

**Table I.** Absorption and Circular Dichroism Data for Cobalt(III) Complexes Containing TMDDA or EDDA

Compd	Absorption		CD	
	kK	$\epsilon$	kK	$\Delta\epsilon$
(+) <sub>589</sub> - <i>uns-cis</i> -[Co(TMDDA)(en)]Cl·1.5H <sub>2</sub> O	20.04	127	20.00	+1.48
	27.78	132	27.55	-0.48
(+) <sub>589</sub> - <i>uns-cis</i> -[Co(TMDDA)(tn)]Cl·H <sub>2</sub> O	19.69	112	18.02	+0.53
			20.16	-1.94
(+) <sub>589</sub> - <i>uns-cis</i> -[Co(TMDDA)(NH <sub>3</sub> ) <sub>2</sub> ]Cl·2H <sub>2</sub> O	27.70	142	27.78	+0.56
	19.76	112	18.22	+0.89
(-) <sub>589</sub> - <i>uns-cis</i> -[Co(TMDDA)(dipy)]I		126	20.58	-1.28
	27.78	128	27.78	+0.48
(+) <sub>589</sub> - <i>uns-cis</i> -[Co(TMDDA)(phen)]I·H <sub>2</sub> O	19.72	218	19.65	-2.58
	26.67 sh	218	27.03	+0.54
(-) <sub>589</sub> - <i>uns-cis</i> -[Co(EDDA)(NH <sub>3</sub> ) <sub>2</sub> ]Cl·1.5H <sub>2</sub> O	19.69	120	19.31	+2.89
	25.64 sh	135	26.60	-0.63
(-) <sub>589</sub> - <i>uns-cis</i> -[Co(EDDA)(tn)]I·1.5H <sub>2</sub> O	20.04	154	18.05	-0.64
			20.70	+1.87
(-) <sub>589</sub> - <i>uns-cis</i> -[Co(EDDA)(tn)]I·1.5H <sub>2</sub> O	27.93	157	27.93	-0.72
	19.90	160	17.30	+0.029
			20.41	-2.00
	27.93	187	28.09	+0.77

es. The CD spectra of the two complexes show only one band in the first absorption band region as is the case for the corresponding ethylenediamine complex. Close examination of the CD spectrum of the phenanthroline complex plotted on graph paper shows, however, deformation of the band on the higher energy side. Furthermore the CD band maximum is shifted to lower energy by *ca.* 0.4 kK from the first absorption maximum. These facts suggest that there is a small component of the same sign as that of the main component on the higher energy side. In the type of chromophore, *cis*-[Co(N<sub>4</sub>O<sub>2</sub>)], the A<sub>2</sub>(D<sub>4h</sub>) component should exist on the lower energy side of the E(D<sub>4h</sub>) component. Therefore the small component at the higher energy side might arise from the splitting of E(D<sub>4h</sub>). The actual symmetry of the complex is C<sub>1</sub>.

The TMDDA complexes shown in Figures 3 and 4 with net positive rotational strengths in the T<sub>1g</sub> absorption band region can be assigned the  $\Lambda\Lambda\Lambda$  configuration<sup>19</sup> (Figure 2)

as in the case of the *uns-cis*-EDDA complexes above.

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**Registry No.** H<sub>2</sub>TMDDA·2HCl, 7597-26-4; H[Co(TMDDA)-Cl<sub>2</sub>], 43200-14-2; (+)-*uns-cis*-[Co(TMDDA)(en)]Cl, 43156-67-8; (-)-*uns-cis*-[Co(TMDDA)(en)]Cl, 43156-68-9; (-)-*uns-cis*-[Co(TMDDA)(tn)]Cl, 43200-15-3; (+)-*uns-cis*-[Co(TMDDA)(tn)]Cl, 43156-69-0; (+)-*uns-cis*-[Co(TMDDA)(NH<sub>3</sub>)<sub>2</sub>]Cl, 43200-16-4; (-)-*uns-cis*-[Co(TMDDA)(dipy)]Cl, 43200-17-5; (+)-*uns-cis*-[Co(TMDDA)(phen)]I, 43200-18-6; (-)-*uns-cis*-[Co(EDDA)(NH<sub>3</sub>)<sub>2</sub>]Cl, 43156-70-3; (+)-*uns-cis*-[Co(EDDA)(tn)]I, 43200-19-7; (-)-*uns-cis*-[Co(EDDA)(tn)]I, 43200-20-0; (-)-*uns-cis*-[Co(TMDDA)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 43200-21-1; (+)-*uns-cis*-[Co(TMDDA)(dipy)]<sup>+</sup>, 43156-71-4.

