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Electronic Spectra of Substituted Cyanocobaltate(III) Complexes

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The electronic spectra of a variety of substituted cyanocobaltate(III) complexes are reported and interpreted. Large tetragonal splittings of the dσ* orbitals are inferred from the ligand field spectra, with the "axially localized" $^1A_1 \rightarrow {}^1E^a$ component of $^1A_{1g} \rightarrow {}^1T_{1g}$ being the lowest spin-allowed transition in all cases. In only one case, $Co(CN)_5Cl^{3-}$, is the $^1A_1 \rightarrow {}^1A_2$ transition also observed, the apparent $^1T_{1g}$ splitting being 6800 cm^{-1}. Ligand-to-metal charge-transfer bands are observed at slightly higher energies than $^1A_1 \rightarrow {}^1E^a$, only slightly blue-shifted from the analogous transitions of $Co(NH_3)_5X^{2+}$ complexes, to which detailed comparisons have been made. Both $\pi \rightarrow d_{z^2}$(weak) and $\sigma \rightarrow d_{z^2}$(intense) transitions are observed for halide complexes, whereas intense charge transfer from sulfur-localized, σ-donor orbitals is observed near 35,000 cm^{-1} for $Co(CN)_5SO_3^{4-}$ and $Co(CN)_5SCN^{3-}$. Additionally, weak $\pi \rightarrow d_{x^2-y^2}$ transitions are assigned for pseudohalide complexes. A metal-to-ligand charge-transfer assignment is suggested for the 35,200-cm^{-1} band of $Co(CN)_5NO_2^{3-}$. Most of the cyanocobaltate(III) complexes exhibit an intense band near 50,000 cm^{-1}, which is attributable to $d\pi \rightarrow \pi^*(CN)$ charge transfer.

Introduction

The electronic spectra of octahedral and distorted octahedral complexes of d^6 metal ions have been the subject of innumerable investigations. Indeed, much of our present understanding of the electronic structure of transition metal complexes is based upon the study of low-spin d^6 systems, particularly the monoacidopentaammine and *trans*-diacidotetraammine complexes of trivalent cobalt. The experimentally observed ligand field (LF) absorption bands are well separated from those attributable to other types of excitations in the cobalt–ammine series, and the agreement between theory and experiment is extremely good.[1]

For the analogous cyanocobaltate(III) complexes, however, the situation has not been nearly as favorable. The ligand field bands are relatively poorly resolved from charge-transfer (CT) absorption, and obtaining the compounds in pure form has proved to be difficult.[2] Our interest in these complexes was initially stimulated by a desire for reliable descriptions of their low-lying LF excited states, to assist in the interpretation of their photochemical reactivity, and was enhanced by the possibilities which subsequently became apparent for the study of CT transitions. We have therefore made a detailed investigation of the electronic absorption spectra of a large number of acidopentacyanocobaltate(III) complexes, including examples where CT absorption does not overlap the low-lying LF bands. We report here an internally consistent assignment scheme, which establishes simple guidelines as to the nature and relative energies of both LF and CT excited states of these complexes.

Experimental Section

Preparation of Compounds. The compounds $K_3[Co(CN)_5Cl]$ and $K_3[Co(CN)_5Br]$ were prepared by the method of Grassi, Haim, and Wilmarth.[2] The compound $K_3[Co(CN)_5NO_2]$ was similarly prepared from the corresponding acidopentamminecobalt(III) salt. *Anal.* Calcd for $K_3[Co(CN)_5Cl]$: Co, 17.24; C, 17.57; N, 20.49; Cl, 10.37; H, 0.00. Found: Co, 17.40; C, 17.66; N, 20.20; Cl, 10.39; H, 0.00. Calcd for $K_3[Co(CN)_5Br]$: Co, 15.25; C, 15.54; N, 18.13; Br, 20.68; H, 0.00. Found: Co, 15.66; C, 15.78; N, 17.83; Br, 20.34; H, 0.00. Calcd for $K_3[Co(CN)_5NO_2]$: Co, 16.73; C, 17.05; N, 23.85; H, 0.00. Found: Co, 16.73; C, 18.90; N, 25.03; H, 0.18.

The $Co(CN)_5OH_2^{2-}$ ion was prepared in solution by exhaustive photolysis of a dilute aqueous solution of $K_3[Co(CN)_6]$ at 305 nm with a UV-Products lamp. In agreement with Adamson, *et al.*,[3] we have found that photolysis of dilute $Co(CN)_6^{3-}$ solutions is an excellent preparative procedure for $Co(CN)_5OH_2^{2-}$, involving exposure of the product to neither concentration nor other "drastic" conditions. From knowledge of the efficiencies of the photolytic reaction and of back-reaction with cyanide, we are confident that $Co(CN)_6^{3-}$ was not present in any significant amount in our product solutions.

