M(II)---M(II) distances in these complexes are quite similar, the factor that governs the distances is attributed to the organic groups in the ligand. The complexes show sharp absorption bands near  $19,000\text{ cm}^{-1}$  in the solid, but these rather strong absorption bands are not observed in solution. The bands originate from M(II)---M(II) interactions. Furthermore, the absorption bands are dichroic with the perpendicular component having high intensity.

Zahner and Drickamer examined the pressure dependence of these complexes as solids (15). They used diluted salt pellets for the measurements. For all the complexes, the absorption band near  $19,000\text{ cm}^{-1}$  shifted towards lower energy with pressure. The observed pressure effects may be summarised as follows:

[a] A very large red shift was observed at first ( $6100\text{ cm}^{-1}$  and  $9800\text{ cm}^{-1}$  for the Ni(II) and Pd(II) complexes, respectively) at 100 kbar, see Figure 1.

[b] The red shift started to level off at ca. 120–150 kbar for the Ni(II) and Pd(II) complexes.

[c] For the Pt(II) complex, a reversal in shift was observed after a red shift of  $8700\text{ cm}^{-1}$  at 63 kbar; the blue shift at higher pressures was very large.

[d] The external pressure induced a broadening of this absorption band in the order of Ni(II) < Pd(II) < Pt(II). As this band is related to the M(II)---M(II) interactions, the observations were explained by a decrease in the M(II)---M(II) distance with pressure, see Figure 2. In the original  $D_{4h}$  complexes d-d transitions are Laporte forbidden, while the d-p transitions are allowed. However, in complexes with  $D_{4h}$  symmetry the

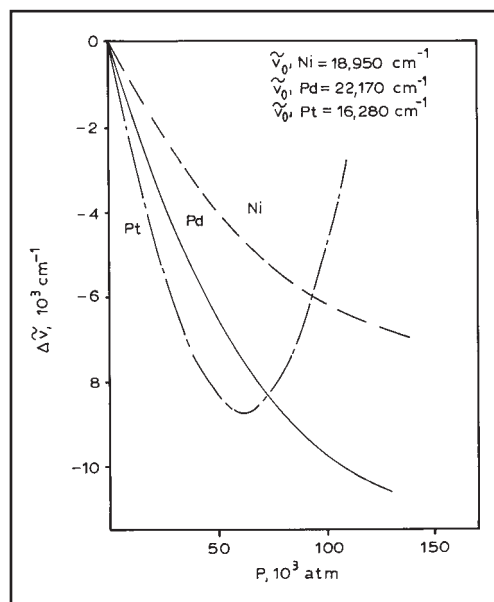


Fig. 1 Frequency shift for  $[\text{Ni}(\text{dmg})_2]$ ,  $[\text{Pd}(\text{dmg})_2]$  and  $[\text{Pt}(\text{dmg})_2]$  vs. pressure. From J. C. Zahner and H. G. Drickamer; *J. Chem. Phys.*, 1960, 33, 1625  
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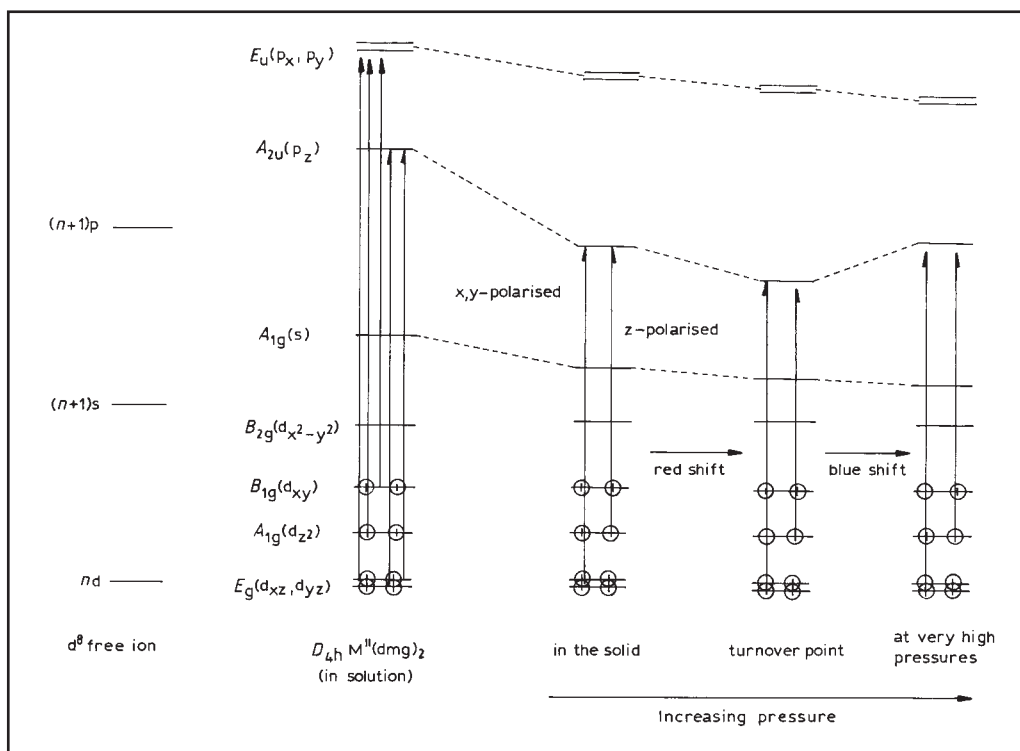


