*Ultraviolet Absorption Spectra and the Electronic Structure of Metallic Complexes. II. Cyanide Complexes**

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(Received August 13, 1957)

In the preceding paper of this series[1], we have calculated the energy levels of the chloroammine cobalt(III) complexes by the semi-empirical moleculer orbital (M. O.) method taking π-orbitals of the ligands into consideration. In those complexes, however, the π-bonding between the metal orbital and the π-orbital of the ligand is relatively weak. On the contrary it is well known that the unsaturated ligands such as CN^- and CO coordinate strongly to the central metal. Recent infrared study of potassium tetracyano platinum (III) trihydrate $K_2[Pt(CN)_4]\cdot 3H_2O$ by Sweeny et al.[2] has shown that the Pt–CN stretching force constant is comparable to that of the usual covalent bonding of organic molecules. Pauling[3] has pointed out that this fact can be explained reasonably by considering the resonance formula containing the double bond between the ligands and the metallic ion. A similar discussion has been made by Williams[4] from the standpoint of the molecular orbital theory. But both of their descriptions are qualitative, and moreover no calculation has been done on these complexes.

In the present study, we calculated the energy levels of hexacyano chromium (III) $[Cr(CN)_6]^{3-}$, hexacyano cobalt(III) $[Co(CN)_6]^{3-}$, tetracyano nickel(II) $[Ni(CN)_4]^{3-}$, tetracyano copper(I) $[Cu(CN)_4]^{2-}$, *trans*-dicyano-diethylene-diamine cobalt(III) *trans*-$[Co\ en_2(CN)_2]^+$ and hexa-ammine cobalt(III) $[Co(NH_3)_6]^{3+}$ ions by the semi-empirical M. O. method, and the stability of the complex ions and the nature of their absorption bands were discussed.

Procedure

The method is the same in principle as that of the preceding paper[1]. The sets of molecular orbitals for each complex are shown in Table I and Fig. 1. The secular equation of the form $|H_{ij}-G_{ij}E|=0$ was solved for each class of the irreducible representation. Here, H_{ij} was approximated by the following equation.

$$H_{ij}=F_x\cdot G_{ij}(H_{ii}+H_{jj})/2$$

The values of F_x is 1.67 for $H_{\sigma\sigma}$ and 2.00 for $H_{\pi\pi}$. G_{ij} are group overlap integrals which can be expressed by the usual overlap integrals.

The values of H_{ii} for metallic ion were selected from the values of Kuroda and Ito[5]. However, they were slightly modified not to contradict the charge distribution obtained from Pauling's neutrality principle, i.e., "the central atom is almost neutralized by the donation of electrons from the ligand". The values of H_{ii} of the ligand were selected from Mulliken's

* Presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April 6, 1957.

1) K. Nakamoto, J. Fujita, M. Kobayashi and R. Tsuchida. *J. Chem. Phys.*, **27**, 439 (1957).

2) D. M. Sweeny, I. Nakagawa, S. Mizushima and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 889 (1956).

3) L. Pauling "The Nature of the Chemical Bond" Cornell University Press, New York (1940).

4) R. J. Williams, *J. Chem. Soc.*, **1956**, 8.

5) Y. Kuroda and K. Ito, *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 545, 763 (1955).

TABLE
MOLECULAR ORBITAL

Complex Ion (point group)	Irred. Rep.	Metal orbitals	Ligand orbitals σ_{NH_3}	Ligand orbitals σ_{CN}
$[M(NH_3)_6]$ (O_h)	a_{1g}	$4s$	$\frac{1}{\sqrt{6}}(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	
	e_g	$3d_{z^2}$	$\frac{1}{\sqrt{12}}(\sigma_2+\sigma_3+\sigma_4+\sigma_5-2\sigma_1+2\sigma_6)$	
		$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_2-\sigma_3+\sigma_4-\sigma_5)$	
	f_{1u}	$4p_x$	$\frac{1}{\sqrt{2}}(\sigma_2-\sigma_4)$	
		$4p_y$	$\frac{1}{\sqrt{2}}(\sigma_3-\sigma_5)$	
		$4p_z$	$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_6)$	
	f_{2g}	$3d_{xy}$ $3d_{yz}$ $3d_{xz}$		
trans $[M\,en_2(CN)_2]^+$ (D_{4h})	a_{1g}	$4s$. $3d_{z^2}$	$\frac{1}{2}(\sigma_2+\sigma_3+\sigma_4+\sigma_5)$	$\frac{1}{\sqrt{2}}(\sigma_1+\sigma_6)$
	b_{1g}	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_2-\sigma_3+\sigma_4-\sigma_5)$	
	a_{2u}	$4p_z$		$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_6)$
	e_u	$4p_x$	$\frac{1}{\sqrt{2}}(\sigma_3-\sigma_5)$	
		$4p_y$	$\frac{1}{\sqrt{2}}(\sigma_2-\sigma_4)$	
	e_g	$3d_{xz}$		
		$3d_{yz}$		
	b_{2g}	$3d_{xy}$		
$[M(CN)_6]$ (O_h)	a_{1g}	$4s$		$\frac{1}{\sqrt{6}}(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$
	e_g	$3d_{z^2}$		$\frac{1}{\sqrt{12}}(\sigma_2+\sigma_3+\sigma_4+\sigma_5-2\sigma_1-2\sigma_6)$
		$3d_{x^2-y^2}$		$\frac{1}{2}(\sigma_2-\sigma_3+\sigma_4-\sigma_5)$
	f_{1g}			
	f_{1u}	$4p_x$		$\frac{1}{\sqrt{2}}(\sigma_2-\sigma_4)$
		$4p_y$		$\frac{1}{\sqrt{2}}(\sigma_3-\sigma_5)$
		$4p_z$		$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_6)$

