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Synthesis, Characterization and Study of the Pt–Pt Interaction in *cis*-$[(aa)(bb)FCr{-}NC{-}Pt(CN)_3]$ (aa, bb = bidentate amine)

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Abstract

Two new dinuclear μ-cyano complexes, *cis*-$[(en)(tn)FCr{-}NC{-}Pt(CN)_3]$ and *cis*-$[(chxn)(tn)FCr{-}NC{-}Pt(CN)_3]$ (en = ethylenediamine, tn = 1,3-diaminepropane and chxn = 1,2-cyclohexanediamine) have been obtained by solid state heating of the *trans*-$[Cr(aa)(bb)F(H_2O)][Pt(CN)_4]$ salts. These complexes have been characterized by chemical analysis, electronic and IR spectra. The dinuclear complexes show strong Pt–Pt interaction both in the solid state and in solution. The association constant of the oligomers formed has been calculated and correlated with the size of the amine ligands. An orbital explanation is proposed to account for the enhancement of the Pt–Pt interaction in the dinuclear complexes relative to the complex salts.

Introduction

In previous works [1–7] we described the synthesis and characterization of several dinuclear complexes with μ-cyano ligand, derived from the reaction of $[Pt(CN)_4]^{2-}$ with aquamines of Cr(III), Co(III), Rh(III), Ir(III). This synthesis can be made by solid state heating of parent doubly complexed salts, as in the following reaction

$$trans\text{-}[Cr(en)_2F(H_2O)][Pt(CN)_4] \longrightarrow cis\text{-}[(en)_2FCr{-}NC{-}Pt(CN)_3] + H_2O$$

With the $[M(NH_3)_5(H_2O)]^{3+}$ cations (M = Co, Rh, Ir) we have observed that there is a strong Pt–Pt interaction, both in the doubly complexed salts or in the derived dinuclear complexes [4, 5]. Instead, in the *trans*-$[Cr(aa)_2F(H_2O)][Pt(CN)_4]$ (aa = en, tn, chxn) [1, 2, 7] this Pt–Pt interaction is only found in the dinuclear μ-cyano derivatives, but never in the doubly complexed salts. In order to better understand this phenomenon we have synthesized several new dinuclear μ-cyano complexes of Cr(III) with mixed amine ligands. A theoretical model to explain why the Pt–Pt interaction is present only in the μ-cyano dinuclear complexes is given.

Taking into account that this Pt–Pt interaction is observed both in the solid state and in solution, the corresponding association constants have been calculated. In this work we compare these association constants with those previously reported by us [2, 4, 6, 7] and we try to correlate these values with the size of the amine ligands.

Experimental

Starting Materials

trans-$[CrF(en)(tn)(H_2O)](ClO_4)_2$ and *trans*-$[CrF(chxn)(tn)(H_2O)](ClO_4)_2$ were obtained as previously described in the literature [8, 9]. $K_2[Pt(CN)_4]$aq was used from Johnson-Matthey, without further purification.

New Complexes

trans-$[CrF(en)(tn)(H_2O)](ClO_4)_2$

0.15 g of $K_2[Pt(CN)_4]\cdot 2H_2O$ were dissolved in the minimum amount of water. The solution was passed through a cation exchange resin in its acid form. The $H_2[Pt(CN)_4]$ so obtained was cooled in an ice-cold bath. To this cold solution, 0.15 g of solid *trans*-$[CrF(en)(tn)(H_2O)](ClO_4)_2$ was added with constant stirring and, finally, 100 ml of acetone were added, in order to precipitate the new compound. The precipitate was filtered, washed with acetone and ether and air-dried. *Anal.* Calc. (found): C, 20.93(20.6); H, 3.84(3.7); N, 21.49(21.3)%.

cis-$[(en)(tn)FCr{-}NC{-}Pt(CN)_3]$

By solid state heating of the previous *trans* complex for 2 h at 130 °C, the new *cis* complex was obtained. *Anal.* Calc. (found): C, 21.43(21.3); H, 3.57(3.5) and N, 22.22(21.9)%.

cis-$[(chxn)(tn)FCr{-}NC{-}Pt(CN)_3]$

This complex was obtained as the previous en–tn complex. There is, however, a significant difference.

