Inorganica Chimica Acta, 104 (1985) 143–147

Dinuclear Complexes with a μ-Cyano Ligand.
Part X. Synthesis and Characterization of several Derivatives of *cis*-Diaquaamminecobalt(III) Complexes. Influence of pH

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Received November 16, 1984

Abstract

Six new dinuclear complexes, derived from *cis*-$[Co(H_2O)_2(NH_3)_4]^{3+}$, *cis*-$[Co(H_2O)_2(en)_2]^{3+}$ and $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) were prepared and characterized by means of chemical analysis, electronic and IR measurements. The influence of the pH on the rate of the reaction was studied for the two derivatives of $[Pd(CN)_4]^{2-}$, showing that the best conditions to obtain the dinuclear compounds are at pH near 6, where the predominant species are *cis*-$[Co(OH)(H_2O)(amine)_2]^{2+}$. The $[Pt(CN)_4]^{2-}$ derivatives show Pt–Pt interactions both in the solid state and in solution.

Introduction

Previous work on the formation of dinuclear complexes in solution [1, 2] permitted us to synthesize and characterize $[(en)_2(H_2O)M{-}NC{-}M(CN)_5]$ [M,M = Co(III), Cr(III)] and $[(NH_3)_4(H_2O)Co{-}NC{-}Co(CN)_5]$ from reaction in solution of the corresponding diaquocomplexes and cyanurated anions. In a similar way, Tsuchiya and co-workers [3] prepared several doubly-complexed salts and dinuclear complexes from $[Co(CN)_6]^{3-}$ and $[Co(H_2O)_2(amine)]^{3+}$.

In order to complete these earlier studies we have examined the reaction in solution of two cobalt(III) cations, *i.e.*, $[Co(H_2O)_2(NH_3)_4]^{3+}$ and $[Co(H_2O)_2(en)_2]^{3+}$ with the planar cyano anions, $[M(CN)_4]^{2-}$, M = Ni, Pd, Pt(II). Taking into account the impossibility of working with $[Ni(CN)_4]^{2-}$ at acid pH values (due to decomposition into HCN and $Ni(CN)_2$ [4]) and the likelihood of occurrence of Pt–Pt interactions between the anionic part which make the resulting species very insoluble [5], we tried to study the influence of the pH in the rate of the reaction with the very stable $[Pd(CN)_4]^{2-}$ anion.

There are many kinetic studies in the literature [6–11] on reactions of the type:

$$[ML_4(H_2O)_2]^{3+} + L' \longrightarrow [ML_4L'(H_2O)]^{2,3+}$$

$$[ML_4(H_2O)_2]^{3+} + 2L' \longrightarrow [ML_4L_2']^{1,2,3+}$$

These processes have a strong pH dependence. In approximately neutral solutions the predominant species are the hydroxoaqua, which present the group H_2O and the labilizing group OH. As the acidity is increased, the concentration of hydroxoaqua species decreases and so does the rate. If the medium is strongly basic the species present is the dihydroxo, which does not give the desired reaction.

The experiments with diaquaamine cations of Co(III) and $Pd(CN)_4^{2-}$ were carried out with varying pH in order to identify the general mechanism which controls the formation of μ-cyano species in solution.

Experimental

Preparation of the New Dinuclear Complexes cis-$[(NH_3)_4(H_2O)Co{-}NC{-}M(CN)_3]_2[M(CN)_4]$ and cis-$[(en)_2(H_2O)Co{-}NC{-}M(CN)_3]_2[M(CN)_4]$ (M = Ni, Pd, Pt)

A concentrated solution of diaquo complexes $[Co(H_2O)_2(NH_3)_4](ClO_4)_3$ and $[Co(H_2O)_2(en)_2](ClO_4)_3$ [12, 13] was mixed with a concentrated solution of $Na_2[M(CN)_4]$ (M = Ni, Pd, Pt)** [14, 15]. The molar ratio must be 2:3. In Table 1 we indicate the optimum pH, the time required for the reaction and temperature, and the colour of the final products. All the new products precipitate with 50% yield on leaving the corresponding solution in the refrigerator for 1–2 h. The yield may be improved (30%) by adding ethanol/ether (1:1) to the mother

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**We used commercial $K_2[Pt(CN)_4]$aq by Johnson-Matthey.

0020-1693/85/$3.30

TABLE I. Optimum Conditions to Obtain the Dinuclear Complexes.