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## Preparation and Spectral Studies of Some Acidopentacyanorhodate(III) and -iridate(III) Complexes

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Complexes of the type [M(CN)<sub>5</sub>X]<sup>n-</sup> [M = Rh(III), Ir(III); X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, OH<sup>-</sup>, NCCH<sub>3</sub>] are readily prepared by thermal anation reactions of [M(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup>, the aquo complexes being formed by uv irradiation of acidic solutions of [M(CN)<sub>6</sub>]<sup>3-</sup>. The K<sup>+</sup> and Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> salts of several of the [M(CN)<sub>5</sub>X]<sup>n-</sup> complexes have been isolated and their ir spectra have been recorded and assigned. The uv spectra of all [M(CN)<sub>5</sub>X]<sup>n-</sup> and [M(CN)<sub>6</sub>]<sup>3-</sup> complexes have been measured in aqueous solution. The lowest energy electronic absorption band in the [Rh(CN)<sub>5</sub>X]<sup>n-</sup> complexes is assigned to the ligand field transition <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E<sup>a</sup>, whereas in [Ir(CN)<sub>5</sub>X]<sup>n-</sup> both <sup>1</sup>A<sub>1</sub> → <sup>3</sup>E<sup>a</sup> and <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E<sup>a</sup> absorptions are observed. The position of the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E<sup>a</sup> transition establishes the order of decreasing ligand field strength of X as NCCH<sub>3</sub> > OH<sup>-</sup> > H<sub>2</sub>O > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> for both Rh(III) and Ir(III) complexes. Halide-to-metal charge-transfer bands are observed for [M(CN)<sub>5</sub>X]<sup>n-</sup> complexes with X = Br<sup>-</sup> and I<sup>-</sup>.

In view of the large number of [Co(CN)<sub>5</sub>X]<sup>n-</sup> complexes, it is surprising that the only pentacyanorhodate(III) and -iridate(III) derivatives reported to date have been [Rh(CN)<sub>5</sub>C<sub>2</sub>F<sub>4</sub>H]<sup>3-</sup>,<sup>1</sup> [Rh(CN)<sub>5</sub>NO<sub>2</sub>]<sup>3-</sup>,<sup>1</sup> [Rh(CN)<sub>5</sub>COCH<sub>3</sub>]<sup>3-</sup>,<sup>2</sup>

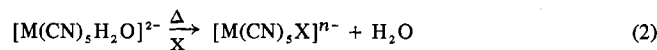
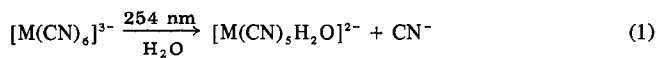
[Rh(CN)<sub>5</sub>H]<sup>3-</sup>,<sup>2</sup> and [Ir(CN)<sub>5</sub>H]<sup>3-</sup>.<sup>3</sup> Utilizing the photolability of the parent [M(CN)<sub>6</sub>]<sup>3-</sup> species, we have been able

(2) R. A. Jewsbury and J. P. Maher, *J. Chem. Soc. A*, 2847 (1971); 2089 (1972).

(3) (a) M. L. H. Green, *Angew. Chem.*, 72, 719 (1960); (b) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, 3, 22 (1964).

(1) D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem. Soc. A*, 52 (1966).

to prepare an extensive series of  $[M(CN)_5X]^{n-}$  [ $M = Rh(III), Ir(III)$ ;  $X = NCCH_3, OH^-, H_2O, Cl^-, Br^-, I^-$ ] complexes by the general procedure



We report here the infrared and electronic absorption spectra of these new acidopentacyanorhodate(III) and -iridate(III) complexes. Assignments for both  $[M(CN)_5X]^{n-}$  and  $[M(CN)_6]^{3-}$  complexes will be discussed.

### Experimental Section

**Purification of Starting Materials.** The starting materials  $K_3[Rh(CN)_6]$  and  $K_3[Ir(CN)_6]$  were obtained from Varlacoid Chemical Co., Elizabeth, N. J. For most of the preparations these compounds were used without further purification. For measurement of the ultraviolet absorption spectra of  $[Rh(CN)_6]^{3-}$ ,  $[Rh(CN)_5H_2O]^{2-}$ , and  $[Ir(CN)_5H_2O]^{2-}$ , the starting materials were chromatographed first on alumina and then on silica gel, with water as the eluent. After the solutions were concentrated and added to a large excess of acetone, the resultant precipitate was collected, washed with acetone, and dried over  $P_2O_5$  under vacuum. This process was repeated until infrared spectra showed negligible amounts of impurities. All other chemicals used were reagent grade.

**Irradiation of Solutions.** All irradiations were conducted in a hood using either quartz (1-cm path length) cells, or 20- or 100-ml quartz beakers, using an Ultraviolet Products lamp with principal output at 254 nm. The solutions were either buffered at pH 6 with  $K_2HPO_4$ - $KH_2PO_4$ , acidified to pH 1.5-3.0 with  $HClO_4$ , or left unbuffered (pH 9-10 for  $[M(CN)_6]^{3-}$ ).

$[Rh(CN)_5H_2O]^{2-}$  and  $[Ir(CN)_5H_2O]^{2-}$ . Acidic or pH 6 buffered solutions were irradiated until the absorption band corresponding to  $[M(CN)_5H_2O]^{2-}$  reached a maximum value. This required approximately 3 hr for a  $10^{-3} M K_3[Rh(CN)_6]$  solution and 95 hr for a  $10^{-3} M K_3[Ir(CN)_6]$  solution. All attempts to isolate the  $[M(CN)_5H_2O]^{2-}$  complexes from aqueous solution were unsuccessful. The irradiated solutions showed no absorption changes after being stored in the dark for several months. Band maxima and extinction coefficients for  $[Rh(CN)_5H_2O]^{2-}$  and  $[Ir(CN)_5H_2O]^{2-}$  were determined by irradiating a carefully prepared pH 6 buffered solution of the corresponding  $[M(CN)_6]^{3-}$  complex until the absorption spectra showed no further changes with continued irradiation. Only one detectable band eluted when these solutions were chromatographed on silica gel or alumina.

