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Dinuclear Complexes with μ-Cyano Ligand.
I. Synthesis and Characterization of *cis*[$(en)_2XCrNCNi(CN)_3$] aq (X = F, Cl, Br)

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Three new dinuclear complexes containing Cr(III), Ni(II) and μ-CN bridge have been prepared: cis-*[$(en)_2FCrNCNi(CN)_3$] $2H_2O$, obtained by heating* trans*[$CrF(H_2O)(en)_2$] [$Ni(CN)_4$] in the solid state and* cis*[$(en)_2XCrNCNi(CN)_3$] $2H_2O$ (X = Cl, Br) prepared from* cis*[$CrX(H_2O)(en)_2$]Br_2 (X = Cl, Br) by treatment with solutions of $(NH_4)_2$[$Ni(CN)_4$]. The new compounds have been characterized by chemical analysis, electronic and infrared spectra and conductivity measurements. The non-precipitation of $Ni(CN)_2aq$ with dilute or concentrated acids is noteworthy.*

Introduction

A number of dinuclear complexes with CN bridging ligand are known. The structures of some of them – $(NH_3)_5CoNCCo(CN)_5$ and $(NH_3)_5CoCNCo(CN)_5$ prepared by A. Haim and coworkers [1, 2] – have been determined by X-ray diffraction [3, 4]. Two of the authors [5] have also prepared dinuclear complexes with formulae $(NH_3)_4(H_2O)CoNCCo(CN)_5$ and $(NH_3)_4Co(NC)_2Co(CN)_4$ from *cis*[$Co(H_2O)_2(NH_3)_4$]$^{3+}$ and [$Co(CN)_6$]$^{3-}$ respectively.

In the past dinuclear complexes with cyano bridges have only been characterized in solution as all attempts to prepare solid species are unsuccessful. Recently, A. Haim *et al.* [6] have shown the existence of $(H_2O)_5CrNCCo(CN)_5$ and $(H_2O)_5CrCNCo(CN)_5$ in aqueous solution without being able to isolate them in the solid state.

There are fundamentally two methods to prepare such compounds: a) solid state heating of double complexed salts of the type, for example [$Co(H_2O)(NH_3)_5$] [$Co(CN)_6$], leading to $(NH_3)_5CoNCCo(CN)_5$ [1], and b) treatment of both reacting species in aqueous solution followed by precipitation of the resulting dinuclear complex with a suitable reagent, as in the case of $(NH_3)_5CoCNCo(CN)_5$ [2].

Attempts to obtain dinuclear ammine species of Cr(III) similar to those of Co(III) described by A. Haim [1, 2] were unsuccessful: thermal treatment of doubly complexed salts of the type [$Cr(H_2O)(NH_3)_5$] [$Co(CN)_6$] indicates water loss and introduction of the CN groups as well as simultaneous ammonia loss with formation of polymeric species. Such behaviour is due to a greater lability of the Cr–NH_3 bond as compared to the Co–NH_3 one. The above facts led us to think of using ethylenediamine rather than ammonia since amine complexes of Cr(III) with "en" as ligand are more stable than those with NH_3. As a result, three new dinuclear complexes – *cis*[$(en)_2XCrNCNi(CN)_3$] aq (X = F, Cl, Br) – have been obtained from *trans*[$CrF(H_2O)(en)_2$]$^{2+}$ and *cis*-[$CrX(H_2O)(en)_2$]$^{2+}$ (X = Cl, Br) by treatment with $Ni(CN)_4^{2-}$.

Experimental

Preparation of the New Compounds

trans[$CrF(H_2O)(en)_2$] [$Ni(CN)_4$]

One gram of *trans*[$CrF(H_2O)(en)_2$]$(ClO_4)_2$ [7] was slowly added with stirring to an ice-cold solution of $(NH_4)_2Ni(CN)_4$ obtained by passing 1 g of $K_2Ni(CN)_4$ dissolved in 10 ml of water through Lewatit S 100 G1 ion exchanger in the NH_4^+ form. The red-orange precipitate was filtered, washed with ethanol, ether and air-dried.

