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Thermal and Photochemical Dimer Formation in $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ and $(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$

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The thermal and the photochemical reactivity of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ and $(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$ have been investigated in CH_2Cl_2 solution. Experimental evidence is found for the formation of –CN– bridged binuclear Co(III) complexes. $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ reacts thermally to give a reaction product which can be identified from its infrared spectrum as $(n\text{-}Bu_4N)_5[(NC)_5Co\text{–}NC\text{–}Co(CN)_4Cl]$. Its identification and the kinetics of its formation are discussed. Irradiation at 405 nm yields the same product ($\phi \leqslant 10^{-3}$ at 273 K).

$(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$ is thermally stable in CH_2Cl_2 solutions at room temperature. Irradiation at 405 nm causes the formation of the dimer product $(n\text{-}Bu_4N)_5[Co_2(CN)_{10}NCS]$. The quantum yield at room temperature is found to be 0.30.

Introduction

The ligand substitution of the acidopentacyanocobaltate(III) complexes $Co(CN)_5X^{n-}$ (X being an anion or a neutral molecule) has been used as a test case for the investigation of the mechanism of this type of substitution reaction [1].

In aqueous solution, the thermal reactions of these complexes are restricted to the exchange of the acidoligand for a water molecule (aquation), or in the case of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5OH^{3-}$, the replacement of the heteroligand by another ligating species present in the solution (anation).

These reactions are found to be accelerated when the complex is excited with light in the ligand field region [2]. In addition to these reactions, photosubstitution of a cyanide ligand by water is possible for the aquo- and hydroxopentacyanocobaltate(III) complexes in the absence of coordinating ligands [3].

Unless water is replaced by another solvent, the number of possible reaction products obtainable by substitution – either thermally or photochemically – is rather limited. The photosolvation of $Co(CN)_6^{3-}$ in a series of organic solvents by Nakamaru *et al.* [4] can be cited as a case in point. It was found here that in the case of coordinating solvents, photosolvolysis occurs with a quantum yield comparable to the value for the aquation reaction. In a non-coordinating solvent such as chloroform, no reaction takes place.

We considered the usefulness of such inert solvents as a matrix to study the chemistry and the photoreactivity of the acidopentacyanocobaltate(III) complexes, and we wish to report here some preliminary results on the thermal and photochemical behaviour of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ and $(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$ in methylene chloride solution.

In both cases we found strong experimental evidence for the formation of binuclear –CN– bridged Co(III) complexes with a net formula $(n\text{-}Bu_4N)_5[Co_2(CN)_{10}X]$.

Experimental

The synthesis of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ and $(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$ is described elsewhere [5].

Dichloromethane usually contains a small amount of water which interferes with the reactions under investigation. These traces are conveniently removed by means of adsorption chromatography on Al_2O_3 (acidic form). The absence of water was checked with I.R. spectroscopy (using a 1 mm NaCl cell) in the 3600 cm^{-1} range.

For the irradiations an Osram HBO 200W mercury arc was used. The 405 nm line was isolated with an appropriate set of filters. To measure the quantum yield, the light source was provided with a Bausch and Lomb High Intensity monochromator and a mobile mirror system. A fraction of the light beam thus collected irradiates the actinometer in a reference cell. Ferrioxalate was used as actinometric standard. All quantum yield data were corrected for inner filter effects.

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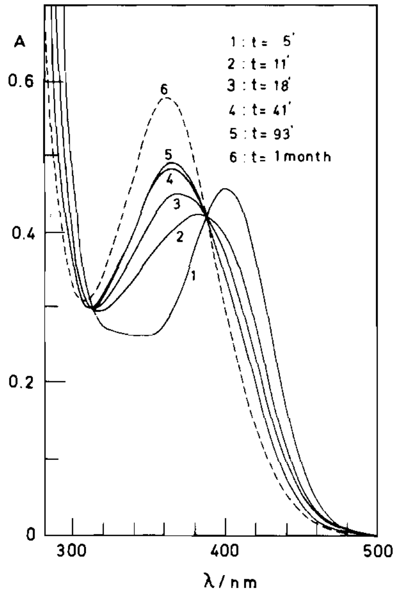

Fig. 1. Thermal reaction of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ at 293 K. L.F. absorption changes as a function of time.