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All attempts to separate the *trans*-[CrF(chxn)(tn)(H_2O)] [Pt(CN)$_4$] were unsuccessful. Precipitation with acetone or other solvents always gave a mixture of *trans*-[CrF(chxn)(tn)(H_2O)] [Pt(CN)$_4$] and *cis*-[(chxn)(tn)FCr–NC–Pt(CN)$_3$]. The analysis of these mixtures always agreed with the ratio C/N and N/H. To obtain the pure dinuclear complex, it is sufficient to heat the previous mixture at 130 °C for 2 h. *Anal.* Calc. (found): C, 27.95(28.1); H, 4.30(4.4) and N, 20.07(19.9)%.

Techniques

Infrared spectra were recorded on a Beckman IR20-A spectrophotometer purged with dry air. Samples were prepared using the KBr technique. Electron absorption spectra were recorded in solution and in the solid state (KBr disk) on a Beckman 5230 UV spectrophotometer.

Molecular Association Constant

If the long-wavelength feature is due to a single oligomer formed according to the equilibrium

$$n[\mathrm{Pt(CN)_4}]^{2-} \overset{K_a}{\rightleftharpoons} [\mathrm{Pt(CN)_4}]_n^{2n-}$$

the association constant, K_a can be determined from the equation

$$CA^{-1/n} = n\epsilon^{-1}A^{(n-1)/n} + (K_a\epsilon)^{-1/n}$$

(C = stoichiometric concentration of the dinuclear complex, A = measured absorbance at 305 nm; ϵ = molar absorptivity of the oligomer complex at 305 nm and K_a = association constant). The derivation of this equation is straightforward and assumes that a 1 cm cell is used and the absorption at 305 nm is due only to the oligomer. Plots of $CA^{-1/n}$ *vs.* $A^{(n-1)/n}$ were linear, the slope giving the value of ϵ and the intercept the value of K_a.

Results and Discussion

IR Spectra

The IR spectrum of *trans*-[Cr(en)(tn)F(H_2O)]-[Pt(CN)$_4$] presents the bands due to the ethylenediamine and 1,3-diaminepropane ligands and the typical features of the $[Pt(CN)_4]^{2-}$ anion. Effectively, the cyanide region of the spectrum shows a very strong band around 2120 cm^{-1}, due to the asymmetric stretching ν(CN) in excellent agreement with those reported in the literature for the same $[Pt(CN)_4]^{2-}$ anion with simple cations [10]. The other possible bands of the anion are masked by the bands of coordinated amine. When the cyano complex is coordinated in the anation reaction, dinuclear complexes with a μ-cyano ligand are formed. The IR spectra of these two new complexes show a significant difference with respect to the doubly complexed salts, *i.e.* the presence of a very intense and perfectly defined doublet in the ν(CN) region: 2125 cm^{-1} and 2180 cm^{-1} for the en–tn complex and 2120 cm^{-1} and 2175 cm^{-1} for the chxn–tn complex. The clear splitting of the ν(CN) stretching frequency is good evidence for the presence of a bridging cyano group [1–7, 11]. According to the literature data the component occurring at lower frequency may be assigned to ν(CN) of the terminal cyano group, while that appearing at high frequency (*ca.* 2200 cm^{-1}) may be attributed to ν(CN) of the bridging cyano group [1–7, 11].

Electronic Spectra in Solution

The electronic spectra of the new complexes together with those of the parent species are given in Table I. The doubly complexed salt *trans*-[CrF(en)-(tn)(H_2O)] [Pt(CN)$_4$] presents the features of the *trans* complexes, as the parent *trans*-[CrF(en)(tn)-(H_2O)](ClO$_4$)$_2$ starting complex. The splitting into two components of the first d–d Cr(III) band is good evidence for the *trans* character. Instead the two new dinuclear μ-cyano complexes present only a well defined and symmetric band in this zone, characteristic of complexes of the type *cis*-[CrXX'-(amine)$_2$]$^{n+}$. This fact indicates the transformation of the starting *trans* into the *cis* dinuclear complex. A similar process has been reported for the salts of the type *trans*-[CrF(aa)$_2$(H_2O)] [Pt(CN)$_4$] (aa = en, tn, chxn) [1–3, 7].

On the other hand, in the μ-cyano dinuclear complexes a new band at 305 nm, that does not correspond either to the amminated or to the cyanurated part, can be observed. This band can be attributed to a Pt–Pt interaction as will be discussed below. In the solid state, this new band also appears at 340 nm.

Association Constant in Solution

Taking into account the theory of Adamson about Pt–Pt interactions [12], the 280 nm absorption band is independent of the Pt–Pt interaction and varies with the concentration according to Beer's law. Instead, the concentration dependence for the 305 nm band, clearly indicates the failure of Beer's law. On the other hand, the 250 nm and 220 nm bands are also concentration dependent. These three bands are, consequently, affected by the Pt–Pt interactions.