$K_3[Rh(CN)_5I]$  and  $K_3[Ir(CN)_5I]$ . A solution containing 0.2 g of  $K_3[Rh(CN)_6]$  or  $K_3[Ir(CN)_6]$  in 20 ml of aqueous  $HClO_4$  with an initial pH of 2 was irradiated until the absorption band corresponding to  $[M(CN)_5H_2O]^{2-}$  reached a maximum. The solution was then brought to pH 7 with KOH, concentrated by evaporation to a volume of about 2 ml, and cooled in an ice bath. The solution was then decanted from the  $KClO_4$  precipitate and a large (~100 fold) excess of KI was added, after which the reaction mixture was left in the dark for 24 hr. The 2-ml solution was then poured into 150 ml of acetone, and the resultant precipitate was collected and washed with acetone and with methanol. Elemental analyses on these and the other  $K_n[M(CN)_5X]$  compounds reported herein showed a significant amount of the anating agent KX present. Repeated attempts at removing the KX were unsuccessful. However, satisfactory analyses for several  $[Co(NH_3)_6]^{3+}$  salts, as outlined below, were obtained.

$[Co(NH_3)_6][Rh(CN)_5I]$  and  $[Co(NH_3)_6][Ir(CN)_5I]$ . The  $K_3[M(CN)_5I]$  salts from above were dissolved in a small amount of water (~2 ml), filtered, and then added to a saturated aqueous solution of  $[Co(NH_3)_6]Cl_3$ . *Anal.* Calcd. Co, 22.03; N, 31.41; H, 6.73; Cl, 39.83. Found: Co, 21.82; N, 31.52; H, 7.01; Cl, 39.70. The solution was stirred and placed in an ice bath for 2 hr after which the resultant yellow crystals were filtered, washed with cold water, and dried over  $P_2O_5$ . *Anal.* Calcd. for  $[Co(NH_3)_6][Rh(CN)_5I]$ : Co, 11.31; N, 29.56; Rh, 19.75; C, 11.52; I, 24.36. Found: Co, 11.10; N, 29.43; Rh, 20.24; C, 11.88; I, 24.32. Calcd. for  $[Co(NH_3)_6][Ir(CN)_5I]$ : Co, 9.66; N, 25.24; Ir, 31.51; C, 9.84; I, 20.80. Found: Co, 10.22; N, 25.59; Ir, 32.01; C, 10.94; I, 20.42.

$K_3[Rh(CN)_5Br]$ ,  $K_3[Ir(CN)_5Br]$ ,  $K_3[Rh(CN)_5Cl]$ , and  $K_3[Ir(CN)_5Cl]$ . Preparation of these complexes was similar to the method used to make the iodo complexes, except that KBr and LiCl were used in the anation reaction.  $[Ir(CN)_5H_2O]^{2-}$  reacts very slowly

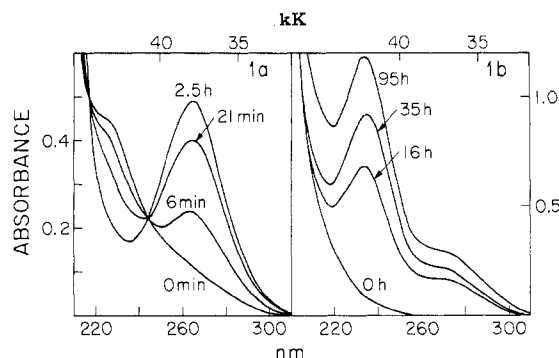


Figure 1. Spectral changes during 254-nm irradiation of pH 6 buffered solutions: a,  $8.1 \times 10^{-4} M K_3[Rh(CN)_6]$ ; b,  $1.5 \times 10^{-3} M K_3[Ir(CN)_6]$ . The final spectrum in each case did not change with continued irradiation.

Table I. Isosbestic Points for the Conversion

$[M(CN)_5X]^{n-}$	Isosbestic point, nm
$[Rh(CN)_5NCCH_3]^{2-}$	222, 252
$[Rh(CN)_5Cl]^{3-}$	240, 277
$[Rh(CN)_5Br]^{3-}$	255, 280
$[Rh(CN)_5I]^{3-}$	a
$[Ir(CN)_5NCCH_3]^{2-}$	223
$[Ir(CN)_5Cl]^{3-}$	217, 250, 260
$[Ir(CN)_5Br]^{3-}$	226, 250
$[Ir(CN)_5I]^{3-}$	a

<sup>a</sup> Spectra of  $[M(CN)_5X]^{n-}$  and  $[M(CN)_5H_2O]^{2-}$  do not cross at any of the wavelengths under investigation.

with  $Cl^-$  at room temperature, so the conversion was carried out for 48 hr at 60°.

$[Co(NH_3)_6][Rh(CN)_5Br]$ ,  $[Co(NH_3)_6][Ir(CN)_5Br]$ ,  $[Co(NH_3)_6][Rh(CN)_5Cl]$ , and  $[Co(NH_3)_6][Ir(CN)_5Cl]$ . These complexes were prepared in a manner similar to that used for the iodo complexes. *Anal.* Calcd. for  $[Co(NH_3)_6][Ir(CN)_5Br]$ : Co, 10.47; N, 27.35; Ir, 34.14; C, 10.66; Br, 14.19. Found: Co, 10.63; N, 28.68; Ir, 34.91; C, 11.72; Br, 12.13. Calcd. for  $[Co(NH_3)_6][Rh(CN)_5Br]$ : Co, 12.44; N, 32.51; Rh, 21.72; C, 12.67; Br, 16.87. Found: Co, 12.17; N, 32.65; Rh, 21.70; C, 12.62; Br, 16.81. Calcd. for  $[Co(NH_3)_6][Ir(CN)_5Cl]$ : Co, 11.36; N, 29.70; Ir, 37.06; C, 11.57; Cl, 6.84. Found: Co, 10.88; N, 29.89; Ir, 37.07; C, 11.57; Cl, 6.80.