The sodium salt of *trans*-$Co(CN)_4(SO_3)_2^{5-}$ was obtained by a published procedure.[4] This procedure was modified to produce the potassium salt, which was obtained as a monohydrate after drying. *Anal.* Calcd for $K_5[Co(CN)_4(SO_3)_2]\cdot H_2O$: C, 8.95; N, 10.44; S, 11.95; H, 0.89. Found: C, 9.30; N, 10.78; S, 10.64; H, 0.40. The compound $K_4[Co(CN)_5SO_3]$ was prepared by allowing K_5[*trans*-$Co(CN)_4(SO_3)_2]\cdot H_2O$ to stand in concentrated aqueous KCN at 70° for 1 hr and fractionally precipitating with ethanol. The compound was recrystallized from aqueous ethanol. $Na_5[Fe(CN)_5SO_3]\cdot 9H_2O$ was prepared by a published method.[5] Infrared spectra indicate that all the above sulfito complexes are S bonded.[6]

Measurements. Ultraviolet, visible, and near-infrared spectra were measured on a Cary Model 17 spectrophotometer. Low-temperature spectra were obtained using a quartz dewar with optical quality windows. The samples were completely immersed in liquid nitrogen, which was supercooled prior to measurement by pumping or by blowing helium gas through the liquid in order to avoid bubbling. The solvent used for low-temperature glasses was a 1:1 mixture of saturated aqueous LiCl and water. Spectra were routinely corrected for base line effects and solvent contraction (2.5% for the LiCl solvent).

Results and Discussion

Ligand Field Spectra. An octahedral low-spin cobalt(III) complex is expected to show two low-lying spin-allowed LF transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, both excited states arising from the strong-field $t_{2g}^5e_g$ configuration. Lowering of the molecular symmetry to C_{4v}, as in a monosubstituted complex, splits the first transition into $^1A_1 \rightarrow {}^1E^a$ and $^1A_1 \rightarrow {}^1A_2$, whereas the second splits into $^1A_1 \rightarrow {}^1E^b$ and $^1A_1 \rightarrow {}^1B_2$. Within the LF formalism, the energies of these transitions in C_{4v} may then be expressed in terms of the parameters Ds and Dt, together with the usual $10Dq$, B, and C.[7] The theoretical expression for the energy of the $^1A_1 \rightarrow {}^1A_2$ transition is the same as that for $^1A_{1g} \rightarrow {}^1T_{1g}$, $10Dq - C$; in addition, if configuration interaction is neglected, the energy of $^1A_1 \rightarrow {}^1E^a$ is equal to $10Dq - C - {}^{35}/_{4}Dt$. (The energies of the $^1A_1 \rightarrow {}^1E^b$ and $^1A_1 \rightarrow {}^1B_2$ transitions are more complicated functions of both Dt and Ds.) As C is generally rather insensitive to field strength,[1] $10Dq - C$ should be roughly invariant for a series of monosubstituted derivatives. It follows that such a series should show $^1A_1 \rightarrow {}^1A_2$ at the position of the $^1A_1 \rightarrow {}^1T_{1g}$ transition of the unsubstituted (parent) complex, with $^1A_1 \rightarrow {}^1E^a$ moving to higher or lower energy depending on the value of Dt. Furthermore, Dt can be estimated from the expression

$$Dt(ML_5X) = {}^2/_7(Dq(ML_6) - Dq(MX_6))$$

Cobalt–ammine complexes, in particular, obey this simple model extremely well.[1]

Assuming that the simple model can be extended to the acidopentacyanocobaltate(III) complexes, we expect that $^1A_1$

Table I. Ligand Field Absorption Bands of Selected $Co(CN)_5X^{n-}$ Complexes in Aqueous Solution at 300°K

X	Assignment	λ, nm	$\bar{\nu}$, kK	ε
CN^- [a]	$^1A_{1g} \rightarrow {}^1T_{1g}$	312	32.1	243
	$^1A_{1g} \rightarrow {}^1T_{2g}$	260	38.9	180
$-SO_3{}^{2-}$	$^1A_1 \rightarrow {}^1E^a$	335	29.9	430
$-NO_2{}^-$	$^1A_1 \rightarrow {}^1E^a$	~345 sh	29.0	490
NH_3 [b]	$^1A_1 \rightarrow {}^1E^a$	345	29.0	250
	$^1A_1 \rightarrow \{^1E^b, {}^1B_2\}$	268	37.3	155
$-NCS^-$ [c]	$^1A_1 \rightarrow {}^1E^a$	363	27.6	500
$-SCN^-$ [c]	$^1A_1 \rightarrow {}^1E^a$	378	26.5	191
OH_2	$^1A_1 \rightarrow {}^1E^a$	380	26.3	280
	$^1A_1 \rightarrow {}^1A_2$	~310 sh	32.3	110
Cl^-	$^1A_1 \rightarrow {}^1E^a$	392	25.5	200
	$^1A_1 \rightarrow {}^1A_2$	~316 sh	31.7	97
Br^- [d]	$^1A_1 \rightarrow {}^1E^a$	395	25.3	170
I^- [e]	$^1A_1 \rightarrow {}^1E^a$	~440 sh	~23	~200
		500	20.0	95

[a] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 4260 (1968). [b] Reference 8. [c] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, 93, 3364 (1971). [d] A. W. Adamson and A. Sporer, *ibid.*, 80, 3865 (1958). [e] Reference 3.