cis[$(en)_2FCrNCNi(CN)_3$] $2H_2O$

2 g of *trans*[$CrF(H_2O)(en)_2$] [$Ni(CN)_4$] (see above) was heated at 150 °C for 9–10 hours. A gradual change of colour occurred during this time and the sample lost 4.8–5% in weight (corresponding to 1 mol of water). The resulting, very soluble product was dissolved in 40 ml of ice-cold water, filtered from insoluble residues, reprecipitated with 95% ethanol (*ca.* 200 ml), filtered, washed with ethanol and ether and air-dried. Yield: 1.2 g. *Anal:* Calc. Cr: 13.34; C: 24.63; N: 28.74; H: 5.17; Ni: 15.06. Found Cr: 13.11; C: 24.66; N: 28.86; H: 4.80; Ni: 15.15%.

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cis[$(en)_2ClCrNCNi(CN)_3$] $2H_2O$

1 g of solid *cis*[$CrCl(H_2O)(en)_2$]Br_2 [8] was added to an ice-cold solution of $(NH_4)_2Ni(CN)_4$ prepared as above, from 0.68 g of $K_2Ni(CN)_4$. The resulting solution after being filtered to remove any insoluble impurity, was poured over a 1:1 mixture of isopropanol:acetone at –20 °C. The immediately formed pink solid was stirred for a few minutes, filtered and washed with ethanol and ether. The product obtained is sufficiently pure but may be recrystallized by dissolving it in the minimum amount of ice-cold water (10–15 ml) and after filtering pouring over isopropanol: acetone at –20 °C. Yield: 1 g. *Anal.* Calc. Cl: 8.73; Cr: 12.80; C: 23.63; N: 27.57; H: 4.90; Ni: 14.45. Found. Cl: 8.52; Cr: 12.97; C: 23.65; N: 27.20; H: 4.75; Ni: 14.10%.

cis[$(en)_2BrCrNCNi(CN)_3$] $2H_2O$

This was obtained similarly to the chloro analogue but using *cis*[$CrBr(H_2O)(en)_2$]Br_2 [9] rather than *cis*[$CrCl(H_2O)(en)_2$]Br_2. The purity of the product is confirmed by its analysis, visible and IR spectra. Recrystallization is unsuccessful due to aquation of the bromo ligand (faster than that of the chloro analogue) [10, 11] which favours the attack of further CN groups, eventually leading to insoluble polymeric products. *Anal.* Calc. Br: 17.73; Cr: 11.53; C: 21.29; N: 24.84; H: 4.43; Ni:13.02. Found. Br: 17.10; Cr: 11.46; C: 20.80; N: 24.80; H: 4.18; Ni: 12.86%.

Analysis

Cr was determined by titration with Fe^{2+} after oxidation with $S_2O_8^{2-}$ in H_2SO_4; Ni was determined by atomic absorption and/or gravimetrically with dimethylglyoxime; Cl and Br were determined by Volhard's method [12].

Other Methods

Infrared spectra were recorded on a Beckman IR 20 A spectrophotometer purged with dry air. Samples were prepared using the KBr technique. Electronic absorption spectra were recorded on a Beckman DB-GT spectrophotometer. Conductivity measurements were obtained with a Radiometer model CDM/3 conductivity bridge. Thermogravimetric analyses were recorded on a model Netzsch STA-429 with thermocouples of Pt/Pt–Rh.

Results and Discussion

cis[$(en)_2FCrNCNi(CN)_3$]aq was prepared from *trans*[$CrF(H_2O)(en)_2$] [$Ni(CN)_4$] previously obtained in this work (as indicated in the experimental part). The *trans* isomer was used since the *cis* species is poorly characterized in solution [13] and no other salt of the cation is known in the solid state. Furthermore all the literature data agree that treatment of the salts *trans*[$CrF(H_2O)(en)_2$]X_2 either by heating in the solid state or in acidic solution leads to replacement of H_2O by X and isomerization to give the corresponding *cis* species [7].