Complex	pH	Time/temp.	Colour
cis-$[(NH_3)_4(H_2O)Co-NC-Ni(CN)_3]_2[Ni(CN)_4]\cdot 2H_2O$	5.5	30 min/30 °C	orange
cis-$[(NH_3)_4(H_2O)Co-NC-Pd(CN)_3]_2[Pd(CN)_4]\cdot 2H_2O$	5.0	30 min/30 °C	orange
cis-$[(NH_3)_4(H_2O)Co-NC-Pt(CN)_3]_2[Pt(CN)_4]\cdot 2H_2O$	5.0	30 min/30 °C	brown
cis-$[(H_2O)(en)_2Co-NC-Ni(CN)_3]_2[Ni(CN)_4]\cdot 3H_2O$	5.5	90 min/40 °C	red-orange
cis-$[(H_2O)(en)_2Co-NC-Pd(CN)_3]_2[Pd(CN)_4]\cdot 3H_2O$	6.5	90 min/40 °C	red-orange
cis-$[(H_2O)(en)_2Co-NC-Pt(CN)_3]_2[Pt(CN)_4]\cdot 3H_2O$	6.5	90 min/40 °C	brown

TABLE II. Analytical Data ((%) Calculated (Found)).

Complex	Co	C	N	H
$[(NH_3)_4(H_2O)Co-NC-Ni(CN)_3]_2[Ni(CN)_4]\cdot 2H_2O$	14.47(14.6)	17.69(17.5)	34.40(34.6)	3.93(4.1)
$[(NH_3)_4(H_2O)Co-NC-Pd(CN)_3]_2[Pd(CN)_4]\cdot 2H_2O$	12.31(12.2)	15.05(15.3)	29.26(29.5)	3.34(3.4)
$[(NH_3)_4(H_2O)Co-NC-Pt(CN)_3]_2[Pt(CN)_4]\cdot 2H_2O$	9.63(9.5)	11.77(11.9)	22.89(23.0)	2.62(2.7)
$[(H_2O)(en)_2Co-NC-Ni(CN)_3]_2[Ni(CN)_4]\cdot 3H_2O$	12.59(12.8)	25.64(25.4)	29.92(30.1)	4.49(4.3)
$[(H_2O)(en)_2Co-NC-Pd(CN)_3]_2[Pd(CN)_4]\cdot 3H_2O$	10.92(10.8)	22.24(22.4)	25.95(25.6)	3.89(4.0)
$[(H_2O)(en)_2Co-NC-Pt(CN)_3]_2[Pt(CN)_4]\cdot 3H_2O$	8.76(8.9)	17.84(18.1)	20.81(21.3)	3.11(3.2)

TABLE III. Infrared and Electronic Spectra.

Complex	IR (cm^{-1})	Electronic (nm)				
cis-$[(NH_3)_4(H_2O)Co\text{-}NC\text{-}Ni(CN)_3]_2[Ni(CN)_4]\cdot 2H_2O$	2120(vs), 2200(m)	491		310	284	266
cis-$[(NH_3)_4(H_2O)Co\text{-}NC\text{-}Pd(CN)_3]_2[Pd(CN)_4]\cdot 2H_2O$	2125(vs), 2200(m)	491	348			260
cis-$[(NH_3)_4(H_2O)Co\text{-}NC\text{-}Pt(CN)_3]_2[Pt(CN)_4]\cdot 2H_2O$	2130(vs), 2200(m)	493		330	278	255
cis-$[(H_2O)(en)_2Co\text{-}NC\text{-}Ni(CN)_3]_2[Ni(CN)_4]\cdot 3H_2O$	2130(vs), 2180(m)	481		310	280	265
cis-$[(H_2O)(en)_2Co\text{-}NC\text{-}Pd(CN)_3]_2[Pd(CN)_4]\cdot 3H_2O$	2135(vs), 2180(m)	482	350			240
cis-$[(H_2O)(en)_2Co\text{-}NC\text{-}Pt(CN)_3]_2[Pt(CN)_4]\cdot 3H_2O$	2130(vs), 2200(m)	482		300	280	258

liquors. The control of the pH is very important for the Ni complexes, because at acid pH the formation of the very insoluble $Ni(CN)_2$ is observed. This control is also important with the cation *cis*-$[Co(H_2O)_2(NH_3)_4]^{3+}$, because at basic pH the complex decomposes with elimination of ammonia. Maintaining a basic pH is not so important with the *cis*-$[Co(H_2O)_2(en)_2]^{3+}$ cation, because the metal–nitrogen bond is in this case more stable.