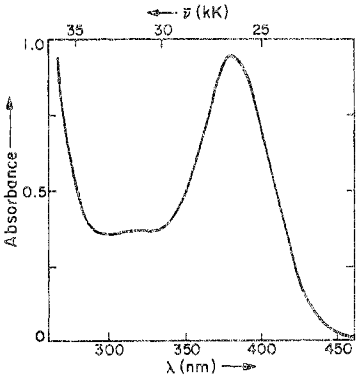

Figure 1. Electronic spectrum of a 3.3×10^{-3} *M* aqueous solution (pH 7) of $Co(CN)_5OH_2{}^{2-}$ at 300°K.

→ $^1E^a$ will almost always be the lowest spin-allowed LF transition, in view of the extremely high *Dq* value of cyanide relative to most substituents. For experimental confirmation of this prediction, we turn to a few complexes whose CT absorption occurs at much higher energies than the lowest LF transition.

Ligand field spectral data for several $Co(CN)_5X^{n-}$ complexes are set out in Table I. The complex $Co(CN)_5NH_3{}^{2-}$ shows two LF bands, at 29.0 and 37.3 kK,[8] which are red-shifted from the $Co(CN)_6{}^{3-}$ bands at 32.1 and 38.9 kK.[9] The two bands in the $Co(CN)_5NH_3{}^{2-}$ spectrum are of comparable intensity, with the 29.0-kK absorption being broad and somewhat asymmetric toward higher energy. The 29.0-kK band may be assigned to $^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$, and it is probable that the 37.3-kK feature represents the $^1A_1 \rightarrow \{^1B_2, {}^1E^b\}$ transition. The $^1A_1 \rightarrow \{^1B_2, {}^1E^b\}$ bands in aqueous solution spectra of $Co(NH_3)_5X^{2+}$ complexes always appear unsplit and generally are shifted only very slightly to lower energy of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition in $Co(NH_3)_6{}^{3+}$.[1]

The lack of pronounced splitting in the low-energy band ($^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$) can be attributed to there only being a small shift of $^1A_1 \rightarrow {}^1E^a$ to lower energy for the relatively high-field ligand NH_3 and also in some degree to the expected unequal oscillator strengths of the two components. The $^1A_1 \rightarrow {}^1A_2$ transition is only vibronically allowed, mainly *via* coupling with equatorial metal–cyanide stretching modes, and could easily be hidden in the tail of the strong, nearby $^1A_1 \rightarrow {}^1E^a$ component.

A somewhat larger splitting of the first band system is expected in the $Co(CN)_5OH_2{}^{2-}$ ion, and here we do see evidence of a weak second component (Figure 1). A distinct shoulder is observed at room temperature at ~32.3 kK, the oscillator strength being roughly one-third that of the low-energy band at 26.3 kK. As $Co(CN)_5OH_2{}^{2-}$ cannot be isolated as a solid salt without extensive decomposition[4,10] and is subject to polymerization in concentrated solution, there is some uncertainty associated with assigning the 32.3-kK shoulder as $^1A_1 \rightarrow {}^1A_2$ in the monomeric ion. Fortunately, we have a better documented example of a large $^1E^a - {}^1A_2$ splitting.

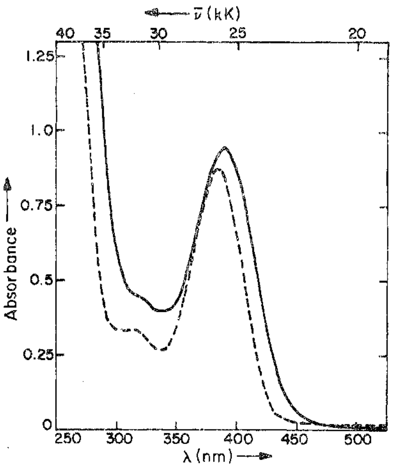

Figure 2. Electronic spectrum of 4.64×10^{-3} *M* $K_3[Co(CN)_5Cl]$ in 50% saturated aqueous LiCl: 300°K, ——; 77°K, - - -.

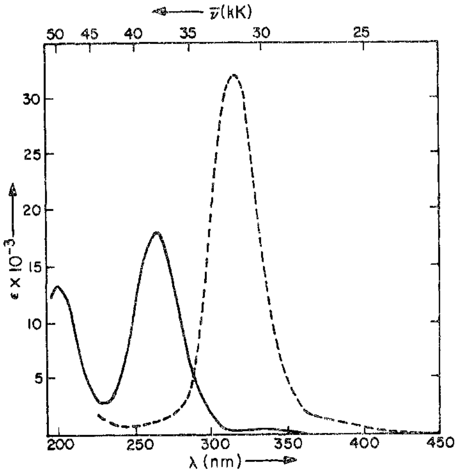

Figure 3. Electronic spectra: $K_4[Co(CN)_5SO_3]$ in aqueous solution at 300°K, ——; $K_5[trans\text{-}Co(CN)_4(SO_3)_2]\cdot H_2O$ in 1 *M* NaOH solution at 300°K, - - -.