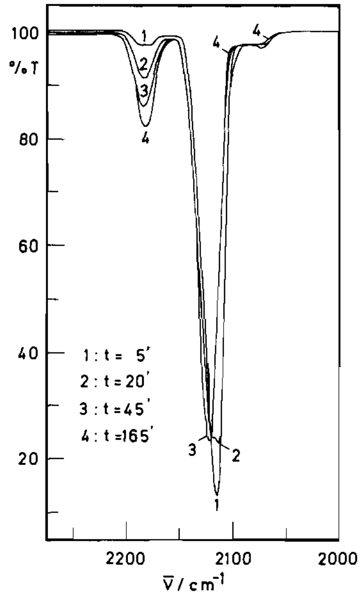

Fig. 2. Thermal reaction of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ at 293 K. Infrared transmission changes as a function of time.

The UV–visible spectra were recorded on a Unicam SP-8/100 spectrophotometer. A Beckman I.R. 4250 was used for the infrared spectra.

To measure the amount of $(n\text{-}Bu_4N)SCN$ released in the reaction we used a modification of a spectrophotometric technique based on the formation of the $Cu(py)_2(SCN)_2$ complex [6]. Since all test samples were CH_2Cl_2 solutions we had to replace the $CHCl_3$ used in the original modus for the extraction of the Cu complex by CH_2Cl_2.

Results and Discussion

Thermal Reaction

The two acidopentacyanocobaltate(III) complexes we have studied exhibit a strikingly different thermal behaviour in methylene chloride solution. Whereas the isothiocyanato complex is stable for a period of days and shows no spectral changes in its ligand field absorption spectrum, the chloro complex reacts quickly and its colour changes from bright yellow to a faint yellow cast. The conversion takes place over isosbestic points, and the initial maximum of the ligand field band at 400 nm disappears to produce a new band at 364 nm (Fig. 1, spectra 1–5). The reaction product is not indefinitely stable; prolonged ageing (1 month) at room temperature leads to further spectral changes (Fig. 1, spectrum 6).

From the spectral changes in the infrared (see below), strong evidence is brought forward that the observed reaction product is a binuclear complex, in which two cobalt(III) metal centers are bridged by a –CN– ligand. Thus the overall reactions can be written as:

$$2(n\text{-}Bu_4N)_3[Co(CN)_5Cl] \xrightarrow{\Delta} (n\text{-}Bu_4N)_5[(NC)_5Co\text{-}NC\text{-}Co(CN)_4Cl] + (n\text{-}Bu_4N)Cl \qquad (I)$$

The dimer complex exhibits a single ligand field absorption band at 364 nm (ϵ = 399 M^{-1} cm^{-1}). This value was calculated assuming complete conversion to the end product at thermal equilibrium, the charge transfer band(s) being hidden under the absorption band of the solvent.

Due to the high reactivity in CH_2Cl_2, it was impossible to record the spectrum of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ at room temperature. At 273 K however the reaction rate is slowed down sufficiently to make the registration possible. The first ligand field band was found at 400 nm (ϵ = 184 M^{-1} cm^{-1}). This value is lower than in aqueous solution (ϵ_{394} = 210 M^{-1} cm^{-1}). The second band is observed as a shoulder at 320 nm ($\epsilon \cong 88\, M^{-1}$ cm^{-1}).

The spectra of two comparable binuclear complexes, $(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5$ and $(NC)_5Co(\mu\text{-}NC)Co(NH_3)_5$ were found to be the simple addition of the two composing moieties [7]. If we apply this principle to $[(NC)_5Co(\mu\text{-}NC)Co(CN)_4Cl]^{5+}$ we should observe the superposition of the spectra of $[Co(CN)_5NC]^{3+}$ and $[Co(CN)_5Cl]^{3+}$, and hence bands around 343 and 400 nm should appear. This

TABLE I. Experimental Second Order Rate Constants for the Dimerization of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ in CH_2Cl_2 at 293 K as a Function of the Initial Concentration.

