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Oxidations of Hexakis(aryl isocyanide)chromium(0) Complexes

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Oxidation of $Cr(CNR)_6$ complexes (R = C_6H_5, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, and p-ClC_6H_4) with 1 equiv of $AgPF_6$ in acetone yields the 17-electron chromium(I) complexes $[Cr(CNR)_6]PF_6$. Oxidation by air, followed by metathesis with NH_4PF_6, likewise gives these complexes. Further oxidation of these complexes by $AgPF_6$, or direct reaction of $Cr(CNR)_6$ and $AgPF_6$ in a 1:2 molar ratio, gives the corresponding 16-electron chromium(II) complexes $[Cr(CNR)_6](PF_6)_2$. Both series of new complexes had been anticipated from earlier electrochemical studies. Conductivity studies verify the formulation of these complexes as 1:1 and 1:2 electrolytes respectively and magnetic moment measurements are in accord with assigned metal oxidation states. A progressive shift to higher frequency for ν_{CN} is noted, going from the chromium(0) to chromium(I) to chromium(II) complexes.

Introduction

Although hexakis(aryl isocyanide)chromium(0) complexes were prepared over 20 years ago,[1] reference to oxidations of these species has been made only in the past several years. In 1972, electrochemical studies carried out in our group[2] established that these complexes undergo an electrochemically reversible one-electron oxidation, presumably to the chromium(I) complexes, $[Cr(CNR)_6]^+$. Subsequently it was reported that a second one-electron oxidation was also accessible for one of these species,[3] oxidation to the chromium(II) complex $[Cr(CNR)_6]^{2+}$ being presumed to occur in this process. It may be noted in passing that the $Cr(CNR)_6$ complexes were also shown to undergo a one-electron reduction.[2]

Considering the well-defined electrochemical data concerning these processes, it is remarkable that few chemical oxidations have been attempted, and that no well-defined chromium(I) or chromium(II) isocyanide complexes have yet been isolated and characterized. Indeed, failure to obtain such complexes was noted in one instance; the reaction of $AgPF_6$ with hexakis(p-tolyl isocyanide)chromium(0) in dichloromethane is said to give only decomposition products.[3] In an interesting preliminary communication,[4] air oxidation of hexakis(aryl isocyanide)chromium(0) species is reported to give a product having a ν_{CN} of about 2060 cm^{-1}. Although the substance formed on air oxidation was not isolated, an unstable and apparently uncharacterized product $Cr(CNC_6H_5)_5I$ is also reported to be formed on oxidation of $Cr(CNC_6H_5)_6$ with iodine; in turn on treatment of this compound with sodium tetraphenylborate, a complex characterized as $[Cr(CNC_6H_5)_5]B(C_6H_5)_4$ was obtained. Notably, this complex also had a strong ν_{CN} absorption near 2060 cm^{-1}, and the obvious inference is that both the air oxidation product and $Cr(CNC_6H_5)_5I$ contain the same cation. It is further argued[4] that the cation $[Cr(CNC_6H_5)_5]^+$ is a dimer, $[Cr_2(CNC_6H_5)_{10}]^{2+}$, based on coincidences in the infrared and Raman spectra. A structure is proposed wherein the two units are linked by bridging isocyanides, but not by an accompanying metal–metal single bond which is necessarily precluded by the magnetism of this species.

On two points this work seems less than satisfactory, however. The first is the unusual stoichiometry ascribed to the complex; a formulation with six ligands seems more reasonable. Cyclic voltammetry on the $Cr(CNR)_6$ species[2] is well-behaved and implies the likelihood of a simple one-electron transfer process, i.e., $Cr(CNR)_6 \rightleftharpoons Cr(CNR)_6^+ + e$. This suggests, in turn, that the $Cr(CNR)_6^+$ complexes have reasonable stability, and probably these species should exist, though of course complexes of a different stoichiometry such as $[Cr(CNR)_5]^+$ are not precluded from having a stable existence as well. Second, the presumed dimeric structure of the chromium(I) species seems quite unlikely. Attention is

directed to the recent article by Cotton and Hunter[5] on bridging carbonyls, wherein it is suggested that such a functionality must always be accompanied by a metal–metal bond. Reasonably, the same rule should also apply to complexes with bridging isocyanides.

Because of the lack of definitive work in this area and the apparent discrepancies noted above, we elected to study the oxidation processes of the hexakis(aryl isocyanide)chromium(0) complexes in more detail. Herein we report the results of this study, and the characterization of two groups of complexes, of stoichiometry $[Cr(CNR)_6]PF_6$ and $[Cr(CNR)_6](PF_6)_2$, derivatives of chromium(I) and chromium(II), respectively. We also offer evidence that the product of air oxidation of the $Cr(CNR)_6$ species is also $[Cr(CNR)_6]^+$, and suggest that the iodine oxidation product has a similar constitution.

Experimental Section

All reactions were carried out under nitrogen except where noted. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. High-resolution infrared spectra (± 1 cm^{-1}) in the range 2200–1850 cm^{-1} on dichloromethane solutions were recorded using a Digilab FTS-20 spectrometer; other infrared spectral measurements were made on a Perkin-Elmer Model 457 or Beckman IR-10 spectrometer, also employing dichloromethane solutions.

