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Electronic Structures and Spectra of Hexakisphenylisocyanide Complexes of Cr(0), Mo(0), W(0), Mn(I), and Mn(II)

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Electronic absorption spectra of $M(CNPh)_6$ [M = Cr(0), Mo(0), W(0)], $[Mn(CNPh)_6]Cl$, and $[Mn(CNPh)_6](PF_6)_2$ are reported. Each of the $M(CNPh)_6$ complexes exhibits three intense metal-to-ligand charge transfer (MLCT) absorption bands between 20.8 and 32.7 kK. The lowest MLCT bands are observed at 29.9 and 31.1 kK in the electronic spectrum of $Mn(CNPh)_6^+$. Low energy bands at 18.2 and 20.4 kK in $[Mn(CNPh)_6]^{2+}$ are assigned to vibronic components of a $\sigma(CNPh) \rightarrow d\pi$ charge transfer transition. The unique electronic structural properties of arylisocyanide complexes are apparently related to the π conjugation of aromatic ring orbitals with the out-of-plane π(CN) function.*

Introduction

We have begun a systematic investigation of the electronic absorption and emission properties of four- and six-coordinate isocyanide complexes of the transition metals. Surprisingly little is known in this area, in spite of the strong current interest in the coordination chemistry of isocyanides and the obvious relationship of these ligands to cyanide and carbon monoxide.[2–12] Previous theoretical work on isocyanide complexes appears to be limited to a few semi-empirical molecular orbital calculations,[5–9] and only incomplete electronic spectral data are available.[5,8–12]

This paper is concerned primarily with the measurement and interpretation of the low temperature electronic absorption spectra of the six-coordinate complexes $M(CNPh)_6^z$ [M = Cr(0), Mo(0), W(0), Mn(I), Mn(II)]. We also present an improved preparative method for $Mo(CNPh)_6$.

Experimental

All chemicals used were reagent grade or better. Anhydrous MnI_2 was obtained from ROC/RIC Chemical Corporation and was used without further purification. $Cr_2(C_2H_3O_2)_2 \cdot 2H_2O$ was prepared according to Jolly,[13] and $Mo_2(C_2H_3O_2)_4$ was synthesized by oxidation of $Mo(CO)_6$ with acetic acid.[14] Phenylisocyanide was synthesized according to Ugi, *et al.*[15] and purified by vacuum distillation.

$Cr(CNPh)_6$

This complex was prepared in excellent yield by reaction of $Cr_2(C_2H_3O_2) \cdot 2H_2O$ with CNPh under conditions described by Malatesta.[16] Heating to 40° C, however, was required to initiate the reaction. The product was recrystallized from benzene and obtained as red crystals with green reflectances. M.P. = 178 to 180° C; $\nu_{C\equiv N}$ = 2005, 1950 cm^{-1}, Nujol: Lit. values, M.P. = 178.5° C[2]; $\nu_{C\equiv N}$ = 2012, 1965 cm^{-1}, $CHCl_3$ solution[17]. *Anal.* Calcd for $Cr(CNPh)_6$: Cr, 7.75; C, 75.21; N, 12.53; H, 4.51. Found: Cr, 7.61; C, 75.06; N, 12.52; H, 4.40.

$Mo(CNPh)_6$

This complex was obtained in about 30% yield as follows. To a stirred slurry of $Mo_2(C_2H_3O_2)_4$ in methanol under argon, an excess (10:1) of phenylisocyanide was added. The solution immediately turned red-brown and was stirred under argon for approximately one hour. Filtration of the solution in air gave a red powder and recrystallization from toluene *in the dark* yielded bright red crystals. M.P. = 165° C with decomposition; $\nu_{C\equiv N}$ = 2008, 1950 cm^{-1}, Nujol. *Anal.* Calcd for $Mo(CNPh)_6$: C, 70.59; N, 11.76; H, 4.23. Found: C, 70.89; N, 11.62; H, 4.23.