$C_o/10^{-3}$ *M*	k_{exp}/M^{-1} min^{-1}	$k_{exp} \cdot C_o/10^{-2}$ min^{-1}
1.10	41.2 ± 0.5	4.53
3.05	15.0 ± 0.2	4.58
6.16	8.14 ± 0.09	5.01
30.6	1.52 ± 0.05	4.65

is not the case for the new dimer since only one band at 364 nm is observed. Its shape however is asymmetrical, probably due to the superposition of two or more adjacent bands.

As mentioned before, the identity of the reaction product is revealed by I.R. spectroscopy. In Fig. 2 the changes in the cyanide stretching region (2250–2000 cm^{-1}) due to the reaction are displayed. The appearance of the new band at 2182 cm^{-1} is very characteristic of a binuclear cyano-bridged compound. Indeed, for several Co–CN–Co and Co–CN–Cr complexes with mixed ammine and cyanide ligands, experimental values of ν_{CN}^{br} of ~2180 cm^{-1} are found [8].

A simplified calculation of the expected cyanide-stretch for a linear Co–CN–Co system leads to a value of 2160 cm^{-1}. Using a more elaborate potential function with an interacting free force constant between the MC and the CN bonds, Wilmarth obtained values of ν_{CN}^{br} of 2170 or 2150 cm^{-1}, depending on the values accepted for the interaction force constant [9]. Differences between calculated and experimental values are to be expected, since the Co–CN–Co bond is not perfectly linear (evidenced by X-ray structural analysis on some mixed cyano–ammine binuclear Co(III) complexes [10]).

The dimerization reaction follows a second-order rate expression, although the observed rate constant (k_{exp}) is inversely proportional to the initial complex concentration. The data for a set of experiments at 293 K are collected in Table I. The concentration changes are followed spectrophotometrically.

The dependence of k_{exp} on the initial complex concentration can be explained if a purely dissociative mechanism (S_N1) is accepted. This pattern is analogous to the thermal anation of $Co(CN)_5OH_2^{2-}$ in aqueous solution, and the aquation of the different $Co(CN)_5X^{3-}$ complexes.

$$(n\text{-}Bu_4N)_3[Co(CN)_5Cl] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (n\text{-}Bu_4N)_2[Co(CN)_5] + (n\text{-}Bu_4N)Cl$$

$$(n\text{-}Bu_4N)_2[Co(CN)_5] + (n\text{-}Bu_4N)_3[Co(CN)_5Cl] \xrightarrow{k_2} (n\text{-}Bu_4N)_5[Co_2(CN)_{10}Cl] \qquad \text{(II)}$$

Application of the steady state principle to this reaction sequence leads to the rate equation:

$$\frac{-d[M]}{dt} = \frac{2k_1k_2[M]^2}{\frac{k_{-1}}{2}[M]_o + \left(k_2 - \frac{k_{-1}}{2}\right)[M]} \qquad \text{(III)}$$

where $[M]_o$ and $[M]$ are the initial and the running concentration of the monomer complex. (It is assumed that no $(n\text{-}Bu_4N)Cl$ has been added to the complex solution). If further it is assumed that k_2 is of the same order of magnitude as $k_{-1}/2$, eqn. (III) can, to a good approximation be reduced to:

$$\frac{-d[M]}{dt} = \frac{4k_1 \cdot k_2[M]^2}{k_{-1}[M]_o} = k_{exp} \cdot [M]^2$$

The experimental data of Table I fit this expression. Using these numbers, we find $4k_1 \cdot k_2/k_{-1} = 4.69 \times 10^{-2}$ min^{-1}. Since we supposed $k_2 \cong k_{-1}/2$ the rate constant for the initial dissociation of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ is $k_1 \cong 2.3 \times 10^{-2}$ min^{-1}.

This value agrees remarkably well with the value reported by Grassi, Haim and Wilmarth for the dissociation rate constant of $Co(CN)_5Cl^{3-}$ in water at 313 K. ($k = 2.7 \times 10^{-2}$ min^{-1}) [11].

