Pressure Sensitive Palladium Complex

By Ichimin Shirotani

Applied Science for Energy, Muroran Institute of Technology, Mizumoto, Muroran-shi, Japan

The complex bis(1,2-cyclohexanedionedioximato)palladium(II) has been prepared and its absorption spectra examined. The preliminary results, which are reported here, show that the colours of thin films of this complex are a function of the applied pressure, a property which may find application as an indicator of pressure and pressure distributions up to perhaps seventy thousand atmospheres.

The development of diamond-anvil pressure cells enables the effect of pressure on various materials to be observed, in situ, visually. This is especially important for the study of polymorphs and crystal growth. Quantitative pressure measurement in a diamond-anvil cell has been carried out by Barnett, Block and Piermarini using ruby as a pressure sensor (1). The pressure is determined by measuring the pressure shift in the sharp R-line fluorescence spectrum of ruby. The pressure shift of an optical absorption band in bis(dimethylglyoximato)nickel(II), $Ni(dmg)_2$, had already been studied as one approach to pressure measurement in the cell (2).

Various d^8 square complexes are formed when Ni^{2+}, Pd^{2+} and Pt^{2+} react with 1,2-dionedioximes such as dimethylglyoxime. The complexes are chemically stable, and have various colours at atmospheric pressure. The effect of pressure on the absorption spectra of these complexes has already been studied (3,4,5). The absorption bands show a large red shift with increasing pressure. The colours of the complexes change with pressure shifts of spectra. For example, the colour of $Ni(dmg)_2$ which is initially red turns to green at pressures around 1.7 GPa. It would be convenient if a semiquantitative value of pressure could be determined visually from a change in the colour

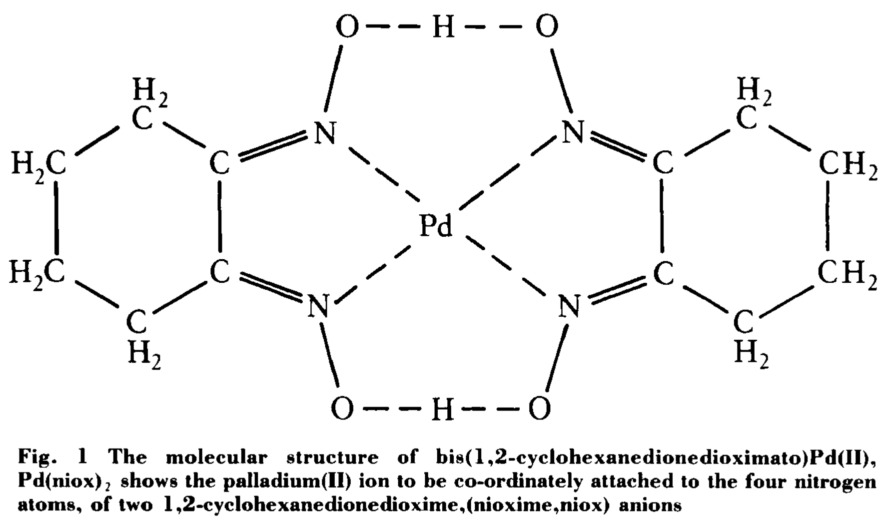

Fig. 1 The molecular structure of bis(1,2-cyclohexanedionedioximato)Pd(II), $Pd(niox)_2$ shows the palladium(II) ion to be co-ordinately attached to the four nitrogen atoms, of two 1,2-cyclohexanedionedioxime,(nioxime,niox) anions

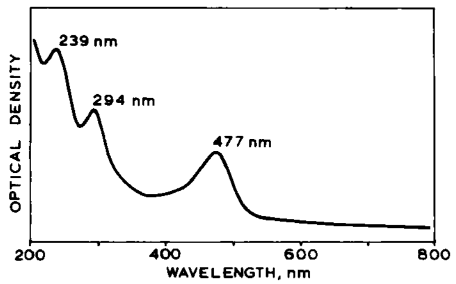

Fig. 2 The absorption spectrum of a 1000Å thin film of $Pd(niox)_2$ at atmospheric pressure is shown

of a material with change in pressure.

Bis (1,2-cyclohexanedionedioximato) Pd(II), $Pd(niox)_2$, may be an excellent pressure indicator in the range 0 to 8 GPa. The complex turns from yellow to orange and then to successive colours in the visible spectrum with increasing pressure. In this article we report preliminary results for colours and absorption spectra in this complex at high pressures.

The molecular structure of $Pd(niox)_2$ is illustrated in Figure 1. A palladium(II) ion is coordinated to the four nitrogen atoms of two 1,2-cyclohexanedionedioxime(nioxime, niox) anions. The square planar complex molecules stack face to face in parallel columns, linking the metal ions in extended linear chains throughout the crystal lattice.