$W(CNPh)_6$

A slurry of absolute ethanol (80 ml) and magnesium powder (4 g) in a three-necked flask was cooled to −15° C in an ice salt bath and 28 ml of phenylisocyanide, 8 g of WCl_6, and a few drops of acetic acid were slowly added. The slurry turned red-brown and the reaction mixture was stirred for one hour. Care was taken to maintain the temperature of the vessel below 0° C. The red solid obtained on filtration of the reaction mixture was washed with ethanol and then dissolved in benzene. The benzene solution was passed through an alumina column using benzene as the eluant. Red crystals were obtained by adding ethanol to the benzene solution. Yield, 10%; M.P. = 139° C; $\nu_{C\equiv N}$ = 2013, 1938 cm^{-1}, KBr disk; $\nu_{C\equiv N}$ = 2025, 1945 cm^{-1}, $CHCl_3$ solution. *Anal.* Calcd for $W(CNPh)_6$: C, 62.92; H, 3.76; N, 10.48. Found: C, 63.04; H, 3.96; N, 9.98.

$[Mn(CNPh)_6]Cl$

This complex was prepared from MnI_2 by the method of Sacco.[18] M.P. = 177–179° C, $\nu_{C\equiv N}$ = 2080 cm^{-1}, Nujol mull. Lit. values: M.P. = 178° C,[18] $\nu_{C\equiv N}$ = 2080 cm^{-1} $CHCl_3$ solution[19]. *Anal.* Calcd for $[Mn(CNPh)_6]Cl$: Mn, 7.75; C, 71.14; N, 11.85; H, 4.26; Cl, 5.00. Found: Mn, 6.90; C, 69.61; N, 11.51; H, 4.36; Cl, 4.91.

$[Mn(CNPh)_6](PF_6)_2$

This complex was obtained by oxidizing a solution of $[Mn(CNPh)_6]Cl$ in glacial acetic acid with an equal volume of concentrated nitric acid. Addition of this red solution to a saturated aqueous solution of $NaPF_6$ gave a red precipitate. Recrystallization from hot ethanol gave red crystals. M.P. = 205–210° C with decomposition; $\nu_{C\equiv N}$ = 2176 cm^{-1}, Nujol. Lit. $\nu_{C\equiv N}$ = 2165 cm^{-1}, $CHCl_3$[6]. *Anal.* Calcd for $[Mn(CNPh)_6](PF_6)_2$: Mn, 5.70; C, 52.35; N, 8.72; H, 3.13. Found: Mn, 5.67; C, 51.81; N, 8.63; H, 3.15.

Spectral Measurements

Infrared spectra were recorded on a Perkin–Elmer 225 spectrophotometer. Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Spectra at liquid nitrogen temperature were obtained using a low temperature dewar fitted with Suprasil quartz windows and modified to hold a standard 1.0 cm cell. Solution spectra were recorded in Spectrograde solvents, and low temperature glasses used were EPA, 8:2:1 ethanol/methanol/diethylether, and 1:1 isopentane/diethylether. For the ionic compounds solutions were obtained by first dissolving the compound in a few drops of CH_2Cl_2 and then adding the glassing solvent. *All solutions* were made up in a dark room because of their extreme sensitivity to light. The solutions were either used immediately or frozen at liquid nitrogen temperature where photochemistry was observed to be slow. A few drops of nitric acid were added to each of the $Mn(CNPh)_6^{2+}$ solutions to prevent slow reduction to the Mn(I) complex.

Results and Discussion

Infrared spectra of Nujol mulls of $Cr(CNPh)_6$, $[Mn(CNPh_6]Cl$, and $[Mn(CNPh)_6](PF_6)_2$ in the region 1800–2200 cm^{-1} are shown in Figure 1. In each case the spectrum in $CHCl_3$ is not significantly

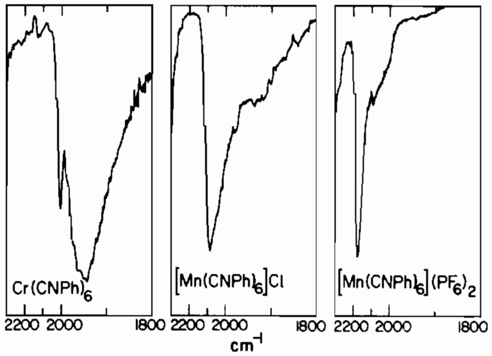

Figure 1. Infrared spectra of Nujol mulls of $Cr(CNPh)_6$, $[Mn(CNPh)_6]Cl$, and $[Mn(CNPh)_6](PF_6)_2$.

