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X-ray Structural Characterization of $[Cr(CNPh)_6][CF_3SO_3]$, $[Cr(CNPh)_6][PF_6]_2$, and $[Cr(CNPh)_6][SbCl_6]_3\cdot CH_2Cl_2$. Completion of a Unique Series of Complexes in Which the Metal Attains Four Different Oxidation States While Maintaining Identical Ligation

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The crystal structures of $[Cr(CNC_6H_5)_6][CF_3SO_3]$ (A), $[Cr(CNC_6H_5)][PF_6]_2$ (B), and $[Cr(CNC_6H_5)_6][SbCl_6]_3\cdot CH_2Cl_2$ (C) have been determined by single-crystal X-ray diffraction techniques. Compound A crystallizes in the $P2_1/n$ (No. 14) space group with $Z = 2$, $V = 2061$ (2) Å^3, $a = 10.757$ (3) Å, $b = 19.994$ (6) Å, $c = 10.242$ (3) Å, and $\beta = 110.69$ (20)°. Full-matrix least-squares refinement (264 variables, 3679 reflections) converged to give R and R_w values of 0.042 and 0.061, respectively. The structure of A consists of discrete $[Cr(CNC_6H_5)_6]^+$ cations and disordered $[CF_3SO_3]^-$ anions. A minor Jahn–Teller distortion is observed in the Cr–C bond lengths, which average 1.975 Å. Compound B crystallizes in the $P2_1/n$ (No. 14) space group with $Z = 4$, $V = 4365$ (5) Å^3, $a = 13.888$ (4) Å, $b = 19.638$ (4) Å, $c = 16.009$ (11) Å, and $\beta = 91.20$ (4)°. Least-squares refinement (329 variables, 2335 reflections) gave $R = 0.060$ and $R_w = 0.070$. The Cr site is a general position in the unit cell. The ligands show a pronounced C_{2v} angular distortion with the C–Cr–C bond angles ranging from 83.7 to 97.0°. The Cr–C bonds average 2.014 Å. Compound C crystallizes in the *Cccm* (No. 66) space group with $Z = 4$, $V = 6483$ (6) Å^3, $a = 14.818$ (6) Å, $b = 18.450$ (5) Å, $c = 23.714$ (7) Å, and $\beta = 90.0$°. Full-matrix least-squares refinement (180 variables, 1445 reflections) converged to give $R = 0.058$ and $R_w = 0.059$. The CH_2Cl_2 of crystallization was disordered. The four crystallographically related equatorial ligands exhibit Cr–C bonds of 2.049 (10) Å relative to the long Cr–C axial bonds of 2.091 (14) Å. Changes in the Cr–C and C≡N bond lengths are discussed in relation to the d-electron configuration of the central metal. The origin of the large positive value previously obtained for the $Cr(CNPh)_6^{3+}/Cr(CNPh)_6^{2+}$ reduction potential is discussed in relation to the large negative value reported for the $Cr(CN)_6^{3-}/Cr(CN)_6^{4-}$ couple.

Introduction

Recently, we have extended[1] previous investigations[2] of the electrochemical behavior of ring-substituted, six-coordinate aryl isocyanide complexes of Cr(0), Cr(I), Cr(II), and Cr(III). During the course of this work, we developed high-yield syntheses for the previously unavailable, highly reactive Cr(III) complexes.[3] We became interested in broadening our research effort in this area because the $Cr(CNAr)_6^{n+}$ series offers an opportunity unique in organometallic transition-metal chemistry: structure, bonding, and reactivity studies are feasible on compounds in which the metal center retains identical ligation in four different oxidation states.[4]

As an important part of these studies, we set out to complete the structural characterization of the $Cr(CNPh)_6^{n+}$ ($n = 0$–3) series by X-ray diffraction techniques. Of these four complexes, only the structure of $Cr(CNPh)_6$ had been previously determined.[5] Herein we report the X-ray crystal structure determinations of $[Cr(CNPh)_6][CF_3SO_3]$, $[Cr(CNPh)_6][PF_6]_2$, and $[Cr(CNPh)_6][SbCl_6]_3\cdot CH_2Cl_2$.

Experimental Section

General Considerations. Omnisolv dichloromethane and hexane were purchased from MCB and dried over activated alumina. $AgCF_3SO_3$ and $AgPF_6$ were purchased from Alfa Products. $Cr(CNPh)_6$ was synthesized by the method of Malatesta.[6] $[Cr(CNPh)_6][CF_3SO_3]$ and $[Cr(CNPh)_6][PF_6]_2$ were prepared by the method of Treichel[2b] ($AgCF_3SO_3$ was substituted for $AgPF_6$ in the first case).

Suitable crystals of $[Cr(CNPh)_6][CF_3SO_3]$ (yellow-brown) and $[Cr(CNPh)_6][PF_6]_2$ (yellow) for X-ray crystallographic studies were grown by allowing hexane to slowly diffuse with dichloromethane solutions of the compounds at 0 °C over a period of several days.

The crystal of $[Cr(CNPh)_6][SbCl_6]_3\cdot CH_2Cl_2$ (red) used in this study was grown by carefully layering −20 °C solutions of $Cr(CNPh)_6^0$ (top) and $SbCl_5$ in dry CH_2Cl_2 in a Schlenk tube. Crystals of $[Cr(CNPh)_6][SbCl_6]_3\cdot CH_2Cl_2$ grew at the solution interface over a period of 3 weeks. Attempts to grow crystals of several other salts (PF_6^-, SbF_6^-, AsF_6^-) of the $Cr(CNPh)_6^{3+}$ cation were unsuccessful.[7]

Crystal Handling. Crystals of $[Cr(CNPh)_6][CF_3SO_3]$ and $[Cr(CNPh)_6][PF_6]_2$ were mounted on standard glass fibers with use of an epoxy resin. Neither of these compounds in the solid state showed sensitivity to water or air when exposed to normal laboratory conditions.

The Cr(III) compound is extremely reactive toward atmospheric water and uncured epoxy resins. The crystal of $[Cr(CNPh)_6][SbCl_6]_3\cdot CH_2Cl_2$ was suspended in dry Nujol and then wedged into a glass capillary tube; the capillary was then sealed at both ends with epoxy. Crystals mounted in this way were found to be stable over the data collection period.

Summaries of the crystal data and collection parameters for the three compounds are found in Table I.