From the 280 nm band (ϵ = 1590) we calculated the concentration of the solutions. In Tables II and III the values of the absorbance at 280 nm and 305 nm for the two μ-cyano dinuclear complexes are given.

The calculated r^2, K_a and ϵ are given in Table IV, supposing the formation of trimers, according to Adamson's model (effectively, the value of the regression coefficient, r^2, is higher if the formation of trimers is assumed). These results can be compared

TABLE I. Electronic Spectra in Solution

Compounds	Assignment λ (nm)								Reference
	$^4A_{2g}-^4T_{2g}\left\{\begin{matrix}^4E_g\\ ^4B_g\end{matrix}\right.$			$^4A_{2g}-^4T_{1g}$	$(1b_2-2a_1)^a$	$A_{1g}-E_u$	$A_{1g}-A_{2u}$	$A_{1g}-A_{2u}$	
trans-$[CrF(en)(tn)(H_2O)]^{2+}$	519		456	368					9
trans-$[CrF(en)(tn)(H_2O)][Pt(CN)_4]$	520		460	363		280	250	223	b
cis-$[(en)(tn)FCr–NC–Pt(CN)_3]$		490			305^a	280	250	220	b
trans-$[CrF(chxn)(tn)(H_2O)]^{2+}$	521		457	370					9
cis-$[(chxn)(tn)FCr–NC–Pt(CN)_3]$		495			305^a	280	255	218	b

[a] Band due to the Pt–Pt interaction, see text. [b] This work.

TABLE II. Variation of Absorbance (A) (λ = 280 nm and 305 nm) with the Concentration (C) for the *cis*-[(en)(tn)-FCr–NC–Pt(CN)$_3$] Complex

$A_{280\ nm}$	$A_{305\ nm}$	$C \times 10^{-3}$ M
2.371	0.983	1.491
1.619	0.566	1.018
1.247	0.391	0.784
0.923	0.254	0.580
0.815	0.213	0.513
0.704	0.173	0.443
0.587	0.127	0.369

TABLE III. Variation of the Absorbance (A) (λ = 280 nm and 305 nm) with the Concentration (C) for the *cis*-[(chxn)-(tn)FCr–NC–Pt(CN)$_3$] Complex

$A_{280\ nm}$	$A_{305\ nm}$	$C \times 10^{-4}$ M
1.395	0.415	8.774
1.107	0.297	6.962
0.904	0.226	5.686
0.607	0.147	4.214
0.529	0.104	3.327
0.447	0.076	2.811
0.427	0.072	2.686
0.321	0.044	2.019

with those previously reported by us for several analogous complexes (Table IV). In all cases, the K_a values are very high, following the order tn > en > chxn ⩾ chxn–tn > en–tn. From these data, we can deduce that the K_a is lower for the complexes with mixed amine. On the other hand, taking into account that the K_a for the complexes with en and tn are greater than for chxn, it would seem reasonable that K_a(en–tn) > K_a(chxn–tn), but experimentally the result is the opposite. This fact can be explained due to the lower symmetry of the chxn–tn complex, in which the two amines are very voluminous and diffuse and, consequently, this compound is more similar to the *bis*-(1,2-cyclohexanediamine) complex.

Finally, the complexes with chxn and tn being more voluminous than the en analogues, the experimental K_a, tn > en > chxn does not follow the expected order according to their size. A possible explanation is that the chxn amine produces a similar surrounding to the en amine with regard to the central chromium(III), but its greater volume hinders the possible Pt–Pt interactions between the neighbour Pt ions.

Theoretical Model for the Pt–Pt Interaction

We have previously commented (see 'Electronic Spectra') that the dinuclear *cis*-[(aa)(bb)FCr–NC–Pt(CN)$_3$] complexes present Pt–Pt interaction. This