A further confirmation of the validity of the proposed mechanism is given by the fact that the addition of an excess $(n\text{-}Bu_4N)Cl$ to the solution inhibits the dimerization reaction strongly, and will even reverse the reaction:

$$(n\text{-}Bu_4N)_5[Co_2(CN)_{10}Cl] + (n\text{-}Bu_4N)Cl \rightarrow 2(n\text{-}Bu_4N)_3[Co(CN)_5Cl] \qquad \text{(V)}$$

Since a large excess $(n\text{-}Bu_4N)Cl$ is required to induce reaction (V), this step can be neglected in the normal dimerization mechanism.

Photochemical Reaction

Both the isothiocyanato- and the chloropentacyanocobaltate(III) complexes will react upon irradiation in their ligand field absorption bands.

$(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$

At room temperature, the investigation of the photochemistry is hampered by the thermal instability of the complex. At 273 K the thermal dimerization is slowed down sufficiently to allow the observation of the photolysis reaction. Irradiation at 405 nm causes spectral changes in the UV–visible region, identical to the changes observed during the thermal dimerization reaction. Isosbestic points are maintained throughout the course of the reaction and the maximum of the reaction product is again at 364 nm.

The I.R. spectrum also approaches the spectrum found earlier. The bridging cyanide stretching band is now found at 2184 cm^{-1}.

These observations lead to the obvious conclusion that the product of the photochemical reaction is the same as for the thermal reaction. The quantum yield at 273 K is too low ($\phi < 10^{-3}$) to be measured accurately with our equipment.

$(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$

The isothiocyanato complex is thermally perfectly stable in CH_2Cl_2 solution at room temperature. This facilitates the study of its photochemistry.

The absorption spectrum features an almost 30% decrease in the L.F. band: $\epsilon_{363} = 501\ M^{-1}\ cm^{-1}$ in water and $\epsilon_{366} = 357\ M^{-1}\ cm^{-1}$ in CH_2Cl_2. The charge transfer band at 265 nm ($\epsilon = 2800\ M^{-1}\ cm^{-1}$) shifts to 261 nm and decreases to 2500 $M^{-1}\ cm^{-1}$ when CH_2Cl_2 is used as solvent instead of water.

Irradiation at 405 nm causes the complex to undergo an efficient photoreaction. Again, the infrared spectral data point to the occurrence of a dimerization reaction:

$$2(n\text{-}Bu_4N)_3[Co(CN)_5NCS] \xrightarrow[CH_2Cl_2]{h\nu\ 405} (n\text{-}Bu_4N)_5[Co_2(CN)_{10}NCS] + (n\text{-}Bu_4N)\,SCN \qquad (V)$$

Since the monomer complex is thermally stable, it was possible to follow the reaction by monitoring the $(n\text{-}Bu_4N)SCN$ production. During the entire course of the reaction the amount of thiocyanate released corresponds exactly to the amount of dimer formed.

As can be seen in Fig. 3 the spectral changes evolve over isosbestic points. The new maxima are found at 372 nm ($\epsilon = 376\ M^{-1}\ cm^{-1}$) and 265 nm ($\epsilon = 9.56 \times 10^3\ M^{-1}\ cm^{-1}$).

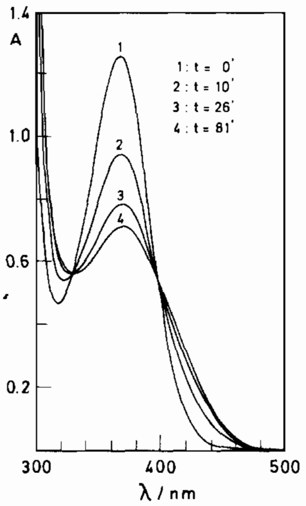

Fig. 3. Photochemical reaction of $(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$ at 293 K. Irradiation wavelength: 405 nm. L.F. absorption changes as a function of irradiation time.

Irradiation with light of shorter wavelengths (366 or 313 nm) causes a more complex reaction scheme, as is evidenced by the disappearance of the isosbestic points at later stages of the reaction. A redox side-path might well be involved.