Fig. 2 Energies of the  $nd$ ,  $(n+1)s$  and  $(n+1)p$  orbitals on  $[M^{II}(dmg)_2]$  complexes. Allowed transitions from  $E_g$  to  $E_u$ , from  $A_{1g}$  to  $E_u$ , and from  $B_{1g}$  to  $E_u$  are  $z$ -,  $x,y$ -, and  $x,y$ -polarised, respectively. The  $d-d$  transitions as well as the  $d-s$  transition are Laporte forbidden. The turnover point was observed at lower pressure for Pt(II), mainly because of the relativistic effect described in the text

energy of  $d-p$  transitions is very large and only weak absorption bands corresponding to the forbidden  $d-d$  transitions are observed in the visible region. This situation explains the absorption spectra in solution.

In the solid, the distance between the M(II) ions is very small. The positive charges located on the  $z$  axis of the planar complex cause an energy decrease in the vacant  $p_z$  and  $s$  orbitals, although the energy levels of the  $p_x$  and  $p_y$  orbitals are little influenced by the adjacent M(II). Therefore, the specific absorption band observed in the solid is assigned to the allowed ( $z$ - and  $x,y$ -polarised)  $d-p_z$  transitions; the  $d-s$  transition is Laporte forbidden.

When external pressure is applied to the solid specimen, the effect of the positive charge on the vacant  $p_z$  and  $s$  orbitals increases: as the distance between two M(II) ions decreases, the energy level of the vacant  $p_z$  orbital continuously decreases until a point where the vacant  $p_z$  orbital and the

occupied  $d_{z^2}$  orbital on the adjacent M(II) ions start to overlap. Further compression of the solid then leads to an increase of the  $p_z$  energy level and induces a blue shift of the absorption band. As the principal quantum number increases, it is expected that the corresponding  $s$ ,  $p$  and  $d$  orbitals gradually expand. However, such a tendency does not apply to the  $6s$  orbital of the third-row transition metals.

The larger relativistic effect for the third-row transition elements causes a contraction of the  $6s$  orbital and the  $5d$  and  $6p$  orbitals become relatively higher in energy than is expected for these elements. Therefore, it seems that for  $M = Pt$ , the overlap of the vacant  $6p_z$  orbital and the occupied  $5d_{z^2}$  orbital on adjacent M(II) ions takes place at a rather low pressure. The pressure broadening of the absorption bands was explained by delocalisation of the electron density from  $A_{1g}$  and  $E_g$  in the one-dimensional metallic lattice. A similar pressure

