Inter- and Intramolecular Rhodium-Rhodium Interactions in Bis(bidentate isocyanide)rhodium(I) Hexafluorophosphates

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The reaction of $[RhCl(1,5\text{-}C_8H_{12})]_2$ with the stoichiometric amount of bidentate isocyanide followed by metathesis affords complexes of the types $[Rh(L\text{–}L)_2]PF_6$ ($L\text{–}L=CN(CH_2)_8NC$ (**1**), $CN(CH_2)_7NC$ (**2**)) and $[Rh_2(L\text{–}L)_4](PF_6)_2$ ($L\text{–}L=CN(CH_2)_6NC$ (**3**), $CN(CH_2)_4NC$ (**4**)). The electronic spectra at various concentrations reveal that in dilute solutions **1** and **2** exist as monomers with chelating isocyanides, while **3** and **4** form dimers with bridging isocyanides through intramolecular rhodium–rhodium interactions as the smallest unit. On the other hand, in concentrated solutions **1** and **2** form dimers and **4** tetramers through intermolecular Rh–Rh interactions.

Much attention has been paid to one-dimensional inorganic complexes in order to synthesize materials of anisotropic electrical conductivity. One of the most promising compounds is square planar d^8 metal complexes, the representative example of which is $K_2Pt(CN)_4\cdot Br_{0.30}\cdot 3H_2O$.[1] In this respect tetrakis(isocyanide)rhodium(I) and -iridium(I) cations are interesting because of their deep coloration.[2] Actually they have been found to exhibit oligomerization in solution.[3–5] Rhodium(I) complexes containing monodentate isocyanides are well known,[2,6] however, studies are relatively sparse on those containing bidentate isocyanides.[5] This paper reports the synthesis of some rhodium(I) complexes coordinated by bidentate isocyanides, $CN(CH_2)_nNC$ (n=4, 6, 7, or 8) and their electronic spectra, which reveal the presence of rhodium-rhodium interactions in these complexes in solution.

Experimental

Materials. Rhodium trichloride trihydrate was of reagent grade and used as supplied. Di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I), $[RhCl(1,5\text{-}C_8H_{12})]_2$, was prepared according to the literature.[7] The bidentate isocyanides $CN(CH_2)_nNC$ (n=4, 6, 7, or 8) were prepared by slightly modifying the literature method.[8] Dimethyl sulfoxide (DMSO) was distilled twice under reduced pressure after drying over $CaSO_4$ to give specific conductance, $k=1.1\times10^{-6}$ ohm^{-1} cm^{-1}.

Physical Measurements. Physical data were obtained in DMSO solutions. Infrared spectra (1×10^{-2} M) were measured on a Hitachi Perkin-Elmer 225 Spectrophotometer, electric conductivity (1×10^{-3} M) by using a Yokogawa F-255A universal bridge and a cell with the cell constant of 0.322 cm^{-1}, and electronic spectra on a Hitachi 124 Spectrophotometer by using 1, 0.1, and 0.01 cm quarz cells.

Preparation of $[Rh(L\text{–}L)_2]PF_6$ *(*$L\text{–}L=CN(CH_2)_8NC$ *(1),* $CN(CH_2)_7NC$ *(2)) and* $[Rh_2(L\text{–}L)_4](PF_6)_2$ *(*$L\text{–}L=CN(CH_2)_6NC$ *(3),* $CN(CH_2)_4NC$ *(4)).* An ethanol (10 ml) solution of hexamethylene diisocyanide (0.32 g, 2.4 mmol) was added dropwise to a stirred suspension of $[RhCl(1,5\text{-}C_8H_{12})]_2$ (0.29 g, 0.58 mmol) in ethanol (10 ml). The mixture was stirred for 1 h, followed by the addition of NH_4PF_6 (2.30 g, 1.4 mmol) in water (5 ml). The resulting product was reprecipitated from a mixture of dichloromethane and heptane to give a dark blue powder of **3** (60%): ν(NC), 2169 cm^{-1}; Λ_M=62 cm^2 ohm^{-1}·mol^{-1}. Found: C, 36.84; H, 4.78; N, 10.71%. Calcd for $C_{32}H_{48}F_{12}N_8P_2Rh_2$: C, 36.94; H, 4.65; N, 10.77%.