Structure Solutions General Remarks. The automatic peak searching, centering, and indexing routines available on the Enraf-Nonius SDP-CAD4 automatic diffractometer[8] were used to find and center 25 reflections, which were used to determine the unit cell parameters. Space group assignments were made by examining the data collected for systematic absences and confirmed by the successful solution and refinement of the structures. Data processing and reduction,[9] Patterson function, Fourier and difference Fourier syntheses,

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Table I. Crystal Data and Collection Parameters

	Cr(I)	Cr(II)	Cr(III)
compd	$[Cr(CNPh)_6][CF_3SO_3]$	$[Cr(CNPh)_6][PF_6]_2$	$[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$
formula	$C_{43}H_{30}N_6F_3O_3SCr$	$C_{42}H_{30}N_6F_{12}P_2Cr$	$C_{43}H_{32}N_6Cl_{20}Sb_3Cr$
fw	819.81	960.67	1759.12
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Cccm* (No. 66)
a, Å	10.757 (3)	13.888 (4)	14.818 (6)
b, Å	19.994 (6)	19.638 (4)	18.450 (5)
c, Å	10.242 (3)	16.009 (11)	23.714 (7)
β, deg	110.69 (20)	91.20 (4)	90.00
V, Å^3	2061 (2)	4365 (5)	6483 (6)
Z	2	4	4
d(calcd), g cm^{-3}	1.321 (1)	1.452 (2)	1.802 (2)
d(obsd), g cm^{-3}	1.314 (5)	1.423 (5)	1.746 (5)
cryst size, mm	0.26 × 0.26 × 0.31	0.08 × 0.10 × 0.31	0.16 × 0.31 × 0.36
μ, cm^{-1}	33.6	37.7	22.7
radiation (graphite monochromated)	Cu (λ = 1.541 84 Å)	Cu (λ = 1.541 84 Å)	Mo (λ = 0.710 73 Å)
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
collection range, deg	$2\theta = 0-156$	$2\theta = 0-96$	$2\theta = 0-50$
no. of unique data	4735	4493	3149
no. of data for $F^2 > \sigma(F^2)$	3679	2335	1445
P	0.05	0.05	0.04
no. of variables	264	329	180
R	0.042	0.060	0.058
R_w	0.061	0.070	0.059

and least-squares refinement[10] were carried out with use of the computer programs available in the Enraf-Nonius structure-solving package. Scattering factors were from Cromer and Waber[11] and included the effects of anomalous dispersion.[12]

$[Cr(CNPh)_6][SO_3CF_3]$. Over the course of data collection, the check reflections showed a maximum decrease of 7%. The data were corrected for this decomposition. No absorption corrections were made. A total of 4735 independent reflections were collected by the $\omega-2\theta$ scan technique in the scan range $2\theta = 0-156°$. Space group $P2_1/n$ (No. 14) was indicated by the systematic absences in the data, which were collected in the *hkl* and $\bar{h}kl$ octants. The trial solution, which placed the Cr atom at the origin, yielded $R = 0.55$ and allowed 11 more atoms to be placed by examination of the differences Fourier. Sequences of least-squares refinement, Fourier, and difference Fourier allowed the placement of all the non-hydrogen atoms. Full-matrix least-squares refinement (264 variables) utilizing anisotropic temperature factors for all non-hydrogen atoms and idealized placement of the H atoms with temperature factors (B) fixed at 8.0 Å^2 converged to give R and R_w values of 0.042 and 0.061, respectively. The error in an observation of unit weight was 1.742, based on a value of 0.05 for p in the $\sigma(I)$ equation.[9]

Disorder was found in the $CF_3SO_3^-$ counterion.[13] The nature of the disorder is based on the approximate equality of the SO_3 and CF_3 halves of the ion. The conformation of $CF_3SO_3^-$ is staggered so that the CF_3 and SO_3 groups are randomly disordered about the pseudo inversion center. The apparent C and S atoms were modeled with the assumption of half-occupied anisotropic S and a half-occupied C with a fixed isotroic temperature factor (B) of 10.0 Å^2. The apparent F and O sites were similarly modeled, but with a fully occupied anisotropic O–F average atom. The model for the disorder was judged adequate by the absence of any significant electron density peaks in the final difference Fourier in this region of the unit cell.

$[Cr(CNPh)_6][PF_6]_2$. During data collection no decrease or fluctuations were observed in the check reflections. A total of 4493 independent reflections were collected by the $\omega-2\theta$ scan technique in the rather limited range $2\theta = 0-96°$. High-angle scattering ($2\theta > 96°$) was poor, perhaps because of the small crystal size. Larger crystals were unavailable. Absorption corrections were not made. The space group $P2_1/n$ (No. 14) was indicated by the systematic absences in the data, which were collected in octants *hkl* and $hk\bar{l}$. Examination of the Patterson function led to no physically reasonable solution of the structure; direct methods were then employed. The program MULTAN[14] was used to generate an electron density map, which allowed the placement of the Cr atom, 1 of the 2 P atoms, and 41 of the light atoms into chemically reasonable positions.

Sequences of least-squares refinement and Fourier and difference Fourier allowed the placement of all non-hydrogen atoms. Full-matrix least-squares refinement (329 variables), which utilized anisotropic temperature factors for Cr, P, and F, isotropic temperature factors for C and N, and idealized placement of the H atoms with temperature factors (B) fixed at 6.0 Å^2, converged to give $R = 0.06$ and $R_w = 0.070$. The error in an observation of unit weight was 1.954, based on a value of 0.05 for the p in the $\sigma(I)$ equation.[9]

$[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$. During data collection no decrease or fluctuations were observed in the check reflections. A total of 3149 independent reflections were collected by the $\omega-2\theta$ scan technique ($2\theta = 0-50°$). Systematic absences in the data (octant *hkl*) indicated

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(9) The intensity data were processed as described in: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity I is given as

$$I = \frac{K}{\mathrm{NPI}}(C - 2B)$$

where K = 20.1166(attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by

$$\sigma^2(I) = \frac{K}{\mathrm{NPI}}[C + 4B + (pI)^2]$$

where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by

$$F_o = (I/Lp)^{1/2}$$

where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$:

$$\sigma(F_o) = \frac{1}{2}\frac{\sigma(I)}{I}F_o$$

(10) The function minimized was $w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as

$$R = (\sum||F_o| - |F_c||)/\sum|F_o|$$

$$R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum|F_o|^2)]^{1/2}$$

The error in an observation of unit weight is

$$[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$$

where NO and NV are the number of observations and variables, respectively.

