Inorganica Chimica Acta, 145 (1988) 163–164

Cobalt Chelates as Hydrogenation Catalysts. VII.* Adduct Equilibria with the Solvent

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(Received November 2, 1987)

As has been shown in previous publications [1–5] the macrocyclic cobalt(II) complexes [Co(dmgH)$_2$] and [Co(dpnH)]$^+$ react with pyridine by forming 1:1 and 2:1 adducts†. The adduct formation constants, however, which are determined by different methods, not only have different values, but also yield quite different $\Delta_R H^\circ$ and $\Delta_R S^\circ$ values [1, 3]. It is supposed that the reason for this is the neglect of analogous adduct equilibria with the solvent (eqn. (1)).

$$\mathrm{Co} + 2\mathrm{L} \rightleftharpoons \mathrm{CoL} + \mathrm{L} \rightleftharpoons \mathrm{CoL_2} \qquad (1)$$

Since the adduct formation of these complexes with pyridine in water/n-propanol (50% *v*/*v*) has been followed by spectrophotometry in the range of their charge transfer band, we first of all studied the temperature dependence of this band between 15 000 and 33 000 cm^{-1}. In the case of [Co(dpnH)]$^+$ the molar absorptivity decreases from 4100 to 3700 l mol^{-1} cm^{-1} (*ca.* 10%) and the band maximum is shifted by only 50 cm^{-1} to higher wavenumbers by increasing the temperature from 290 to 340 K. This decrease of the absorbance and the shift of the band maximum corresponds to the changes observed by the formation of the monopyridine adduct. Although these changes are out of the error limits of the method, they are too small to follow a shift of a solvent adduct equilibrium.

However, more distinct changes of the spectrum can be observed in the near-infrared (see Fig. 1). The ligand field band [6] of the [Co(dpnH)]$^+$ complex at 10 600 cm^{-1} at room temperature decreases with increasing temperature and a new band arises with a maximum <7600 cm^{-1}. The reaction spectrum shows two isosbestic points at 9800 and 13 200 cm^{-1} indicating an equilibrium, but the corresponding plot of absorbance differences (Fig. 2) does not yield the straight lines which are expected if only one equilibrium is present [7, 8]. The determination of the rank of the absorbance matrix [9] provides the same result. In the case of the [Co(dmgH)$_2$] complex, in addition to the band at 10 600 cm^{-1} a second one with a maximum at *ca.* 7600 cm^{-1} is already observed at 293 K. Its intensity also increases with temperature, whereas the intensity of the first one decreases correspondingly (Fig. 3). Here an isosbestic point also appears at first at 9600 cm^{-1}, but it disappears at temperatures higher than 306 K. A plot of absorbance differences (Fig. 4) shows more marked deviations from the straight line and the analysis of the absorption matrix gives the rank three, *i.e.* in the case of [Co(dmgH)$_2$] two equilibria (or reactions) are responsible for the spectral changes in the near-infrared. Since the dissociation of solvent adducts increases with increasing temperature, shifting the

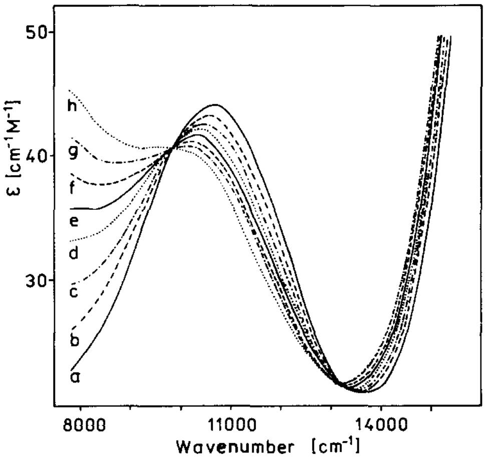

Fig. 1. Temperature dependence of the near-infrared spectrum of [Co(dpnH)]$^+$. Solvent: water–n-propanol (50% *v*/*v*), $I = 0.05$ (NaClO$_4$); temperatures (K): a = 294.4; b = 303.3; c = 312.3; d = 320.2; e = 326.8; f = 333.9; g = 341.3; h = 350.5.