TABLE IV. Association Parameters for the Trimer Formation

	r^2	K_a	ϵ
cis-[(en)(tn)FCr–NC–Pt(CN)$_3$]	0.9942	3.1 x 10^6	2852
cis-[(chxn)(tn)FCr–NC–Pt(CN)$_3$]	0.9984	7.2 x 10^6	2123
cis-[(en)$_2$FCr–NC–Pt(CN)$_3$]	0.9908	4.0 x 10^7	3500
cis-[(tn)$_2$FCr–NC–Pt(CN)$_3$]	0.9919	1.2 x 10^8	4600
cis-[(chxn)$_2$FCr–NC–Pt(CN)$_3$]	0.9981	7.4 x 10^6	2717

interaction is due to the overlap between the p_z and d_{z^2} orbitals of neighbour Pt ions [13, 14]. In the Introduction we have pointed out that this interaction, when the amine complexes of Cr(III) are the counterion of the $[Pt(CN)_4]^{2-}$ anion, only takes place in the μ-cyano dinuclear complexes but not in the precursor mixed complexes salts, *trans*-[CrF(aa)(bb)(H$_2$O)][Pt(CN)$_4$]. A qualitative molecular orbital study has been carried out in search of an explanation to this unprecedented behaviour (see Appendix).

One of the bands assigned to free $[Pt(CN)_4]^{2-}$, at 258 nm, z-polarized is attributed to the $d_{z^2}(Pt)$–$a_{2u}(\pi)$ transition [12]. $a_{2u}(\pi)$ is, in fact, a mixture of the Pt(II)–p_z orbital with the π^* orbitals of cyanide (Fig. 1, right part). According to Adamson and coworkers [12] this band is very sensitive to the Pt–Pt interaction and, consequently, does not follow Beer's law. The band at 216 nm is also z-polarized and its intensity is sensitive to the Pt–Pt interaction.

If the dimer $[Pt(CN)_4]_2^{4-}$ formation is assumed (in staggered conformation, in order to minimize the steric hindrances) both the d_{z^2} and a_{2u} orbitals give a symmetrical (a_1) and an antisymmetrical (b_2) combination (Fig. 1, center).

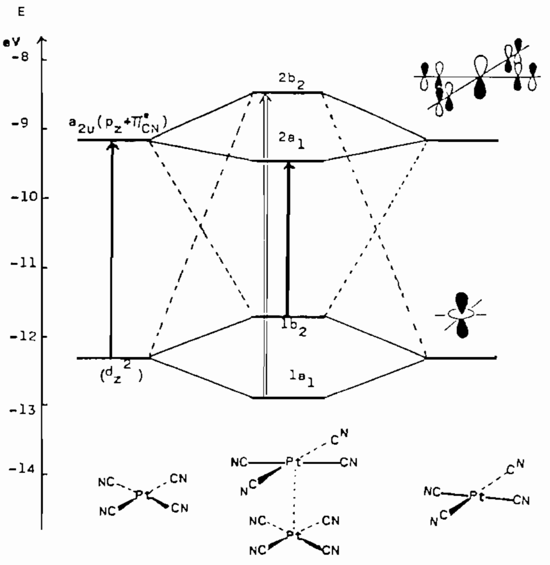
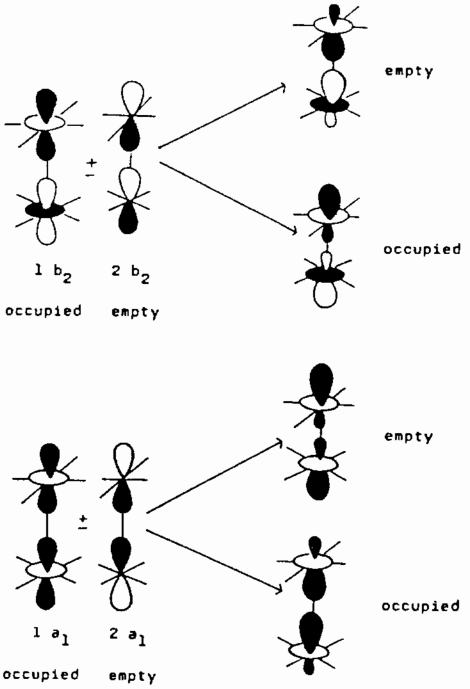


Fig. 1. Molecular orbitals of $[Pt(CN)_4]^{2-}$ and $[Pt(CN)_4]_2^{4-}$ with the orbital allowed transitions.

Now, there are four possible transitions, but only $1a_1 \rightarrow 2b_2$ and $1b_2 \rightarrow 2a_1$ are orbitally allowed. The first one is highly energetic and, probably, falls in the far UV. On the other hand, the new band at 305 nm (soln) can be assigned to the $1b_2 \rightarrow 2a_1$ transition.

We shall now take a closer look at the nature of the weak Pt–Pt bond formed. The interaction between the occupied d_{z^2} orbitals should originate a repulsion. Only the mixing of the corresponding molecular orbitals $1a_1$ and $1b_2$ with the empty $2a_1$ and $2b_2$ orbitals, respectively, alleviates the four electron-repulsion and originates the weak Pt–Pt bond.