Conductivity measurements were determined at 24.5° using a Beckman conductivity bridge, Model RC-18A, and a Beckman conductivity cell with cell constant $k = 0.20$, and employed dry acetonitrile as the solvent. Magnetic susceptibility measurements were performed at five field strengths between 5.9 and 7.9 kOe on a Faraday balance calibrated against $Hg[Co(SCN)_4]$. Three of the complexes exhibited slight field dependence which was corrected for by the standard method of Honda and Owen.[6,7]

Electrochemical measurements were made using a three-electrode configuration, employing a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (KCl) reference electrode. Voltage and current functions were controlled using a Princeton Applied Research Electrochemistry System, Model 170, incorporating compensation for internal resistive potential drop. Dichloromethane was used as the solvent with the solution 5×10^{-3} M in substrate. Tetrabutylammonium perchlorate (0.1 M) was employed as the base electrolyte. Sweep rates were usually varied from 50 to 200 mV/sec in order to achieve the optimum peak shapes. However, a more detailed study was made for the compound Cr-(o-$CH_3C_6H_4NC$)$_6$. As the scan rate was changed from 10 V/sec to 10 mV/sec, the potential separation between the anodic and cathodic peaks for the process 0 → +1 varied from 700 to 136 mV, respectively. The ratios between the anodic and cathodic peak currents, $i_{p,a}/i_{p,c}$ in all cases were unity. Thus, the electrochemical nature of the complexes indicates a quasi-reversible system, i.e., moderately slow electron transfer compared to the rate of potential change.[8] All measurements were made at 25°C.

Preparation of Known $Cr(CNR)_6$ Compounds. The hexakis(aryl isocyanide)chromium(0) species used as starting materials were prepared by the method of Malatesta and coworkers[1] from chro-

mous(II) acetate and the corresponding aryl isocyanide. These compounds were recrystallized from a benzene–hexane mixture under nitrogen to give bright red crystalline substances.

Preparation of New [Cr(CNR)6]PF6 Complexes. [Cr-(C6H5NC)6]PF6. To a solution of Cr(C6H5NC)6 (1.0 g, 1.5 mmol) in deaerated acetone (70 ml) was added 1 equiv of AgPF6 (0.38 g, 1.5 mmol) whereupon the initial red solution immediately turned to a green-black color due to liberated Ag metal. The reaction was stirred 1.0 hr at room temperature. Filtration of the Ag metal gave an intense yellow-orange solution. Addition of hexane gave a precipitate of the product (1.05 g, 86%), which was recrystallized from an acetone–hexane mixture, washed with benzene and diethyl ether, and vacuum dried. The resultant brown-gold prisms upon heating darkened at 170° and decomposed at 213°.

Anal. Calcd for C42H30N6F6PCr: C, 61.84; H, 3.71; N, 10.30. Found: C, 61.47; H, 2.99; N, 10.09.

Ir: νC≡N 2065 s and 1985 m cm^{-1}; other bands 1596 w, 1486 w, and 840 m (νP–F) cm^{-1}.

Data on other compounds prepared by this route are given below.

[Cr(o-CH3C6H4NC)6]PF6. Obtained as brown-gold prisms from acetone–hexane in 62% yield after reaction for 1.5 hr. The compound darkened at 160° and decomposed at 208°.

Anal. Calcd for C48H42N6F6PCr: C, 64.06; H, 4.71; N, 9.34. Found: C, 63.97; H, 4.96; N, 9.30.

Ir: νC≡N 2055 s and 2014 m cm^{-1}; other bands 1595 w, 1575 w, 1485 m, 1145 w, 1100 vw, and 840 s (νP–F) cm^{-1}.

[Cr(p-CH3C6H4NC)6]PF6. Obtained as yellow prisms from acetone–hexane in 87% yield after reaction for 1.0 hr. The compound darkens at 155° and decomposes at 184°.

Anal. Calcd for C48H42N6F6PCr: C, 64.06; H, 4.71; P, 3.44. Found: C, 63.54; H, 4.42; P, 3.37.

Ir: νC≡N 2070 s and 2029 m cm^{-1}; other bands 1595 w, 1500 m, 1210 m, 1150 w, 840 m (νP–F), and 810 w cm^{-1}.

[Cr(p-CH3OC6H4NC)6]PF6. Obtained as blood red prisms from acetone–hexane in 73% yield after reaction for 1.5 hr. The compound darkens at 145° and decomposes at 193°.

Anal. Calcd for C48H40O6N6F6PCr: C, 57.89; H, 4.25; N, 8.44. Found: C, 58.29; H, 4.52; N, 8.22.

Ir: νC≡N 2069 s cm^{-1}; other bands 1600 m, 1580 w, 1500 m, 1290 m, 1200 w, 1180 w, 1160 m, 1100 w, 1020 m, and 840 (νP–F) cm^{-1}.

[Cr(p-ClC6H4NC)6]PF6. Obtained as yellow-orange prisms from acetone–hexane in 64% yield after reaction for 1.5 hr. The compound darkens at 190° and decomposes at 210°.