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	atom	x	y	z
			A. $[Cr(CNPh)_6][SO_3CF_3]$				
Cr	0.0000 (0)	0.0000 (0)	0.0000 (0)	C5B	−0.5594 (2)	0.0987 (2)	0.0954 (3)
S	0.5848 (1)	0.01906 (6)	0.5252 (1)	C6B	−0.4329 (2)	0.0793 (1)	0.1066 (3)
O1	0.6394 (2)	−0.0083 (1)	0.4335 (2)	C1C	0.2037 (2)	0.1794 (1)	0.2558 (2)
O2	0.3478 (2)	−0.0036 (1)	0.3425 (2)	C2C	0.1930 (2)	0.2422 (1)	0.1983 (3)
O3	0.5635 (2)	0.0867 (1)	0.5045 (3)	C3C	0.2563 (3)	0.2953 (1)	0.2834 (4)
N1A	−0.0203 (2)	0.08034 (11)	−0.2689 (2)	C4C	0.3282 (3)	0.2841 (1)	0.4209 (4)
N1B	−0.2759 (2)	0.05507 (9)	−0.0059 (2)	C5C	0.3396 (3)	0.2225 (2)	0.4745 (4)
N1C	0.1387 (2)	0.12535 (9)	0.1729 (2)	C6C	0.2765 (3)	0.1681 (1)	0.3944 (3)
C7A	−0.0142 (2)	0.0500 (1)	−0.1697 (2)	C	0.584 (1)	0.0237 (5)	0.516 (1)
C7B	−0.1748 (2)	0.0349 (1)	−0.0047 (2)	H2A	0.0542 (0)	0.2013 (0)	−0.2750 (0)
C7C	0.0878 (2)	0.0784 (1)	0.1110 (2)	H3A	0.0354 (0)	0.2668 (0)	−0.4722 (0)
C1A	−0.0292 (2)	0.1179 (1)	−0.3864 (2)	H4A	−0.0498 (0)	0.2212 (0)	−0.6894 (0)
C2A	0.0171 (3)	0.1831 (2)	−0.3662 (3)	H5A	−0.1298 (0)	0.1163 (0)	−0.7240 (0)
C3A	0.0063 (4)	0.2215 (2)	−0.4829 (4)	H6A	−0.1092 (0)	0.0446 (0)	−0.5298 (0)
C4A	−0.0454 (4)	0.1941 (3)	−0.6113 (4)	H2B	−0.4714 (0)	0.0905 (0)	−0.2234 (0)
C5A	−0.0904 (4)	0.1316 (3)	−0.6309 (4)	H3B	−0.6845 (0)	0.1226 (0)	−0.2379 (0)
C6A	−0.0809 (4)	0.0903 (2)	−0.5166 (3)	H4B	−0.7380 (0)	0.1292 (0)	−0.0389 (0)
C1B	−0.4020 (2)	0.0763 (1)	−0.0132 (2)	H5B	−0.5833 (0)	0.1004 (0)	0.1766 (0)
C2B	−0.4941 (2)	0.0924 (1)	−0.1418 (3)	H6B	−0.3684 (0)	0.0680 (0)	0.1946 (0)
C3B	−0.6198 (3)	0.1116 (2)	−0.1497 (3)	H2C	0.1433 (0)	0.2491 (0)	0.1017 (0)
C4B	−0.6517 (2)	0.1153 (1)	−0.0322 (3)	H3C	0.2491 (0)	0.3393 (0)	0.2467 (0)
				H4C	0.3699 (0)	0.3205 (0)	0.4792 (0)
			B. $[Cr(CNPh)_6][PF_6]_2$				
Cr	0.1411 (1)	0.25640 (7)	0.05202 (8)	C2D	0.4665 (8)	0.1177 (5)	−0.0305 (6)
P1A	0.3870 (2)	0.2589 (1)	0.7870 (2)	C3D	0.5564 (8)	0.0832 (5)	−0.0162 (6)
P1B	0.2392 (2)	0.9787 (1)	0.2389 (2)	C4D	0.5765 (8)	0.0600 (5)	0.0560 (7)
F1A	0.3071 (4)	0.3154 (3)	0.7990 (4)	C5D	0.5219 (8)	0.0617 (6)	0.1233 (7)
F2A	0.3617 (6)	0.2527 (3)	0.6917 (4)	C6D	0.4337 (7)	0.0951 (5)	0.1143 (6)
F3A	0.3115 (5)	0.2012 (3)	0.8057 (4)	C1E	−0.0520 (6)	0.0690 (4)	0.0839 (5)
F4A	0.4658 (4)	0.2013 (3)	0.7778 (4)	C2E	−0.1091 (6)	0.0482 (4)	0.0180 (5)
F5A	0.4134 (5)	0.2636 (3)	0.8843 (3)	C3E	−0.1601 (6)	−0.0122 (4)	0.0283 (5)
F6A	0.4622 (5)	0.3165 (3)	0.7709 (4)	C4E	−0.1519 (6)	−0.0487 (4)	0.1002 (5)
F1B	0.2113 (5)	1.0440 (3)	0.1858 (4)	C5E	−0.0940 (7)	−0.0282 (5)	0.1643 (6)
F2B	0.1687 (5)	0.9343 (3)	0.1839 (4)	C6E	−0.0411 (7)	0.0331 (4)	0.1579 (5)
F3B	0.2666 (5)	0.9143 (3)	0.2924 (4)	C1F	0.2351 (6)	0.2388 (4)	0.3261 (5)
F4B	0.1556 (5)	0.9930 (4)	0.2971 (4)	C2F	0.2194 (7)	0.2904 (5)	0.3806 (6)
F5B	0.1799 (5)	0.4627 (4)	0.3210 (4)	C3F	0.2593 (7)	0.2854 (5)	0.4609 (6)
F6B	0.1903 (5)	0.5241 (3)	0.2074 (4)	C4F	0.3103 (7)	0.2304 (5)	0.4852 (6)
N1A	0.0023 (5)	0.3770 (3)	0.1028 (4)	C5F	0.3262 (7)	0.1790 (5)	0.4297 (6)
N1B	0.2735 (5)	0.3818 (3)	0.0070 (4)	C6F	0.2866 (7)	0.1825 (5)	0.3490 (6)
N1C	0.0777 (5)	0.2455 (3)	−0.1388 (4)	H2A	0.0483 (0)	0.5014 (0)	0.0822 (0)
N1D	0.3213 (5)	0.1597 (3)	0.0336 (4)	H3A	−0.0384 (0)	0.5998 (0)	0.1219 (0)
N1E	0.0038 (5)	0.1291 (3)	0.0754 (4)	H4A	−0.1818 (0)	0.5887 (0)	0.1880 (0)
N1F	0.2020 (5)	0.2446 (3)	0.2437 (4)	H5A	−0.2419 (0)	0.4848 (0)	0.2173 (0)
C7A	0.0467 (6)	0.3307 (4)	0.0809 (5)	H6A	−0.1605 (0)	0.3836 (0)	0.1810 (0)
C7B	0.2280 (6)	0.3350 (4)	0.0251 (5)	H2B	0.4186 (0)	0.3840 (0)	−0.0939 (0)
C7C	0.1014 (6)	0.2519 (4)	−0.0693 (5)	H3B	0.5041 (0)	0.4801 (0)	−0.1407 (0)
C7D	0.2520 (6)	0.1921 (4)	0.0355 (5)	H4B	0.4539 (0)	0.5842 (0)	−0.1045 (0)
C7E	0.0516 (6)	0.1769 (4)	0.0693 (5)	H5B	0.3371 (0)	0.6031 (0)	−0.0097 (0)
C7F	0.1777 (6)	0.2511 (4)	0.1739 (5)	H6B	0.2513 (0)	0.5084 (0)	0.0454 (0)
C1A	−0.0490 (6)	0.4350 (4)	0.1269 (5)	H2C	−0.0722 (0)	0.1798 (0)	−0.1929 (0)
C2A	−0.0118 (7)	0.4971 (5)	0.1102 (6)	H3C	−0.1250 (0)	0.1642 (0)	−0.3307 (0)
C3A	−0.0630 (8)	0.5558 (5)	0.1337 (6)	H4C	−0.0461 (0)	0.2120 (0)	−0.4383 (0)
C4A	−0.1467 (8)	0.5493 (5)	0.1721 (6)	H5C	0.0968 (0)	0.2700 (0)	−0.4159 (0)
C5A	−0.1824 (8)	0.4887 (5)	0.1899 (7)	H6C	0.1557 (0)	0.2879 (0)	−0.2770 (0)
C6A	−0.1347 (7)	0.4276 (5)	0.1681 (6)	H2D	0.4464 (0)	0.1342 (0)	−0.0844 (0)
C1B	0.3270 (6)	0.4390 (4)	−0.0213 (5)	H3D	0.5996 (0)	0.0789 (0)	−0.0605 (0)
C2B	0.4012 (7)	0.4280 (4)	−0.0756 (6)	H4D	0.6379 (0)	0.0390 (0)	0.0621 (0)
C3B	0.4507 (8)	0.4850 (5)	−0.1047 (6)	H5D	0.5406 (0)	0.0406 (0)	0.1749 (0)
C4B	0.4222 (7)	0.5456 (5)	−0.0812 (6)	H6D	0.3921 (0)	0.1006 (0)	0.1604 (0)
C5B	0.3526 (7)	0.5584 (5)	−0.0261 (6)	H2E	−0.1115 (0)	0.0766 (0)	−0.0313 (0)
C6B	0.3015 (7)	0.5022 (5)	0.0062 (6)	H3E	−0.2048 (0)	−0.0298 (0)	−0.0155 (0)
C1C	0.0455 (6)	0.2361 (4)	−0.2236 (5)	H4E	−0.1879 (0)	−0.0900 (0)	0.1040 (0)
C2C	−0.0376 (6)	0.1989 (4)	−0.2377 (5)	H5E	−0.0925 (0)	−0.0579 (0)	0.2130 (0)
C3C	−0.0685 (6)	0.1900 (4)	−0.3200 (5)	H6E	0.0052 (0)	0.0499 (0)	0.2006 (0)
C4C	−0.0208 (6)	0.2173 (4)	−0.3828 (5)	H2F	0.1833 (0)	0.3300 (0)	0.3633 (0)
C5C	0.0627 (7)	0.2526 (5)	−0.3692 (6)	H3F	0.2503 (0)	0.3218 (0)	0.4995 (0)
C6C	0.0986 (6)	0.2631 (4)	−0.2875 (5)	H4F	0.3352 (0)	0.2267 (0)	0.5408 (0)
C1D	0.4086 (6)	0.1233 (4)	0.0378 (5)	H5F	0.3627 (0)	0.1403 (0)	0.4458 (0)
				H6F	0.2968 (0)	0.1463 (0)	0.3094 (0)