A weak bonding interaction between both platinum atoms is reflected in the small positive value of the Pt–Pt overlap population (0.06) found in our calculations for $[Pt(CN)_4]_2^{4-}$. A more convenient way to monitor the extent of the Pt–Pt interaction is to look at the electronic population of the platinum p_z orbital since it reflects the amount of $p_z + d_{z^2}$ mixing responsible of the Pt–Pt bond, as shown in Scheme 1. The population of the platinum p_z orbital



Scheme 1.

TABLE V. Electronic Population of the Atomic Orbitals Involved in the Pt–Pt Interaction

Compound	Orbital	
	p_z	d_{z^2}
$[Pt(CN)_4]^{2-}$	0.01	1.93
$[Pt(CN)_4]_2^{4-}$	0.05	1.88
$[(NC)_3Pt–CN–CrH_4F]^{4-}$	0.01	1.93
$[(NC)_3Pt–CN–CrH_4F]_2^{8-}$	0.06	1.88

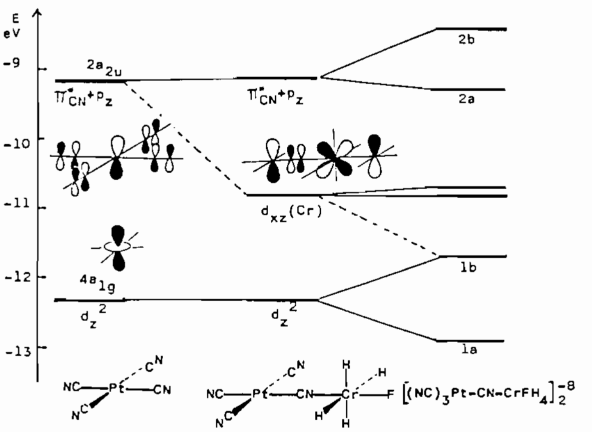


Fig. 2. Molecular orbital diagram for $[Pt(CN)_4]^{2-}$, $[(NC)_3Pt–CN–CrFH_4]^{4-}$ and $[(NC)_3Pt–CN–CrFH_4]_2^{8-}$ showing the mixing between $p_z + d_{z^2}$ Pt(II) orbitals.

is indeed significantly increased upon dimerisation of $[Pt(CN)_4]^{2-}$ while the occupation of d_{z^2} is decreased (Table V). Consequently, we can expect that all the factors which favour the mixing between the p_z(Pt) (empty) and the d_{z^2} (filled) orbitals will diminish this repulsion and enhance the Pt–Pt interaction.

The formation of the μ-cyano dinuclear complex has been studied with a $[H_4FCr–NC–Pt(CN)_3]^{4-}$ model. In this case, a new orbital, d_{xz}(Cr) (Fig. 2) with a sizeable contribution from p_z(Pt) and at lower energy than the a_{2u}, appears (Fig. 2). Due to its better energy match with the $1a_1$ and $1b_2$ orbitals, this new Cr(III) orbital will favour the mixing between d_{z^2} and p_z and, consequently, the Pt–Pt interaction as seen in the larger increase of the p_z(Pt) population upon dimerization compared to that of the unbridged $[Pt(CN)_4]^{2-}$ (Table V).

If π-basic ligands are introduced in the coordination sphere of Cr(III), substituting Br^- for H^- in our model bridged compound, the contribution from the p_z(Pt) orbital to the d_{xz}(Cr) orbital increases and, consequently, the Pt–Pt interaction will also be reinforced.

In conclusion, we have found an electronic factor, a weak one though, which can explain the greater tendency of the dinuclear cyano-bridged complexes to give a Pt–Pt interaction. In any case, other factors cannot be ruled out, such as the interaction of Pt with hydration water molecules or the difference between the ionic character of the mixed complexed salts and the neutral character of the dinuclear complexes, since it is well known that in the ionic salts of $[Pt(CN)_4]^{2-}$ the Pt–Pt interaction can vary appreciably with the counterion [15].

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Appendix

Extended Hückel calculations [16] with weighted H_{ij} formula [17] were used throughout. Slater exponents and coefficients as well as H_{ii} values were taken from previous works [18]. Regular geometries and the following bond distances were used: Pt–C, 2.02; C≡N, 1.15; Pt–Pt, 2.9; Cr–F, 1.85; Cr–H, 1.80; Cr–N, 2.02; Cr–Br, 2.60 Å.