Anal. Calcd for C42H24N6Cl6F6PCr: C, 49.34; H, 2.37; N, 8.22. Found: C, 49.34; H, 2.51; N, 8.07.

Ir: νC≡N 2072 s and 2004 w cm^{-1}; other bands 1600 w, 1485 m, 1215 m, 1090 w, 1010 w, 840 m (νP–F), and 825 w cm^{-1}.

Alternate Preparation of [Cr(p-CH3C6H4NC)6]PF6. A solution of Cr(p-CH3C6H4NC)6 (0.76 g, 1 mmol) was prepared in 25 ml of CHCl3. Air was bubbled continuously through the solution and the mixture was stirred for 3.0 hr at room temperature, following the progress of the reaction by the changes in the νCN absorptions (Figure 1). During the course of the reaction the initial red solution changed to a lighter, orange color. Removal of the solvent and extraction of the brown-red oil with ethanol gave a dark yellow solution. Addition of NH4PF6 in ethanol followed by hexane gave golden-brown crystals (0.2 g, 22%). The infrared spectrum and cyclic voltammetry trace for this compound were identical with those of the known [Cr(p-CH3C6H4NC)6]PF6.

Preparation of [Cr(C6H5NC)6]B(C6H5)4. To a solution of Cr(C6H5NC)6 (0.67 g, 1.0 mmol) in deaerated CH2Cl2 (50 ml) was added 1 equiv of I2 (0.13 g, 0.5 mmol). The reaction was stirred for 15 min at room temperature and as the reaction proceeded the solution changed color from red to yellow-brown. Addition of a saturated solution of Na[B(C6H5)4] (0.4 g, excess) in a CH2Cl2–acetone mixture followed by addition of hexane yielded a gold-brown precipitate (0.5 g, 50%). This product was recrystallized from warm EtOH containing some excess Na[B(C6H5)4], and upon cooling, gold needle-like crystals were filtered out, washed with ether, and vacuum dried. Upon heating, the compound darkened over a range beginning at 154° and decomposed at 172°.

Anal. Calcd for C66H50N6BCr: C, 80.07; H, 5.09; N, 8.49. Found: C 80.72; H, 5.36; N, 8.38.

Ir: νC≡N 2065 s and 1985 m cm^{-1}; other bands 1596 m, 1486 m, 1025 w, and 985 w cm^{-1}.

Preparation of [Cr(RC6H4NC)6](PF6)2 Complexes. [Cr-
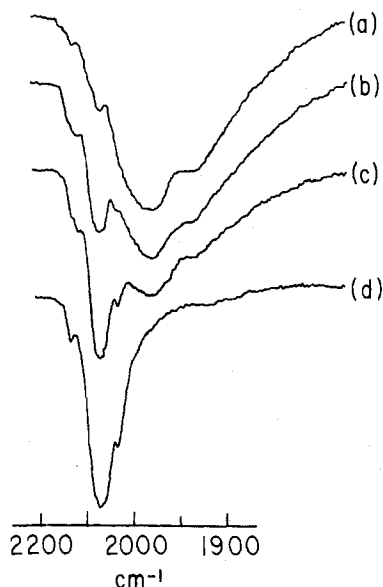
Figure 1. Air oxidation of Cr(p-CH3C6H4NC)6 in CHCl3: (a) $T =$ 0; (b) $T = 15$ min; (c) $T = 60$ min; (d) $T = 180$ min.

(C6H5NC)6](PF6)2. To a solution of Cr(C6H5NC)6 (1.0 g, 1.5 mmol) in deaerated acetone (50 ml) was added 2 equiv of AgPF6 (0.76 g, 3.0 mmol); the reaction mixture changed color to green-black. The mixture was stirred at room temperature for 1.5 hr. Removal of the Ag metal gave a yellow-green solution. Addition of hexane gave a precipitate of the desired product (1.1 g, 77%), which was recrystallized from an acetone–hexane mixture, washed with benzene and diethyl ether, and vacuum dried. (Washing with benzene removed an impurity, phenyl formamide, probably formed through hydration of free isocyanide present in the solution). The resultant yellow-green prisms upon heating darkened at 160° and decomposed at 192°.

Anal. Calcd for C42H30N6F12P2Cr: C, 52.51; H, 3.15; N, 8.75. Found: C, 51.96; H, 3.33; N, 8.49.

Ir: νC≡N 2161 s cm^{-1}; other bands 1596 w, 1486 w, and 840 vs (νP–F) cm^{-1}.

[Cr(o-CH3C6H4NC)6](PF6)2. Obtained as yellow prisms from acetone–hexane in 94% yield after reaction for 1.0 hr. The compound darkens at 127° and decomposes at 160°.

Anal. Calcd for C48H42N6F12P2Cr: C, 55.17; H, 4.05; N, 8.05. Found: C, 55.31, H, 4.25; N, 7.68.

Ir: νC≡N 2147 s cm^{-1}; other bands 1595 w, 1485 w, 1150 w, 1100 vw, and 840 vs (νP–F) cm^{-1}.

[Cr(p-CH3C6H4NC)6](PF6)2. Obtained as yellow-orange prisms from acetone–hexane in 72% yield after reaction for 1.0 hr. The compound darkens at 162° and decomposes at 209°.