Table II (*Continued*)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C. $[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$							
Sb1	0.0000 (0)	0.00000 (0)	0.0000 (0)	C5A	−0.1370 (9)	0.4837 (7)	0.3248 (6)
Sb2	0.0000 (0)	0.22897 (5)	0.2500 (0)	C6A	−0.1466 (9)	0.5461 (7)	0.3549 (5)
Cr	−0.2500 (0)	0.7500 (0)	0.5000 (0)	C7A	−0.2468 (7)	0.6724 (5)	0.4376 (4)
Cl1A	0.0187 (2)	0.0895 (2)	−0.0702 (1)	C1B	−0.5566 (11)	0.7888 (9)	0.5000 (0)
Cl1B	0.1582 (3)	−0.0203 (3)	0.0000 (0)	C2B	−0.5948 (9)	0.7981 (8)	0.5514 (6)
Cl2A	0.0000 (0)	0.3567 (2)	0.2500 (0)	C3B	−0.6807 (11)	0.8289 (9)	0.5509 (7)
Cl2B	0.0000 (0)	0.1018 (2)	0.2500 (0)	C4B	−0.7229 (14)	0.8438 (13)	0.5000 (0)
Cl2C	0.1329 (2)	0.2302 (2)	0.1961 (2)	C7B	−0.3906 (10)	0.7529 (9)	0.5000 (0)
Cl2D	0.0864 (3)	0.2313 (2)	0.3339 (2)	C	0.5000 (0)	0.0000 (0)	0.544 (3)
Cl	0.4218 (5)	0.0452 (5)	0.5000 (0)	H2A	−0.3641 (0)	0.5432 (0)	0.3651 (0)
N1A	−0.2400 (6)	0.6268 (4)	0.4052 (3)	H3A	−0.3460 (0)	0.4405 (0)	0.3116 (0)
N1B	−0.4653 (9)	0.7661 (6)	0.5000 (0)	H4A	−0.1987 (0)	0.3969 (0)	0.2910 (0)
C1A	−0.2317 (7)	0.5674 (6)	0.3697 (4)	H5A	−0.0779 (0)	0.4688 (0)	0.3158 (0)
C2A	−0.3050 (8)	0.5278 (6)	0.3531 (5)	H6A	−0.0957 (0)	0.5763 (0)	0.3639 (0)
C3A	−0.2935 (9)	0.4662 (7)	0.3234 (6)	H2B	−0.5651 (0)	0.7842 (0)	0.5846 (0)
C4A	−0.2080 (9)	0.4419 (6)	0.3095 (5)	H3B	−0.7095 (0)	0.8406 (0)	0.5848 (0)
				H4B	−0.7831 (0)	0.8618 (0)	0.5000 (0)

either No. 37 or No. 66 as the space group. An empirical absorption correction was made. Successful solution and refinement was subsequently carried out in *Cccm* (No. 66). Examination of the Patterson function followed the placement of the two crystallographically unique Sb atoms. Sequences of least-squares refinement and Fourier and difference Fourier allowed placement of the remaining non-hydrogen atoms. Full-matrix least-squares refinement (180 variables) utilizing anisotropic temperature factors for all non-hydrogen atoms and idealized placement of the H atoms with variable isotropic temperature factors converged to give $R = 0.058$ and $R_w = 0.059$. The error in an observation of unit weight was 0.771, based on a value of 0.04 for p in the $\sigma(I)$ equation.[9]

