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Inorganica Chimica Acta 225 (1994) 89–93

Inorganica Chimica Acta

The use of pressure-tuning spectroscopy to distinguish between one- and two-electron transfer processes

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Received 24 February 1994

Abstract

The first use of pressure-tuning spectroscopy as a diagnostic tool in the evaluation of an intervalence transition band to determine the number of electrons transferred is described. The trinuclear complex $[(CN)_5FeCNPt(NH_3)_4NCFe(CN)_5]^{4-}$ was subjected in solution to hydrostatic pressures from ambient to 1.5 kbar giving a $\Delta V^* = -5.7 \pm 0.2$ cm^3 mol^{-1}. Calculated values from various models ranged from -5.6 to -6.7 cm^3 mol^{-1} assuming a one-electron transfer event and a negligible inner-sphere reorganizational energy compared with the apparently very large outer-sphere rearrangements that must occur.

Keywords: Pressure-tuning spectroscopy; Electron transfer; Iron complexes; Platinum complexes; Cyano complexes

1. Introduction

The use of pressure as an experimental variable to study intervalence redox reactions has been limited to only a few systems [1–8]. The first report of such a study was that of Hendrickson and co-workers [4] who attempted to employ pressure-induced freezing of solutions containing the ferrocenium dinuclear or the complex $(bpy)_2ClRu(pyz)RuCl(bpy)_2^{3+}$ in order to observe expected huge shifts of the intervalence-transition (IT) band because of the large changes in static dielectric constants that occur between solvents in the liquid and solid states. Energetically, the formation of the transition state involves two events [9,10], i.e. changes in bond lengths occur in the inner coordination shell of the binuclear itself as the oxidation states of the metals change (called λ_{in}) and rearrangements of solvent and other molecules in solution (called λ_{out}) are necessary to accommodate the new shape and polarity of the binuclear. The total reorganizational energy is given by λ where

$$\lambda = \lambda_{in} + \lambda_{out} \tag{1}$$

Application of the continuum model of solvent properties surrounding the reaction molecule and assuming a hard-spheres model of the two metal centers gives the classical Marcus expression for the outer-sphere term [10].

$$\lambda_{out} = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{2}$$

where Δe is the charge transferred, a_1 and a_2 are the radii of the two reactants, R is the distance between their centers, D_{op} is the optical dielectric constant and D_s is the static dielectric constant of the medium. The failure to observe the predicted large shifts in the energies of IT bands on going from the liquid to the solid state by the pressure-induced freezing technique led Hendrickson and co-workers [4] to conclude that the continuum model is inadequate in accounting for the inner- and outer-sphere energies of the localized intervalence electron transfer processes.

The same group later [7] used pressure tuning spectroscopy (PTS) to examine the Creutz–Taube ion, $[(NH_3)_5RupyzRu(NH_3)_5]^{5+}$, where pyz is pyrazine which is a borderline Class II (localized)/Class III (delocalized) system in the Robin and Day classification [11]. As the pressure was increased from 1 to 7000 bar in liquid D_2O, a small shift of the IT band maximum occurred 35 cm^{-1} to higher energy. Pressures of this magnitude are sufficient to cause compressions in bond lengths. The conclusion of this study, then, which employed extensive PKS calculations was that the degree of electronic coupling between the metal centers was

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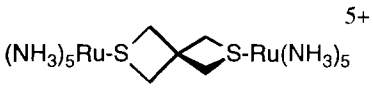
Elsevier Science S.A.
SSDI 0020-1693(94)04034-S

enhanced by these bond compressions and the degree of vibronic coupling changed only slightly.

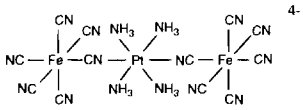
Our group subsequently [1] examined the effect of pressure on the IT band of a very weakly coupled Class I binuclear, complex **I** in which the major mechanism for electron transfer was tunneling. A large red shift



I

of more than 200 cm^{-1} over 1500 bar was observed when this complex was subjected to pressure in D_2O. This unexpected result was interpreted in terms of H bonding interactions between the ruthenium ammine groups and solvent molecules. In contrast to the Creutz–Taube ion, the coupling between the metal centers in the spiro complex is so weak that this renders the electron transfer process very sensitive to subtle changes in the surrounding medium such as ionic strength and salt effects [12]. Ordinarily, under pressure, optical transitions are expected to shift to higher energies since the bulk modulus always increases, i.e. the vibrational and rotational movements of both solute and solvent molecules become increasingly restricted making it more difficult for them to undergo the rearrangements necessary for the transfer of charge. In the case of H bonding interactions, however, the application of moderate pressures initially enhances this process energetically, leading to the apparently anomalous shifts of optical bands to lower energy. It was also demonstrated that recent improvements of the original Marcus theory were quite accurate in the explanation of our experimental results [1].