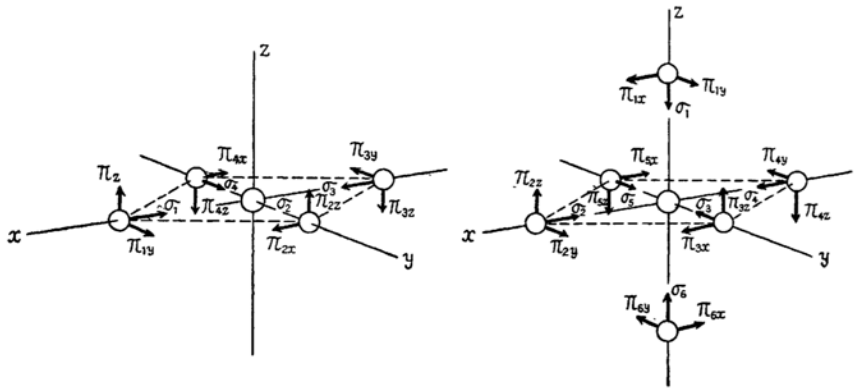
I.

COMBINATIONS

π_C	π_N
$\frac{1}{\sqrt{2}}(\pi_{1x}-\pi_{6x})$	$\frac{1}{\sqrt{2}}(\pi_{1x}-\pi_{6x})$
$\frac{1}{\sqrt{2}}(\pi_{1y}-\pi_{6y})$	$\frac{1}{\sqrt{2}}(\pi_{1y}-\pi_{6y})$
$\frac{1}{\sqrt{2}}(\pi_{1x}+\pi_{6x})$	$\frac{1}{\sqrt{2}}(\pi_{1x}+\pi_{6x})$
$\frac{1}{\sqrt{2}}(\pi_{1y}+\pi_{6y})$	$\frac{1}{\sqrt{2}}(\pi_{1y}+\pi_{6y})$
$\frac{1}{2}(\pi_{2z}+\pi_{4z}-\pi_{1x}-\pi_{6x})$	$\frac{1}{2}(\pi_{2z}+\pi_{4z}-\pi_{1x}-\pi_{6x})$
$\frac{1}{2}(\pi_{3z}+\pi_{5z}-\pi_{1y}-\pi_{6y})$	$\frac{1}{2}(\pi_{3z}+\pi_{5z}-\pi_{1y}-\pi_{6y})$
$\frac{1}{2}(\pi_{2y}+\pi_{4y}-\pi_{3x}-\pi_{5x})$	$\frac{1}{2}(\pi_{2y}+\pi_{4y}-\pi_{3x}-\pi_{5x})$
$\frac{1}{2}(\pi_{3x}-\pi_{5x}+\pi_{1x}-\pi_{6x})$	$\frac{1}{2}(\pi_{3x}-\pi_{5x}+\pi_{1x}-\pi_{6x})$
$\frac{1}{2}(\pi_{2y}-\pi_{4y}+\pi_{1y}-\pi_{6y})$	$\frac{1}{2}(\pi_{2y}-\pi_{4y}+\pi_{1y}-\pi_{6y})$
$\frac{1}{2}(\pi_{2z}+\pi_{3z}-\pi_{4z}-\pi_{5z})$	$\frac{1}{2}(\pi_{2z}+\pi_{3z}-\pi_{4z}-\pi_{5z})$