$K_3[Rh(CN)_5NCCH_3]$  and  $K_3[Ir(CN)_5NCCH_3]$ . Preparation of these complexes was similar to the method used to make the iodo complexes, except that 10 ml of acetonitrile was added to the 2 ml of aqueous solution of  $[M(CN)_5H_2O]^{2-}$ . The aqueous acetonitrile solution was either left in the dark for 24 hr or was irradiated for 1 hr at 254 nm and then allowed to stand for 4 hr. In either case conversion to  $[M(CN)_5NCCH_3]^{2-}$  was found to be essentially complete. The solution was then concentrated to a volume of about 2 ml and poured slowly into 150 ml of acetone. The resultant precipitate was collected, washed with acetone, and dried over  $P_2O_5$ . Attempts at preparing  $[Co(NH_3)_6][M(CN)_5NCCH_3]$  salts were unsuccessful and satisfactory analyses were not obtained for  $K_n[M(CN)_5NCCH_3]$ . The ir and uv spectral data, however, are consistent with the formulation  $[M(CN)_5NCCH_3]^{2-}$  for the anions.

$[Rh(CN)_5OH]^{3-}$  and  $[Ir(CN)_5OH]^{3-}$ . Solutions containing  $[M(CN)_5H_2O]^{2-}$  were made alkaline to pH 12 by addition of KOH. By monitoring the uv spectral changes during the addition of base, titration curves for the coordinated water were obtained. At pH 12 conversion to  $[M(CN)_5OH]^{3-}$  is essentially complete, the  $pK_a$  values being 10.4 for  $[Rh(CN)_5H_2O]^{2-}$  and 9.8 for  $[Ir(CN)_5H_2O]^{2-}$ . All attempts at isolation of solid salts of the hydroxo complexes were unsuccessful.

**Spectral Measurements.** Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer using KBr pellets prepared from ir Spectrograde KBr powder (Matheson Coleman and Bell). 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 1.00-cm cell. A solution prepared

Table II. Infrared Spectra of  $K_n[M(CN)_5X]$  in KBr Pellets in the Range 200–3000  $\text{cm}^{-1}$ 

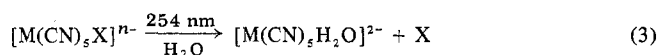
Compd	Absorptions of $M(CN)_5^{2-}$			Absorptions of X	Other peaks
	$\nu_{C\equiv N}$	$\delta_{MCN}$	$\nu_{M-C}$		
$K_3[Rh(CN)_6]$	2133 s	524 m 513 m	386 s		2110 w 2095 w
$K_3[Rh(CN)_5Cl]$	2157 w 2130 s	522 w 510 m	386 s 366 m 352 m		2091 w
$K_3[Rh(CN)_5Br]$	2155 w 2128 s	523 w 519 m 510 w	438 m 386 s 360 m 350 m		2090 w
$K_3[Rh(CN)_5I]$	2156 m 2128 s	519 m 500 m	426 m 389 s 349 m		2088 w
$K_2[Rh(CN)_5NCCH_3]$	2172 m 2185 m 2138 s 2131 s	521 m 514 m	467 m 382 s 347 w 398 s	2935 $m^a$ 2325 $m^b$ 2300 $w^c$	
$K_3[Ir(CN)_6]$	2131 s	525 m 511 m	398 s		2108 w 2093 w
$K_3[Ir(CN)_5Cl]$	2160 w 2127 s	519 m 508 w	472 w 397 s 372 w		
$K_3[Ir(CN)_5Br]$	2159 m 2130 w, sh 2125 s	525 m 516 m	470 w 398 m 370 w		485 w
$K_3[Ir(CN)_5I]$	2160 w 2132 s 2126 s	522 m, sh 517 m	402 m 372 w		482 w
$K_2[Ir(CN)_5NCCH_3]$	2168 m 2129 s	524 m 515 m	470 m 398 s	2935 $m^a$ 2331 $m^b$	

<sup>a</sup>  $\nu_{C-H}$ . <sup>b</sup>  $\nu_{C\equiv N}$ . <sup>c</sup>  $\nu_{C-C} + \delta_{CH_3}$ .

by mixing equal volumes of saturated aqueous LiCl and water was used for low-temperature glasses. The 77°K spectra were not corrected for solvent contraction.

### Results and Discussion

Irradiation of  $[Rh(CN)_6]^{3-}$  or  $[Ir(CN)_6]^{3-}$  in acidic solutions provides a convenient synthesis of  $[M(CN)_5H_2O]^{2-}$ . Spectral changes which occur during the photolysis of solutions containing  $[M(CN)_6]^{3-}$  are shown in Figure 1. Solutions of the aquo complexes undergo no further changes upon either standing or continued irradiation. Measurement of pH changes during irradiation indicates loss of  $1.0 \pm 0.2$  cyanide from  $[M(CN)_6]^{3-}$ , consistent with the formation of  $[M(CN)_5H_2O]^{2-}$ . Irradiation in alkaline or neutral media (which quickly turn alkaline due to released  $CN^-$ ) yields other photo-products. As is the case with many  $[Co(CN)_5X]^{n-}$  complexes,<sup>4</sup> electronic absorption spectral data, summarized in Table I, show that irradiation of the  $[M(CN)_5X]^{n-}$  complexes of Rh(III) and Ir(III) in aqueous solution results in a quation (eq 3).