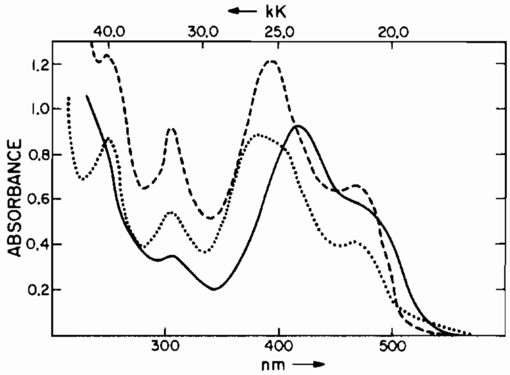

Figure 2. Electronic absorption spectra of $Cr(CNPh)_6$ in 1:1 isopentane/diethyl ether (—), $Mo(CNPh)_6$ in 8:2:1 ethanol/methanol/diethyl ether (---), and $W(CNPh)_6$ in EPA (···) at 77° K.

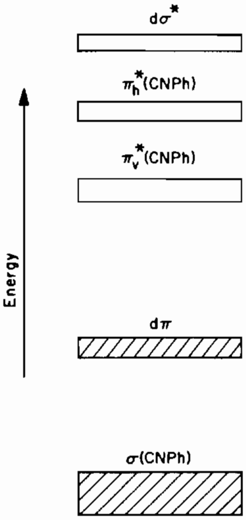

Figure 3. General classification and estimated relative energies of the molecular orbitals in $M(CNPh)_6$ complexes; dπ and σ(CNPh) levels are occupied in the ground state.

different, and it is likely that solid and solution structures are similar. The chromium complex exhibits prominent bands at 2005 and 1950 cm^{-1}, which are attributable to C≡N stretching motions. The fact that at least two bands are observed strongly suggests a solid-state molecular geometry of symmetry lower than T_h. In T_h, as in O_h, only one ν(C≡N) fundamental is ir-allowed (T_{1u} in O_h; T_u in T_h). One possibility is that Cr(CNPh)$_6$ possesses S_6 symmetry, as in this case two ir bands are predicted (E_u and A_u). In this connection it should be noted that a known S_6 complex, $Co(NO_2)_6^{3-}$ (in a crystalline sodium salt[20]), does in fact exhibit two ir bands attribuable to E_u and A_u stretching fundamentals (in this case they are ν(Co–N) bands, at 451 and 373 cm^{-1}).[21] For comparison, $K_3[Co(NO_2)_6]$ has a single ν(Co–N) ir band (418 cm^{-1}),[21] and crystal structure analysis shows[20] the complex anion to fall in the T_h group. The case for S_6 Cr(CNPh)$_6$ is certainly not compelling, however, as the ir data could be accommodated by a number of geometrical structures. Similar structural ambiguities obtain for Mo(CNPh)$_6$ and W(CNPh)$_6$, whose ν(C≡N) ir bands in Nujol mulls are nearly identical both in positions and intensities to those of Cr(CNPh)$_6$.

Only one strong ν(C≡N) ir band is observed for [Mn(CNPh)$_6$]Cl (Figure 1). This band, which peaks at 2080 cm^{-1}, is shouldered on the low-energy side. It is therefore impossible to decide whether Mn(CNPh)$_6^+$ in this solid is T_h or not. A better candidate for T_h symmetry is Mn(CNPh)$_6^{2+}$, as a solid sample of [Mn(CNPh)$_6$](PF$_6$)$_2$ exhibits a relatively sharp ν(C≡N) band at 2176 cm^{-1}.