We now report the first application of PTS to determine whether an intervalence transition (IT) band represents a one- or a two-electron process. Bocarsly and co-workers [13,14] recently reported the first observation of a photo-induced two-electron charge-transfer process based on an intervalence transition (IT) band. The complex they studied was the diiron–platinum trinuclear complex, **II**, which formally may exist either as an Fe(II)Pt(IV)Fe(II) or an Fe(III)Pt(II)Fe(III) system.



II

Electrochemical experiments were interpreted in terms of two non-interacting iron centers and the photochemical experiments were carried out at very low light intensity so that a simultaneous two-electron transfer event was considered unlikely. Bocarsly and co-workers concluded that the IT band arose solely from a one-electron event between the platinum atom and one of the iron centers. Our findings arrive at the same conclusion.

2. Experimental

2.1. Preparations

Complex **II** was prepared according to the published procedure [13]. Formation of the complex is easily achieved as indicated by spectroscopy monitoring, although crystallization is more difficult. All experiments were carried out in water that was house distilled, passed through a Barnstead Nanopure II system and then distilled from alkaline permanganate in an all-glass apparatus.

2.2. Spectral measurements

Fresh solutions of complex **II**, 0.18 mM in concentration, were prepared immediately before use. The spectra were obtained at 25 °C in a Perkin-Elmer Lambda 9 UV–Vis–NIR spectrophotometer interfaced to an IBM PC/XT microcomputer with the slit set in automatic servocontrol. The software for the Lambda 9 instrument was purchased from Softways Inc. High pressure measurements were performed with equipment described in detail previously [1]. In each experiment spectra were taken in 150 bar intervals up to 1.5 kbar. Parallel electronic background correction spectra were run at each pressure and data were checked for both reproducibility and reversibility. The effect of ionic strength on the IT band was tested. Aliquots of solutions of NH_4NO_3 or KNO_3 were added to solutions of complex **II** at different concentrations up to $I = 0.5$ M. No changes in the position of the band energy were observed.

3. Results and discussion

Upon application of hydrostatic pressure from ambient to 1.5 kbar to complex **II** in H_2O, we observed that a symmetrical shift of 184 ± 6 cm^{-1}/kbar to higher energy occurred with no detectable changes in the bandwidth or oscillator strength (see Fig. 1). This is an enormous change compared with the values of less than 5 cm^{-1}/kbar obtained by Drickamer and co-workers for the Creutz–Taube ion [7], $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$, in D_2O or their value of 73 cm^{-1}/kbar observed for the complex $[(bpy)_2ClRu(pyrazine)RuCl(bpy)_2]^{3+}$ in CD_3CN [4].

As was the case with our previous work, theoretical calculations provide some information that is helpful in the understanding of these results. Since this system

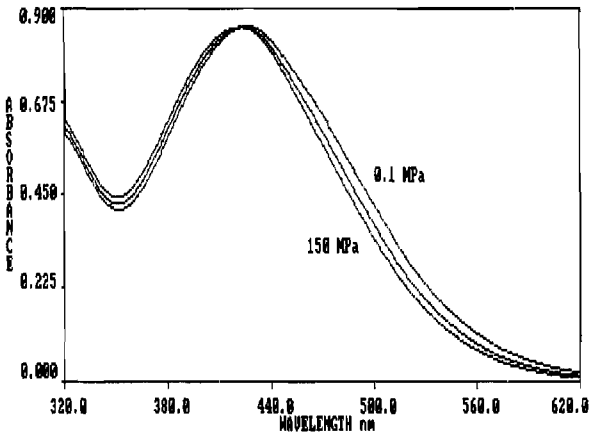


Fig. 1. Pressure response of the intervalence transition band in the complex $[(CN)_5Fe^{II}CNPt^{IV}(NH_3)_4NCFe^{II}(CN)_5]^{4-}$ in water. Concentration of the species was 1.8×10^{-4} M. Pressures were 0.1, 75 and 150 MPa.

is moderately strongly coupled electronically, the Marcus–Hush theory [9,10,15–17] for intervalence electron transfer may be used and an expression for the experimental volume of activation, ΔV^*, may be developed.