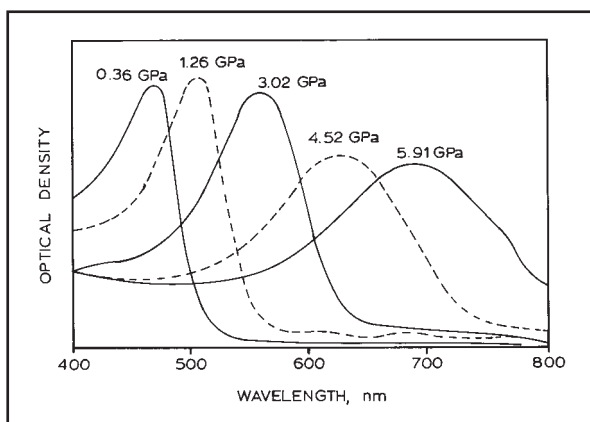


Fig. 3 The absorption spectra of  $[Pd(niox)_2]$  at various pressures (18)

dependence of the absorption spectra was observed for the Ni(II) and Pd(II) complexes with 1,2-cyclohexanedione dioximate ( $L^2: niox^-$ ).

A series of studies, including measurements of the electrical conductivity at very high pressures (up to 14 GPa), was carried out for the complex dimethylglyoximatoplatinum(II) (16, 17). Powder X-ray diffraction at elevated pressures revealed that the Pt–Pt distance continuously decreased by ca. 17% up to 14 GPa. A levelling-off in resistivity with pressure was observed at ca. 6.5 GPa. This was attributed to the phase transition from the one-dimensional “metal” to the “semiconductor.” Most interesting results were reported for the shift of the UV-vis bands at very high pressures: the MLCT (metal to ligand charge transfer) band that appeared at the 320 nm region at ambient pressure was observed at ca. 500 nm at 9 GPa. It seems that the large red shift of the MLCT band is related to the “metal” to “semiconductor” phase transition.

An extension of these studies appeared in this Journal in 1987 (18). The  $d_{z^2}(a_{1g}) \rightarrow p_z(a_{2u})$  absorption in the  $Pd^{II}(niox)_2$  complex exhibited a large pressure dependence. Accordingly, the colour of this complex changed from yellow orange (0.8–1.4 GPa) to red (1.4–2.3), to purple (2–3), to blue (2.7–5.5), to yellow green (5.5–6.5), and to pale yellow (above 7 GPa), see Figure 3 (18).

It has been suggested that the use of this piezochromism would enable us to monitor pressure *in situ*, although further investigations concerning the relationship between the thickness

of the specimen and the observed colours under each pressure may have to be carried out.

## Mixed-Valent Pd(II)/Pd(IV) Complexes

Pressure effects on the conductivity of crystals and powders of various platinum compounds have been investigated in relation to the electronic interactions between two metal sites through bridging ligands. Pt and Pd complexes with  $d^8$  electronic configuration normally prefer square-planar coordination geometry, while metal ions with  $d^7$  and  $d^6$  electronic configuration prefer octahedral 6-coordination. Although early studies of 1-electron oxidised M(II) complexes,  $MAX_3$  ( $M = Pt$  or  $Pd$ ;  $A = (NH_3)_2$ ;  $X = Cl^-, Br^-,$  or  $I^-$ ) suggested the existence of M(III) species (19), later structural analyses revealed that these complexes are mixtures of square-planar M(II) and octahedral M(IV) complexes with chains:  $[---M(II)-X-M(IV)-X---M(II)---]$  in the crystals (20, 21). These complexes are diamagnetic and have been classified as “Class II compounds”, according to the criteria of Robin and Day (22). The observed absorption bands for these compounds are therefore superpositions of the individual absorption bands for M(II) and M(IV) complexes with a M(II) to M(IV) inter-valence transfer (IT) band in the visible region. The intensity of the latter IT bands is high and these compounds are highly coloured.

Interrante and colleagues investigated the possibility of a spectral shift and a change in conductivity upon compression of the crystals along the  $---M(II)-X-M(IV)-X---$  axis for various  $MAX_3$  complexes:

- $[M^{II}(NH_3)_2X_2][M^{IV}(NH_3)_2X_4]$  for Pd and Pt with  $X = Cl^-, Br^-$ ;
- $[M^{II}(en)X_2][M^{IV}(en)X_4]$  for  $M = Pt$ ,  $X = Cl^-$  and  $Br^-$  ( $en = ethylenediamine$ ); and
- $[M^{II}(C_2H_5NH_2)_4][M^{IV}(C_2H_5NH_2)_4X_2]X_4 \cdot 4H_2O$  for  $M = Pt$ ,  $X = Cl^-$  and  $Br^-$  (23). No irreversible phase change with pressure was observed, except in the case of  $[Pt(C_2H_5NH_2)_4]Br_3 \cdot 2H_2O$ . The X-ray powder diffraction pattern for each complex was

examined at ambient pressure and at ca. 60 kbar.