Anal. Calcd for C48H42N6F12P2Cr: C, 55.17; H, 4.05; P, 5.93. Found: C, 54.48; H, 4.42; P, 5.89.

Ir: νC≡N 2153 s cm^{-1}; other bands 1600 w, 1500 w, 1200 w, 1150 w, 840 vs (νP–F), and 815 w cm^{-1}.

[Cr(p-CH3OC6H4NC)6](PF6)2. Obtained as maroon prisms from acetone–hexane in 78% yield after reaction 1.5 hr. The compound darkened at 140° and decomposed at 185°.

Anal. Calcd for C48H42N6O6F12P2Cr: C, 50.53; H, 3.71; N, 7.37. Found: C, 50.27; H, 3.64; N, 7.22.

Ir: νC≡N 2142 s cm^{-1}; other bands 1600 s, 1580 m, 1505 m, 1295 m, 1200 w, 1180 w, 1160 m, 1100 w, 1020 m, and 840 vs (νP–F) cm^{-1}.

[Cr(p-ClC6H4NC)6](PF6)2. Obtained as yellow prisms from acetone–hexane in 72% yield after reaction for 1.0 hr. Compound darkened at 204° and decomposed at 250°.

Anal. Calcd for C42H24N6Cl6F12P6Cr: C, 43.21; H, 2.07; N, 7.20. Found: C, 42.66; H, 2.03; N, 7.02.

Ir: νC≡N 2158 s cm^{-1}; other bands 1590 w, 1490 m, 1210 w, 1090 w, 1010 w, 840 vs (νP–F), and 820 w cm^{-1}.

Alternate Preparation of [Cr(o-CH3C6H4NC)6](PF6)2. To a solution of [Cr(o-CH3C6H4NC)6]PF6 (0.16 g, 0.18 mmol) in deaerated acetone was added an excess of AgPF6 (0.1 g, 0.4 mmol). The yellow-orange solution immediately darkened. After stirring for 1.0 hr at room temperature, the reaction was stopped. Filtration of the Ag metal which had formed and addition of hexane to the filtrate gave a yellow

precipitate which from observation of its infrared spectrum appeared to be a mixture of the desired product and o-CH3C6H4NHCHO. It was subsequently recrystallized from acetone–hexane, washed with benzene and diethyl ether, and vacuum dried. The resulting yellow crystals gave an infrared spectrum and cyclic voltammogram identical with those for [Cr(o-CH3C6H4NC)6](PF6)2 which had been prepared by the aforementioned method. Yield 0.07 g, 38%.

Results and Discussion

The synthesis of these chromium(I) and chromium(II) complexes, [Cr(CNR)6]PF6 and [Cr(CNR)6](PF6)2 (R = C6H5, o-CH3C6H4, p-CH3C6H4, p-CH3OC6H4, and p-ClC6H4), proved remarkably straightforward. The known zerovalent chromium complexes may be oxidized to either of these products by AgPF6 in acetone, with the product formed dependent on the molar ratio of reactants; viz.

$$Cr(CNR)_6 + AgPF_6 \rightarrow [Cr(CNR)_6]PF_6 + Ag$$

$$Cr(CNR)_6 + 2AgPF_6 \rightarrow [Cr(CNR)_6](PF_6)_2 + 2Ag$$

$$(R = C_6H_5, o\text{-}CH_3C_6H_4, p\text{-}CH_3C_6H_4, p\text{-}CH_3OC_6H_4, p\text{-}ClC_6H_4)$$
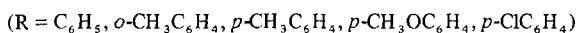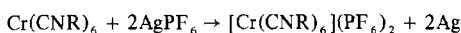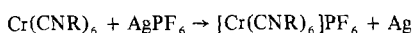
The chromium(I) complexes can also be formed, in poorer yield, by oxidations of the chromium(0) isocyanide species with oxygen, followed by metathesis with NH4PF6 to give the hexafluorophosphate salt

$$Cr(p\text{-}CH_3C_6H_4NC)_6 \xrightarrow{O_2} [Cr(p\text{-}CH_3C_6H_4NC)_6]^+ \xrightarrow{PF_6^-}$$
$$[Cr(p\text{-}CH_3C_6H_4NC)_6]PF_6$$
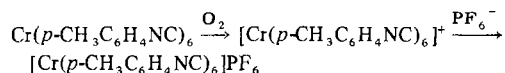
It is convenient to follow this reaction by infrared spectroscopy, observing the appearance of a ν_{CN} absorption at about 2060 cm^{-1} and the disappearance of the broad ν_{CN} absorption for the starting material at 1975 cm^{-1} (Figure 1). Prolonged treatment with air should be avoided, since this leads eventually to total degradation. The fate of the added oxygen was not pursued.