	f_{2g}	$3d_{yx}$ $3d_{yz}$ $3a_{zx}$	
	f_{2u}		
$[M(CN)_4]$ Planar (D_{4h})	a_{1g}	$4s$, $3d_{z^2}$	$\frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)$
	a_{2g}		
	a_{2u}	$4p_z$	
	b_{2g}	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1+\sigma_3-\sigma_2-\sigma_4)$
	b_{2g}	$3d_{xy}$	
	b_{2u}		
	e_g	$3d_{xz}$ $3d_{yz}$	
	e_u	$4p_x$ $4p_y$	$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_3)$ $\frac{1}{\sqrt{2}}(\sigma_2-\sigma_4)$
$[M(CN)_4]$ tetrahedral (T_d)	a_1	$4s$	$\frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)$
	e	$3d_{z^2}$ $3d_{x^2-y^2}$	
	f_2	$4p_x$, $3d_{yz}$ $4p_y$, $3d_{xy}$ $4p_z$, $3d_{xy}$	$\frac{1}{2}(\sigma_1+\sigma_3-\sigma_2-\sigma_4)$ $\frac{1}{2}(\sigma_1+\sigma_2-\sigma_3-\sigma_4)$ $\frac{1}{2}(\sigma_1+\sigma_4-\sigma_2-\sigma_3)$
	f_1		

$\frac{1}{2}(\pi_{2y}+\pi_{3x}+\pi_{4y}+\pi_{5x})$	$\frac{1}{2}(\pi_{2x}+\pi_{4x}+\pi_{1x}+\pi_{6x})$
$\frac{1}{2}(\pi_{2x}+\pi_{4x}+\pi_{1x}+\pi_{6x})$	$\frac{1}{2}(\pi_{2x}+\pi_{4x}+\pi_{1x}+\pi_{6x})$
$\frac{1}{2}(\pi_{3z}+\pi_{5z}+\pi_{1y}+\pi_{6y})$	$\frac{1}{2}(\pi_{3z}+\pi_{5z}+\pi_{1z}+\pi_{6y})$
$\frac{1}{2}(\pi_{3x}-\pi_{5x}-\pi_{1x}+\pi_{6x})$	$\frac{1}{2}(\pi_{3x}-\pi_{5x}-\pi_{1x}+\pi_{6x})$
$\frac{1}{2}(\pi_{2y}-\pi_{4y}-\pi_{1y}+\pi_{6y})$	$\frac{1}{2}(\pi_{2y}-\pi_{4y}-\pi_{1y}+\pi_{6y})$
$\frac{1}{2}(\pi_{2z}-\pi_{4z}-\pi_{3z}+\pi_{5z})$	$\frac{1}{2}(\pi_{2z}-\pi_{4z}-\pi_{3z}+\pi_{5z})$
$\frac{1}{2}(\pi_{1y}-\pi_{2x}+\pi_{3y}-\pi_{4x})$	$\frac{1}{2}(\pi_{1y}-\pi_{2x}+\pi_{3y}-\pi_{4x})$
$\frac{1}{2}(\pi_{1z}+\pi^2{}_z-\pi_{3z}-\pi_{4z})$	$\frac{1}{2}(\pi_{1z}+\pi_{2z}-\pi_{3z}-\pi_{4z})$
$\frac{1}{2}(\pi_{1y}+\pi_{2x}+\pi_{3y}+\pi_{4x})$	$\frac{1}{2}(\pi_{1y}+\pi_{2x}+\pi_{3y}+\pi_{4x})$