In Figure 2 we show the electronic spectrum of $Co(CN)_5Cl^{3-}$ at room temperature and 77°K. Considerable care was taken to ensure the purity of the complex, particularly in regard to avoiding possible contamination with the hexacyanide. We observe a shoulder at room temperature at ~31.3 kK, which sharpens at 77°K into a peak at 31.9 kK. The weaker peak has an integrated intensity of less than one-third of that of the ligand field band at 25.6 kK, and we feel confident in assigning these absorptions as the $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E^a$ transitions. We note that the $^1A_1 \rightarrow {}^1E^a$ band has an ε of only 200. As the Laporte-forbidden $^1A_1 \rightarrow {}^1T_{1g}$ band of $Co(CN)_6{}^{3-}$ has an ε of 243, it is clear that the formal orbital allowedness of $^1A_1 \rightarrow {}^1E^a$ does not make a large contribution to its intensity. The integrated intensity of the $^1A_1 \rightarrow {}^1E^a$ band sharply decreases at 77°K, attesting to the importance of a vibronic intensity-giving mechanism.

The reasoning we outlined in the beginning of this section can be extended to more highly substituted cyanocobaltate(III) complexes.[1,11,12] The predictions of main interest to us are that, for trans-disubstituted complexes, the splitting of the $^1T_{1g}$

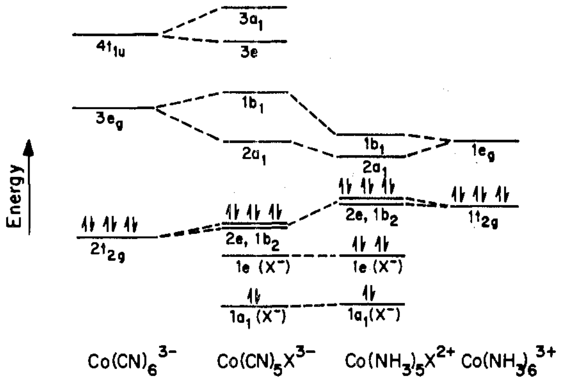

Figure 4. Molecular orbital energy level correlation diagram for cyanocobaltate(III) and cobalt(III)-ammine complexes.

state simply doubles (the energy of the $^1A_{2(g)}$ state remaining invariant); for cis-disubstituted complexes, the "$^1E^a$" state remains at the same energy as in the monosubstituted case, whereas the "$^1A_2$" now moves to *lower* energy.

In Figure 3, we show the electronic spectra of $Co(CN)_5SO_3^{4-}$ and *trans*-$Co(CN)_4(SO_3)_2^{5-}$. The $^1A_1 \rightarrow {}^1E^a$ band in the monosulfito complex at 29.9 kK corresponds to a splitting of 2.6 kK, assuming a $^1A_1 \rightarrow {}^1A_2$ band at 32.1 kK, whereas the transition at ~26.7 kK in the disulfito case implies a splitting of 5.4 kK, in rather close agreement with the expected doubling. Such close agreement would not be expected if $10Dq - C$ were varying greatly or if configuration interaction were very important. The spectrum of $Co(CN)_4en^-$[13] shows a maximum at 28.4 kK, comparing nicely to the $^1A_1 \rightarrow {}^1E^a$ band of $Co(CN)_5NH_3^{2-}$ at 29.0 kK. The spectra of these complexes thus demonstrate the utility of the simple LF model, even without direct observation of a transition to $^1A_2$, and place on rather firm ground the assignment of the single band observed as the $^1A_{1(g)} \rightarrow {}^1E_{(g)}{}^a$ component.

Examination of Table I reveals that the $^1A_1 \rightarrow {}^1E^a$ transition in $Co(CN)_5X^{n-}$ complexes decreases in energy according to $CN^- > -SO_3^{2-} > -NO_2^- > NH_3 > -NCS^- > OH_2 \sim -SCN^- > Cl^- > Br^- > I^-$. This spectrochemical ordering is very similar to the standard version based on the bands in substituted cobalt(III) ammines.[1] An important consequence of such normal spectroscopic behavior is that we can estimate energies for LF excited states in substituted cyanocobaltate(III) complexes even when charge-transfer absorption makes them unobservable. Furthermore, we have established that the one-electron splitting of the e_g orbitals in $Co(CN)_5X^{3-}$ is much larger than that of the t_{2g} orbitals. In this respect the present study accords well with the magnetic susceptibility and epr characterization of the ground states of $Fe(CN)_5NCS^{3-}$ and $Fe(CN)_5N_3^{3-}$, where relatively small $^2T_{2g}(d^5)$ splittings attributable to axial distortion were found.[14] Finally, our energy estimates suggest that the low-lying LF excited states of the $Co(CN)_5X^{3-}$ complexes are well separated. Thus we can realistically label the lowest observed transition as $d_{xz,yz} \rightarrow d_{z^2}$, an identification which is of considerable importance in considerations of the photochemistry of these complexes.[15,16]