From classical thermodynamics

$$\Delta V^* = -\left(\frac{\delta\Delta G^*}{\delta P}\right)_T \tag{3}$$

and the simple Marcus–Hush relationship [9,10,15–17]

$$\Delta G^* = \frac{E_{op}^2}{4(E_{op}-\Delta G^\circ)} \tag{4}$$

where ΔG^* is the free energy of activation for electron transfer, E_{op} is the optical energy of the intervalence transfer (IT) band and ΔG° is the free energy change for the non-homogeneous redox reaction, Eq. (5) may be derived by substitution and differentiation.

$$\Delta V^* = \frac{1}{4}\left(\frac{E_{op}^2-2E_{op}(E_{op}-\Delta G^\circ)}{(E_{op}-\Delta G^\circ)^2}\right)\left(\frac{\delta E_{op}}{\delta P}\right)_T - \frac{E_{op}^2}{(E_{op}-\Delta G^\circ)^2}\left(\frac{\delta\Delta G^\circ}{\delta P}\right)_T \tag{5}$$

All the parameters for Eq. (5) are experimentally available, except for the term $(\delta\Delta G^\circ/\delta P)_T$, which is the same as ΔV°, the partial molal volume change for intramolecular electron transfer in complex **II**. Since the complex is negatively charged in solution, electrostrictive contributions to ΔV° are expected to be very small. Indeed, our attempts to measure ΔV° experimentally by means of densitometry in the 0.1–1.0 mM concentration range proved futile due to the negligible changes in density. Our estimate of ΔV° from published bond length data [18] for the assumed oxidation states undergoing a one-electron transfer process is about 0.9 cm^3 mol^{-1}. We reached this conclusion by estimating the difference in calculated volumes between an ellipsoid minimally enclosing the $(CN)_5Fe^{II}$–CN–$Pt^{IV}(NH_3)_4$ moiety and one minimally enclosing the proposed $(CN)_5Fe^{III}$–CN–$Pt^{III}(NH_3)_4$ species. Putting this value ΔV° into Eq. (5) and calculating ΔV^* by this expression results in a number which differs by less than 4% from the abbreviated Eq. (6) (vide infra). In most cases of electron transfer within a binuclear, this second term will be small because one end of the ellipsoid will always be increasing due to a decrease in oxidation state whereas the other end will be decreasing due to an increase in oxidation state.

Therefore, dropping the second term in Eq. (5) we finally arrive at

$$\Delta V^* = \frac{1}{4}\left(\frac{E_{op}^2-2(E_{op}-\Delta G^\circ)}{(E_{op}-\Delta G^\circ)^2}\right)\left(\frac{\delta E_{op}}{\delta P}\right)_T \tag{6}$$

where $E_{op}=23.58$ +/− 0.01 kK. The value for the Fe(II)/Fe(III) exchange was reported to be 0.55 V versus SCE by Bocarsly and co-workers. In order to calculate ΔG°, the $E_{1/2}$ for the Pt(IV)/Pt(III) half-reaction is also needed and this is not available experimentally since this redox potential is inaccessible electrochemically due to sluggish charge-transfer rates. To solve this problem in their work, Pfennig and Bocarsly [14] employed a theoretical estimate based on one-electron, outer-sphere quenching of luminescent Group 8 polypyridyl complexes, with may not be the most desirable model for the present compound. Using their value of −0.56 V versus SCE for the Pt(IV)/Pt(III) redox potential produces a ΔG° of 25.6 kcal mol^{-1} and a ΔV^* of −4.0 cm^3 mol^{-1} for the present molecule using Eq. (6). However, this potential appears to be far removed from the values where the tetraammineplatinum moiety is known to be electroactive [19,20]. It is likely that there will be very little energy difference between the addition of the first and second electrons in going from Pt(IV) to Pt(II). The first step is probably slower because the electron has to go into an empty anti-bonding orbital and the second step would be predicted to be faster because this kinetic barrier is overcome by the pairing energy released when the second electron is added.