$Pd(niox)_2$ was prepared from a hot aqueous solution of K_2PdCl_4 and a hot alcoholic solution of nioxime(1,2-cyclohexanedionedioxime). The diamond-anvil pressure cell was used for the study of optical properties in the complex at high pressures; the optical system consisted of a standard microscope and a monochrometer with an associated photodetection system. The pressure was measured by means of the pressure shift of the sharp R-line fluorescence spectrum of ruby. Water was used as the pressure transmitting medium.

The absorption spectrum of an evaporated thin film of $Pd(niox)_2$ at atmospheric pressure is shown in Figure 2. This spectrum is similar to that of bis(dimethylglyoximato)Pd(II), $Pd(dmg)_2$, which has already been determined by Ohashi, Hanazaki and Nagakura (6). The band at 294 nm in $Pd(niox)_2$ may be ascribed to a metal to ligand charge transfer transition; on the other hand the band at 477 nm is assigned to the $4d_{z^2}$-$5p_z$ transition. Figure 3 exhibits the absorption spectra of $Pd(niox)_2$ in the visible region at high pressures. The absorption band always showed a large red shift with increasing pressure. Visual observation of the sample in the diamond-anvil cell indicated that with increasing pressure the colour of $Pd(niox)_2$ turned from yellow to orange (at 0.8 to 1.4 GPa), to red (at 1.4 to 2.3 GPa), to purple (at 2 to 3 GPa), to blue (at 2.7 to 5.5 GPa), to