It is noted that both the one-electron and two-electron oxidations had been predicted earlier by electrochemical studies.[2,3]

These complexes are notable exceptions to the effective atomic number, or 18 e, rule; the [Cr(CNR)6]PF6 species are formally regarded as having 17 e in their valence shell, while the [Cr(CNR)6](PF6)2 compounds correspond to 16 e complexes. As crystalline solids, both the [Cr(CNR)6]PF6 and [Cr(CNR)6](PF6)2 complexes appear to be thermally stable indefinitely. They are also air stable in the solid state in contrast to most chromium complexes in these oxidation states. Colors generally range from yellow through gold to orange for the oxidized species, in contrast to the brilliant red of the zerovalent complexes; however, the complexes derived from p-CH3OC6H4NC are dull red. The diminution of color upon sequential oxidation is a clearly visible, though more subtle, indication of the oxidation process.

In solution both series of complexes are less stable with substantial decomposition being noted within hours by the presence of insoluble residues. The nature of this decomposition was not investigated.

Both series of complexes were characterized by elemental analyses (C, H, N). Conductivity measurements for the [Cr(CNR)6]PF6 species in acetonitrile confirmed the identification as 1:1 electrolytes. Magnetic moments of about 2.0 μ_B were found; these values are similar to those for other chromium(I) complexes.[9] The properties of the chromium(II) complexes were also in accord with their formulations; conductivity values of about 300 cm^2 ohm^{-1} mol^{-1} in acetonitrile were appropriate for 1:2 electrolytes[10] and magnetic moments of about 3.0 μ_B were similar to the values for other low-spin chromium(II) complexes.[9] These data are presented in Tables I and II.

In accord with these formulations, a sharp ν_{CN} absorption

Table I. Conductivity Data in Acetonitrile

Compd[a]	Λ, ohm^{-1} cm^2 mol^{-1} [b]
[Cr(C6H5NC)6]PF6	140
[Cr(C6H5NC)6]B(C6H5)4	133[c]
[Cr(o-CH3C6H4NC)6]PF6	138
[Cr(p-CH3C6H4NC)6]PF6	140
[Cr(p-CH3OC6H4NC)6]PF6	130
[Cr(p-ClC6H4NC)6]PF6	136
[Cr(C6H5NC)6](PF6)2	278
[Cr(o-CH3C6H4NC)6](PF6)2	314
[Cr(p-CH3C6H4NC)6](PF6)2	292
[Cr(p-CH3OC6H4NC)6](PF6)2	300
[Cr(p-ClC6H4NC)6](PF6)2	296

[a] Concentrations between 4×10^{-4} and 6×10^{-4} M. [b] Values reported for 1:1 electrolytes and 2:1 electrolytes in acetonitrile are 135–155 and 250–310, respectively.[10] [c] Literature[4] value 13 cm^2 ohm^{-1} mol^{-1}, in nitrobenzene.

Table II. Magnetic Susceptibility Data

Compd[a]	μ_{eff}^{295},[b] μ_B
[Cr(C6H5NC)6]PF6	2.07
[Cr(C6H5NC)6]B(C6H5)4	2.14
[Cr(o-CH3C6H4NC)6]PF6	2.14
[Cr(p-CH3C6H4NC)6]PF6	2.09[c]
[Cr(p-CH3OC6H4NC)6]PF6	2.04
[Cr(p-ClC6H4NC)6]PF6	2.18[c]
[Cr(C6H5NC)6](PF6)2	3.05
[Cr(o-CH3C6H4NC)6](PF6)2	3.13
[Cr(p-CH3C6H4NC)6](PF6)2	3.12[c]
[Cr(p-CH3OC6H4NC)6](PF6)2	3.10
[Cr(p-ClC6H4NC)6](PF6)2	3.14

[a] Reported values[9] are 2.0–2.1 for [Cr(Dipy)3]ClO4 and 2.9 for [Cr(Dipy)3](ClO4)2. [b] $\mu_{eff}^{295} = 2.825(\chi_M^{corr}T)^{1/2}$. [c] Honda–Owen extrapolation,[6,7] i.e., at $1/H = 0$.

is observed in the infrared spectrum of both the chromium(I) and chromium(II) species. In the former series ν_{CN} appears at about 2060 cm^{-1}, compared to the 1975 cm^{-1} absorption in the zerovalent species; in the latter the ν_{CN} absorption is found at about 2150 cm^{-1}. Thus each one-electron oxidation is accompanied by a rise of about 90 cm^{-1} in this value. The ν_{CN} absorption for the free isocyanides is found at about 2125 cm^{-1}, and only for the [Cr(CNR)6](PF6)2 species are the values of ν_{CN} higher than the value for the free ligand. This is not an unexpected result; an increase of ν_{CN} for cyanide ion upon coordination is noted.[11] The lowering of ν_{CN} upon coordination to the lower oxidation state metal is of course a consequence of increased π donation to the ligand.

Commentary on characterization might end at this point; however, there remains still the somewhat disconcerting difference in stoichiometry between the chromium(I) species here reported and the previously described complex, [Cr(CNC6H5)5]B(C6H5)4.[4] Because of this difference we feel compelled to argue further in favor of the stoichiometry, [Cr(CNR)6]+, reported here. We must also cast some doubt upon the unusual formulation offered in the earlier work.

First to point out the obvious, neither magnetic data nor conductivity will serve to distinguish one formulation from the other. Analyses for the five compounds prepared here do provide some support for the [Cr(CNR)6]PF6 formulation, but this is less than convincing. For example, the two possible stoichiometries [Cr(CNC6H5)6]PF6 and [Cr(CNC6H5)5]PF6 differ significantly only in the carbon percentage, 61.83% for the former, 58.98% for the latter (here found, 61.47%). Analyses for hydrogen differ only by about 0.2%, and analyses for nitrogen differ by only 0.5%.