Other complexes were similarly prepared. **1** was reprecipitated from acetonitrile–water (73%): ν(NC), 2165 cm^{-1}; Λ_M= 31 cm^2 ohm^{-1} mol^{-1}. Found: C, 41.81; H, 5.78; N, 9.82%. Calcd for $C_{20}H_{32}F_6N_4PRh$: C, 41.68; H, 5.60; N, 9.72%. **2** was purified as **3** and contains a half molecule of dichloromethane (82%): ν(NC), 2170 cm^{-1}; Λ_M=34 cm^2 ohm^{-1} mol^{-1}. Found: C, 37.71; H, 4.89; N, 9.23%. Calcd for $C_{18.5}H_{29}ClF_6N_4PRh$: C, 37.61; H, 4.95; N, 9.48%. **4** was purified as **3** (81%): ν(NC), 2175 cm^{-1}; Λ_M=58 cm^2 ohm^{-1} mol^{-1}. Found: C, 31.77; H, 3.97; N, 11.80%. Calcd for $C_{24}H_{32}F_{12}N_8P_2Rh_2$: C, 31.05; H, 3.47; N, 12.07%.

Results and Discussion

The complexes obtained exhibit dark violet or blue color in the solid state, which is reminicent of metal-metal interactions. Conductivity measurements indicated that they are all electrolytes in DMSO. Infrared spectra of the complexes in DMSO showed only one strong band in the ν(N≡C) region, implying the equivalence of four isocyanide groups coordinated to the rhodium atom.

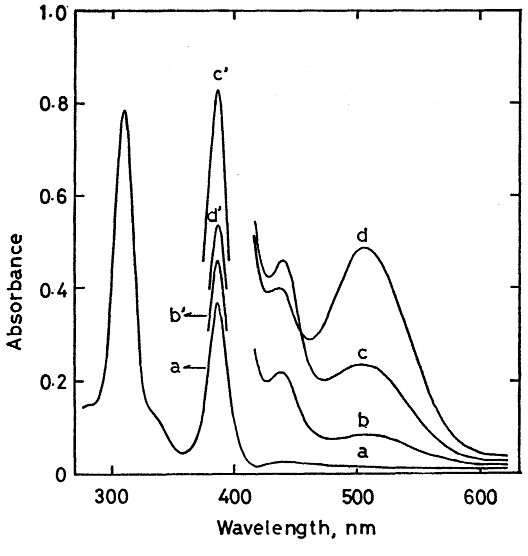


Fig. 1. Electronic spectra of $[Rh(CN(CH_2)_7NC)_2]PF_6$ (**2**) in DMSO at various concentrations at 25 °C (cell length, cm): a (1), 3.5×10^{-5} M; b (1) and b′ (0.1), 5.1×10^{-4} M; c (1) and c′ (0.1), 1.2×10^{-3} M; d (0.1) and d′ (0.01), 8×10^{-3} M.

TABLE 1. THE WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS OF THE ABSORPTION MAXIMA OF THE CATIONS

No.	Cation	$\lambda_{\max}$, nm($\varepsilon \times 10^{-4}$)					
1	$[Rh(CN(CH_2)_8NC)_2]^+$	312 (2.7)	338 sh	387 (1.2)	440 (<0.1)	505[b]	
2	$[Rh(CN(CH_2)_7NC)_2]^+$	311 (2.3)	338 sh	387 (1.1)	440 (<0.1)	505[b]	
3	$[Rh_2(CN(CH_2)_6NC)_4]^{2+}$	313 (4.2)	338 sh	386 (0.3)[a]		526 (1.5)	
4	$[Rh_2(CN(CH_2)_4NC)_4]^{2+}$	314 (2.2)	340 sh	383 (0.2)[a]		564 (1.9)	765[b]

a) See text. b) Observable only in concentrated solutions.