Charge-Transfer Spectra. The charge-transfer spectra of both $Co(CN)_5X^{3-}$ and $Co(NH_3)_5X^{2+}$ complexes can be interpreted with the aid of the qualitative molecular orbital energy level diagram shown in Figure 4. For monohalo derivatives, there are two types of ligand-to-metal excitations into $d\sigma^*$ metal orbitals; σ LMCT originates in the halogen $p_z(a_1)$ orbital, whereas π LMCT originates in the halogen p_x, $p_y(e)$ level. The allowed σLMCT transition, $^1A_1 \rightarrow {}^1A_1$ ($\sigma \rightarrow d_{z^2}$), should give rise to an intense absorption band, as it involves large overlap. The σ LMCT transition to the $d_{x^2-y^2}$ orbital ($^1A_1 \rightarrow {}^1B_1$) is orbitally forbidden. Both allowed π LMCT transitions, $^1A_1 \rightarrow {}^1E$ ($\pi \rightarrow d_{z^2}$) and $^1A_1 \rightarrow {}^1E$ ($\pi \rightarrow d_{x^2-y^2}$), should be much weaker than $\sigma \rightarrow d_{z^2}$, owing to poor overlap.

Table II. Charge-Transfer Absorption Bands of $Co(CN)_5X^{n-}$ and $Co(NH_3)_5X^{n+}$ Complexes in Aqueous Solution at 300°K

		$Co(CN)_5X^{n-}$			$Co(NH_3)_5X^{n+}$		
X	Assignment	$\bar{\nu}$, kK	ϵ	Ref	$\bar{\nu}$, kK	ϵ	Ref
Cl^-	$\pi \rightarrow d_{z^2}$	37.7	866	*a*	36.0	400	*d*
	$\sigma \rightarrow d_{z^2}$	44.6	16,100	*a*	43.9	12,900	*d*
	$d\pi \rightarrow \pi^*(CN)$	51.0	13,000	*a*			
Br^-	$\pi \rightarrow d_{z^2}$	33.9	822	*a*	31.8	560	*d*
	$\sigma \rightarrow d_{z^2}$	41.3	13,210	*a*	39.5	12,600	*d*
	$d\pi \rightarrow \pi^*(CN)$	50.5	11,700	*a*			
I^-	$\pi \rightarrow d_{z^2}$	30.3	2,950	*b*	26.1	1,450	*d*
	$\sigma \rightarrow d_{z^2}$	38.5	17,500	*b*	34.9	12,600	*d*
$-NCS^-$	$2\pi \rightarrow d_{z^2}$	37.7	2,340	*c*	32.7	1,550	*e*
	$2\pi \rightarrow d_{x^2-y^2}$	44.0	6,200	*c*			
	$d\pi \rightarrow \pi^*(CN)$	49.5	28,100	*c*			
$-SCN^-$	$2\pi \rightarrow d_{z^2}$	37.7	17,100	*c*	34.7	15,600	*f*
	$2\pi \rightarrow d_{x^2-y^2}$	44.0	4,300	*c*			
	$d\pi \rightarrow \pi^*(CN)$	50.0	16,700	*c*			
$-NO_2^-$	$d\pi \rightarrow \pi^*(NO_2^-)$	35.2	2,700	*a*	30.7	1,590	*g*
	$\sigma \rightarrow d_{z^2}$	43.7	22,700	*a*	42.0	9,400	*g*
$-SO_3^{2-}$	$\sigma \rightarrow d_{z^2}$	37.7	18,100	*a*	36.5	12,000	*g*
	$d\pi \rightarrow \pi^*(CN)$	50.0	13,300	*a*			

[a] This work. [b] Reference 3. [c] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, 93, 3364 (1971). [d] L. E. Orgel, Reports to the Tenth Solvay Council, Stoops, Brussels, 1956, p 289. [e] K. Schug, M. D. Gilmore, and L. A. Olson, *Inorg. Chem.*, 6, 2180 (1967). [f] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *ibid.*, 9, 655 (1970). [g] V. A. V. Kiss and D. R. Czegledy, *Z. Anorg. Allg. Chem.*, 235, 407 (1938).

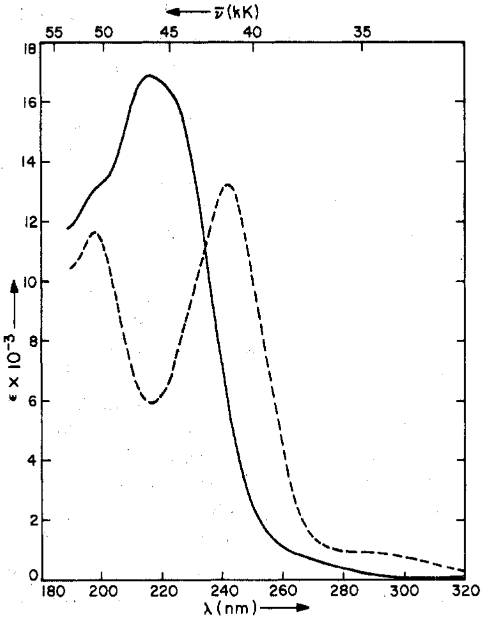

Figure 5. Ultraviolet spectra of $K_3[Co(CN)_5Cl]$ (——) and $K_3[Co(CN)_5Br]$ (- - -) in aqueous solution at 300°K.