Analyses for [Cr(CNC6H5)5]B(C6H5)4 and [Cr(CNC6-H5)6]B(C6H5)4 are even less descriminating, with neither carbon nor hydrogen differing by more than 0.2% and nitrogen differing by only 0.6%.

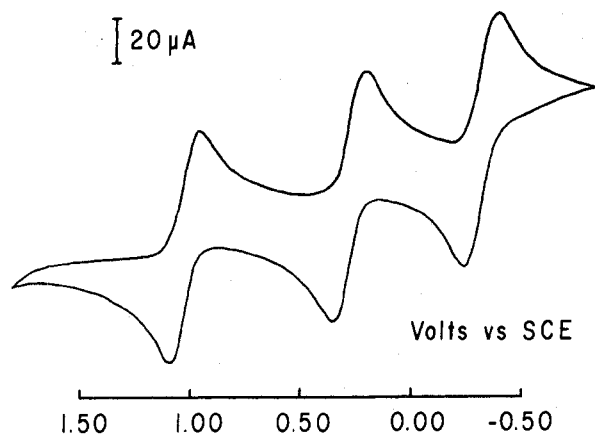The fact that the hexakis(ligand)chromium(I) formulation

Figure 2. The cyclic voltammogram of $[Cr(CNC_6H_5)_6]PF_6$ in CH_2Cl_2 with a scan rate of 200 mV/sec and 0.1 M $[Bu_4N][ClO_4]$.

Table III. Voltammetric Data[a]

Compd	$\frac{1}{2}[E_{p,c} + E_{p,a}]$[b]	$[E_{p,c} - E_{p,a}]$	Process
$Cr(C_6H_5NC)_6$	-0.32^d	0.084	$-1 \to 0$
	$+0.27^d$	0.078	$0 \to +1$
	$+0.98$	0.075	$+1 \to +2$
$[Cr(C_6H_5NC)_6]PF_6$	-0.34	0.160	$-1 \to 0$
	$+0.27$	0.125	$0 \to +1$
	$+0.99$	0.132	$+1 \to +1$
$[Cr(C_6H_5NC)_6]$-$B(C_6H_5)_4$	-0.32	0.110	$-1 \to 0$
	$+0.27$	0.115	$0 \to +1$
	$+0.98$	0.090	$+1 \to +2$
$[Cr(C_6H_5NC)_6]$-$(PF_6)_2$	-0.35	0.126	$-1 \to 0$
	$+0.25$	0.137	$0 \to +1$
	$+1.00$	0.117	$+1 \to +2$
$Cr(o\text{-}CH_3C_6H_4NC)_6$	-0.36	0.197	$-1 \to 0$
	$+0.33$	0.167	$0 \to +1$
	$+1.12$	0.118	$+1 \to +2$
$[Cr(o\text{-}CH_3C_6H_4NC)_6]$-$PF_6$	-0.39	0.157	$-1 \to 0$
	$+0.32$	0.152	$0 \to +1$
	$+1.12$	0.145	$+1 \to +2$
$[Cr(o\text{-}CH_3C_6H_4NC)_6]$-$(PF_6)_2$	-0.41^c	0.540	$-1 \to 0$
	$+0.31^c$	0.493	$0 \to +1$
	$+1.11$	0.138	$+1 \to +2$
$Cr(p\text{-}CH_3C_6H_4NC)_6$	-0.38^d	0.203	$-1 \to 0$
	$+0.22^d$	0.188	$0 \to +1$
	$+1.00^e$	0.167	$+1 \to +2$
$[Cr(p\text{-}CH_3C_6H_4NC)_6]$-$PF_6$	-0.43	0.160	$-1 \to 0$
	$+0.19$	0.142	$0 \to +1$
	$+0.99$	0.157	$+1 \to +2$
$[Cr(p\text{-}CH_3C_6H_4NC)_6]$-$(PF_6)_2$	-0.44^c	0.622	$-1 \to 0$
	$+0.19^c$	0.590	$0 \to +1$
	$+0.98^c$	0.390	$+1 \to +2$
$Cr(p\text{-}CH_3OC_6H_4NC)_6$	-0.45	0.255	$-1 \to 0$
	$+0.11$	0.220	$0 \to +1$
	$+0.84$	0.205	$+1 \to +2$
$[Cr(p\text{-}CH_3OC_6H_4NC)_6]$-$PF_6$	-0.48	0.142	$-1 \to 0$
	$+0.10$	0.139	$0 \to +1$
	$+0.89$	0.135	$+1 \to +2$
$[Cr(p\text{-}CH_3OC_6H_4NC)_6]$-$(PF_6)_2$	-0.48^c	0.455	$-1 \to 0$
	$+0.08^c$	0.437	$0 \to +1$
	$+0.88$	0.306	$+1 \to +2$
$Cr(p\text{-}ClC_6H_4NC)_6$	-0.20^d	0.130	$-1 \to 0$
	$+0.30^d$	0.135	$0 \to +1$
	$+0.99$	0.132	$+1 \to +2$
$[Cr(p\text{-}ClC_6H_4NC)_6]$-$PF_6$	-0.20	0.135	$-1 \to 0$
	$+0.30$	0.134	$0 \to +1$
	$+0.99$	0.125	$+1 \to +2$
$[Cr(p\text{-}ClC_6H_4NC)_6]$-$(PF_6)_2$	-0.21	0.238	$-1 \to 0$
	$+0.29$	0.251	$0 \to +1$
	$+1.00$	0.200	$+1 \to +2$