**Infrared Spectra.** Infrared spectral results for the  $K_3[M(CN)_6]$  and  $K_n[M(CN)_5X]$  complexes are set out in Table II. The ir spectra of  $K_3[Rh(CN)_6]$  and  $K_3[Ir(CN)_6]$  are in excellent agreement with published data,<sup>5</sup> and the spectra of the  $[M(CN)_5X]^{n-}$  [ $M = Rh(III), Ir(III)$ ] complexes are qualitatively very similar to those observed<sup>6</sup> for analogous  $[Co(CN)_5X]^{n-}$  complexes. In addition, the positions of the ir peaks attributable to the complex anions in the analyzed samples  $[Co(NH_3)_6][M(CN)_5X]$  accord well with values

(4) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, Chapter 11.

(5) L. H. Jones, *J. Chem. Phys.*, **41**, 856 (1964).

(6) V. M. Miskowski and H. B. Gray, to be submitted for publication.

given in Table II for the corresponding potassium salts.

Assignments for the  $M(CN)_5^{2-}$  modes follow closely the standard interpretation.<sup>7</sup> A band of medium or low intensity around 2155  $\text{cm}^{-1}$  and an intense band at about 2130  $\text{cm}^{-1}$  are attributable to cyano stretching,  $\nu_{C\equiv N}$ ; the 2130- $\text{cm}^{-1}$  band probably represents the  $e$  mode in  $C_{4v}$  symmetry. Two or three medium-intensity bands, often with prominent shoulders, are observed between 500 and 550  $\text{cm}^{-1}$ . These bands are assigned to the  $\delta_{MCN}$  modes. From two to four bands are observed in the 325–475- $\text{cm}^{-1}$  region and this group is assigned to the  $\nu_{M-C}$  modes.

The  $[M(CN)_5NCCH_3]^{2-}$  complexes exhibit a sharp  $\nu_{C-H}$  band at 2935  $\text{cm}^{-1}$  and a band at approximately 2325  $\text{cm}^{-1}$  which may be assigned to  $\nu_{C\equiv N}$  of the coordinated acetonitrile. The bands at 2325 and 2300  $\text{cm}^{-1}$  in  $[Rh(CN)_5NCCH_3]^{2-}$  may be compared with those at 2323 and 2300  $\text{cm}^{-1}$  in  $[Rh(NH_3)_5NCCH_3][ClO_4]_3$ .<sup>8</sup>

**Electronic Spectra.** Electronic spectral data for the various cyanometalates in aqueous solution are set out in Table III.<sup>9</sup> The assignments given for the low-energy absorption bands are based on the ligand field (LF) energy level diagram shown in Figure 2. Because of the interference of charge transfer (CT) absorption, we shall only be concerned with the LF bands in the  $C_{4v}$  complexes derived from the  $^1A_{1g} \rightarrow ^3T_{1g}$  and  $^1A_{1g} \rightarrow ^1T_{1g}$  octahedral transitions. For all the  $[M(CN)_5X]^{n-}$  complexes under consideration, X has a weaker LF strength than  $CN^-$ . Thus we expect the spin-triplet and spin-singlet  $E^a (e^3b_2^2a_1)$  levels to be of substantially lower

(7) D. M. Adams, "Metal Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, Chapter 3.

(8) R. D. Foust, Jr., and P. C. Ford, *Inorg. Chem.*, **11**, 899 (1972).

(9) Solution spectra for the  $[Co(NH_3)_6][M(CN)_5X]$  complexes were difficult to obtain, owing to the very low solubilities of these salts. However, we were able to measure the uv spectra of the compounds containing  $[Rh(CN)_5Br]^{3-}$ ,  $[Rh(CN)_5I]^{3-}$ , and  $[Ir(CN)_5I]^{3-}$ . In these three cases, the positions and intensities of the uv bands attributable to the complex anions are in excellent agreement with corresponding values given in Table III.

Table III. Electronic Absorption Spectra of  $[M(CN)_5X]^{n-}$  Complexes in pH 6 Aqueous Solution at 300°K