Although the cyclic voltammetry experiments of Pfennig and Bocarsly [14] showed a single redox event which was assigned to direct simultaneous electrochemical oxidation of the two iron centers, it was not too distant from the area where the Pt(IV)/Pt(II) couple has been reported to be electroactive and the peak-to-peak separation was much larger than expected, equally consistent with a quasi-reversible one- or two-electron transfer process. For example, the $E_{1/2}$ for the oxidation of the $Pt(NH_3)_6^{2+}/Pt(NH_3)_6^{4+}$ couple was reported to be 0.16 V versus SCE, which would result in a ΔG° of 9.0 kcal mol^{-1} and a ΔV^* of −5.6 cm^3 mol^{-1} for

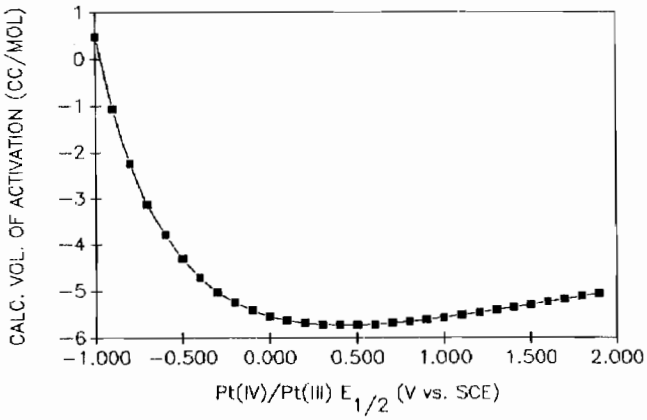


Fig. 2. The possible Pt(IV)/Pt(III) redox couples plotted as a function of ΔV^* obtained from Eq. (6) when this possible value is employed in the equation.

the present system again using Eq. (6). Likewise, the cyclic voltammetry of complex **II** itself after electropolymerization on an inert electrode of SnO_2 on glass showed two one-electron redox events at 0.86 and 1.09 V versus SCE. The most realistic number seems to be $E_{1/2}=0.40$ V versus SCE which was reported by Pfennig and Bocarsly for the Pt(II)/Pt(IV) couple from an indirect titration technique. Using this final estimate results in a $\Delta G°$ of 3.5 kcal mol^{-1} and a ΔV^* of -5.7 cm^3 mol^{-1}. The most important observation from these calculations is that Eq. (6) does not seem to be very sensitive to the exact value of $\Delta G°$. If the change in the calculated ΔV^* is plotted as a function of $E_{1/2}$ for the possible range of values for the Pt(IV)/Pt(III) couple, the result is Fig. 2. Thus, the value of ΔV^* is essentially unchanged regardless of what the value of the Pt(IV)/Pt(III) couple happens to be unless it is very negative which as we have argued is unlikely.

The ΔV^* can also be estimated from purely geometrical considerations by various models [2], assuming that the inner-sphere reorganizational energy is negligible. This is expected to be the case for this binuclear because the metal–ligand bond length changes are small during this redox process. Therefore, the hard spheres model of Stranks [21] based on traditional Marcus–Hush ideas and the ellipsoidal cavity models of Cannon [22] and German [23] might all be expected to give reasonable estimates of ΔV^* (see Table 1).

In the hard spheres model, the electrostatic influence of the spheres on each other is neglected but the electronic polarization of the solvent, as the instantaneous charge distribution on each ion changes, is considered. Cannon [22] was the first to apply the ellipsoidal cavity model of Kirkwood and Westheimer [24] to mixed-valence dinuclear complexes. The cavity employed in his calculations was generated by setting the volume of the ellipsoid equal to the sum of the volumes of the two spheres in the corresponding hard spheres model (the 'hard spheres equal volume' (HSEV) method, see dotted line in Fig. 3). This method tends to underestimate the volume occupied by the non-bridging ligands on the metal. A better method of generating the ellipsoid was later suggested by Brunschwig et al. [25] and is known as the 'minimum enclosing volume' (MEV) method (see solid line in Fig. 3). This ellipsoid tends to overestimate the amount of solvent present in the region of the bridge but generally gives numbers closer to those observed experimentally than does the equal volume (HSEV) method. We have therefore used the MEV method in the present work to estimate the volume of the ellipsoid for both the Cannon and German models. The main difference remaining between these two methods, then, arises from the assumed positions of the metal atoms. Cannon assumes that the change in dipole moment from precursor to successor complex could be replaced with little error by another dipole of equal moment but with charges (i.e. the metal atoms) located at the foci of the ellipsoid. In the German model, the Kirkwood–Westheimer theory is generalized to the case in which the charges may be located anywhere in the ellipsoidal cavity.