$\frac{1}{2}(\pi_{1z}-\pi_{2z}-\pi_{3z}+\pi_{4z})$	$\frac{1}{2}(\pi_{1z}-\pi_{2z}-\pi_{3z}+\pi_{4z})$
$\frac{1}{\sqrt{2}}(\pi_{1z}+\pi_{3z})$	$\frac{1}{\sqrt{2}}(\pi_{1z}+\pi_{3z})$
$\frac{1}{\sqrt{2}}(\pi_{2z}+\pi_{4z})$	$\frac{1}{\sqrt{2}}(\pi_{3z}+\pi_{4z})$
$\frac{1}{\sqrt{2}}(\pi_{2x}-\pi_{4x})$	$\frac{1}{\sqrt{2}}(\pi_{2x}-\pi_{4x})$
$\frac{1}{\sqrt{2}}(\pi_{1y}-\pi_{3y})$	$\frac{1}{\sqrt{2}}(\pi_{1y}-\pi_{3y})$
$\frac{1}{4}\{\pi_{1x}+\pi_{3x}+\pi_{2x}+\pi_{4x}-\sqrt{3}(\pi_{1y}+\pi_{2y}+\pi_{3y}+\pi_{4y})\}$	$\frac{1}{4}\{\pi_{1x}+\pi_{3x}+\pi_{2x}+\pi_{4x}-\sqrt{3}(\pi_{1y}+\pi_{2y}+\pi_{3y}+\pi_{4y})\}$
$\frac{1}{4}\{\pi_{1x}+\pi_{3x}+\pi_{2x}+\pi_{4x}+\sqrt{3}(\pi_{1y}+\pi_{2y}+\pi_{3y}+\pi_{4y})\}$	$\frac{1}{4}\{\pi_{1x}+\pi_{3x}+\pi_{2x}+\pi_{4x}+\sqrt{3}(\pi_{1y}+\pi_{2y}+\pi_{3y}+\pi_{4y})\}$
$\frac{1}{4}\{\pi_{4x}+\pi_{2x}-\pi_{1x}-\pi_{3x}+\sqrt{3}(\pi_{4y}+\pi_{2y}-\pi_{1y}-\pi_{3y})\}$	$\frac{1}{4}\{\pi_{4x}+\pi_{2x}-\pi_{1x}-\pi_{3x}+\sqrt{3}(\pi_{4y}+\pi_{2y}-\pi_{1y}-\pi_{3y})\}$
$\frac{1}{2}(\pi_{1x}+\pi_{2x}-\pi_{3x}-\pi_{4x})$	$\frac{1}{2}(\pi_{1x}+\pi_{2x}-\pi_{3x}-\pi_{4x})$
$\frac{1}{4}\{\pi_{3x}+\pi_{2x}-\pi_{1x}-\pi_{4x}+\sqrt{3}(\pi_{4y}+\pi_{1y}-\pi_{2y}-\pi_{3y})\}$	$\frac{1}{4}\{\pi_{3x}+\pi_{2x}-\pi_{1x}-\pi_{4x}+\sqrt{3}(\pi_{4y}+\pi_{1y}-\pi_{2y}-\pi_{3y})\}$
$\frac{1}{4}\{\pi_{2y}+\pi_{4y}-\pi_{3y}-\pi_{1y}+\sqrt{3}(\pi_{1x}+\pi_{3x}-\pi_{2x}-\pi_{4x})\}$	$\frac{1}{4}\{\pi_{2y}+\pi_{4y}-\pi_{3y}-\pi_{1y}+\sqrt{3}(\pi_{1x}+\pi_{3x}-\pi_{2x}-\pi_{4x})\}$
$\frac{1}{2}(\pi_{1y}+\pi_{2y}-\pi_{3y}-\pi_{4y})$	$\frac{1}{2}(\pi_{1y}+\pi_{2y}-\pi_{3y}-\pi_{4y})$
$\frac{1}{4}\{\pi_{2y}+\pi_{3y}-\pi_{1y}-\pi_{4y}+\sqrt{3}(\pi_{2x}+\pi_{3x}-\pi_{1x}-\pi_{4x})\}$	$\frac{1}{4}\{\pi_{2y}+\pi_{3y}-\pi_{1y}-\pi_{4y}+\sqrt{3}(\pi_{2x}-\pi_{3x}-\pi_{1x}-\pi_{4x})\}$