Techniques

Infrared spectra were recorded on a Beckman IR20 A spectrophotometer purged with dry air. Samples were prepared using the KBr technique. Electronic absorption spectra were recorded in solution on a Beckman 5230 UV spectrophotometer. pH measurements (±0.001) were carried out with a digital Radiometer PHM 64, calibrated with appropriate standard solutions (pH = 4.006 and 6.385) at 25 °C.

Results and Discussion

Properties of the New Dinuclear Complexes

The six new dinuclear compounds were characterized by means of chemical analysis (Table II), electronic and IR spectra (Table III). The IR spectra show the two characteristic bands in the CN stretching region (2200–2000 cm^{-1}), caused by splitting of the $\nu_8(CN)$ (Table III). This clear splitting of the CN stretching frequency is good evidence for a bridging cyano group [1, 2, 16]. According to the literature the component occurring at lower frequency may be assigned to $\nu(CN)$ of the terminal cyano group, while that appearing at high frequency (*ca.* 2200 cm^{-1}) may be attributed to $\nu(CN)$ of the bridging cyano group [16]. All other bands due to amine or cyano ligands are in perfect agreement with the literature data [17], and are not modified by coordination (only the rocking of the ammonia ligand is slightly modified due to the sensitivity of this mode to the new coordination [17]).

There are two relevant features in the electronic spectra: the d–d shift of the first cobalt(III) transition and the Pt–Pt interaction. The six new dinuclear complexes present a symmetrical band centered at 491 nm for $[(H_2O)(NH_3)_4Co{-}NC{-}M(CN)_3]^+$ cations and 487 nm for *cis*-$[(H_2O)(en)_2Co{-}NC{-}M(CN)_3]^+$ cations, whose intensities are very similar to the parent diaquacobalt(III) cations. This shift of nearly 15 nm towards lower wavelengths (504 nm and 492 nm for *cis*-$[Co(H_2O)_2(NH_3)_4]^{3+}$ and *cis*-$[Co(H_2O)_2(en)_2]^{3+}$, respectively) has been observed in many other dinuclear compounds with μ-cyano bridge [18] and agrees with the position of –NC in relation to water in the spectrochemical series. The second d–d transition of cobalt(III) is observed only in the Pd compound: the intense 310 nm band of $[Ni(CN)_4]^{2-}$ completely obscures this second band in the Ni compound and the Pt–Pt interactions (see below) also obscures this band in the Pt complex. In the Ni and Pd compounds the bands attributable to $[M(CN)_4]^{2-}$ are observed in the same positions as those given in the literature [4]. The Pt case is different, due to the presence of the metal–metal interactions in the solid state and solution. The electronic spectrum of the $[Pt(CN)_4]^{2-}$ anion shows intense, diffuse bands with maxima at approximately 280, 258, 242 and 217 nm [4, 19].

In the solid state the two complexes derived from $[Pt(CN)_4]^{2-}$ anion present one strong band at *ca.* 375 nm, which causes the brown colour of these complexes instead of the orange colour of the Ni and Pd analogues. When these complexes are dissolved in water this new band at 375 nm disappears and a new, very broad band at *ca.* 300 nm appears (Table III).

These Pt–Pt interactions have already been studied in a series of similar complexes of Co(III), Cr(III), Rh(III) and Ir(III) with μ-CN derived of $[Pt(CN)_4]^{2-}$ and other amine as ligand [20]. These Pt–Pt interactions in the solid state have been explained by several authors [21–23] by the approximate treatment of Davidov, *i.e.* in terms of the charge-transfer bands of the isolated molecules shifted to lower frequencies by specific interactions among molecules in the crystal.

The occurrence of the 300 nm band in solution can be interpreted in terms of an oligomer association equilibrium in solution similar to that reported for $[Pt(CNR)_4][Pt(CN)_4]$ [23] and $Ba[Pt(CN)_4]$ [24].