Electronic spectra of these complexes in DMSO show concentration dependence, which is illustrated by the spectra of **2** in DMSO at various concentrations (Fig. 1). A dilute solution (3.5×10^{-5} M) exhibit four absorption bands. The wavelengths and molar extinction coefficients of these bands (Table 1) are close to the charge transfer bands of tetrakis(ethyl isocyanide)-rhodium(I) perchlorate observed in acetonitrile (308 (ε 24000), 333^{sh}, 380 (8400), 435 nm (260)). This complex was reported to exist as the discrete rhodium(I) cation.[9] In addition, a molecular model suggests that the methylene chain of $CN(CH_2)_7NC$ is long enough for chelation to the rhodium(I) ion. Thus, the four absorption bands observed in dilute solutions are due to monomeric $[Rh(CN(CH_2)_7NC)_2]^+$. A more concentrated solution of **2** exhibits a new broad band at 505 nm, which is intensified relatively at the expense of the 387 and 440 nm bands as the concentration increases. The 505 nm band may therefore be assigned to dimeric $[Rh(CN(CH_2)_7NC)_2]_2^{2+}$ by analogy with $[Rh(C_6H_5NC)_4]^+$, which was reported to exhibit an absorption arising from its dimer at 568 nm in concentrated acetonitrile solutions.[4] If one can assume that an equilibrium exists between monomeric $[Rh(CN(CH_2)_7NC)_2]^+$ and its dimeric dication, the equilibrium constant, K_1, is expressed by the following equation (Eq. 1), where C, A, and ε stand for the concentration, absorbance, and molar extinction coefficient of the monomeric and dimeric species denoted by the subscripts M and D, respectively.

$$K_1 = \frac{C_D}{C_M^2} = \frac{A_D/\varepsilon_D}{(A_M/\varepsilon_M)^2} \tag{1}$$

Equation 1 can be transformed as follows:

$$A_M^2 = \frac{\varepsilon_M^2}{K_1 \varepsilon_D} \times A_D. \tag{2}$$

This equation predicts a linear relationship between A_M^2 and A_D. In fact, a plot of the absorbance at 505 nm *vs.* the square of that at 387 nm[10] gave a straight line shown in Fig. 2. It is therefore suggested that **2** exists as an equilibrium mixture of the monomeric and dimeric species in concentrated solutions. The association of $[Rh(CN(CH_2)_7NC)_2]^+$ may be formed through Rh–Rh interactions as illustrated in **A**. A similar result was obtained for **1** (see Table 1). Unfortunately, the K_1 and ε_D values have not been determined in the present study, because limited solubilities of **1** and **2** have precluded the spectral measurements over a concentration range wide enough to warrant the least squares analysis[11] to calculate these two values.

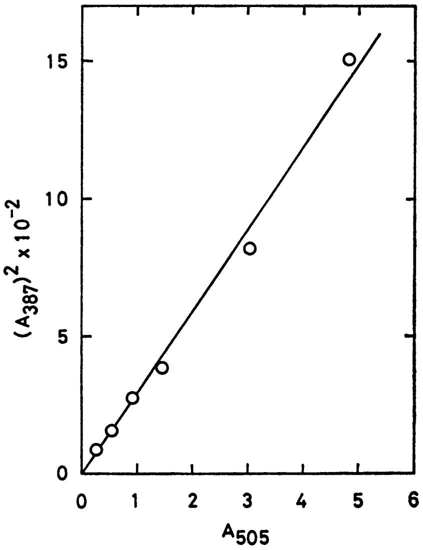
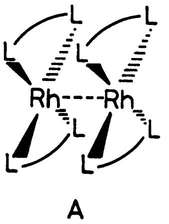


Fig. 2. A plot of the absorbance at 505 nm, A_{505}, *vs.* the square of that at 377 nm, $(A_{387})^2$, for $[Rh(CN(CH_2)_7NC)_2]PF_6$ (**2**) in DMSO at 25 °C.