Table 1

Model	Form of expression[a]	Calculated ΔV^* (cm^3 mol^{-1})
Cannon[b]	$\Delta V^* = \left(\frac{e^2}{4}\right)\left(\frac{d^2}{2AB^2}\right)S(l_0)\frac{\delta}{\delta P}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$	−5.6
German[c]	$\Delta V^* = \left(\frac{e^2}{4}\right)\left(\frac{1}{R}\right)S(l_0)\frac{\delta}{\delta P}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$	−6.7
Stranks[d]	$\Delta V^* = \left(\frac{e^2}{4}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right)\frac{\delta}{\delta P}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$	−6.1

[a]Calculated ΔV^* assumes a one-electron transfer: e is the charge on the electron, $S(l_0)$ is the 'shape' factor in terms of Legendre polynomials, the form of which is given in Ref. [2]; D_{op} is the optical dielectric constant; D_s is the static dielectric constant.

[b]Taken from Ref. [2]; d is the intermetal distance; A and B are the semimajor and semiminor axes of the ellipse, respectively.

[c]Taken from Ref. [2]; R is the interfocal distance.

[d]Taken from Ref. [2]; a_1 and a_2 are the radii of the two spheres; d is the intermetal distance.

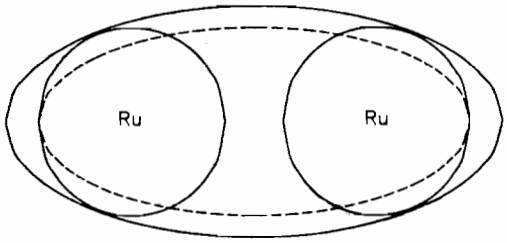


Fig. 3. Geometry considerations of the possible models for complex **II**. The two circles represent the hard spheres model. The dotted line gives the shape of the ellipsoid determined by the hard spheres equal volume (HSEV) method. The solid ellipse describes the ellipsoid generated by the minimum enclosing volume (MEV) method.

For all calculations the radius of the sphere enclosing the Fe moiety was taken as 3.06 Å and that of the Pt sphere was taken to be 2.59 Å. Since the molecule was not symmetrical, the average of these two values was used to construct the ellipses. Using Cannon's mode [22] for example (see Table 1), to construct the minimum enclosing volume of the ellipsoid for an iron and platinum moiety, one obtains a value of $\Delta V^* = -5.6$ cm^3 mol^{-1} for a one-electron transfer process and -11.2 cm^3 mol^{-1} if a simultaneous two-electron transfer reaction occurs. Clearly, the experimental value indicates that the electronic process is unitary and the IT band arises from a one-electron transfer event generating a transient Pt^{III} species. Other models result in the same conclusion being reached (see Table 1). If a significant contribution is being made by inner-sphere rearrangements at the Pt center, the contribution of the outer-sphere reorganizational energy to the measured value of the activation volume is even smaller than -5.6 cm^3 mol^{-1} and the conclusion is unchanged.

4. Conclusions

Analysis of the pressure dependence of the intervalence charge transfer band for complex **I** is consistent with a one-electron process. The value found for the volume of activation is -5.7 cm^3 mol^{-1}, which is in excellent agreement with the values calculated from theoretical models and this probably is due to the well-known geometry of the complex. The proposed transition state for the light-induced electron transfer reaction manifested by the intervalence band is [Fe(II)–Pt(III)–Fe(II)] in agreement with the report of Bocarsly and co-workers [13]. However, our conclusions are based on pressure measurements on the IT band itself and are less subject to rebutal. We note that since the IT band is a vibronic transition, it does not require the introduction of an excited electronic state as implied by the conclusion reached by Bocarsly's group. The amount of energy required to excite two electrons into an excited vibronic state giving rise to a two-electron intervalence transition band is unknown since it has not yet been observed.

It is important to stress the great potential of high pressure studies in the quantitative evaluation of electron transfer processes. Any systematic errors introduced in the calculation of E_{op} and its components are minimized by the term $\delta E_{op}/\delta P$, which is the slope of a linear plot. This may also help to explain the good agreement between the experimental and theoretical results reported herein. We are currently preparing additional molecules capable of undergoing simultaneous two-electron transfer processes to further test these ideas.

Acknowledgement

We thank the National Science Foundation for a Career Advancement Award to N.A.L. (Grant CHE 9011824) which made this work possible.

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