Authors dealing with solution association, particulary Gray [25], have discussed this phenomenon in terms of molecular orbital theory. The splitting of the isolated levels into several components due to the Pt–Pt interactions causes a shift on the charge-transfer transitions towards lower frequencies (red-shift transition). In our case, and assuming the formation of a dimer, the d_{z^2} and π^* orbitals of each $[Pt(CN)_4]^{2-}$ group are split, and if we suppose a C_{2h} symmetry for the dimer then the splitting is $[(1a_g)^2(2b_u)^2(3a_g)^0(4b_u)^0]$. The transition $2b_u \rightarrow 3a_g$ $[{}^1A_g \rightarrow {}^1B_u]$ is dipole-allowed in this symmetry and will produce the strong new band at 300 nm (red-shift with respect to $d_{z^2} \rightarrow \pi^*$ of starting $[Pt(CN)_4]^{2-}$). If formation of trimers is assumed, the reasoning is the same and the red shift is even greater.

Influence of the pH in the Rate of the Anation Reaction

The first experiments indicated that $[Ni(CN)_4]^{2-}$ was unsuitable for this study due to its poor stability at acid pH, as was $[Pt(CN)_4]^{2-}$ due to its great tendency to form insoluble polymers with Pt–Pt interactions. Consequently the study was carried out with the stable $[Pd(CN)_4]^{2-}$ anion by following $[{}^1A_{1g} \rightarrow {}^1T_{1g}]$ of Co(III), at 480–500 nm.

Reaction of $[Pd(CN)_4]^{2-}$ *and* cis-$[Co(H_2O)_2(NH_3)_4]^{3+}$

0.025 M solutions of $Na_2[Pd(CN)_4]$ and *cis*-$[Co(H_2O)_2(NH_3)_4](ClO_4)_3$ were thermostatted at 30 °C. The pH was immediately controlled. In all cases an excess of the anion was added, the concentration of the cation and anion being 7.5×10^{-2} and 1.67×10^{-2} M, respectively. To change the pH, 0.1 M $HClO_4$ or 0.1 M NaOH were gradually added. Previous measurements indicate that at strongly acidic pH (corresponding to 1 M $HClO_4$) there is no reaction (the visible spectrum does not change within several hours). Conversely, at pH greater than 5 the reaction is fast (the anation is complete in less than 20 min). The final spectrum corresponds to $[(H_2O)(NH_3)_4Co{-}NC{-}Pd(CN)_3]^+$. It was also observed that the limiting pH of stability of the cation is about 6–7. At pH greater than 7–8 the complex decomposes evolving ammonia.

We therefore followed the reaction at pH = 5, recording the visible spectrum each 15 min. Isosbestic points were observed at 380, 418 and 525 nm. The 460–470 nm region is the optimum zone to follow the reaction due to the different molar absorption of the two species. The reaction was followed at 460 nm at eight different pH (between 2.82 and 6.72), at 30 °C. The values obtained were recorded graphically (Fig. 1). It was observed that at acid pH (2.8 for instance) there is no variation in 90 min. Conversely, at pH = 6.72 the reaction is complete in 20 min, followed by rapid decomposition of the amine part (liberation of ammonia). The optimum pH zone to study the reaction (Fig. 1) was found to be 4.75–5.75.

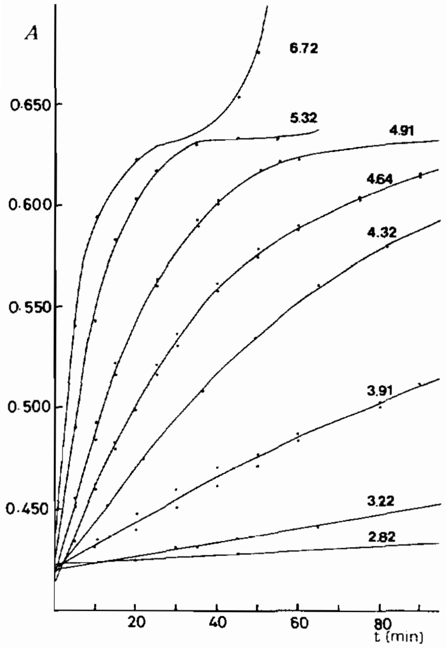

Fig. 1. Variation of the absorbance *vs.* time (min) for the reaction of *cis*-$[Co(H_2O)_2(NH_3)_4]^{3+}$ and $[Pd(CN)_4]^{2-}$ at different pH values (460 nm and 30 °C).