A

Figure 3 displays electronic spectra of **4** in DMSO at various concentrations. A dilute solution (4.2×10^{-4} M) exhibits four absorption bands. These wavelengths

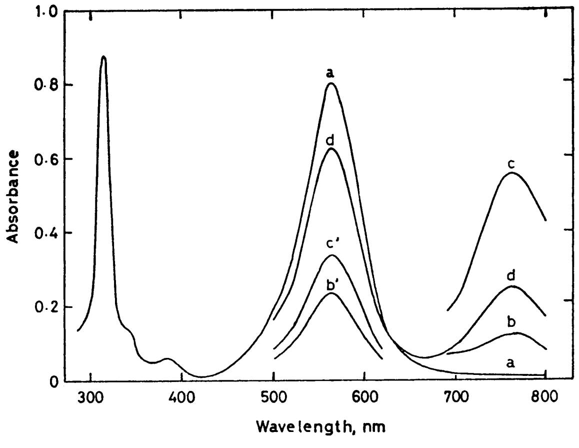
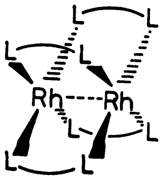
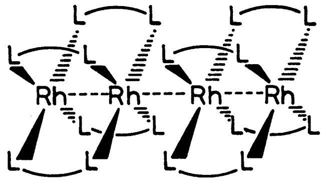


Fig. 3. Electronic spectra of $[Rh_2(CN(CH_2)_4NC)_4](PF_6)_2$ (**4**) in DMSO at various concentrations at 25 °C (cell length, cm): a (0.1), 4.2×10^{-4} M; b (0.1) and b′ (0.01), 8.4×10^{-4} M; c (0.1) and c′ (0.01), 1.7×10^{-3} M; d (0.01), 3.5×10^{-3} M.

(Table 1) except 383 nm (*vide infra*) are close to those of absorptions of the $CN(CH_2)_3NC$ analog in a dilute methanol solution (318, 342, 555 nm), for which a dimeric structure with bridging isocyanides has recently been suggested.5) A molecular model indicates that $CN(CH_2)_4NC$ will not be able to chelate to the rhodium(I) ion. Therefore, **4** probably contains bridging isocyanides to form a dimer with an intramolecular Rh–Rh interaction as the smallest unit in dilute solutions, **B**. The intensity of the rather weak band at 383 nm decreases considerably on addition of $CN(CH_2)_4NC$ to its Rh(I) complex in DMSO. In view of this result and the fact that monomeric **1** and **2** show absorptions at 387 nm (Table 1), the band may arise from such a monomeric species as, for example, $[Rh(CN(CH_2)_4NC)_2(DMSO)_2]^+$ involving unidentate $CN(CH_2)_4NC$. Thus, the 314 and 340 nm bands of **4** (Table 1) may be contributed from the monomeric species to some extent, since monomeric **1** and **2** exhibit absorptions at similar wavelengths. A more concentrated solution of **4** exhibits a new broad band at 765 nm, which is intensified at the expense of the 564 nm band as the concentration increases. The 765 nm band can be assigned to tetrameric $[Rh_2(CN(CH_2)_4NC_4]_2^{4+}$ by analogy with the $CN(CH_2)_3NC$ analog.5) Moreover, a linear relationship was obtained between the absorbance at 765 nm *vs.* the square of that at 564 nm (the dimer band), supporting the assignment. It is therefore suggested that in concentrated solutions the dimeric **4** undergoes an intermolecular association to form the tetramer **C**. No similar association of **3** has been observed in the electronic spectrum because of its poor solubility, although in dilute solutions it exhibited a spectrum similar to that of **4** (Table 1). The absorptions at long wavelengths of these four complexes will be explained to be due to the dimeric and tetrameric species by a simple MO diagram proposed by Gray *et al.*4,5)



B



C

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