For  $\text{Pd}(\text{NH}_3)_2\text{Cl}_3$ , isotropic compression in all three directions of the orthorhombic unit cell was observed, including compression along the intra-chain  $\text{Pd}(\text{II})\text{---Cl---Pd}(\text{IV})$  distance. Observation of the absorption spectra revealed that the IT band was very strong for most of the complexes, even at ambient pressure, and measurement became impossible at elevated pressures.

An exceptional result was obtained for complex  $\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  where an absorption change with pressure in the UV-vis region was observed. The absorption maximum at  $16,000\text{ cm}^{-1}$  at ambient pressure for a single crystal (consistent with the previously reported absorption band corresponding to the  $\text{M}(\text{II})$  to  $\text{M}(\text{IV})$  inter-valence transition) shifted towards longer wavelengths at ca. 30 kbar. This shift in the IT band indicates that the compression along the  $\text{M}(\text{II})\text{---X---M}(\text{IV})\text{---X---}$  axis is due to the applied pressure.

The conductivities of these complexes at ambient temperature reversibly increased with pressure. The plot of the logarithmic value of the conductivity ( $\text{ohm}^{-1}\text{ cm}^{-1}$ ) against the reciprocal temperature at each pressure was linear. The activation barrier for the change in conductance was plotted against pressure, see Figure 4. The activation barrier was initially found to decrease with pressure up to ca. 106 kbar and then to begin to increase with pressure. However, no phase transition to the metallic state was observed, even at 140 kbar. The inhibition of this phase transition may be caused by the increase in the activation barrier at pressures higher than 106 kbar. Therefore, it was not possible to achieve the Class III state (where a complete electronic delocalisation occurs, according to the Robin and Day definition (22)) for this complex even at very high pressures. The  $\text{Pd}(\text{II})\text{---Cl}$  and  $\text{Pd}(\text{IV})\text{---Cl}$  distances have been reported as 322 pm and 199 pm, respectively, at ambient pressure. As compression of the  $\text{Pd}(\text{IV})\text{---Cl}$  distance is difficult, compression of the  $\text{Pd}(\text{II})\text{---Pd}(\text{IV})$  distance by ca. 35 pm at 60 kbar may be attributed to the decrease in the  $\text{Pd}(\text{II})\text{---Cl}$  distance. However, such a change in the  $\text{Pd}(\text{II})\text{---Cl}$  distance is still too small for the transition to the

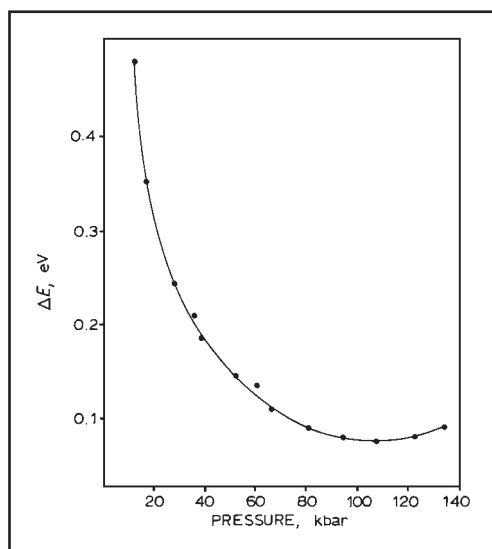


Fig. 4  $\Delta E$  as a function of pressure for  $[\text{Pd}(\text{NH}_3)_2\text{Br}_3]$ . From L. V. Interrante, K. W. Browall and F. P. Bundy, *Inorg. Chem.*, 1974, 13, 1158  
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Class III state, where the Cl atom is expected to sit between a  $\text{Pd}(\text{II})$  and a  $\text{Pd}(\text{IV})$  ion.