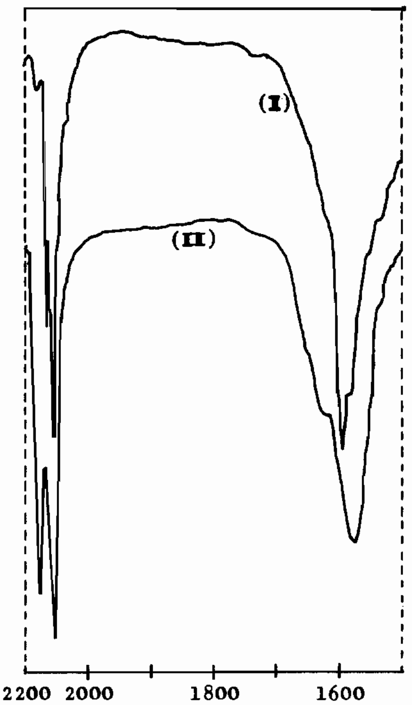

Fig. 1. I.R. Spectra. νCN and δ(NH_2) of I) *trans*[$CrF(H_2O)(en)_2$] [$Ni(CN)_4$], II) *cis*[$(en)_2XCrNCNi(CN)_3$] $2H_2O$ (X = F, Cl, Br).

A weight loss of 4.74% was observed in a previous TG study of *trans*[$CrF(H_2O)(en)_2$] [$Ni(CN)_4$] at temperatures between 25 and 300 °C. This weight loss agrees with one molecule of water (4.80% assuming the above species to be anhydrous as indicated by chemical analysis). On the other hand, IR and visible spectra are evidence of *cis* geometry for the compound studied.

Conductivity Measurements

Molar conductivities of the fluoro, chloro and bromo complexes in water, at 0 °C and concentration 10^{-3} *M*, are respectively 10, 18–20 and 25 ohm^{-1} mol^{-1} cm^2. On the other hand, the conductivity of the fluorocomplex is almost constant with time whereas that of the chloro and bromocomplexes increases with time (the latter specially). These facts agree perfectly with the discrepancies observed in the conductivity measurements of *cis*[$CrX(H_2O)(en)_2$]Br_2 (X = Cl, Br). These compounds show higher values than those expected for species giving three ions in solution, due to aquation of the halide ligand. Kinetic studies of these aquations indicate faster rates for the bromo than for the chlorocomplex [10, 11]. Furthermore in these dinuclear complexes,

TABLE I. Electronic Spectra (maxima in nm).

								Lit.
$Ni(CN)_4^{2-}$	–	–	–	310	285	268	198	[19][a]
t$[CrF(H_2O)(en)_2]^{2+}$	519	454	371	–	–	–	–	[7][a]
t$[CrF(H_2O)(en)_2][Ni(CN)_4]$	521	449	(Nujol suspension)			–	–	[a]
cis$[CrF(H_2O)(en)_2]^{2+}$	503	–	373	–	–	–	–	[22]
cis$[(en)_2FCrNCNi(CN)_3]2H_2O$	491/2	–	–	312	285	266	205	[a]
cis$[CrCl(H_2O)(en)_2]^{2+}$	510/2	–	387	–	–	–	–	[8][a]
cis$[(en)_2ClCrNCNi(CN)_3]2H_2O$	500	–	–	315	285	266	210	[a]
cis$[CrBr(H_2O)(en)_2]^{2+}$	519	–	388	–	–	–	–	[11][a]
cis$[(en)_2BrCrNCNi(CN)_3]2H_2O$	507/8	–	–	312	285	265	215	[a]

[a] This work.

substitution is probably favoured by the presence of terminal –NC groups which coordinate to the Cr ion after the halide has been replaced by water.

Infrared Spectra

Infrared spectra of the three new dinuclear complexes show the presence of a very intense and perfectly defined doublet at 2160, 2120 cm^{-1} (Fig. 1, II) whereas $K_2Ni(CN)_4$ and *trans*$[CrF(H_2O)(en)_2]$ $[Ni(CN)_4]$ (Fig. 1, I) [21] show only one band at 2120 cm^{-1}. In some cases this band may be split due to effects of crystal site or hydrogen bonding interactions, as seen in Fig. 1, I [21]. The clear splitting of the CN stretching vibration towards higher frequencies is good evidence for a bridging cyano group [14].

The bands of coordinated 'en' appear at identical frequencies in the three compounds and the values are in perfect agreement with those in the literature [15, 16].