CH_2Cl_2 of Crystallization. One disordered dichloromethane molecule per formula unit is present in the unit cell. The unique chlorine atom (Cl) lies on the mirror plane and is related to the other chlorine atom by the twofold axis. This arrangement requires the carbon atom (C) to lie on the twofold axis, but it can be disordered either above or below the mirror plane. The electron density of carbon atom C was modeled with a 50% occupancy factor in each position. Because this type of disorder is somewhat surprising,[15] an attempt was made to refine the structure in the corresponding acentric space group (*Ccc*2, No. 37). This refinement did not lead to significantly different parameters for the Cl atom nor did it lead to a well-defined C atom in CH_2Cl_2; therefore, the centric space group was used for the final calculations.

Results

Tables II–IV give the final atomic parameters, bond lengths, and bond angles determined for each structure. (Tables and figures labeled A correspond to the Cr(I) compound, B to the Cr(II) compound, and C to the Cr(III) compound.) Final values for the temperature factors and structure factors are given in the supplementary material.

$[Cr(CNPh)_6][CF_3SO_3]$. The structure of $[Cr(CNPh)_6][CF_3SO_3]$ consists of discrete $[Cr(CNPh)_6]^+$ cations and disordered $[CF_3SO_3]^-$ anions. The disorder in the $[CF_3SO_3]^-$ anion is discussed in the Experimental Section. Examination of the structural parameters suggests no interionic contacts shorter than those expected on the basis of van der Waals radii.

The Cr atom sits on the inversion center, which requires mutually trans ligands to be equivalent (sets A, B, and C labeled in the ORTEP view of the cation (Figure 1A)). The CrC_6 coordination core is very nearly octahedral with the idealized 90° C–Cr–C angles averaging 91.0 (3)°. Two of the three independent Cr–C bond lengths (ligands A and C) are nearly identical ($\sim 4\sigma$) within experimental error (1.968 (3) Å) while the third is slightly longer (1.990 (3) Å), a deviation from the other two of about 7σ. The lengthening of the Cr–C bonds on one axis may be indicative of the small Jahn–Teller distortion expected for the low-spin d^5 $^2T_{2g}$ (in O_h) ground state.[16] The average C≡N and N—C_{ring} distances of 1.159 (3) and 1.397 (3) Å show no systematic variation with ligand and are in the ranges (1.142–1.176 and 1.388–1.420 Å, respectively) normally found in complexes of the phenyl isocyanide ligand.[17] (Further discussion of the systematic trends observed in the Cr—C, C≡N, and N—C_{ring} bond lengths with metal oxidation state is deferred until a later section of this paper.)

The Cr—C≡N and C≡N—C_{ring} linkages are very near the nominal 180° values expected for phenyl isocyanide primarily functioning as a σ-donor ligand. The orientations of the phenyl rings are partially determined by the Cr site symmetry; i.e., the trans rings related by the inversion center are required to be coplanar. A pitch angle may be defined in the idealized geometry (Cr—C≡N—C_{ring} linkage strictly linear) as the angle between the phenyl ring plane normal and the plane normal defined by the $Cr(CN)_4$ square-planar unit containing the phenyl ring (i.e., the angle between the plane normal of phenyl ring A and plane normal of the $Cr(CN)_4$ plane containing ligands A and B). The values of this angle are 3.1, 25.7, and 18.9°, respectively. It is interesting to note that the axis with the shortest Cr–C bond length (*a* axis) is the axis with the pitch angle closest to 0° while the *b* axis phenyl ring with the longest Cr–C bond deviates the most from 0°. Although this may be a consequence of the effect of the phenyl ring orientation on the σ component of the Cr–C bond, more experimental (single-crystal EPR) and theoretical (MO calculations) work is needed to confirm this explanation.

$[Cr(CNPh)_6][PF_6]_2$. The ORTEP view (Figure 1B) and, more vividly, the stereoview of the $[Cr(CNPh)_6]^{2+}$ cation (Figure 2) illustrate the distortion present in this cation. Of the structures determined for the Cr(0), Cr(I), Cr(II), and Cr(III) hexakis(phenyl isocyanide) complexes, the Cr(II) compound is by far the most distorted. The structure consists of discrete $[Cr(CNPh)_6]^{2+}$ cations and PF_6^- anions with no apparent close interionic contacts. The shortest of these is the 3.197 (7) Å contact between F4B and C3D.

The Cr atom site is a general position in the unit cell, requiring no symmetry elements (i.e., the six CNPh ligands are

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(16) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; pp 678–682. Figgis, B. N. *Trans. Faraday Soc.* **1961**, *57*, 204.

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Table III. Selected Interatomic Distances (Å) with Their Estimated Standard Deviations

A. $[Cr(CNPh)_6][SO_3CF_3]$			
$Cr(CNPh)_6^+$			
Cr-C7A	1.964 (2)	C7C-N1C	1.156 (2)
Cr-C7B	1.990 (2)	N1A-C1A	1.393 (2)
Cr-C7C	1.971 (2)	N1B-C1B	1.397 (2)
C7A-N1A	1.165 (2)	N1C-C1C	1.400 (2)
C7B-N1B	1.156 (2)		
Disordered[a] $CF_3SO_3^-$			
"S-C"	1.917 (14)	"S-O2"	1.328 (3)
"S-O1"	1.384 (3)	"S-O3"	1.375 (3)
B. $[Cr(CNPh)_6][PF_6]_2$			
$Cr(CNPh)_6^{2+}$			
Cr-C7A	2.021 (7)	C7D-N1D	1.154 (7)
Cr-C7B	2.011 (7)	C7E-N1E	1.154 (7)
Cr-C7C	2.011 (6)	C7F-N1F	1.167 (7)
Cr-C7D	2.013 (7)	N1A-C1A	1.401 (7)
Cr-C7E	2.019 (7)	N1B-C1B	1.425 (7)
Cr-C7F	2.009 (7)	N1C-C1C	1.433 (7)
C7A-N1A	1.157 (7)	N1D-C1D	1.409 (8)
C7B-N1B	1.156 (7)	N1E-C1E	1.421 (7)
C7C-N1C	1.160 (6)	N1F-C1F	1.392 (7)
C. $[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$			
$Cr(CNPh)_6^{3+}$			
Cr-C7A	2.060 (10)	C7B-N1B	1.134 (14)
Cr-C7B	2.085 (13)	N1A-C1A	1.386 (11)
C7A-N1A	1.144 (10)	N1B-C1B	1.415 (18)
$SbCl_6^-$ 1			
Sb1-Cl1A	2.361 (2)	Sb1-Cl1B	2.373 (3)
$SbCl_6^-$ 2			
Sb2-Cl2A	2.357 (3)	Sb2-Cl2C	2.348 (2)
Sb2-Cl2B	2.345 (4)	Sb2-Cl2D	2.366 (3)
Disordered[a] CH_2Cl_2			
C-Cl	1.767 (33)		

[a] See Experimental Section for the description of the disorder model employed.

