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Note

Pressure and concentration dependent formation of oligomers of tetrakis-(p-methylphenylisocyanide)rhodium(I)

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Abstract

The optical absorption of $[Rh(tol)_4]PF_6$ (tol p-methylphenylisocyanide) dissolved in acetonitrile has been measured as function of concentration ($10^{-4} \leqslant c_0 \leqslant 1.5 \times 10^{-2}$ mol/l) and of applied pressure ($0.1 \leqslant p \leqslant 400$ MPa) at room temperature. Analysis of the spectra indicates the formation of oligomers $[Rh(tol)_4]_n^{n+}$, $n = 2,3$, with increase of both the concentration and the pressure, respectively. Application of pressure increases the dimer–monomer equilibrium constant and yields a blue shift (≈ 0.3 cm^{-1}/MPa) of the monomer absorption but a red shift (≈ -0.6 cm^{-1}/MPa) of the dimer absorption.

Key words Rhodium complexes, Isocyanide complexes; Oligomer formation; Spectroscopic studies

Introduction

The absorption spectra of many transition metal complexes with planar molecular structures exhibit different electronic transitions in the crystalline state compared to the dilute solution [1]. These changes are particularly distinct, when the coupling between the complexes in the crystalline state is strong. An example is given by the tetracyanoplatinates(II). These exhibit a strong inter-complex coupling for Pt–Pt distances of even more than 3.7 Å leading to distinct spectroscopic effects [2]. With increasing concentration it is expected that in solution complexes with planar structures form oligomers as a first step of crystallization. A corresponding oligomerization should also occur by application of high pressure by inducing a change of the equilibrium constant between monomers and oligomers. In the case of an inter-complex interaction the optical properties of the oligomers differ from those of the monomers. Consequently, it should be possible to study the formation of oligomers by optical spectroscopy. In this paper we investigate the optical absorption of $[Rh(tol)_4]PF_6$ (tol: p-methylphenylisocyanide) in solution as a function of the concentration and high pressure.

Experimental

The title compound was prepared according to the procedure described in ref 3. *Anal.* Calc. for $[Rh(tol)_4]PF_6$: C, 53.65; N, 7.82; H, 3.94. Found: C, 53.54; N, 7.83; H, 4.04%. CH_3CN (Merck; uvasol) was used as solvent.

The absorption spectra at ambient pressure were recorded with an Uvikon spectrophotometer (Kontron). The high pressure cell consisted of a thick-wall cylinder with Poulter type windows. The pressure was generated and measured by a standard hydraulic oil system (Cobold) [4, 5]. The absorption spectra were recorded as single beam spectra The transmitted light was analyzed by a Codberg monochromator and was detected by a photomultiplier (Hamamatsu, R446UR, cooled to −25 °C by a Joule-Thomson cooling system, Seefelder Messtechnik). The intensities $I(\lambda)$ and $I_0(\lambda)$ were successively registered and stored on a computer. The absorbance $\log[I_0(\lambda)/I(\lambda)]$ was calculated using as reference the intensity $I_0(\lambda)$ of pure CH_3CN in the high pressure cell at ambient pressure. Due to the intensity profile of the radiation source (wolfram lamp) this absorption spectrometer could be used only for $\lambda \geqslant 400$ nm. All spectra at increased pressure were corrected using the compressibility factors of CH_3CN [6].

Results and discussion

Concentration dependence

The absorption spectra taken at ambient pressure of $[Rh(tol)_4]PF_6$ dissolved in acetonitrile depend strongly on the concentration (Fig. 1). At low concentrations ($c_0 \leqslant 10^{-4}$ mol/l) the absorption spectrum exhibits below 23 000 cm^{-1} only one clearly measurable peak (band I at 21 690 cm^{-1}). With increasing concentration two additional bands occur (band II at 17 800 cm^{-1} and band III at 14 280 cm^{-1}). None of the three absorption bands follow the Lambert–Beer law. For example, the increase of the absorbance of band I is distinctly smaller than expected for a given increase of the formal concentration c_0 of the complex. This

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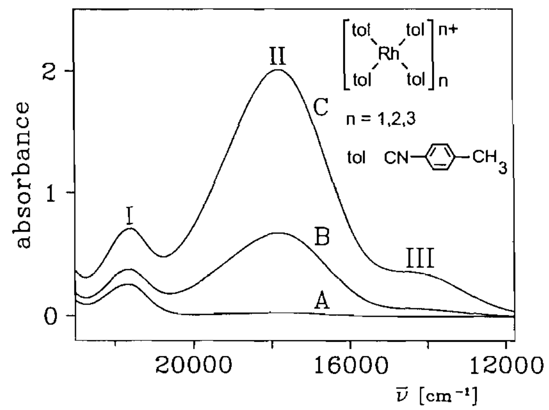

Fig. 1 Absorption spectra of $[Rh(tol)_4]PF_6$ dissolved in acetonitrile ($p = 0.1$ MPa, $T = 298$ K) A $c_0 = 3\times10^{-4}$ mol/l, path length 1 cm, B: $c_0 = 5\times10^{-3}$ mol/l, path length 0.1 cm, C. $c_0 = 1.5\times10^{-2}$ mol/l, path length 0.1 cm

behavior indicates an oligomerization of the rhodium complexes with increasing concentration.