Species	$\lambda_{\max}$ , nm	$\bar{\nu}_{\max}$ , kK	$\epsilon_{\max}$ , $M^{-1} \text{ cm}^{-1}$	Assignment	
$K_3[Rh(CN)_6]$	260	38.5	170	$^1A_{1g} \rightarrow ({}^3T_{1g}, {}^3T_{2g})?$	
	225 sh	44.4	555	$^1A_{1g} \rightarrow {}^1T_{1g}$	
$K_3[Rh(CN)_5NCCH_3]$	245	40.8	550	$^1A_1 \rightarrow {}^1E^a$	
	258	38.8	500	$^1A_1 \rightarrow {}^1E^a$	
	$[Rh(CN)_5OH]^{3-}$	265	37.7	605	$^1A_1 \rightarrow {}^1E^a$
	$[Rh(CN)_5H_2O]^{2-}$	277	36.1	425	$^1A_1 \rightarrow {}^1E^a$
$K_3[Rh(CN)_5Cl]$	278 (280) <sup>b</sup>	34.8 (35.7) <sup>b</sup>	402 (286) <sup>b</sup>	$^1A_1 \rightarrow {}^1E^a$	
	237 sh	42.2 sh	1,700	$\pi$ -LMCT	
$K_3[Rh(CN)_5I]$	205	48.8	24,000	$\sigma$ -LMCT	
	313 (308) <sup>b</sup>	31.9 (32.5) <sup>b</sup>	1,500 (1544) <sup>b</sup>	$^1A_1 \rightarrow {}^1E^a$	
	258	38.8	4,200	$\pi$ -LMCT	
	220	45.5	42,000	$\sigma$ -LMCT	
$K_3[Ir(CN)_6]$	<192	>52.0			
$K_3[Ir(CN)_5NCCH_3]$	240 sh	41.7 sh	250	$^1A_1 \rightarrow {}^3E^a$	
	215 sh	46.5 sh	720	$^1A_1 \rightarrow {}^1E^a$	
$[Ir(CN)_5OH]^{3-}$	260 sh	38.5 sh	180	$^1A_1 \rightarrow {}^3E^a$	
	230 sh	43.5 sh	630	$^1A_1 \rightarrow {}^1E^a$	
	270 sh	37.0 sh	180	$^1A_1 \rightarrow {}^3E^a$	
$[Ir(CN)_5H_2O]^{2-}$	235	42.6	790	$^1A_1 \rightarrow {}^1E^a$	
	280 sh	35.7 sh	95	$^1A_1 \rightarrow {}^3E^a$	
$K_3[Ir(CN)_5Cl]$	245	40.8	370	$^1A_1 \rightarrow {}^1E^a$	
	290 sh (285 sh) <sup>b</sup>	34.5 sh (35.1 sh) <sup>b</sup>	70 (61) <sup>b</sup>	$^1A_1 \rightarrow {}^3E^a$	
$K_3[Ir(CN)_5Br]$	257 (255) <sup>b</sup>	38.9 (39.2) <sup>b</sup>	412 (367) <sup>b</sup>	$^1A_1 \rightarrow {}^1E^a$	
	215 sh	46.5 sh	2,000	$\pi$ -LMCT	
	320 sh (310 sh) <sup>b</sup>	31.3 sh (32.3 sh) <sup>b</sup>	60 (83) <sup>b</sup>	$^1A_1 \rightarrow {}^3E^a$	
	275 (272) <sup>b</sup>	36.4 (36.8) <sup>b</sup>	1,400 (1589) <sup>b</sup>	$^1A_1 \rightarrow {}^1E^a$	
$K_3[Ir(CN)_5I]$	230 sh	43.5 sh	3,000	$\pi$ -LMCT	
	195 sh	51.3 sh	21,800	$\sigma$ -LMCT	

<sup>a</sup> Error limits  $\pm 10\%$ . <sup>b</sup> Quantities in parentheses were measured at 77°K in an aqueous LiCl glass.

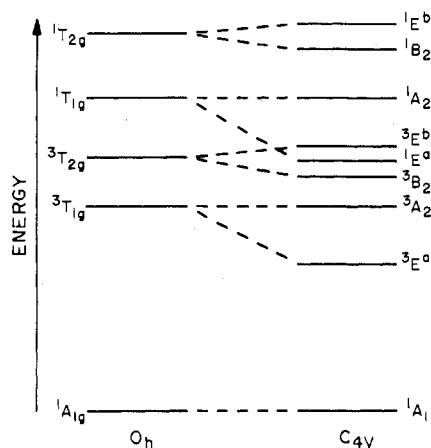


Figure 2. Energy level diagram showing the correlation of ligand field states in  $O_h$  and  $C_{4v}$  symmetries.

energy than their respective  $A_2$  ( $e^4b_2b_1$ ) states, as the  $a_1$  ( $d_{z^2}$ ) orbital should be stabilized relative to  $b_1$  ( $d_{x^2-y^2}$ ). Before taking up the  $C_{4v}$  cases, however, we shall consider briefly the LF spectra of  $[Rh(CN)_6]^{3-}$  and  $[Ir(CN)_6]^{3-}$ .

Interpretation of the spectrum of  $[Rh(CN)_6]^{3-}$  has proved to be troublesome.<sup>10-12</sup> Schmidtke assigned the band at 44.4 kK as the  $^1A_{1g} \rightarrow {}^1T_{1g}$  transition and the ill-defined shoulder at 38.5 kK as  $^1A_{1g} \rightarrow ({}^3T_{1g}, {}^3T_{2g})$ .<sup>11</sup> Our results on the  $C_{4v}$  complexes suggest that 44.4 kK is quite a reasonable position for the  $^1A_{1g} \rightarrow {}^1T_{1g}$  band for  $[Rh(CN)_6]^{3-}$ , and we shall adopt this assignment. There is some uncertainty concerning the assignment of the 38.5 kK absorption, however,

due to the fact that  $[Rh(CN)_5H_2O]^{2-}$ , which has a maximum at 37.7 kK, is a likely impurity. We have found that the relative band intensity at 38.5 kK varies with the purity of  $[Rh(CN)_6]^{3-}$ , although a weak shoulder remains in the most highly purified sample we have obtained. On the other hand, the weak band at 30.8 kK reported earlier<sup>10a</sup> is not observed in rigorously purified samples of  $[Rh(CN)_6]^{3-}$ .