The differences observed between *trans*$[CrF(H_2O)(en)_2][Ni(CN)_4]$ and its derivative *cis*$[(en)_2FCrNCNi(CN)_3]$aq are noteworthy. These differences agree with literature data and allow to distinguish between *cis* and *trans* isomers [16, 17]. Several authors indicate that $\delta_a(NH_2)$ which occurs in the region 1600 cm^{-1} for the Cr(III)–en complexes, appears at higher frequencies in the *trans* than in the *cis* isomer; on the other hand the *cis* isomer sometimes shows a splitting of this band which does not appear in the *trans* isomer. The band assigned to $\delta_a(NH_2)$ appears at 1600 cm^{-1} for *trans*$[CrF(H_2O)(en)_2][Ni(CN)_4]$ whereas it is observed at 1575 cm^{-1} (along with a shoulder at 1600 cm^{-1}) in *cis*$[(en)_2XCrNCNi(CN)_3]$ (X = F, Cl, Br). Characterization is less definite in other regions of the spectrum due to interference with δ(CN) of $Ni(CN)_4^{2-}$ and with crystal water vibrations. The identity of the infrared spectra of the three compounds, the study of the visible spectra which will be treated below and the *cis* geometry of the two starting substances (when X = Cl, Br) lead us to assign a *cis* geometry to the three new dinuclear complexes.

Electronic Spectra

Spectral data of the starting products as well as of the three new compounds prepared are given in Table I. It is observed that:

a) There is only one band in the 550–450 nm region (attributable to the transition $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ of Cr(III) ion). The presence of only one, completely symmetric band in this region is characteristic of complexes of the type *cis*$[CrXX'(en)_2]^{n+}$. On the other hand, the *trans* isomer shows splitting of the same band due to low symmetry components of the ligand field [18]. Such splitting clearly appears both in *trans*$[CrF(H_2O)(en)_2](ClO_4)_2$ and *trans*$[CrF(H_2O)(en)_2][Ni(CN)_4]$ (Table I).

b) The three new compounds exhibit the four characteristic bands of the $Ni(CN)_4^{2-}$ ion, at 310, 285, 265 and 200 nm [19] (Table I). The first band which appears at 310 nm in the free ion is somewhat displaced to longer wavelengths in the compounds studied due to coordination. Furthermore, this band at 310 nm completely overlaps the far less intense second transition $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ of Cr(III) which usually occurs at about 340–370 nm.

c) Substitution of aquo for isocyano ligand shifts the first d–d transition of Cr(III) towards higher frequencies (*ca.* 10–15 nm) (Table I), as can be expected from spectrochemical series considerations. The ligands –NC and NH_3 occupy almost identical positions in the spectrochemical series, the first one being somewhat stronger. A. Haim and coworkers [1, 2, 6] have always found, in their studies of replacement of H_2O by –NC, good correlation between the visible spectra of the resulting complexes and those in which H_2O has been replaced by NH_3. The same correlation has been found between the series *cis*$[CrX(NH_3)(en)_2]^{2+}$ (X = F, Cl, Br) (first maxima at 494, 506 and 514 nm respectively) [20] and the new series *cis*$[(en)_2XCrNCNi(CN)_3]$aq (X = F, Cl, Br) (first maxima at 491–2, 500 and 507–8, respectively).

Reactivity

The fluorocomplex is very stable in aqueous solution at room temperature whereas the chloro and bromo analogues slowly form an orange precipitate. This precipitate is probably a polymer (formed by direct or indirect replacement of the halide ligands by –NC groups) since the I.R. spectrum shows both a strong band at 2160–2170 cm^{-1} (characteristic of bridging CN) and a weak band at 2120 cm^{-1} (typical of terminal CN ligand).

It is noteworthy that gelatinous $Ni(CN)_2$aq does not precipitate on adding dilute or concentrated acids (even 60% $HClO_4$) to any of the three new compounds; in contrast, $Ni(CN)_4^{2-}$ decomposes immediately with acids giving $Ni(CN)_2$aq [21]. This facts allows to test the product obtained for free $Ni(CN)_4^{2-}$. Furthermore, this is evidence that aquation of the CN bridge must be very slow and that the insoluble products obtained are due to polymerization processes.

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