The charge-transfer energies and peak ϵ's for several $Co(NH_3)_5X^{2+}$ and $Co(CN)_5X^{3-}$ complexes are set out in Table II. Charge-transfer spectra of $Co(CN)_5Cl^{3-}$ and $Co(CN)_5Br^{3-}$, which have not previously been reported, are illustrated in Figure 5. The halopentacyanocobaltates typically exhibit two CT bands, shifted to higher energy by 2–4 kK relative to corresponding bands in the pentaammines. We suggest that the lower band represents $\pi \rightarrow d_{z^2}$, with $\pi \rightarrow d_{x^2-y^2}$ hidden under the intense absorption, which must be assigned to $\sigma \rightarrow d_{z^2}$. We can unambiguously rule out the possibility that the observed π LMCT transition terminates in $d_{x^2-y^2}$ (with, perhaps, a very weak and unobserved $\pi \rightarrow d_{z^2}$ transition), because for such an assignment the difference in energy between the σ and π LMCT would be expected to decrease along the series Cl^-, Br^-, I^-, as a result of the increased $d\sigma^*$ splitting. In contrast, this difference *increases* very slightly along the series, quite in keeping with results for hexahalometalate complexes[17] and also with the trend in the halo-substituted ammines. Thus it is apparent that both observed LMCT transitions in the halopentacyanocobaltates terminate in the d_{z^2} orbital.

For pseudohalide derivatives, such as the N- and S-bonded thiocyanates, bands attributable to $2\pi(X) \rightarrow d\sigma^*$ LMCT transitions are observed.[18] The principal LMCT band varies in intensity, being much stronger for S-bonded thiocyanate complexes than for corresponding N-bonded ones. This intensity variation probably is related to the much greater spatial overlap of the 2π orbital, which is somewhat concentrated on the sulfur,[18] for S-bonding and also to the fact that the Co–SCN unit is nonlinear. As the Co–SCN linkage is bent, the 2π orbital is split into bonding and nonbonding components, where the bonding interaction should properly be described as of the σ type.[19] For the N-bonded isomer, on the other hand, a nitrogen-localized orbital is σ bonding, and the 2π orbital only engages in weak interaction. The transition in the S-bonded complex thus takes on considerable σ LMCT character.

The $Co(CN)_5SCN^{3-}$ spectrum shows a well-resolved peak at 44 kK, in addition to the main band at 37.7 kK. For other pseudohalide derivatives $Co(CN)_5X^{3-}$, a more or less well-resolved shoulder is also observed at energies 6–9 kK higher than the main band.[18] In each case the less intense, higher energy feature can be assigned to the transition $2\pi \rightarrow d_{x^2-y^2}$, which from spatial overlap considerations would be expected to be weaker than $2\pi \rightarrow d_{z^2}$. Some support for this interpretation may be derived from the electronic spectrum of $Rh(CN)_5SCN^{3-}$, which shows two components of LMCT at 44.4 (ϵ 18,000) and 49.5 kK (ϵ 9800).[20] The fact that both bands shift similarly to higher energy in the Rh(III) case accords well with expectation for $2\pi \rightarrow d_{z^2}$ and $2\pi \rightarrow d_{x^2-y^2}$ assignments and argues against either band being assigned[18] to a ligand-localized $\pi \rightarrow \pi^*$ transition.

The spectra of the complexes $Co(CN)_5SO_3^{4-}$ and *trans*-$Co(CN)_4(SO_3)_2^{5-}$ exhibit intense bands at 37.7 and 31.5 kK, respectively (Figure 3). Assignment of the 37.7-kK band in $Co(CN)_5SO_3^{4-}$ to σ LMCT ($\{a_1\ \sigma$ donor orbital of $SO_3^{2-}\} \rightarrow d_{z^2}$) is strongly suggested upon examination of the spectrum of $Fe(CN)_5SO_3^{5-}$, which does not exhibit an intense band below 40 kK. The energy order Co(III) < Fe(II) would not be consistent with an MLCT assignment for $Co(CN)_5SO_3^{4-}$ but is expected for LMCT. The large red shift of the intense band in going from $Co(CN)_5SO_3^{4-}$ to *trans*-$Co(CN)_4(SO_3)_2^{5-}$ is fully consistent with an assignment of the $\sigma \rightarrow d_{z^2}$ type, as the d_{z^2} orbital should be much less energetic in the latter complex (*vide supra*).