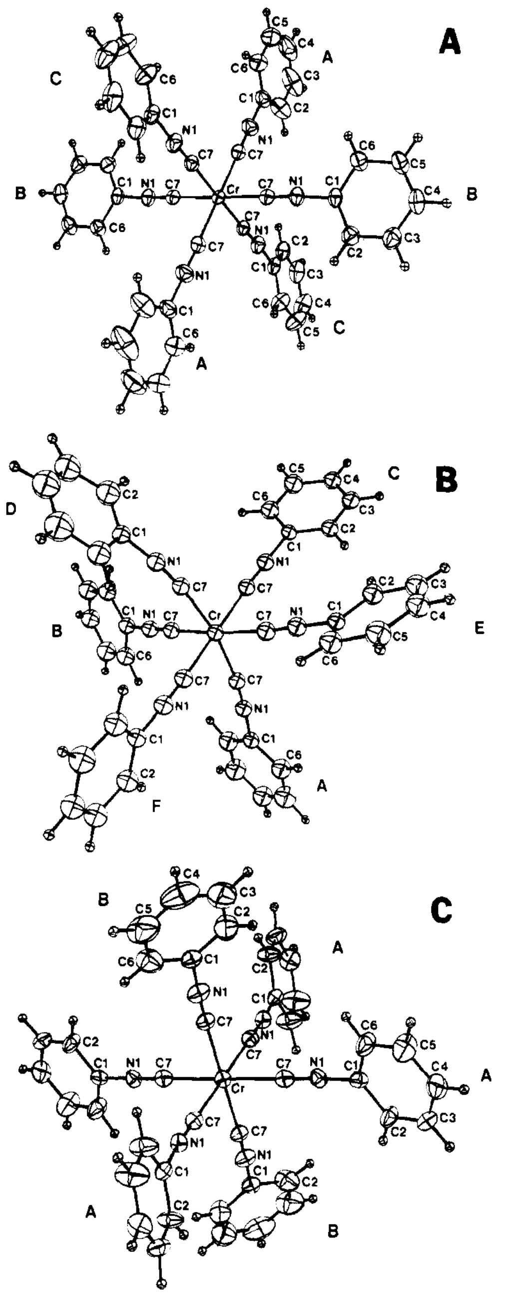

Figure 1. ORTEP view of the $Cr(CNPh)_6^+$ (A), $Cr(CNPh)_6^{2+}$ (B), and $Cr(CNPh)_6^{3+}$ (C) cations down a pseudo threefold axis, with the numbering scheme illustrated. The thermal ellipsoids for Cr, C, and N are drawn at the 50% level; H ellipsoids are arbitrarily set. Hydrogens are not labeled but are numbered as H followed by the label for the carbon atom to which it is attached. Example: H attached to C4A is numbered H4A.

independent). The Cr–C distances are nearly identical (average 2.014 (7) Å) and show no apparent systematic variation with ligand position. The most striking features of the cation structure are the distortions in the C–Cr–C bond angles and the warping of the C_{ring}—N≡C—Cr—C≡N—C_{ring} units into the shape of an archer's bow.

The angular distortions in the C—N≡C—Cr—C≡N—C units are quite dramatic. The unit involving trans ligands A and D is distorted the most while the C,F and B,E ligand trans axes are distorted to a lesser but significant amount. The "90°" C–Cr–C angles (given in part B of Table IV) range from a high value of 97.0° for C7A–Cr–C7E to a low value of 83.7° for the C7A–Cr–C7B angle. The most distorted "180°" C–Cr–C angle is 169.9° (C7A–Cr–C7D) while the *least* distorted angle is the C7B–Cr–C7E angle of 175.5°.

The most concise description of the CrC_6 coordination core is octahedral, with a significant C_{2v} angular distortion of the C–Cr–C bond angles. The twofold pseudo symmetry axis of the cation bisects the largest "90°" C–Cr–C angle, the 97.0° C7A–Cr–C7E angle. This description of the geometry is only approximate due to the extreme warping of C—N≡C—Cr—C≡N—C axes.

The exact origins of these distortions are in some doubt; however, they are likely due to packing forces or to the electronic requirements of the Cr(II) ion. Although structural determinations of the $Cr(CNPh)_6^{2+}$ cation with different anions present in the lattice would be needed to determine the relative importance of packing and electronic effects at Cr, the latter are consistent as the cause of the structural distortion. The standard reduction potential of the $Cr(CNPh)_6^{2+}/Cr(CNPh)_6^+$ couple[1] of −0.05 V vs. AgCl/Ag indicates that the six-coordinate Cr(II) center in $Cr(CNPh)_6^{2+}$ is electron deficient.[18] The six-coordinate, 16e $Cr(CNPh)_6^{2+}$ ion might be expected to show a tendency to bind a seventh ligand to attain the 18e configuration, as in the structurally characterized[18] $Cr(CN\text{-}t\text{-}Bu)_7(PF_6)_2$. Because the very weakly coordinating PF_6^- anion present in the crystal does not interact with the Cr(II) center, electron density can only be gained via distortion of the six phenyl isocyanide ligands to make them more efficient electron donators. By distortion of the C—Cr—C, Cr—C≡N, and C≡N—C angles, the overlap of the π_b C≡N orbitals with the Cr d orbitals can be increased. The improved overlap that occurs via these distortions may increase

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Table IV. Selected Interatomic Angles (deg) with Their Estimated Standard Deviations