[a] Solutions in CH_2Cl_2; concentration of compound approximately 5×10^{-3} M; $[Bu_4N]ClO_4$ (0.1 M) used as supporting electrolyte. [b] Cathodic and anodic peak potentials are in volts vs. saturated calomel electrode (aqueous KCl). [c] Anodic and/or cathodic peak poorly defined. [d] Values reported previously without internal ir compensation.[2] [e] Value previously reported.[3]

seems more logical, and the support obtained through analyses is reassuring, but the strongest evidence for this formulation comes from the electrochemical data (Table III). We have previously noted that the $Cr(CNR)_6$ complexes show two well-defined sequential one-electron oxidations as well as a reduction. More impressive, however, is the fact that cyclic voltammetry scans for any of the three members of the series $[Cr(CNR)_6]^{n+}$ ($n = 0, 1, 2$) give essentially the same patterns. The $E^{1/2}$ values for each oxidation–reduction process are found to be the same within experimental error, regardless of the starting material chosen. A trace of the cyclic voltammogram for $[Cr(C_6H_5NC)_6]PF_6$ is presented in Figure 2, showing the three well-defined oxidation–reduction processes. It is inconceivable that this could occur if the processes occurring were anything but simple electron transfer processes.

It may be observed that these electrochemical oxidations for each species appear to be quasi-reversible processes. To investigate this matter further we looked more carefully at the $Cr(o\text{-}CH_3C_6H_4NC)_6$ system, varying scan rates between 10 V/sec and 10 mV/sec. For the $0 \to +1$ process the anodic and cathodic potentials decreased from 700 to 136 mV, while the ratio of anodic and cathodic peak currents remained at unity. This is good evidence for a system involving moderately slow electron transfer compared to the rate of potential change,[8] in accord with our expectations.

Serious doubts can be raised concerning the identity of the supposed $[Cr(CNC_6H_5)_5]B(C_6H_5)_4$ species.[4] As indicated earlier, neither analyses nor conductivity nor magnetic data can firmly establish this stoichiometry. We have questioned the dimeric formulation. Apart from the weak 1980-cm⁻¹ band in the infrared spectrum of this species, which is in the same position as the νCN for $Cr(CNC_6H_5)_6$, this compound shows the same absorption as is found in oxygen or $AgPF_6$ oxidation products, which we feel are firmly characterized as having the $[Cr(CNC_6H_5)_6]^+$ cation. Thus we suspected that this species had also been mischaracterized; it is probably a $[Cr(CNC_6H_5)_6]^+$ complex also. To confirm this as far as possible we undertook the synthesis of the supposed $[Cr(CNC_6H_5)_5]BPh_4$ following the vague directions provided in the earlier communication.[4] We were able to isolate a yellow-brown crystalline product, possessing properties similar to those reported. As expected, this complex gave a cyclic voltammetry scan which was virtually superimposable on the scan for $[Cr(C_6H_5)_6]PF_6$. This is the best evidence that we can obtain for its characterization as the anticipated hexacoordinate chromium species, rather than as the species indicated.

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Registry No. $Cr(C_6H_5NC)_6$, 17375-15-4; $[Cr(C_6H_5NC)_6]PF_6$, 57016-33-8; $[Cr(C_6H_5NC)_6]B(C_6H_5)_4$, 57016-34-9; $[Cr(C_6H_5NC)_6](PF_6)_2$, 57016-36-1; $Cr(o\text{-}CH_3C_6H_4NC)_6$, 57016-37-2; $[Cr(o\text{-}CH_3C_6H_4NC)_6]PF_6$, 57016-39-4; $[Cr(o\text{-}CH_3C_6H_4NC)_6](PF_6)_2$, 57016-41-8; $Cr(p\text{-}CH_3C_6H_4NC)_6$, 15531-15-4; $[Cr(p\text{-}CH_3C_6H_4NC)_6]PF_6$, 57016-43-0; $[Cr(p\text{-}CH_3C_6H_4NC)_6](PF_6)_2$, 57016-45-2; $Cr(p\text{-}CH_3OC_6H_4NC)_6$, 18115-32-7; $[Cr(p\text{-}CH_3OC_6H_4NC)_6]PF_6$, 57016-47-4; $[Cr(p\text{-}CH_3OC_6H_4NC)_6](PF_6)_2$, 57016-49-6; $Cr(p\text{-}ClC_6H_4NC)_6$, 36732-52-2; $[Cr(p\text{-}ClC_6H_4NC)_6]PF_6$, 57016-51-0; $[Cr(p\text{-}ClC_6H_4NC)_6](PF_6)_2$, 57016-53-2; $AgPF_6$, 26042-63-7; I_2, 7553-56-2.