The ultraviolet spectrum of the complex ion [(2-mercaptoethylamine)bis(ethylenediamine)-*N*,*S*]cobalt(III) exhibits an intense band at 35.7 kK,[21] which can be attributed again to $S(\sigma) \rightarrow d_{z^2}$ LMCT. The close similarities observed in the CT spectra of S-bound mercapto, thiocyanato, and sulfito complexes indicate that an essentially identical sulfur-localized, σ-donor (lone-pair) orbital is present in all of them. The vastly different nature of the π orbitals of the various ligands is reflected in greatly different ligand field transition energies (Table I).

An interesting special case is provided by the electronic absorption spectrum of $Co(CN)_5NO_2^{3-}$ (Figure 6). The shoulder at ~29 kK is assigned as the $^1A_1 \rightarrow {}^1E^a$ ligand field band, its high energy being consistent with the high position of NO_2^- in the spectrochemical series. Following the Caulton–Fenske assignments[22] for the hexanitrometalates, the 35.2-kK charge-transfer band in $Co(CN)_5NO_2^{3-}$ is attributed to a metal-to-ligand transition (MLCT), whereas the peak at 43.6 kK represents LMCT. Assuming effective C_{2v} symmetry, we suggest that these transitions correspond to $^1A_1 \rightarrow {}^1A_1$, $^1B_2$ [$\{a_2\ (d_{xy}),\ b_1\ (d_{xz})\} \rightarrow b_1^*\ (\pi^*(NO_2^-))$] for the MLCT and to $^1A_1 \rightarrow {}^1A_1$ ($\{a_1\ \sigma(NO_2^-)$ nitrogen σ-donor orbital$\} \rightarrow \{a_1(d_{z^2})\}$) for the LMCT.[23] It is noteworthy that the MLCT transition undergoes a considerably larger shift to higher energy than the LMCT transition in $Co(CN)_5NO_2^{3-}$ *vs.* $Co(NH_3)_5NO_2^{2+}$. This suggests that the $d\pi$ orbitals in the cyano complex are stabilized relative to those of the ammine, presumably as a result of π-back-bonding interactions with the cyanide ligands.

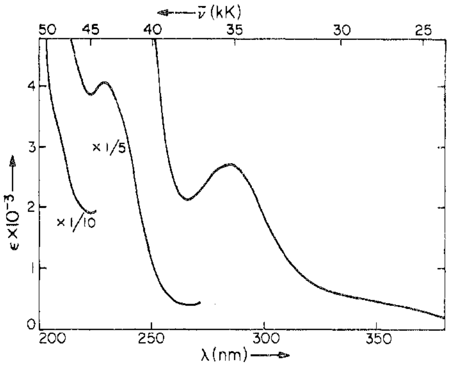

Figure 6. Electronic spectrum of $K_3[Co(CN)_5NO_2]$ in aqueous solution at 300°K.

Finally, we shall consider the CT bands generally observed near 50 kK in the $Co(CN)_5X^{n-}$ complexes. The parent complex $Co(CN)_6^{3-}$ has a $d\pi \rightarrow \pi^*(CN)$ transition at 49.5 kK (ϵ 35,400),[9] whereas the acidopentacyanocobaltates have corresponding maxima between 49 and 52 kK. Considering the large variation in the energy of the d_{z^2} orbital in the various complexes, this approximate energy invariance is rather convincing proof that in each case the transition is indeed of the $d\pi \rightarrow \pi^*(CN)$ type.

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Registry No. $Co(CN)_5(SO_3)^{4-}$, 53078-06-1; $Co(CN)_5(NO_2)^{3-}$, 53011-06-6; $Co(CN)_5(OH_2)^{2-}$, 14842-83-2; $Co(CN)_5Cl^{3-}$, 19400-43-2; $Co(CN)_5Br^{3-}$, 19400-44-3; *trans*-$Co(CN)_4(SO_3)_2^{5-}$, 53011-07-7.

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N-bonded isomer. This shift should, however, be counterbalanced by the lower ligand field strength of $-SCN^-$ relative to $-NCS^-$.[18]

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New Complexes of Dirhodium(II)

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The species $Rh_2(CO_3)_4^{4-}$ forms when CO_3^{2-} in slight excess reacts with $Rh_2^{4+}(aq)$. It is readily produced in good yield also by the reaction of CO_3^{2-} with $Rh_2(OAc)_4$. Solids containing the anion have been prepared and characterized. On treatment with acid, CO_2 is slowly released. The stage $Rh_2(CO_3H)_2^{2+}$ has been characterized in solution but we did not find it possible to prepare the aquo ion by heating the carbonato complex with acid. The complex $Rh_2(SO_4)_4^{4-}$ also has been prepared as have salts containing the species. On treatment with Ba^{2+}, $Ba_2Rh_2(SO_4)_4$ is precipitated, and the aquo ion is not formed.