A. $[Cr(CNPh)_6][SO_3CF_3]$					
C7A-Cr-C7B	91.3 (1)	C7A-Cr-C7A′	180.0 (1)	Cr-C7A-N1A	178.6 (2)
C7A-Cr-C7C	88.7 (1)	C7B-Cr-C7B′	180.0 (1)	Cr-C7B-N1B	179.3 (2)
C7B-Cr-C7C	89.5 (1)	C7C-Cr-C7C′	180.0 (1)	Cr-C7C-N1C	178.1 (2)
C7A-N1A-C1A	178.6 (2)	N1A-C1A-C2A	117.9 (2)	N1A-C1A-C6A	120.4 (2)
C7B-N1B-C1B	176.4 (2)	N1B-C1B-C2B	118.6 (2)	N1B-C1B-C6B	119.9 (2)
C7C-N1C-C1C	176.1 (2)	N1C-C1C-C2C	119.8 (2)	N1C-C1C-C6C	118.7 (2)
B. $[Cr(CNPh)_6][PF_6]_2$					
C7A-Cr-C7B	83.7 (3)	C7B-Cr-C7E	175.5 (3)	C7E-Cr-C7F	88.4 (3)
C7A-Cr-C7C	95.0 (3)	C7B-Cr-C7F	96.2 (3)	Cr-C7A-N1A	171.3 (6)
C7A-Cr-C7D	169.9 (3)	C7C-Cr-C7D	92.3 (3)	Cr-C7B-N1B	175.9 (6)
C7A-Cr-C7E	97.0 (2)	C7C-Cr-C7E	86.6 (3)	Cr-C7C-N1C	176.3 (6)
C7A-Cr-C7F	88.2 (3)	C7C-Cr-C7F	174.3 (3)	Cr-C7D-N1D	171.6 (6)
C7B-Cr-C7C	88.9 (3)	C7D-Cr-C7E	90.4 (3)	Cr-C7E-N1E	175.6 (6)
C7B-Cr-C7D	89.4 (3)	C7D-Cr-C7F	85.2 (3)	Cr-C7F-N1F	176.0 (6)
C7A-N1A-C1A	177.4 (6)	N1A-C1A-C2A	118.7 (7)	N1A-C1A-C6A	119.6 (7)
C7B-N1B-C1B	176.0 (7)	N1B-C1B-C2B	118.6 (7)	N1B-C1B-C6B	118.3 (7)
C7C-N1C-C1C	177.9 (6)	N1C-C1C-C2C	117.7 (6)	N1C-C1C-C6C	119.5 (6)
C7D-N1D-C1D	174.9 (7)	N1D-C1D-C2D	121.3 (7)	N1D-C1D-C6D	116.5 (7)
C7E-N1E-C1E	177.9 (6)	N1E-C1E-C2E	118.8 (6)	N1E-C1E-C6E	117.1 (6)
C7F-N1F-C1F	177.0 (6)	N1F-C1F-C2F	119.6 (6)	N1F-C1F-C6F	118.8 (6)
C. $[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$					
C7A-Cr-C7A	91.9 (4)	C7A-N1A-C1A	175.2 (9)	C7B-N1B-C1B	175.3 (14)
C7A-Cr-C7B	92.3 (4)				
Cr-C7A-N1A	174.8 (8)	N1A-C1A-C2A	121.8 (8)	N1B-C1B-C2B	115.9 (8)
Cr-C7B-N1B	169.0 (13)	N1A-C1A-C6A	117.6 (8)		

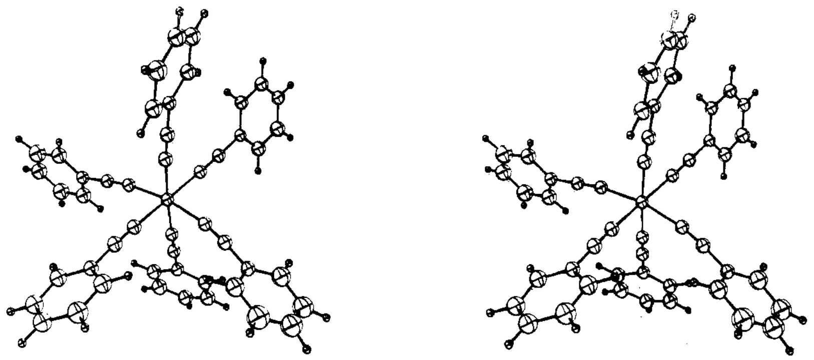

Figure 2. Stereoscopic view of the $Cr(CNPh)_6^{2+}$ cation.

Table V. Comparison of Structural Data for Several $M(CNR)_6{}^{n+}$ and $M(CN)_6{}^{m-}$ Complexes[a]

complex	electronic confign	av M–C, Å	av C≡N, Å	av N–C, Å
$Cr(CNPh)_6{}^0$	lsd^6	1.938 (3)	1.176 (4)	1.388 (4)
$Cr(CNPh)_6{}^+$	lsd^5	1.975 (2)	1.159 (2)	1.397 (2)
$Cr(CNPh)_6{}^{2+}$	lsd^4	2.014 (7)	1.158 (7)	1.414 (7)
$Cr(CNPh)_6{}^{3+}$	d^3	2.068 (11)	1.141 (12)	1.396 (15)
$Mn(CNPh)_6{}^+$	lsd^6	1.901 (4)	1.162 (6)	1.411 (6)
$Cr(CN)_6{}^{4-}$	lsd^4	2.053 (6)	1.156 (8)	
$Cr(CN)_6{}^{3-}$	d^3	2.071 (1)	1.156 (1)	

[a] Standard deviations quoted are the average of the standard deviation for the individual values; ls = low spin.

the electron density at the Cr(II) center to approach that of a seven-coordinate complex. In an equivalent view, the distortion enables each CNPh ligand to donate slightly more electron density to Cr(II).

$[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$. The structure of $[Cr(CNPh)_6][SbCl_6]_3 \cdot CH_2Cl_2$ consists of $[Cr(CNPh)_6]^{3+}$ cations, $SbCl_6^-$ anions, and CH_2Cl_2 molecules of crystallization. There appear to be no specific interactions between these structural units (shortest contact is 3.340 Å between Cl1B and N1A).

The location of the cations and anions on special positions in the relatively high-symmetry *Cccm* space group imposes C_{2h} site symmetry on the $[Cr(CNPh)_6]^{3+}$ cation and one $SbCl_6^-$ anion, while the second $SbCl_6^-$ is on a site of C_s symmetry. The two crystallographically independent anions are closely octahedral with the Sb–Cl bond lengths averaging 2.360 (4) Å and the angles within 1° of the expected 90 and 180°.

The symmetry at the Cr(III) center is nearly D_{2h} (a pair of twofold axes bisect the small 88.1° C7A–Cr–C7A′ angle and the larger 91.9° C7A–Cr–C7A′, while a third twofold axis is coincident with the C7B–Cr–C7B′ vector). The $Cr(C)_6$ coordination core exhibits a marginally significant tetragonal distortion (~3σ) in the Cr–C bond lengths, with long axial bonds of 2.085 (13) Å (Cr–C7B) and shorter equatorial bonds of 2.060 (10) Å (Cr–C7A). The angular distortions in the Cr—C≡N and C≡N—C angles are small for the A ligand (~5°) but are relatively more significant for the B ligand, particularly in the Cr—C≡N linkage (11°). The effect of these angular distortions is to produce two smaller trigonal face pockets related to each other by an inversion center. The origins of these distortions as in the previously discussed Cr(II) complex are not readily apparent but again may be due in part to the extremely electron-deficient Cr(III) center in this compound (the Cr(III)/Cr(II) couple[1] is +0.73 V vs. AgCl/Ag).