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Lattice Effects on the
Electron Resonance of Halopentaamminechromium(III) Complexes

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Powder electron resonance spectra have been used to study the effect of different counterions on the spin-Hamiltonian parameters of $[Cr(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_5Br]^{2+}$ in the isomorphous hosts $[Co(NH_3)_5X]Y_2$ with $Y^- = Cl^-$, Br^-, I^-, and NO_3^-. X-ray powder patterns were used to determine the variations in the lattice dimensions. To explain the lattice effects a model with two different lattice deformations is necessary. The lattice effects are observed primarily through variations of the zero-field splitting tensor. Several possible lattice perturbation mechanisms are examined in the context of the origins of the zero-field splitting.

Introduction

Awareness of the effects of the lattice or environment on the electron paramagnetic resonance (EPR) spectra of molecular complexes of chromium(III) has been slow to develop. Most of the early studies of these systems were concerned with the contributions of the internal electronic structure to the spin-Hamiltonian parameters of the systems.[1,2] The large amount of effort involved in obtaining and interpreting single-crystal EPR data precluded comparison of the spectra in various host lattices. Thus, it was tacitly assumed that the paramagnetic complex adopted an intrinsic set of properties when it was substituted into an isomorphous host lattice. With the advent of random orientation spectra in glasses[3] and powders[4] it became feasible to begin comparison of the EPR spectra of a variety of related complexes.[3-10] The zero-field splittings of mixed-ligand complexes such as *trans*-[Cr-(en)$_2$A$_2$]$^{n+}$,[3] $[Cr(NH_3)_5A]^{n+}$,[5,10] $[Cr(NH_3)_4AA']^{n+}$,[8,9] and $[Cr(py)_4AA']^{n+}$ [9] (en = ethylenediamine, py = pyridine) were found to vary systematically with the ligand field strength of the A ligand, but changes of up to 20% in the zero-field splittings were found for the same chromium complex in different host lattices or in the same lattice at different temperatures.[6-8] The relative magnitude of the lattice effects leaves intact the idea that the spin-Hamiltonian parameters are molecular properties, but at the same time, this sensitivity to the environment will be useful for the study of guest–host interactions and may yield information about the relative importance of the intramolecular origins of the spin Hamiltonian.

The retention of an essentially molecular spin Hamiltonian implies that the primary effect of the lattice is to perturb the intramolecular origins of this Hamiltonian. Thus, it is requisite that we review these origins. Attention is focused upon the zero-field splitting for convenience of discussion and because no significant lattice effects have been observed for the *g* tensor. The zero-field splitting is primarily a spin–orbit effect, being a remnant of the free-ion spin–orbit splitting. Formally, the crystal field quenches the coupling between spin and orbital angular momenta by destroying the spatial similarity of the d orbitals, but this quenching is incomplete because the spin–orbit interaction is strong enough to retain some rotational symmetry. This effect is described by an admixture of excited crystal field states back into the ground state. (For d^3 ions, the only nonvanishing spin–orbit matrix elements with the $^4A_2(O_h)$ ground state involve excited states of $^2T_2$ and $^4T_2(O_h)$ symmetry.) The axial zero-field parameter, D, reflects the difference between the spin–orbit effect about the z axis and about an axis in the xy plane while the rhombic parameter measures similar differences about the x and y directions.

The magnitude of the spin–orbit interaction is considerably altered by several molecular effects.[1,2] (a) Unpaired spin is transferred off the metal ion onto the ligands reducing the metal wave function coefficients in the molecular orbitals of both the ground state and the admixed excited states. This delocalization naturally reduces the spin–orbit matrix elements on the metal center. Stephens incorporated this effect into the crystal field descriptions by including an orbital reduction factor.[11] (b) Both the interelectron repulsion parameters observed in the optical spectra and the spin–orbit parameter, which depend upon $\langle r^{-1} \rangle$ and $\langle r^{-3} \rangle$, respectively, are reduced by radial expansion of the metal d orbitals.[12] The relationship between the optical nephelauxetic effect[13] and the spin–orbit parameter reduction has been quantified[14] so that the appropriate spin–orbit parameter for a complex ion may be estimated from the optical data. (c) Spin density which is delocalized onto the ligands is subjected to a potential characteristic of the ligand and thus suffers a spin–orbit interaction characteristic of the ligand center. This ligand spin–orbit effect opposes the spin–orbit interaction on the metal center in matrix elements connecting excited crystal field states to the ground state but augments the interaction on the metal in matrix elements involving (d) charge-transfer states. The contributions of the spin–orbit interaction on ligand centers and of the charge-transfer state admixture were first recognized and formulated by Lacroix and Emch.[15] Subsequent quantitative estimates indicate that the charge-transfer state matrix elements may account for as much as 40% of the axial zero-field splittings.[2,5] (e) Doublet-state admixture into the quartet ground state via the spin–orbit interaction has been considered by several authors[1,2,16] with discordant results, but this effect probably does not contribute more than 10% of the zero-field splitting of the chemically anisotropic systems under consideration in this paper. (f) The dipole–dipole interaction between the unpaired spins can also contribute to the zero-field