$M(CN)_6$—type (planar)

$M(CN)_6$—type (Octahedral)

Fig. 1. Orientation of the orbital.

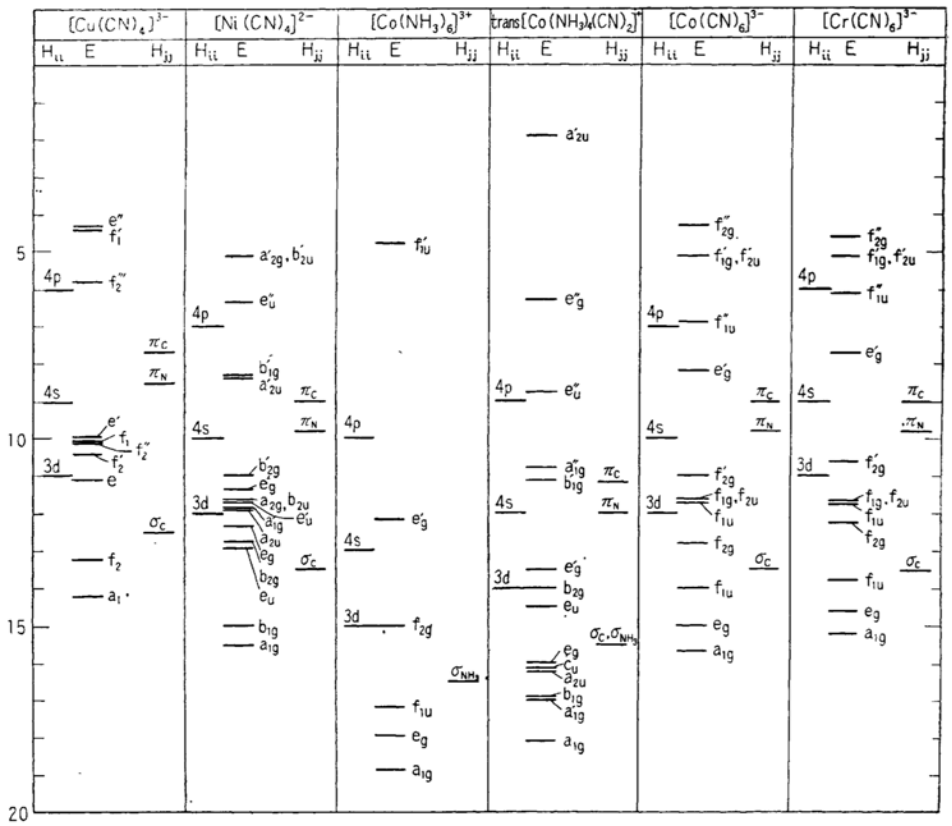


Fig. 2. The orbital energy levels.

ionization potentials[6], according to the charge distribution postulated above. For example, the charge of the individual atom in hexacyano cobalt(III) complex $[Co(CN)_6]^{3-}$, was assumed to be $[Co^{0.20+}(C^{0.22-}N^{0.32-})_6]$. According to this assumption, H_{ii}'s were obtained as shown below:

$$H_{3d3d} = {}_{3d}I_{Co} \times 0.80 + {}_{3d}I_{Co^{+}} \times 0.20 = 9.0 \times 0.80 + 25.0 \times 0.20 \fallingdotseq 12$$

$$H_{\pi_C\pi_C} = {}_{2p}I_C \times 0.78 {}_{2p}I_{C^{-}} \times 0.22 = 11.17 \times 0.78 + 0.69 \times 0.22 \fallingdotseq 9.0$$

$$H_{\pi_N\pi_N} = {}_{2p}I_N \times 0.68 + {}_{2p}I_{N^{-}} \times 0.32 = 13.81 \times 0.68 + 0.99 \times 0.32 \fallingdotseq 9.8$$

$$H_{\sigma\sigma} = \frac{({}_{2p}I_C + {}_{2s}I_C)}{2} \times 0.78$$

6) R. S. Mulliken, *J. Chem. Phys.*, **2**, 792 (1934).

$$+\frac{({}_{2p}I_{C^-}+{}_{2s}I_{C^-})}{2}\times 0.22$$
$$=\frac{(11.17+21.06)}{2}\times 0.78$$
$$+\frac{(8.74+0.69)}{2}\times 0.22\fallingdotseq 13.5$$

Here, ${}_{3d}I_{Co}$ etc. are the ionization potentials of electrons in the orbitals shown by the subscripts. The validity of such a procedure may be doubtful. However, no better method is known at present.

Complete sp hydridization was assumed for σ-orbital of the ligand. Interaction between the ligands have been entirely ignored. The values of the overlap integrals were obtained mostly from the tables of Mulliken, Orloff and Orloff[7], and Jaffé and Doak[8] except $S(3d_\pi/5p_\pi)$ which was calculated from the master formula of Jaffé[8]. The metal–C and C–N distances, 1.92 and 1.16 Å, respectively, were taken from the X-ray analysis on potassium ferrocyanate $K_4[Fe(CN)_6]\cdot 3H_2O$[9].

After the secular equation was solved, the charge distribution was calculated. The result was then compared with the formerly postulated charge distribution. If the calculated result was very different from the formerly postulated one, the calculation was repeated using a new charge distribution until the agreement was satisfactory. The final result of the postulated and the calculated charge distribution is shown in Table II.

TABLE II
CHARGE DISTRIBUTION

	Atom	Postulated	Calculated
$[Cr(CN_6)]^{3-}$	Cr	+0.12	+0.12
	C	−0.21	−0.36
	N	−0.31	−0.16
$[Co(CN)_6]^{3-}$	Co	+0.20	+0.18
	C	−0.22	−0.21
	N	−0.32	−0.32
$[Co(NH_3)_6]^{3+}$	Co	+0.44	+0.60
	NH_3	+0.43	+0.40
$[Ni(CN)_4]^{2-}$	Ni	+0.15	−0.18
	C	−0.22	−0.20
	N	−0.31	0.00
$[Cu(CN)_4]^{3-}$	Cu	0.00	−0.42
	C	−0.32	−0.24
	N	−0.43	−0.41

7) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, ibid., **17**, 1248 (1949).
8) H. H. Jaffe and D. O. Doak, ibid., **21**, 196 (1953).
9) V. A. Pospelov and G. S. Zhdanov, *J. Phys Chem.* (USSR) **21**, 879 (1947).