Each of the complexes M(CNPh)$_6$ [M = Cr(0), Mo(0), W(0)] exhibits three strong electronic absorption bands above 300 nm in frozen solution at 77° K (Figure 2). The bands below 300 nm are attributable to $\pi \rightarrow \pi^*$ transitions localized primarily in the ligand system. The positions and intensities at 300 and 77° K for all the observed bands of M(CNPh)$_6$, [Mn(CNPh)$_6$]Cl, and [Mn(CNPh)$_6$](PF$_6$)$_2$ are set out in Table I.

Our interpretation of the electronic spectra of the M(CNPh)$_6$ complexes is based on the molecular orbital energy level diagram shown in Figure 3. In view of the geometrical structural uncertainties, only the general labels σ, π, dπ, dσ^*, and π^* are used. The diagram was constructed by estimating the interaction of the highest occupied and lowest unoccupied molecular orbitals of six CNPh ligands with the central

TABLE I. Electronic Absorption Spectra of M(CNPh)$_6^z$ Complexes.

Complex	300° K			77° K[a]			Assignment
	λ_{max}, nm	$\bar{\nu}_{max}$, kK	$\varepsilon_{max} \times 10^{-3}$	λ_{max}, nm	$\bar{\nu}_{max}$, kK	$\varepsilon_{max} \times 10^{-3}$	
Cr(CNPh)$_6$[b]	458 sh	21.8	46.0	480	20.8	36.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
	394	25.4	73.0	419	23.9	61.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
	310	32.3	36.0	307	32.6	23.0	d$\pi \rightarrow \pi_h^*$ (CNPh)
Mo(CNPh)$_6$[c]	453 sh	22.1	d	470	21.3	42.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
	378	26.5	d	396	25.3	78.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
	313 sh	31.9	d	307	32.6	53.0	d$\pi \rightarrow \pi_h^*$ (CNPh)
	255 sh	39.2	d	250	40.0	81.0	intraligand
W(CNPh)$_6$[e]	446	22.4	44.0	467	21.4	35.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
				405	24.7		
	367	27.2	58.0	380	26.3		d$\pi \rightarrow \pi_v^*$ (CNPh)
	320	81.3	41.0	306	32.7	46.0	d$\pi \rightarrow \pi_h^*$ (CNPh)
	250	40.0	–	250	40.0	–	intraligand
[Mn(CNPh)$_6$]Cl[c]	340 sh	29.4	61.0	345	29.0	46.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
	322	31.1	66.0	325	30.8	46.0	d$\pi \rightarrow \pi_v^*$ (CNPh)
	249 sh	40.2	51.0	250	40.0	–	intraligand
	234 sh	42.7	71.0	235	42.6	–	
	225	44.4	75.0	–	–	–	
[Mn(CNPh)$_6$][PF$_6$]$_2$[c,f]	–	–	–	548	18.2	5.3	σ(CNPh)$\rightarrow$dπ
	490	20.4	4.6	490	20.4	6.4	

[a] Spectra corrected for solvent contraction. [b] 1 : 1 isopentane/diethylether solution. [c] 8 : 2 : 1 ethanol/methanol/diethyl ether solution. [d] Solutions were too photosensitive to allow measurement. [e] EPA solution. [f] Ultraviolet spectra are not reported, owing to interfering absorption of the nitric acid added to the solutions.

metal. The ground state for each complex has the $(d\pi)^6$ configuration. As is the case with the related $M(CO)_6$ complexes,[22] the lowest energy excited states are derived either from *d–d* ($d\pi\rightarrow d\sigma^*$) or metal-to-ligand charge transfer (MLCT) transitions. It can reasonably be assumed that the *d–d* states lie above 25,000 cm^{-1}, and transitions to them should give rise to relatively weak bands. Therefore, it is not likely that any of the three intense bands in the $M(CNPh)_6$ complexes is due to a *d–d* transition.