A more recent analysis of the complex  $[\text{Pd}(\text{chxn})_2][\text{Pd}(\text{chxn})_2\text{Br}_2]\text{Br}_4$  ( $L^3$ :  $\text{chxn} = 1R,2R$ -cyclohexanediamine) indicates that  $\text{Pd}(\text{II})$  and  $\text{Pd}(\text{IV})$  in the one-dimensional chain are energetically close and produce  $10^{-3}$  of paramagnetic  $\text{Pd}(\text{III})$  (24). Moreover, this mixed-valence palladium complex, which is dark brown at ambient pressure, turns light green upon exposure to  $\text{Br}_2$ : an uptake of two  $\text{Br}_2$  molecules to each  $[\text{Pd}(\text{chxn})_2][\text{Pd}(\text{chxn})_2\text{Br}_2]$  (25). This process induced the oxidation of  $\text{Pd}(\text{III})$  to  $\text{Pd}(\text{IV})$ .

Electronic conduction in solid samples generally takes place through:

- [1] the direct interaction of the  $d_{z^2}$  orbitals via bridged ligands as seen in  $\text{MgCl}_3$  and/or through
- [2] the interaction of  $\pi$  orbitals as found in tetra-benzoporphyrin (26).

In the former case, the application of external pressures may strengthen the interactions between  $d_{z^2}$  orbitals by axial compression: the phase transition to achieve the ultimate electronic delocalisation may be expected to occur. In the latter case, the ultimate state/condition for this type of interaction is as “organic metal”, such as the

TCNQ-TTF (tetracyanoquinodimethane-tetrathiafulvalene).

A mixed-valence palladium complex with a conjugated planar macrocyclic ligand, tetrabenzobenzene- $[b,f,j,\eta]-1,5,9,13$ -tetraazacyclohexadecine ( $L^4$ : TAAB), was examined at elevated pressures (27). The mixed-valence complex was prepared by the partial oxidation of the corresponding Pd(II) complex by  $I_2$ . Powder and crystalline samples of the resulting  $[\text{Pd}(\text{TAAB})]^{2.7+}(\text{I}_3^-)_{2.7}$  was examined by IR and Raman spectroscopic methods. It was revealed that the  $\text{I}_3^-$  anion exists as a linear unit in the crystal, based on the selection rules. Although X-ray analysis was not carried out for this mixed-valence complex, it was concluded that the  $\text{I}_3^-$  ion is located in space with little perturbation from the neighbouring group. Therefore, this mixed-valence complex does not have a one-dimensional chain structure. The mixed-valence complex is dark red and this colour may relate to the ML/LMCT band. The conductivity of the complex increased from  $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  at ambient pressure to  $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 10 kbar. The conductivity of solid  $[\text{Pd}^{\text{II}}(\text{TAAB})]^{2+}$  was  $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  at ambient pressure and was independent of pressure. Moreover, the spectra of the mixed-valence complex hardly changed with pressure. Therefore, the small pressure-dependent conductivity of this mixed-valence complex was attributed to the crystal packing effect.

### Pressure Effects on Emission Spectra, Emission Intensities and Lifetimes of Excited Pd(II) Complexes

One of the most intensively studied Pd(II) complexes in the last decade is  $[\text{Pd}^{\text{II}}\text{L}_4]^{2+}$  ( $\text{L} = \text{SCN}^-$  or  $\text{SeCN}^-$ ). The  $\text{XCN}^-$  ligands are ambidentate and may coordinate through X or N, depending on the polarisability of the central metal ion. Crystal structures of the  $[\text{Pd}(\text{XCN})_4]^{2-}$  fragments have  $D_{4h}$  symmetry; the average Pd–S and Pd–Se distances are 2.33 and 2.44 Å, respectively, and the M–X–C angles were  $109^\circ$  and  $105$ – $107^\circ$  for the tetra-*n*-butylammonium salt of the  $\text{SCN}^-$  and  $\text{SeCN}^-$  complexes, respectively (28).