Discussion

Table V summarizes crystallographic data pertinent to the discussion of the $Cr(CNPh)_6{}^n$ (n = 0, 1+, 2+, 3+) series. Data obtained in the present study and the previous determinations[5] of the $Cr(CNPh)_6{}^0$ structure indicate that the sequential oxidation of the Cr center results in a systematic *increase* in the

Cr–C and $N–C_{ring}$ bond lengths and a *decrease* in the C≡N bond lengths. As previously discussed[5a] in the comparison of the structural parameters for the isoelectronic $Cr(CNPh)_6^0$ and $Mn(CNPh)_6^+$ complexes, the trends observed for the Cr(0), Cr(I), Cr(II), and Cr(III) series in the Cr—C, C≡N, and $N—C_{ring}$ bond lengths are consistent with a M $d\pi \rightarrow L\pi^*$ interaction between Cr and CNAr, which decreases with each increase in the formal Cr oxidation state. The lengthening in the Cr–C bond with an increase in the formal oxidation state of Cr is the reverse of the trend normally observed in the primarily $L(\sigma) \rightarrow M$ bonds found in coordination compounds.[19] The decrease in the C≡N bond length with an increase in formal oxidation state in the $Cr(CNPh)_6^{n+}$ series also correlates with the previous observation[2b,3] of a systematic increase in the $\bar{\nu}$(CN) infrared stretching frequency.

The anomalous properties that we have observed[3] for $Cr(CNAr)_6^{3+}$ complexes are explicable in the context of the structural studies reported here. The properties of interest are (1) the very low kinetic and thermodynamic stability of the $Cr(CNAr)_6^{3+}$ complexes relative to the more stable $Cr(CNAr)_6^{2+}$ complexes[3] (the opposite stability order is normally found) and (2) the subsequently very high Cr(III)/Cr(II) formal potentials (~+1.0 V vs. NHE) for the CNAr complexes[1] (typical Cr(III)/Cr(II) formal reduction potentials are in the range −0.4 to −1.1 V vs. NHE).[20] Clearly the inverted stability order (Cr(III) < Cr(II)) mentioned in (1) determines the positive shift in the Cr(III)/Cr(II) potential; however, the magnitude of the shift (~2.0 V)[21] between the $Cr(CN)_6^{3-}/Cr(CN)_6^{4-}$ and $Cr(CNPh)_6^{3+}/Cr(CNPh)_6^{2+}$ reduction potentials is surprising and indicates very large relative stability changes in the Cr–C bonds of the CN^- complexes compared with those of the CNPh complexes.

Although variations in Cr(III)–L bond lengths (Cr(III)–F^- = 1.906 Å;[22] Cr(III)–CH_3 = 2.300 Å[23] and in Cr(III)–L bond stability[24] are observed, stability and bond length do not always correlate. For example, the average Cr(III)–C bonds of the $Cr(CN)_6^{3-}$[25] and $Cr(CNPh)_6^{3+}$ ions are nearly identical in length (2.071 vs. 2.068 Å) but they differ many orders of magnitude in substitutional lability.[3,20,24] Previously, the hybridization of the σ_b ligand orbital and the electronegativity of the ligating atom trans to the Cr(III)–C bond have been suggested as factors important in determining Cr(III)–C bond stability.[26] Both of these factors are approximately constant in $Cr(CN)_6^{3-}$ and $Cr(CNPh)_6^{3+}$. The determining factor in the present case must be the relative energies of the carbon lone pair of CN^- compared with that of CNPh. Without measurements of the predominantly carbon lone-pair molecular orbital energies in the two ligands relative to the energy of the appropriate Cr(III) valence orbitals, we can only speculate that the energy match between the Cr(III) orbitals and the σ_b ligand orbital is considerably more favorable in the CN^- case. The lone pair on carbon in free CNPh is stabilized relative to its energy in CN^- due to the strong electron-withdrawing effect of the Ph^+ group bound to nitrogen. The CNPh carbon lone pair is able to gain very little additional stability on coordination to Cr(III) in comparison to a large stabilization gain for coordination of the CN^- carbon lone pair.

A portion of the enhanced stability of $Cr(CNPh)_6^{2+}$ relative to the less stable $Cr(CN)_6^{4-}$[20] ion must also be due to the relative energies of the Cr(II) orbitals and the ligand σ_b orbital; however, in this case an additional stabilizing factor is present. The Cr(II)–C bond in the CNPh complex is significantly shorter (2.014 vs. 2.053 Å) than in the CN^- case.[27] This shortening of the Cr(II)–C bonds in $Cr(CNPh)_6^{2+}$ may result in better σ and π overlap between the Cr(II) orbitals and the CNPh ligand orbitals.

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Supplementary Material Available: Listings of additional interatomic distances and angles, thermal parameters, and observed and calculated structure factors and stereoscopic views of the $Cr(CNPh)_6^+$ and $Cr(CNPh)_6^{3+}$ cations (41 pages). Ordering information is given on any current masthead page.

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(19) For example, changes in the metal–ligand bond lengths for a number of coordination compounds in which only the $(t_{2g})^n$ configuration changes are as follows. $Fe(H_2O)_6^{n+}$, d(2+)–d(3+) = 0.14 Å: Hair, N. J.; Beattie, J. K. *Inorg. Chem.* **1977**, *16*, 245. Bauer, W. H. *Acta Crystallogr.* **1964**, *17*, 1167. Montgomery, H.; Chastain, R. V.; Nalt, J. J.; Witowska, A. M.; Lingafelter, E. C. *Ibid.* **1967**, *22*, 775. Hamilton, W. C. *Ibid.* **1962**, *15*, 353. $Ru(NH_3)_6^{n+}$, d(2+)–d(3+) = 0.04 Å: Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304. $Ru(H_2O)_6^{n+}$, d(2+)–d(3+) ≅ 0.01 Å: Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798 and references cited therein.

(20) $E°$ values for $Cr(H_2O)_6^{3+}/Cr(H_2O)_6^{2+}$ and $Cr(CN)_6^{3-}/Cr(CN)_6^{2-}$ are −0.41 V vs. NHE and −1.130 V vs. NHE, respectively. Hume, D. N.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1943**, *65*, 1897.

(21) We estimate that up to ~1.0 V (23 kcal/mol) of this potential shift might be due to differences in the solvation energy between the two couples, because they involve highly charged negative ions in one case and highly charged positive ions in the other case.

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