The third-row complex  $[Ir(CN)_6]^{3-}$  exhibits no band maxima at energies less than 52.0 kK. Our assignment of the 37.0-kK band in  $[Ir(CN)_5H_2O]^{2-}$  as  $^1A_1 \rightarrow {}^3E^a$  suggests that the  $^1A_{1g} \rightarrow {}^3T_{1g}$  transition in  $[Ir(CN)_6]^{3-}$  occurs well above 40 kK and would be overlapped by the tail of the CT absorption band.

The electronic spectra of  $[Rh(CN)_5Cl]^{3-}$  and  $[Ir(CN)_5Cl]^{3-}$  are shown in Figure 3. Only one band is resolved in the spectrum of the Rh(III) complex, at 36.1 kK ( $\epsilon$  425). Both the energy and the intensity of the band are consistent with its assignment as the spin-allowed  $^1A_1 \rightarrow {}^1E^a$  LF transition. The orbitally forbidden, equatorially localized  $^1A_1 \rightarrow {}^1A_2$  excitation would be expected to appear at approximately 44.4 kK, which is the position of the  $^1A_{1g} \rightarrow {}^1T_{1g}$  band in  $[Rh(CN)_6]^{3-}$ . There is no indication in any of the  $[Rh(CN)_5X]^{n-}$  spectra of the  $^1A_1 \rightarrow {}^1A_2$  band, a not altogether surprising result in view of the relatively small oscillator strength anticipated for it. Careful examination of the electronic spectrum of  $[Co(CN)_5Cl]^{3-}$ , however, has revealed both the  $^1A_1 \rightarrow {}^1E^a$  and  $^1A_1 \rightarrow {}^1A_2$  bands, at 25.6 ( $\epsilon$  196) and 31.3 ( $\epsilon$  100) kK, respectively.<sup>6</sup> The position of the  $^1A_1 \rightarrow {}^1A_2$  band in  $[Co(CN)_5Cl]^{3-}$  compares favorably with the 32.1-kK value<sup>10</sup> for  $^1A_1 \rightarrow {}^1T_{1g}$  in  $[Co(CN)_6]^{3-}$ , and the low intensity is also consistent with expectation. Therefore it is probable that a  $^1A_1 \rightarrow {}^1A_2$  band does in fact lie in the neighborhood of 44 kK in each of the  $[Rh(CN)_5X]^{n-}$  complexes but that because of CT tail absorption we were unable to resolve it.

The spectrum of  $[Ir(CN)_5Cl]^{3-}$  is similar to that of  $[Rh(CN)_5Cl]^{3-}$ , except that the  $^1A_1 \rightarrow {}^1E^a$  band is shifted to higher energy (40.8 kK) and is weakly shouldered, at 35.7 kK. The lowest spin-forbidden LF transition,  $^1A_1 \rightarrow {}^3E^a$ ,

(10) (a) J. J. Alexander and H. B. Gray, *Coord. Chem. Rev.*, **2**, 29 (1967); (b) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968).

(11) H.-H. Schmidtke, *Z. Phys. Chem. (Frankfurt am Main)*, **40**, 96 (1964).

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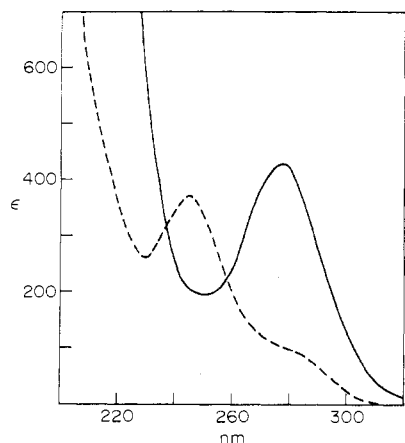


Figure 3. Electronic spectra of  $K_3[Rh(CN)_5Cl]$  (—) and  $K_3[Ir(CN)_5Cl]$  (---) in pH 6 aqueous buffer solutions at 300°K.

would be expected to be more readily observable in Ir(III) than Rh(III), because of the much larger spin-orbit coupling in the third-row central ion. We therefore attribute the weak low-energy feature in each of the  $[Ir(CN)_5X]^{n-}$  complexes to the  $^1A_1 \rightarrow ^3E^a$  transition.

The positions of the  $^1A_1 \rightarrow ^1E^a$  bands in the  $[M(CN)_5X]^{n-}$  complexes (Table III) are consistent with decreasing LF strength of X in the order  $NCCH_3 > OH^- > H_2O > Cl^- > Br^- > I^-$  for both Rh(III) and Ir(III). A similar order has been obtained from an analysis of  $[Co(CN)_5X]^{n-}$  spectra.<sup>6</sup>

For  $[M(CN)_5X]^{n-}$  complexes with X =  $Br^-$  or  $I^-$ , one or two relatively intense absorption bands are observed at higher energies than the  $^1A_1 \rightarrow ^1E^a$  transition. The spectrum of  $[Rh(CN)_5I]^{3-}$ , for example, shows well-resolved bands at 38.8 ( $\epsilon$  4200) and 45.5 ( $\epsilon$  42,000) kK, in addition to a  $^1A_1 \rightarrow ^1E^a$  band at 31.9 ( $\epsilon$  1500) kK (Figure 4). These additional bands are much too intense to be attributable to LF transitions, so they must represent ligand (X)  $\rightarrow$  metal charge transfer (LMCT) excitation processes. There are two allowed LMCT transitions from halide valence p orbitals to  $a_1$  ( $d_{z^2}$ ), which is the lowest metal virtual orbital. These transitions are  $^1A_1 \rightarrow ^1E$  ( $e\pi X \rightarrow a_1 d_{z^2}$ ) and  $^1A_1 \rightarrow ^1A_1$  ( $a_1\sigma X \rightarrow a_1 d_{z^2}$ ), abbreviated  $\pi$ -LMCT and  $\sigma$ -LMCT, respectively. Simple theoretical reasoning, which places the  $\sigma$  bonding  $a_1\sigma X$  or-