A similar investigation was reported by Mann *et al.* [7], who examined $[Rh(CNPh)_4]PF_6$ (CNPh: phenylisocyanide). The assignment given for this related compound fits also to $[Rh(tol)_4]_n^{n+}$, $n = 1, 2, 3$. In particular, band I belongs to a monomer while bands II and III are assigned to dimers and trimers, respectively. The occurrence of the dimer and trimer bands at lower energies than the monomer band is explained by the metal–metal interaction, which leads to a destabilization of the $4d_{z^2}$HOMO and to a stabilization of the $5p_z$, π^* (tol)LUMO (z: Rh–Rh axis). With increasing number of interacting complexes the energy difference between HOMO and LUMO becomes smaller [1, 2, 7, 8]

The equilibrium conditions of monomers $M = [Rh(tol)_4]_1{}^+$, dimers $D = [Rh(tol)_4]_2{}^{2+}$ and trimers $T = [Rh(tol)_4]_3{}^{3+}$ are given by the following relations:

$$2M \overset{K_1}{\rightleftharpoons} D \qquad (1)$$

$$D + M \overset{K_2}{\rightleftharpoons} T \qquad (2)$$

By using the method of Mann *et al.* [7] and Lechner and Gliemann [8] we obtained the ϵ values of the dimers (ϵ_D) and trimers (ϵ_T) and the equilibrium constants K_1 and K_2 at ambient pressure as follows: $\epsilon_D = (9000 \pm 700)$ l (mol cm)$^{-1}$, $K_1 = (53 \pm 7)$ l/mol, $\epsilon_T K_2 = (2.43 \pm 0.34)10^5$ (l/mol)^2 cm^{-1}. Approximating $\epsilon_T \approx \frac{3}{2}\epsilon_D$ [7] we estimate $\epsilon_T \approx 13\,500$ l(mol cm)$^{-1}$ and $K_2 \approx 18$ l/mol. For low concentrations ($c_0 \leqslant 10^{-4}$ mol/l), when only band I (monomer) is detected, one directly obtains $\epsilon_M = (850 \pm 50)$ l(mol cm)$^{-1}$. The equilibrium constants determined for $[Rh(CNPh)_4]PF_6$ [7] are smaller ($K_1 \approx 35$ l/mol and $K_2 \approx 10$ l/mol) by about 35% for K_1 and 45% for K_2, respectively. Thus, additional methyl groups in *para*-position to the isocyanide groups of the phenylisocyanide ligands have a distinct effect on the equilibrium constants.

Pressure dependence

The absorption spectra of $[Rh(tol)_4]PF_6$ in CH_3CN ($c_0 = 1.5\times10^{-3}$ mol/l) at different pressures p are shown in Fig. 2. The spectrum at ambient pressure ($p = 0.1$ MPa) exhibits below 23 000 cm^{-1} the monomer band I and the dimer band II. With pressure increase ($p_{max} = 400$ MPa) the absorbance of the dimer band II increases, whereas the one of monomer band I decreases (Figs. 2 and 3). This results from the decreasing concentration of the monomers and the increasing concentration of the dimers. Using the molar extinction coefficients of monomers and dimers at ambient pressure and the experimental absorbances $A_M(p)$ and $A_D(p)$ for monomer and dimer, respectively, one may determine the pressure dependent equilibrium constant for dimer formation according to

$$K_1(p) = \frac{c_D(p)}{c_M^2(p)} = \frac{A_D(p)}{A_M^2(p)}\,\frac{[\epsilon_M(0.1\ \text{MPa})]^2}{\epsilon_D(0.1\ \text{MPa})}\,d \qquad (3)$$

Here, d denotes the path length ($d = 0.83$ cm). As Fig. 4 shows ln K_1 versus pressure may be approximated by a linear plot in the range between 0.1 and 400 MPa. From the slope of the linear fit of $\ln[K_1(p)]$ and using eqn. (4) (e.g. see ref. 9) we calculate a value of $\Delta V^0 = -(4.4 \pm 0.5)$ cm^3/mol.