The situation regarding MLCT transitions is more complicated than for the $M(CO)_6$ complexes. Molecular orbital calculations[6] suggest that there are two low-lying π^* levels in CNPh. The out-of-plane π^*(CN) function is involved in the lower level, which is designated π_v^* in Figure 3. The π_v^* MO, therefore, is stabilized by conjugation with the π orbitals on the aromatic ring, whereas the in-plane orbital, π_h^*, is localized on the cyano group.

The lowest two bands in each of the three $M(CNPh)_6$ complexes may be assigned to allowed $d\pi\rightarrow\pi_v^*$(CNPh) transitions. The fact that both transitions are substantially blue-shifted in the electronic spectrum of the $(d\pi)^6$ complex $Mn(CNPh)_6^+$ confirms the MLCT interpretation. The lowest $d\pi\rightarrow\pi_v^*$(CNPh) band, for example, is 8 kK higher in $Mn(CNPh)_6^+$ than in $Cr(CNPh)_6$. The magnitude of the shift is very nearly the same as that observed for the lowest ${}^1A_{1g}\rightarrow{}^1T_{1u}$ transitions in $Cr(CO)_6$ (35.7 kK) and $Mn(CO)_6^+$ (44.5 kK).[22] Each of the $M(CNPh)_6$ complexes also exhibits a prominent band at about 33 kK. This band could represent an additional, higher energy component of $d\pi\rightarrow\pi_v^*$, but we prefer to assign it to allowed $d\pi\rightarrow\pi_h^*$ transitions. The relative effects of aromatic-ring substituents could help distinguish the two types of MLCT transitions, and studies along these lines are in progress.

The ground state of $Mn(CNPh)_6^{2+}$ has the low-spin configuration $(d\pi)^5$. The low temperature spectrum of $[Mn(CNPh)_6](PF_6)_2$ exhibits a structured, low energy system (18.2, 20.4 kK) attributable to the LMCT transition σ(CNPh)$\rightarrow d\pi$. Similar low energy LMCT bands have been observed[23] in $Fe(CN)_6^{3-}$ and $Mn(CN)_6^{4-}$. The two observed peaks in the σ(CNPh)$\rightarrow d\pi$ system may be assigned to components of a vibrational progression in the symmetrical C≡N stretching motion. The excited-state value of about 2200 cm^{-1} for this vibration is reasonable.

It is of some interest that the MLCT bands in the $(d\pi)^6$ $M(CNPh)_6^z$ complexes are substantially lower in energy than corresponding peaks in $M(CO)_6^z$ analogs (Table II). The lower energies of $d\pi\rightarrow\pi^*$ transitions are probably due in part to the effects of enhanced σ donation in the CNPh complexes, which would tend to increase the electron density on the central metal, thereby raising the energies of both $d\pi$ and $d\sigma^*$ levels relative to carbonyl analogs. The splitting of $\pi^*CN(\pi_v^*<\pi_h^*)$ by interaction with aromatic ring orbitals must also play an important role, as judged by the high energy of the observed $d\pi\rightarrow\pi^*$ band in $Mn(CNMe)_6^+$ (43.1 kK).[9] Preferential stabilization of π_v^*, of course, is not available to alkylisocyanide ligands. It follows that stabilization of low-oxidation ground states of metals through $d\pi$ back donation to π_v^* should be much more pronounced in aryl- than in alkylisocyanide complexes.

TABLE II. Energies of MLCT Transitions in $M(CO)_6^z$ and $M(CNPh)_6^z$ Complexes.

M	$d\pi\rightarrow\pi^*$ (CO), kK[a]	$d\pi\rightarrow\pi^*$ (CNPh), kK[b]
Cr(0)	35.7	21.8
	43.6	25.4
		32.3
Mo(0)	34.6	22.1
	42.8	26.5
		31.9
W(0)	34.7	22.4
	43.8	27.2
		31.3
Mn(I)	44.5	29.4
	49.9	31.1

[a] Acetonitrile solution, 300° K; Ref. 22. [b] This work.

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