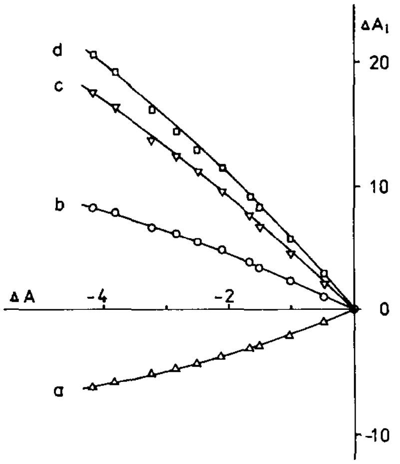

Fig. 2. Plot of absorbance differences for the spectra in Fig. 1. ΔA_i (a = 11 800, b = 9000, c = 8000, d = 7600 cm^{-1}) *vs.* ΔA = 10 600 cm^{-1}.

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*For Part VI see ref. 1.

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†dpnH = DO(DOH)pn = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olate.

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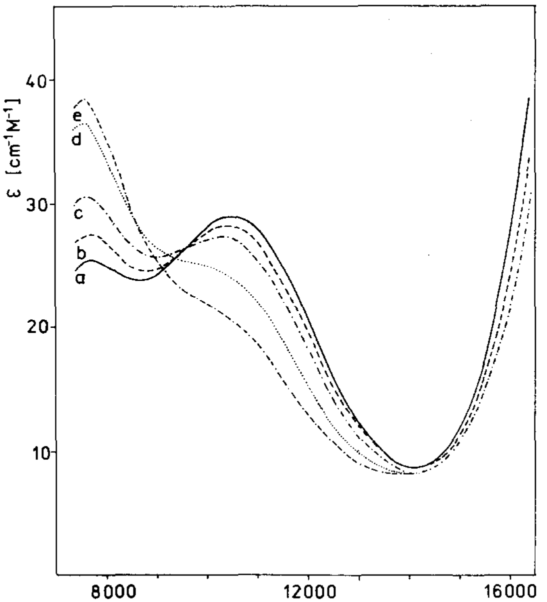

Fig. 3. Temperature dependence of the near-infrared spectrum of [Co(dmgH)$_2$]. Solvent: water–n-propanol (50% v/v), I = 0.05 (NaClO$_4$); temperatures (K): a = 293.4, b = 298.4, c = 306.0, d = 322.3, e = 337.3.

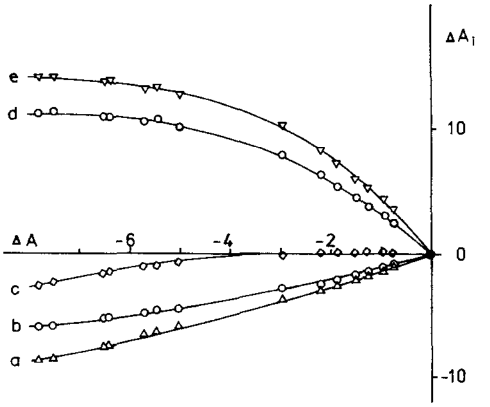

Fig. 4. Plot of absorbance differences for the spectra in Fig. 3. ΔA_i (a = 11 000, b = 12 400, c = 9600, d = 8000, e = 7600 cm^{-1}) vs. ΔA = 10 600 cm^{-1}.

equilibria formulated in eqn. (1) to the left, the decrease of the band at 10 600 cm^{-1} and the increase of the band at *ca.* 7600 cm^{-1}, implies that the last one has to be assigned to a lower coordinated species. Such a shift of the ligand field band with a decreasing coordination number can be expected if the band is assigned to a transition from an energetic lower lying, filled 3d orbital to the half filled 3d$_{z^2}$ orbital [6, 10].

From the relative intensities of both bands it can be derived that the higher coordinated species not only is degraded with increasing temperature, but also that its concentration is smaller in the case of [Co(dmgH)$_2$] than for [Co(dpnH)]$^+$. This is in accordance with the general expectation that the higher charged complex forms the more stable adduct [11].

A more detailed and quantitative evaluation of the solvent adduct formation is hampered at present, because both complexes decompose irreversibly at higher temperatures. This decomposition can be detected in the case of [Co(dmgH)$_2$] at temperatures already above 325 K, for the more stable [Co(dpnH)]$^+$ only above 345 K. We shall report on these and related investigations in more detail in the near future.

The adduct equilibria with the solvent, upon which only few and incomplete informations can be found in the literature [2, 3, 12–14], not only superimpose the adduct formation with other ligands but also the temperature dependence of reactions with these complexes or those catalyzed by them. Therefore thermodynamic ($\Delta_R H^\circ$, $\Delta_R S^\circ$) and kinetic parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) derived from the temperature dependence of such reactions published by us [1, 4] and other authors are incorrect.

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