Rhode and coworkers (28) also reported normal coordinate analyses for these complexes. The force

constants for Pd–S and Pd–Se were ca.  $1.17 \text{ mdyn } \text{Å}^{-1}$ , which is significantly smaller than those for the corresponding Pt(II) complexes: Pt–S is  $1.44 \text{ mdyn } \text{Å}^{-1}$  and Pt–Se is  $1.42 \text{ mdyn } \text{Å}^{-1}$ . The  $a_{1g}$  totally symmetric vibrations of the Pd–S and Pd–Se bonds were  $274$ – $303 \text{ cm}^{-1}$  and  $180$ – $195 \text{ cm}^{-1}$ , respectively, while  $b_{1g}$  non-totally symmetric stretching and  $b_{2g}$  non-totally symmetric bending modes were observed at  $260$ – $290$  and  $170$ – $187 \text{ cm}^{-1}$  for Pd–SCN, and at  $140$ – $150$  and  $100$ – $110 \text{ cm}^{-1}$  for Pd–SeCN complexes, respectively. The ground-state electronic configuration for these complexes is:  $a_{1g}(\text{d}_{z^2})^2 b_{2g}(\text{d}_{xy})^2 e_g(\text{d}_{xz}, \text{d}_{yz})^4 b_{1g}(\text{d}_{x^2-y^2})^0$  (29) and one-electron excitation from the  $e_g$  orbital to the  $\sigma$  antibonding  $b_{1g}$  orbital creates degenerate  $^3E_g$  and  $^1E_g$  excited states. The electron occupancy of the  $\sigma$  antibonding  $b_{1g}$  orbital induces totally symmetric ( $a_{1g}$ ) elongation of all Pd–X bonds, while the doubly degenerate electronic excited states cause Jahn-Teller distortion – that is, elongation/contraction along one diagonal X–Pd–X axis takes place.

The luminescence bands for these complexes are broad, indicating that the potential energy minimum of the lowest excited  $^3E_g$  state is coupled strongly with the Pd–X vibration modes. At ambient temperature, the emission centred at ca.  $12,500 \text{ cm}^{-1}$  is almost unobservable, however the intensities as well as the emission lifetime increase with decreasing temperature. Therefore, effective participation of the non-radiative decay mechanism exists at relatively high temperatures. Furthermore, the low temperature emission spectra of these complexes exhibit well-resolved vibronic structures ( $< 50 \text{ K}$ ).

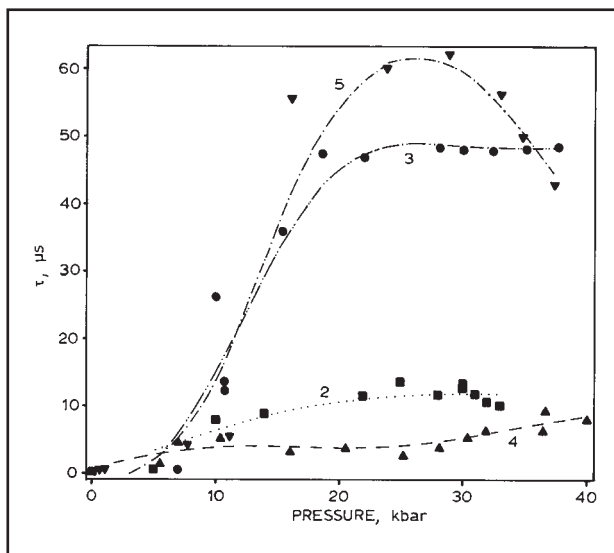
Reber and coworkers examined the pressure effects on the d-d luminescence spectra of these Pd(II)–XCN and Pt(II)–XCN complexes ( $\text{X} = \text{S}$  and  $\text{Se}$ ) up to 40 kbar (30). The intensity of the luminescence increased with pressure for all the complexes. The peak position steadily blue-shifted with pressure:  $24$ ,  $12$ ,  $29$  and  $25 \text{ cm}^{-1} \text{ kbar}^{-1}$  for Pt–SCN, Pd–SCN, Pt–SeCN and Pd–SeCN, respectively. However, such a blue-shift may not be explained by the axial metal–metal interactions that  $[\text{Pt}(\text{CN})_4]^{2-}$  exhibits. Indeed, the metal–metal distance in the crystals of these complexes (ca.

Fig. 5 Pressure-dependent luminescence lifetimes:

- (a)  $[\text{Pt}(\text{SCN})_4](n\text{-Bu}_4\text{N})_2$  2  
 (b)  $[\text{Pd}(\text{SCN})_4](n\text{-Bu}_4\text{N})_2$  3  
 (c)  $[\text{Pt}(\text{SeCN})_4](n\text{-Bu}_4\text{N})_2$  4  
 (d)  $[\text{Pd}(\text{SeCN})_4](n\text{-Bu}_4\text{N})_2$  5

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13 Å) are much longer than in the tetracyanoplatinate complex (ca. 3.1–3.7 Å) (28).