Discussion

The orbital energy level diagram obtained by our calculation is shown in Fig. 2. For hexa-ammine cobalt(III) $[Co(NH_3)_6]^{3+}$, dicyano tetra-ammine cobalt(III) $[Co(NH_3)_4(CN)_2]^+$, hexacyano cobalt(III) $[Co(CN)_6]^{3-}$, tetracyano nickel(III) $[Ni(CN)_4]^{2-}$ and tetracyano copper(I) $[Cu(CN)_4]^{3-}$ ions the highest occupied levels—f_{2g}, e'_g, f'_{2g}, b'_{2g} and e', respectively,—are filled up with electrons. This fact explains the diamagnetism of these complexes which was formerly interpreted by Van Vleck[10] and Pauling[3] using the M. O. and the V. B. method, respectively, but both ignored the π-bonding. If one or more electrons are added to these complexes, they must enter into the next higher level which is located far above the ground level. This will make the energy state of the complex much higher than before. Thus, hexacyano cobalt(II) $[Co(CN)_6]^{4-}$ and tetracyano copper(I) $[Cu(CN)_4]^{3-}$ ions (square planar) are less stable than hexacyano cobalt(III) $[Co(CN)_6]^{3-}$ and tetracyano nickel(II) $[Ni(CN)_4]^{2-}$, respectively.

The U. V. absorption spectra of the cyanide complexes were investigated by Kashimoto and Tsuchida[11], and Kuroya and Tsuchida[12]. They concluded that the bands at 24000, 32500 and 39000 cm^{-1} of hexacyano cobalt(III) $[Co(CN)_6]^{3-}$ ion and at 21700, 31700 and 35100~37500 cm^{-1} of tetracyano nickel(II) $[Ni(CN)_4]^{2-}$ were called "the first, the second and the third bands", respectively. However, the first bands of these two complexes are unusually weak compared with the first bands of the other complexes*. This anomaly of the first band has long been a subject of discussion.

Our present calculation clearly indicates that the bands at 32500 and 39000 cm^{-1} in hexacyano cobalt(III) ion $[Co(CN)_6]^{3-}$ are due to $f'_{2g}\rightarrow e'_g$ forbiden transitions which give rise to two electronic states (singlet) F_{1g} and F_{2g}. Therefore these bands correspond to the first and the second bands of cobalt(III) ammine complexes, since Kuroda and Ito[5], and Yamatera[13] have

10) J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1935).
11) M. Kashimoto and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*) **60**, 347 (1939).
12) H. Kuroya and R. Tsuchida, ibid. **61**, 597 (1940).
13) H. Yamada, Presented at the Symposium of Metallic Complexes. Tokyo, October, (1954).
* In $[Ni(CN)_4]^{2-}$, $\log\varepsilon=-0.05$ and in $[Co(CN)_6]^{3-}$, $\log\varepsilon=-0.28$, but these values are not strictly reproducible.

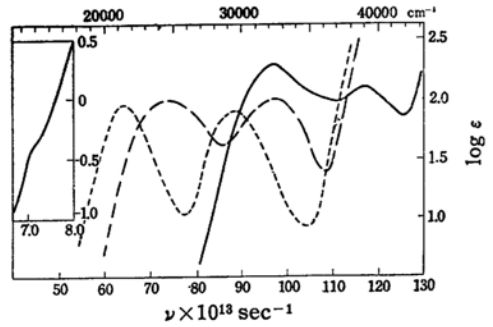


Fig. 3. —— $K_3Co(CN)_6$,
- - - - $[Co\ en_3](ClO_4)_3$
— — — $[Co\ en_2(CN)_2]_2SO_4 \cdot 3H_2O$