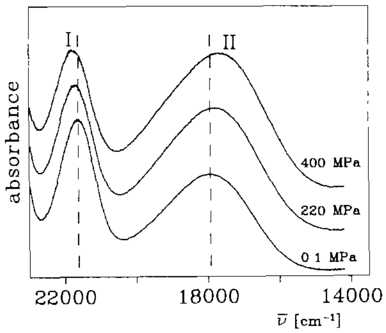

Fig 2 Absorption spectra of $[Rh(tol)_4]PF_6$ dissolved in acetonitrile ($T = 298$ K) at different pressures (100 MPa = 1 kbar), $c_0 = 1.5\times10^{-3}$ mol/l; path length 0.83 cm for all spectra

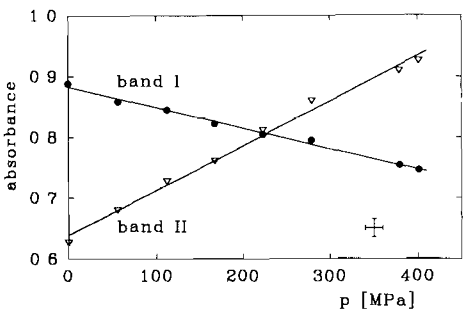

Fig 3. Absorbance of band I (monomer) and band II (dimer) of $[Rh(tol)_4]PF_6$ in acetonitrile ($c_0 = 1.5\times10^{-3}$ mol/l) as a function of pressure; $T = 298$ K, $d = 0.83$ cm

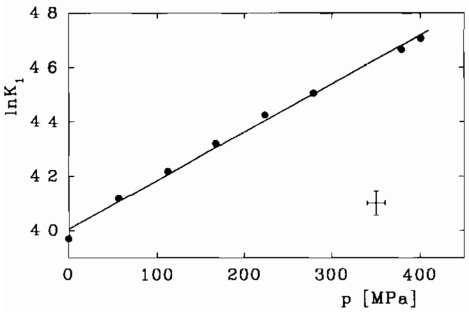

Fig. 4. Logarithm of the dimer–monomer equilibrium constant K_1 of $[Rh(tol)_4]PF_6$ in acetonitrile ($c_0 = 1.5 \times 10^{-3}$ mol/l) as a function of pressure, $T = 298$ K, $d = 0.83$ cm.

$$\left(\frac{\partial \ln K_1}{\partial p}\right)_T = -\frac{\Delta V^0}{RT} \tag{4}$$

This volume change ΔV^0 is associated with the formation of dimers from monomers. Moreover, with increasing pressure, band I (monomer) exhibits a blue shift of $\Delta\bar{\nu}/\Delta p = (0.3 \pm 0.05)$ cm^{-1}/MPa, whereas band II (dimer) shows a red shift of $\Delta\bar{\nu}/\Delta p = -(0.6 \pm 0.1)$ cm^{-1}/MPa (Fig. 2). A blue shift of the monomer band may be explained by interactions of complexes with solvent molecules (e.g. see refs. 8 and 10) while the red shift of the dimer band results from the reduction of the metal–metal distance which leads to a decrease of the HOMO–LUMO energy difference.

Acknowledgements

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References

1 J.W. Schindler, R C Fukuda and A.W. Adamson, *J. Am Chem Soc, 104* (1982) 3596.
2 (a) H Yersin and G Gliemann, *Ann N Y. Acad Sci, 313* (1978) 539; (b) G. Gliemann and H Yersin, *Struct Bonding (Berlin), 62* (1985) 87
3 V M. Miskowski, G L. Nobinger, D.S. Kliger, G S Hammond, N.S. Lewis, K.R. Mann and H B. Gray, *J Am Chem Soc, 100* (1978) 485.
4 W F. Sherman and A.A. Stadtmuller, in *Experimental Techniques in High-Pressure Research*, Wiley, Chichester, UK, 1987
5 H. Englmeier, *Dissertation*, Universitat Regensburg, Germany, 1991
6 R Landau and A. Wurflinger, *Ber Bunsenges Phys. Chem., 84* (1980) 895.
7 K R Mann, N.S Lewis, R.M. Williams, H B Gray and J.G. Gordon II, *Inorg Chem, 17* (1978) 828.
8 A Lechner and G. Gliemann, *J Am Chem Soc, 111* (1989) 7469.
9 G. Wedler, *Lehrbuch der physikalischen Chemie*, VCH, Weinheim, Germany, 1987, p 354.
10 O A. Salman and H.G. Drickamer, *J. Chem. Phys., 77* (1982) 3337.