Rhodium(III) in analogy to Co(III) forms a wide variety of complexes including many with saturated ligands, which are stable enough, at least in the kinetic sense, to be readily characterizable. But the coordination chemistry of Rh(II), in contrast to that of Co(II), is still highly circumscribed. Until the discovery of $Rh_2^{4+}(aq)$,[1] the only example of Rh(II) in combination with saturated ligands was $Rh_2(OAc)_4$,[2] and from this example it was not clear to what extent the Rh–Rh bond owed its stability to the fact that OAc^- acts in a bridging capacity to unite the Rh(II) centers—thus note that Cr(II) is monomeric as the aquo ion but dimeric when combined with an equivalent amount of acetate. The existence of $Rh_2^{4+}(aq)$ makes it clear that direct Rh–Rh interactions are important in the chemistry of aquorhodium(II), but the work of Maspero, *et al.*, did leave open the possibility that significant amounts of Rh^{2+} are in labile equilibrium with $Rh_2^{4+}(aq)$.

The experiments to be described were undertaken in an effort to find a convenient route to preparing $Rh_2^{4+}(aq)$ at relatively high concentration, so that the aquo ion could be studied intensively. Though they failed in this purpose they did reveal some new substitution chemistry of the Rh_2^{4+} unit. In particular, a new series of complexes in which CO_3^{2-} plays a role similar to that of OAc^- in $Rh_2(OAc)_4$ was found. Though there is an obvious analogy between CO_3^{2-} and OAc^-, this analogy has until now not been exploited in the extensive series of complexes of the type $M_2(OAc)_4$ which have been prepared.[17] But there are significant differences between the carbonato and acetato series in that only the former includes anionic species and in that CO_3^{2-} is expected to be removed from the coordination sphere much more readily than is OAc^- by acid.

Experimental Section

Materials. All chemicals were of the highest purity commonly available. Water used as reaction medium was redistilled from alkaline potassium permanganate in an all-glass still. Argon (99.995% pure), purchased from Liquid Carbonic, was freed of oxygen by passing the gas through a tower containing amalgamated zinc and a solution of chromous ion in 0.50 *M* acid. Ion-exchange resins were purchased from Bio-Rad. For anion exchange, Ag 1-X2, 200–400 mesh chloride form was used. This was pretreated by washing with saturated sodium chloride solution and excess water. For cation exchange, AG 50W-X2, 200–400 mesh hydrogen ion form was used. This resin was pretreated as described by Deutsch[3] except that 3% peroxide was used instead of 30%. The resin was stored in the acid form, under water and in the dark, until use. It was then rinsed with the strongest eluting agent to be used and with quantities of water.

Preparation of Anhydrous Tetra-μ-acetato-dirhodium(II). Hydrated rhodium trichloride (Engelhard Industries) was refluxed in a mixture of glacial acetic acid and ethanol following Rempel, *et al.*[4] Yields ranged from 70 to 85%.

Preparation of the Aquodirhodium(II) Cation. The procedure of Maspero, *et al.*,[1] was followed, care being taken to exclude oxygen. Only platinum needles were used in syringe transfers and residence time on the cation-exchange resin was minimized.

Instrumentation and Analysis. Ultraviolet and visible spectra were recorded on Cary 14 and 15 spectrophotometers. Infrared spectra were measured on Perkin-Elmer 457 and 621 machines. Magnetic susceptibilities were measured on solid samples by the Faraday method using the Ventron Corp. Model 7600 system with Model 7570 variable-temperature accessory. For liquid samples the nmr method of Evans[5] was used, as modified by Bailey.[6]

All microanalyses were performed by the Stanford Microanalytical Laboratory. Even though the decomposition temperature was at 940°, it was found necessary to add vanadium pentoxide as a catalyst to obtain reproducible and meaningful carbon analyses with carbonate complexes of rhodium.

Cyclic Voltammetry. For cyclic voltammetry a saturated calomel electrode was placed in a cell compartment connected by a partially fused glass frit to a degassed cell compartment containing platinum auxiliary and indicator electrodes and the solution of interest. The necessary electronics were constructed by Glenn M. Tom out of conventional operational amplifier circuitry, and voltammagrams were displayed on Houston Instument's Omnigraphic 200 X-Y recorder.

Results and Discussion

The Carbonato Complex. When a freshly prepared solution of $Rh_2^{4+}(aq)$ is added under an inert atmosphere to a solution containing excess carbonate ion, the solution immediately changes from wintergreen to dark blue. With an appropriate cation, such as Na^+ or K^+, a purple solid is precipitated and it may be collected on a fritted filter. The solid appears wet. When it is air-dried or washed with methanol and air-dried, it changes into a blue solid having the infrared spectrum shown in Figure 1. (This differs in some details from that of the purple solid, which is a higher hydrate.) The identical material can be prepared by the following more convenient route. Approximately 0.5 g of anhydrous tetra-μ-acetato-dirhodium(II) is suspended in 10 ml of 2 *M* sodium carbonate solution. The solution is heated to near boiling and held at 100° for 10–15 min. Upon cooling and filtering, a solid forms. The resulting precipitate is washed with water until it just begins to dissolve, thus removing excess carbonate. The solid then is redissolved in water, reprecipitated with either methanol, sodium carbonate, or sodium chloride, washed with small amounts of water, rinsed with methanol and ether, and air-dried. Yields are greater than 90%.

Analyses for the various preparations of the carbonato complex are shown in Table I. It is found that they correspond