shown that the first and the second band of hexa-ammine cobalt ion $[Co(NH_3)_6]^{3+}$ were attributable to $f_{2g} \rightarrow e'_g$ transitions. Fig. 3 indicates the correlation of the absorption bands between hexacyano cobalt (III) ions $[Co(CN)_6]^{3-}$, dicyanodiethylenediamine cobalt(III) $[Coen_2(CN)_2]^+$ and trisethylenediamine cobalt(III) $[Co\ en_3]^{3+}$ ions**. It is seen that the absorption bands of trisethylenediamine cobalt(III) $[Co\ en_3]^{3+}$ shift to the shorter wave length as the ethylenediamine is replaced by cyanide. Furthermore, the magnitude of the shift has a linear relation with the number of cyanide, as is generally seen in the absorption spectra of the mixed complex[14,15]. This fact also suggests that these two absorption bands of hexacyano cobalt(III) ion $[Co(CN)_6]^{3-}$ are of similar character to the first and the second band of hexa-ammine cobalt(III) $[Co(NH_3)_6]^{3+}$ ion. Thus we conclude that the weak shoulder at 24000 cm^{-1} may be attributable to the singlet-triplet transition. It should be noted, however, that the f_{2g} orbital of hexacyano cobalt(III) ion $[Co(CN)_6]^{3-}$ consists of 3*d* (cobalt)and 2*p* (ligand) orbitals, whereas th f_{2g} orbital of hexa-ammine cobalt(III) $[Co(NH_3)_6]^{3+}$ includes only non-bonding 3*d* (cobalt)orbital. In dicyanodiethylenediamine cobalt(III) $[Co\ en_2(CN)_2]^+$, the transitions occur from b_{2g} or e'_g to a''_{1g} or b'_{1g} levels according to our calculation. This is not unexpected, because lowering of symmetry from O_h to D_{4h} splits f_{2g} into e_g and b_{2g}, and e_g into a_{1g} and b_{1g}, respectively. Thus, the observed bands at 25000 and 32400 cm^{-1} will be due to these transitions.

As is seen in Fig. 4, the bands at 26300 and 32200 cm^{-1} of hexacyano chromium (III) ion $[Cr(CN)_6]^{3-}$ are also attributable to $f'_{2g} \rightarrow e'_g$ transitions. In this case, our result is in good accord with Tsuchida's former assignment, which ascribed these bands to the first and the second bands.

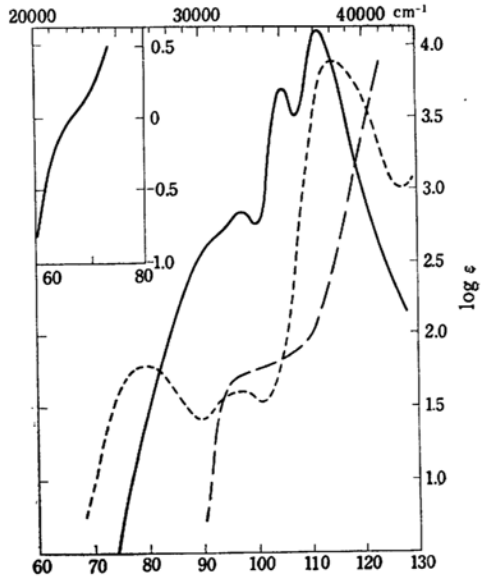


Fig. 4. —— $K_2[Ni(CN)_4]$
- - - - $K_3[Cr(CN)_6]$[12]
— — — $K_3Cu(CN)_4$[11]

In planar tetracyano nickel(II) $[Ni(CN)_4]^{2-}$ ion, the lowest transition occurs from b'_{2g} or e'_g to b'_{1g} or a'_{2u} level. Of these transitions, $e'_g \rightarrow a'_{2u}$ is allowed, and $b'_{2g} \rightarrow b'_{1g}$, $e'_g \rightarrow b'_{1g}$ and $b'_{2g} \rightarrow a'_{2u}$ are forbidden. The intense bands at 35100 ($\log \varepsilon = 3.67$) and 37500 cm^{-1} ($\log \varepsilon = 4.09$) may be due to $e'_g \rightarrow a'_{2u}$ transitions, which substantially correspond to $f'_{2g} \rightarrow f'''_{1u}$ transition of hexacyano cobalt(III) ion $[Co(CN)_6]^{3-}$. Since $b'_{2g} \rightarrow b'_{1g}$ and $e'_g \rightarrow b'_{1g}$ transitions correspond to $f_{2g} \rightarrow e'_g$ transitions of hexa-ammine cobalt(III) $[Co(NH_3)_6]^{3+}$, the band at 31700 cm^{-1} may be "the first band". The second band may be hidden by the strong "specific band" in the region of 33000~40000 cm^{-1}. The weak shoulder at 21700 cm^{-1} may be due to the singlet-triplet transition.

In tetrahedral tetracyano copper(I) $[Cu(CN)_4]^{3-}$ ion, the lowest transition occurs from e', f_1, f'_2 and f''_2 to f'''_2 which contains allowed transitions. The bands

** Though the calculation was made on *trans*-$[Co(NH_3)_4(CN)_2]^+$, absorption measurement was made on *trans*-$[Co\ en_2\ (CN)_2]^+$, because the former complex has not yet been prepared. It has been well known, however, that absorption spectra of ethylenediamine complexes always bear a close resemblance to that of ammine complexes. Therefore, experimental data of $[Co\ en_2\ (CN)_2]^+$ have been used instead of $[Co(NH_3)_4\ (CN)_2]^+$.

14) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

15) S. Kida, ibid., **29**, 805 (1956).

observed at about 32000 cm^{-1} and following higher absorption will be probably due to those transitions. In this case, no band exists corresponding to "the first or the second band" of the octahedral cobalt(III) complexes.

Finally we tabulated the calculated and observed energies of transitions in each complex in Table III. It may be possible to obtain better agreement between these values if the values of the ionization potentials are selected appropriately. However, we did not do so since we thought consideration of the charge distribution obtained from the Pauling's neutrality principle was more important.

TABLE III

COMPARISON OF THE OBSERVED AND THE CALCULATED ENERGIES OF TRASITION IN EV. UNIT

	$[Cr(CN)_6]^{3-}$	$[Co(CN)_6]^{3-}$
	3.25, 3.95*	3.97, 4.80
obs.	(1.76) (1.65)	(2.29) (2.09)
calcd.	2.9(*f*)	2.8(*f*)

	$[Ni(CN)_4]^{2-}$	$[Cu(CN)_4]^{3-}$
	4.00, 4.34, 4.63	4.15, 5.3**
obs.	(2.85) (3.67) (4.09)	(1.67) (4.0)
calcd.	2.6 3.0(*a* & *f*)	4.0 4.3(*a* & *f*)

	$[Co\,en_2(CN)_2]^+$	$[Co(NH_3)_6]^{3+}$	$[Co\,en_3]^{3+}$
	3.09, 4.01	2.61, 3.66***	2.64, 3.66***
obs.	(1.98) (2.00)	(1.78) (1.74)	(1.94) (1.90)
calcd.	2.6 3.2(*f*)	2.8(*f*)	—

Literature of the observed data.

* H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, (*Nippon Kagaku Zassi*) **61**, 597 (1940).

** M. Kashimoto and R. Tsuchida, ibid. **60** 347 (1939).

*** Y. Shimura and R. Tsuchida, This Bulletin, **29**, 313 (1956).

The number in the bracket in the "obs." column indicates logarithm of the molecular extinction coefficient. (*a*) and (*f*) in the "calcd." column denote "allowed" and "forbidden" transitions, respectively.

Experimental

The absorption measurement was made by the Beckmann DK Spectrophotometer.

Potassium hexacyano cobalt(III)ate $K_3[Co(CN)_6]$ and potassium tetracyano nickel(II)-ate $K_2[Ni(CN)_4]$ were prepared according to the description of "Inorganic Syntheses Vol. II". Dicyano-diethylenediamine cobalt(III) sulfate trihydrate $[Co\,en_2(CN)_2]\,1/2\,SO_4 \cdot 3H_2O$ was prepared by the method of Ray et al.[16]. In the preparation of these complexes, the contamination of other metallic ions was avoided by careful purification of the starting materials, cobaltous chloride and nickel sulfate.

Summary

The energy levels of the cyanide complexes—hexacyano chromium(III) $[Cr(CN)_6]^{3-}$, hexacyno cobalt(III) $[Co(CN)_6]^{3-}$, tetracyano nickel(II) $[Ni(CN)_4]^{2-}$, and tetracyano copper(I) $[Cu(CN)_4]^{3-}$ ions—have been calculated by the semi-emprical M. O. method taking π-orbitals of the ligands into consideration. The ionization potentials used have been determined so that the calculated charge distribution does not contradict that obtained from Pauling's neutrality principle. The stability and the magnetic property of these complexes have been well interpreted by our calculation. The results have revealed that the first and the second bands of hexacyano chromium (III) $[Co(CN)_6]^{3-}$ and hexacyano cobalt (III) $[Co(CN)_6]^{3-}$ are attributable to $f'_{2g} \rightarrow e'_g$ transitions which are of the similar character to the first and the second bands of hexammine cobalt(III) $[Co(NH_3)_6]^{3+}$, although the ground level, f'_{2g} combines strongly with the π-orbitals of the ligands. In tetracyano nickel(II) $[Ni(CN)_4]^{2-}$, the "second band" is hidden by the allowed transition. For tetracyano copper(I) $[Cu(CN)_4]^{3-}$, there is no band corresponding to "the first and the second band".

The authors are very grateful to Dr. K. Ito of Nagoya University and Mr. H. Yamatera of the Osaka City University for their kind advice and helpful discussions during the course of this work.

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16) P. Ray and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).