The quantum yield of the reaction is, at least at the beginning of the reaction, wavelength independent and has a value of 0.30 (± 0.01).

The infrared spectrum of the reaction product shows two new bands in the 2250–2000 cm^{-1} cyanide stretching region. One band at 2058 cm^{-1} can be attributed to the absorption of the released SCN^- ligand [12]. The other band at 2181 cm^{-1} is again indicative of a bridging cyanide ligand between the two Co(III) centers. In this case there is the hypothetical possibility of the formation of a thiocyanate bridge whose cyanide stretching is believed to absorb also in this spectral region [13].

Our *GF*-matrix calculations on two simple geometrical models for the bridging thiocyanate ligand between two Co(III) centers (whose masses are supposed to be infinite) are not conclusive. Assuming a linear structure for the Co–SCN–Co system, we calculate a cyanide stretching frequency for the bridging SCN group of 2121 cm^{-1}, which is almost the same value as for the cyanide frequency in a terminal Co–NCS group (2123 cm^{-1}). If on the other hand, the sulfur atom of the bridging thiocyanate is supposed to bind to the Co atom at a Co $\hat{S}$ C angle of 90° (as is the case for most terminal SCN ligands in Co(III) complexes), we find a frequency of 2138 cm^{-1} for the SCN cyanide stretching, a value which is definitely higher than that for a terminal *N*CS and *S*CN ligand, but which cannot explain our experimental value of 2181 cm^{-1}.

In the literature a few values are reported for the position of a cyanide stretching band in a bridging NCS group. Buckley and Wardeska [14] report values of 2170 and 2175 cm^{-1} for two isomeric SCN-bridged binuclear Co(III) complexes and Artz and Burmeister [15] find a value of 2171 cm^{-1} for a similar complex.

In view of our value of 2182 cm^{-1} in the case of the Cl substituted dimer, and considering the values around 2180 cm^{-1} reported for other CN bridging ligands [8], we are tempted to believe that the dimerization of $(n\text{-}Bu_4N)_3[Co(CN)_5NCS]$ proceeds via the formation of a CN bridge.

The infrared spectrum of the photoproduct also shows a shift in the position of the terminal cyanide stretchings (from the CN ligand and from the *N*CS ligand). In the monomer product (CH_2Cl_2 solution) these bands are found at 2138 cm^{-1} (ν_{CN}) and 2121 cm^{-1} (ν_{CN}^{NCS}), in good agreement with the values reported by Melpolder and Burmeister [12]. However, these authors assign their 2134 cm^{-1} band to the cyanide stretch of the *N*CS ligands, which is in contradiction with their assignment in an earlier paper [16]. Also, in the complex $Co(NH_3)_5NCS$, where no interference of cyanide ligands occurs, the ν_{CN}^{NCS} value is reported to be 2125 cm^{-1} [17]. In our dimer reaction product these bands are found at 2116 cm^{-1} (s) with shoulders at 2132 and 2098 cm^{-1}.

Conclusions

The thermal and/or photochemical reaction mode presented in this work does not seem to be limited to the chloro and the isothiocyanato complexes: we have preliminary results on analogous reactions with the bromo and the azido complexes.

$(n\text{-}Bu_4N)_3[Co(CN)_6]$ on the other hand is thermally and photochemically inert in CH_2Cl_2. Nakamaru [4] found this also to be the case in $CHCl_3$. An explanation for this different behaviour as compared to other $Co(CN)_5X^{3-}$ complexes might well be found in the difference of reaction mechanism proposed for the photoreactions of these species in aqueous solution. For the photoaquation of $Co(CN)_5X^{3-}$ a dissociative mechanism is generally accepted [18], whereas for $Co(CN)_6^{3-}$ an interchange mechanism is proposed [19]. In the latter case the expulsion of the cyanide from the first coordination sphere is believed to be made possible by the interaction of a solvent molecule from the outer sphere. The non-complexing properties of CH_2Cl_2 and $CHCl_3$ would explain the stability of $Co(CN)_6^{3-}$ as compared to the other $Co(CN)_5X^{3-}$ complexes.

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