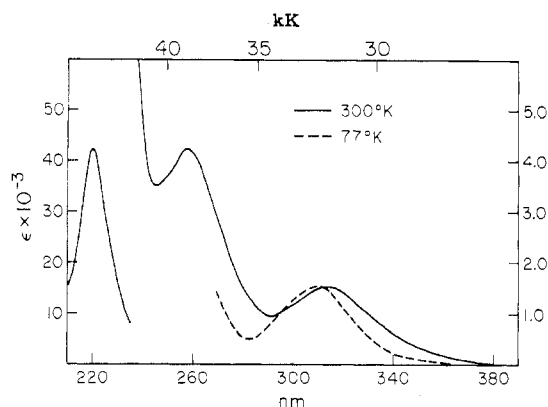


Figure 4. Electronic spectra of  $K_3[Rh(CN)_5I]$  in pH 6 aqueous buffer solution at 300°K and in an aqueous LiCl glass at 77°K.

bitally lower than the  $e\pi X$  level, as well as established experimental patterns in the LMCT spectra of a variety of halometalate complexes,<sup>13</sup> lead us to expect that the  $\sigma$ -LMCT band will be of higher energy and have substantially greater intensity than the  $\pi$ -LMCT absorption. Thus we assign the 38.8- and 45.5-kK bands in  $[Rh(CN)_5I]^{3-}$  to  $\pi$ -LMCT and  $\sigma$ -LMCT transitions, respectively. Analogous LMCT assignments are given in Table III for the intense bands observed in  $[Rh(CN)_5Br]^{3-}$ ,  $[Ir(CN)_5Br]^{3-}$ , and  $[Ir(CN)_5I]^{3-}$ .

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**Registry No.**  $[Rh(CN)_5H_2O]^{2-}$ , 42892-92-2;  $[Rh(CN)_5OH]^{3-}$ , 42892-93-3;  $K_3[Rh(CN)_6]$ , 20792-40-9;  $K_3[Rh(CN)_5Cl]$ , 42892-94-4;  $K_3[Rh(CN)_5Br]$ , 42892-95-5;  $K_3[Rh(CN)_5I]$ , 42892-96-6;  $K_2[Rh(CN)_5NCCH_3]$ , 42892-97-7;  $[Co(NH_3)_6][Rh(CN)_5I]$ , 42892-98-8;  $[Co(NH_3)_6][Rh(CN)_5Br]$ , 42892-99-9;  $[Ir(CN)_5H_2O]^{2-}$ , 42893-00-5;  $[Ir(CN)_5OH]^{3-}$ , 42893-01-6;  $K_3[Ir(CN)_6]$ , 20792-41-0;  $K_3[Ir(CN)_5Cl]$ , 42893-03-8;  $K_3[Ir(CN)_5Br]$ , 42893-04-9;  $K_3[Ir(CN)_5I]$ , 42893-05-0;  $K_2[Ir(CN)_5NCCH_3]$ , 42893-06-1;  $[Co(NH_3)_6][Ir(CN)_5I]$ , 42893-07-2;  $[Co(NH_3)_6][Ir(CN)_5Br]$ , 42893-08-3;  $[Co(NH_3)_6][Ir(CN)_5Cl]$ , 42893-09-4.

(13) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

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## Preparation and Reactivity of Tris(oxalato)iridate(IV) Ion in Aqueous Acidic Solution<sup>1</sup>

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In aqueous acidic sulfate and perchlorate media, Ce(IV) rapidly and quantitatively oxidizes  $Ir^{III}(C_2O_4)_3^{3-}$  to  $Ir^{IV}(C_2O_4)_3^{2-}$ .  $Co_{aq}^{3+}$  also effects this rapid conversion, and the Ir(IV) complex is also produced by anodic oxidation. In solutions of a given acidity  $Ir^{IV}(C_2O_4)_3^{2-}$  undergoes slow pseudo-first-order reaction to produce a highly reactive intermediate which we interpret to be  $Ir^{III}(C_2O_4)_2(C_2O_4^{\cdot-})^{2-}$ . The latter species reacts very rapidly with  $Ir^{IV}(C_2O_4)_3^{2-}$ , Ce(IV), or  $O_2$  with production of  $CO_2$ . In acidic sulfate media, the direct reaction of Ce(IV) with  $Ir^{IV}(C_2O_4)_3^{2-}$  is a moderately slow process, in line with the redox reactivity exhibited by coordinated oxalate in related metal-oxalato complexes.

For some time we have been interested in the chemistry of iridium-oxalato complexes, particularly as the behavior may compare to observations which we and others have made on

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related rhodium and cobalt systems. While brief reports on the iridium system have been made,<sup>2</sup> the present paper represents the first detailed account of our progress. We describe here the preparation of  $Ir(C_2O_4)_3^{2-}$ , its thermal redox de-