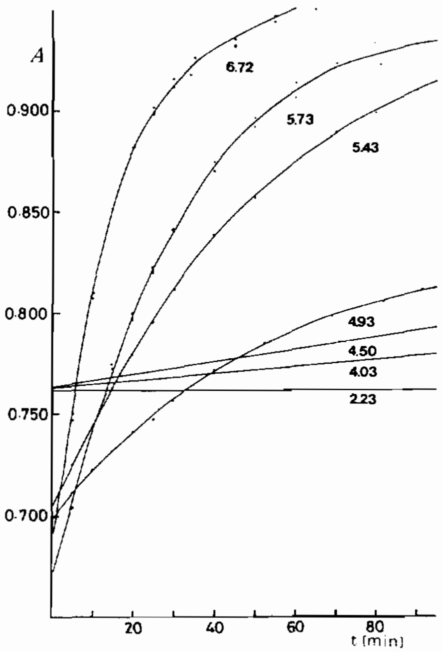

Fig. 2. Variation of the absorbance *vs.* time (min) for the reaction of *cis*-$[Co(H_2O)_2(en)_2]^{3+}$ and $[Pd(CN)_4]^{2-}$ at different acid pH values (465 nm and 40 °C).

Reaction of $[Pd(CN)_4]^{2-}$ *and cis*-$[Co(H_2O)_2(en)_2]^{3+}$

The experimental procedure was the same as in the previous case, but since no decomposition was observed at basic pH, the study was extended to pH 9.

The previous study indicates the great stability of the mixture of the two ions at acid pH and the rapid reaction at pH = 6–7. The final product was $[(H_2O)(en)_2Co{-}NC{-}Pd(CN)_3]^+$ with maxima indicated in Table III. The reaction was followed at pH 5 by recording the spectrum every 15 min. Isosbestic points were observed at 367, 415 and 505 nm. The best zone to study the process (due to the difference between the absorption) is about 465 nm. Taking into account that the first measurements indicate that the reaction is slower than in the previous case, a higher temperature (40 °C) was used, and the variation of absorption at pH between 2.83 and 9.22 was recorded (Figs. 2 and 3). Analogously to the ammonia case, the rate of anation is negligible at acid or basic pH (about 9). The optimum pH is about 6.5 which was the pH used in the experiments.

In order to understand better this difference in the rate at different pH we tried to study the anation reaction of $[Pd(CN)_4]^{2-}$ with $[Co(H_2O)(NH_3)_5]^{3+}$, $[Rh(H_2O)(NH_3)_5]^{3+}$, $[Ir(H_2O)(NH_3)_5]^{3+}$ or $[Co(NH_3)(H_2O)(en)_2]^{3+}$ in similar conditions to those indicated above. In all cases there is no reaction at pH 5 even at 60 °C.

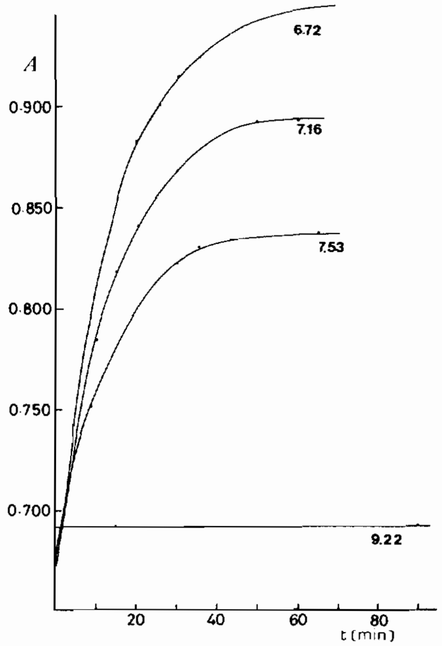

Fig. 3. Variation of the absorbance *vs.* time (min) for the reaction of *cis*-$[Co(H_2O)_2(en)_2]^{3+}$ and $[Pd(CN)_4]^{2-}$ at different basic pH values (465 nm and 40 °C).

Conclusion

We conclude that the pH dependence in the diaquo species and the inertness of the monoaquo species agrees with the mechanism proposed by Balt and co-workers [10, 11]. According to these authors the anation is produced by the presence of hydroxo-aqua species, which are predominant at almost neutral pH, being negligible the contribution of diaqua or dihydroxo species, *i.e.*, the group OH is the labilising group and the H_2O is the leaving group. On these grounds we can easily explain that at acid pH the doubly complexed salts are obtained with the diaqua cations, like those obtained by us and by Tsuchiya [1–3]. On the other hand, at almost neutral pH the dinuclear complexes are always obtained, to a different extent.

Acknowledgements

We thank the University of Barcelona and the Generalitat of Catalunya (DGEU) for financial support.

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