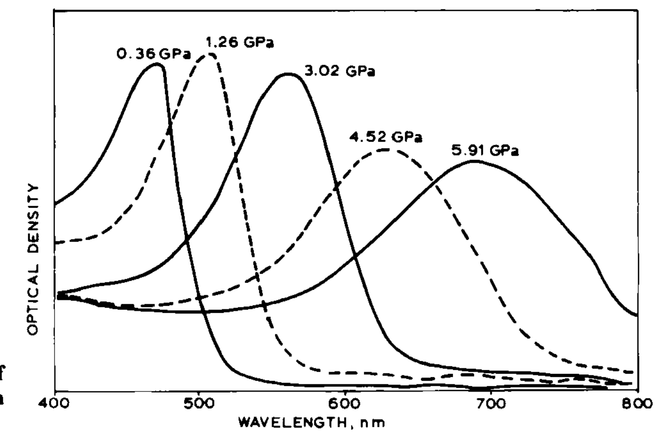

Fig. 3 Absorption spectra of $Pd(niox)_2$ at various high pressures are shown

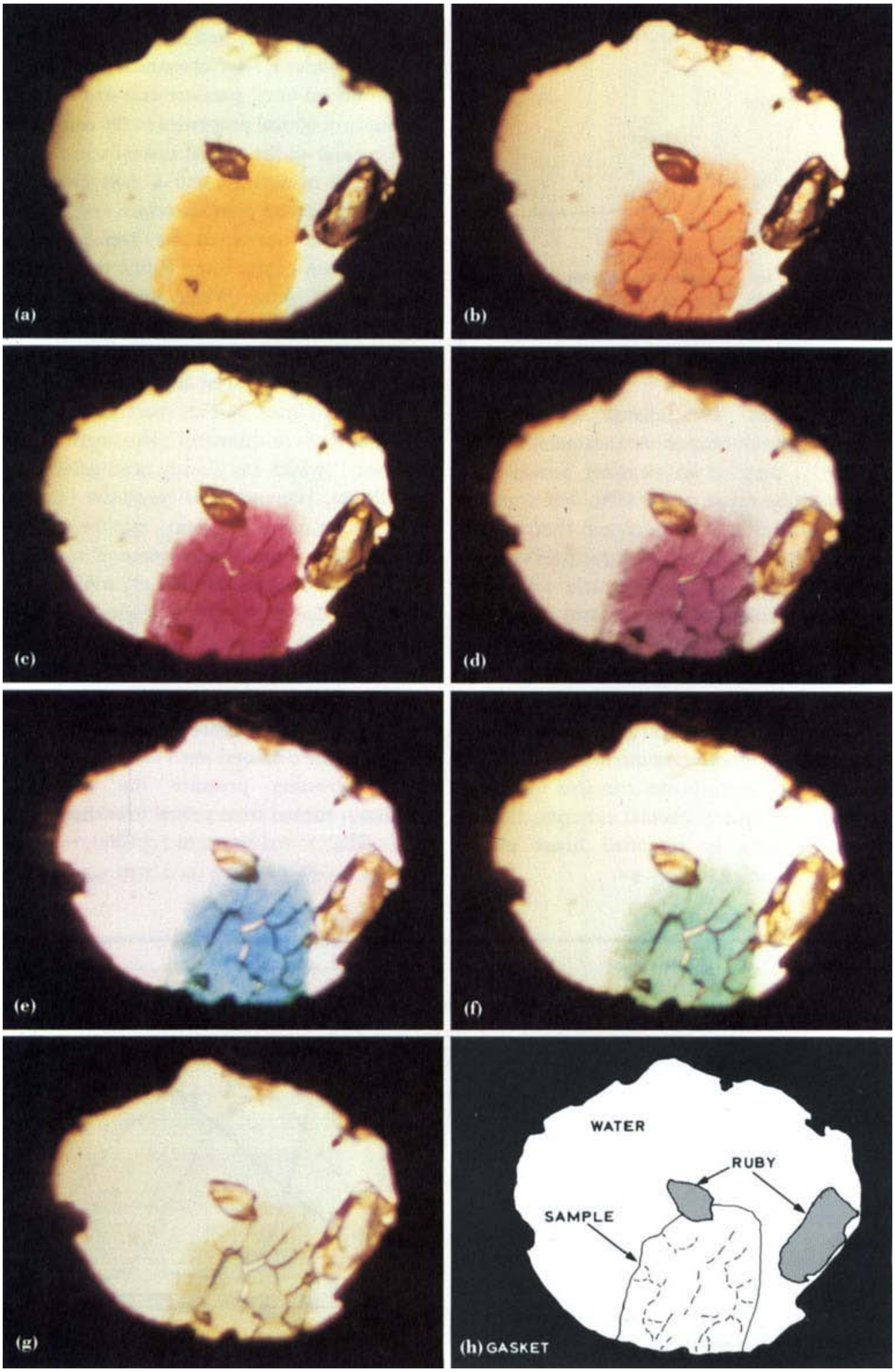
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h) GASKET
WATER
RUBY
SAMPLE

Fig. 4 The series of photographs on the facing page shows the colour of a thin film of Pd(niox)$_2$ at various pressures between 0.2 and 10 GPa: (a) 0.2 GPa, (b) 1 GPa, (c) 2 GPa, (d) 3 GPa, (e) 4 GPa, (f) 6 GPa and (g) 10 GPa; the line drawing identifying the position of the palladium complex and the two reference rubies. The aperture in the gasket measures 0.3 mm from side to side

yellow green (at 5.5 to 6.5 GPa), and to pale yellow (above 7 GPa) with increasing pressure. The variation in the colour of Pd(niox)$_2$ with pressure can be interpreted to show that the absorption band which is ascribed to $4d_{z^2}$-$5p_z$ shifted toward longer wavelength at high pressures.

The relationship between the colour and the pressure is only the preliminary results of our work. The pressure ranges of the colours have not yet been determined in detail. The thickness of our sample is about 1000Å. It should be noted that the tone of a colour depends on a number of factors including thickness of the sample, the pressure transmitting medium and the pressure distribution. If the relationship between colour and pressure is studied in detail, a semiquantitative value of pressure could be obtained from the visual observation of the change in colour with pressure by a colorimetric method similar to pH testing paper. Furthermore, the pressure gradient in a high pressure cell can be directly observed in situ.

Acknowledgement

The present work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Fig. 5 A pressure gradient produced under non-hydrostatic conditions is displayed visually by the change in the colour of the sample: centre (green) about 6 GPa, middle (red) about 2 GPa, outside (yellow) 0–1 GPa

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Anti-Cancer Platinum Compounds

The platinum compound Cisplatin is now widely used for the treatment of specific cancers. However a number of adverse side effects are associated with its use, and since the late 1970s attention has been focused on the identification of other platinum drugs having less toxicity but with at least equivalent clinical activity.

This work has made significant progress and a review of the work carried out between the discovery of the anti-tumour activity of Cisplatin by B. Rosenberg and L. Van Camp in 1969 and the launch of Carboplatin, a second generation platinum drug, has recently been prepared by staff at the Johnson Matthey Technology Centre ("Second Generation Anti-cancer Platinum Compounds", C. F. J. Barnard, M. J. Cleare and P. C. Hydes, *Chem. Brit.*, 1986, **22**, (11), 1001–1004).

Current work is concentrating on Carboplatin and on Iproplatin, another second generation drug. Particular attention is being paid to the use of these platinum drugs in combination with radiotherapy, and to varying the mode of administration to increase their effectiveness. At the same time the search for third generation platinum complexes with higher anti-tumour activity continues.