In  $[\text{Pd}(\text{XCN})_4]^{2-}$  and  $[\text{Pt}(\text{XCN})_4]^{2-}$  the pressure dependence of the luminescence intensities and lifetimes was attributed to the loss of the inversion centres caused by the applied pressure: the probability of the d-d transition increases with the decreasing centrosymmetry of the complex (11). It was shown that the participation of the slow  $b_{2g}$  bending motion coupled with the intermolecular forces induced by the external pressure also contributes to the enhanced intensities of the emission spectra. Such a distortion of the excited state explains the spectral shifts: the bending motion inherent in these complexes may reduce the  $p\pi$ - $d\pi$  interactions between the HOMO ( $e_g$  orbitals) and ligand  $n\pi$  orbital and cause a blue shift of the luminescence bands with pressure. This distortion also enhances the luminescence lifetimes by contributing to the loss of centrosymmetry in the chromophore. No enhancement of the luminescence intensity was observed for  $\text{K}_2[\text{PtBr}_4]$  in which pressure-induced coupling of the  $b_{2g}$  bending mode is not expected.

The luminescence lifetimes of the  $[\text{Pd}(\text{XCN})_4]^{2-}$  complexes were significantly enhanced with pressure: 62 μs and 48 μs at ca. 30 kbar, and 4 μs and 541 ns at 7 kbar, for X = Se and S, respectively, see Figure 5. By contrast, the lifetimes for the corre-

sponding Pt complexes were not enhanced much: 6 μs and 13 μs at ca. 30 kbar, and 2 μs and 750 ns at 5 kbar, for X = Se and S, respectively. The radiation lifetime is expected to decrease when the d-d transition becomes more allowed by the loss of centrosymmetry with pressure. Therefore, the enhanced luminescence lifetimes observed for these complexes indicate the significant decrease in the rate of the non-radiative process with pressure. The validity of this was verified by the use of Englman-Jortner's radiationless decay theory (31).

## Conclusions

In this short review topics concerning piezochromism and related phenomena in solid palladium complexes have been summarised. The data may help towards finding use for these metal complexes, such as for *in situ* pressure sensors or as conductors in extreme environments.

## Acknowledgement

The authors wish to pay their respects to the late Professor Harry G. Drickamer, the pioneer of this research field.

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#### The Authors

Hideo D. Takagi (right) has been an Associate Professor of Inorganic Chemistry at the Research Center for Materials Science, Nagoya University since 2002. His research areas are: synthetic and physical inorganic chemistry, structure/reactivity relations of metal complexes, and inorganic reactions in solution at elevated pressures. He graduated from Tokyo Institute of Technology in 1978 and received his Ph.D. (Nuclear Engineering) from there in 1983. From 1981 to 1982 he was an Exchange Student at the Department of Chemistry, University of East Anglia, U.K., under the supervision of Dr R. D. Cannon. From 1983 to 1985 he was an Instructor at the College of Industrial Technology, Nihon University, and from 1985 to 1992 he was a Post Doctoral Fellow and Research Associate in the Department of Chemistry at the University of Calgary in Canada with Prof. T. W. Swaddle. From 1992 to 2002 he was Associate Professor of Chemistry, Department of Chemistry, Nagoya University.



Kyoko Noda is a Ph.D. student in the Graduate School of Science, Nagoya University. Her research includes syntheses, structural analyses and reactions of metal complexes with novel hybrid ligands having phosphorus as the donating atoms.

Sumitaka Itoh is a Ph.D. student in the Graduate School of Science, Nagoya University. His research involves gated electron transfer reactions at elevated pressures.



Satoshi Iwatsuki is a Post Doctoral Fellow in the Department of Chemistry, Waseda University, (21COE "Practical Nano-Chemistry" from MEXT). His research involves the catalytic reactions of binuclear Pt(III) complexes at elevated pressures. He graduated from the Department of Chemistry, Nagoya University (1997) and obtained his Ph.D. in chemistry in 2003 from the Graduate School of Science, Nagoya University.

