# A Quantitative Scale of the Spectrochemical Series for the Mixed Ligand Complexes of $d^6$ Metals

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Quantitative scale of a new parameter $d$ has been proposed for the spectrochemical series of ligands in the mixed ligand complexes of $d^6$ metals, which enables us to predict the positions of low energy d-d absorption bands of a $d^6$ complex. Introduction of a new reduction parameter $\alpha$ has improved the prediction of the d-d bands of mixed cyano complexes of cobalt(III), mixed halogeno complexes of rhodium(III), iridium(III), and platinum(IV), and also several mixed carbonyl complexes of low-valent $d^6$ metals.

Some quantitative scales were presented for the spectrochemical series of ligands,[1] i.e., ligand field splitting energy $\Delta$(=10 Dq) of a given metal ion, or in an exact sense $f$(ligand) value of Jørgensen's formula $\Delta = f(\text{ligand}) \cdot g(\text{central ion})$,[2] but these are limited for non-mixed ligand complexes only. On the other hand, to predict the position of d-d absorption band of a mixed complex, Yamatera's $\delta$ parameters[3] have frequently been used, but they are also unsatisfactory because it has been reported that the Yamatera rule was not exactly fit for the mixed cyano complexes of cobalt(III)[4] and the mixed halogeno complexes of rhodium(III) or iridium(III).[5] In the present paper, a new quantitative scale will be proposed for the spectrochemical series of ligands in the mixed complexes of $d^6$ metals, which enables us to predict the energy values of long wavelength d-d absorption bands of almost all the $d^6$ complexes.

## Results and Discussion

**Spectrochemical Series of Ligands.** The energies of three components of the first spin-allowed d-d absorption band of an octahedral complex $[ML_{(1)}L_{(2)}L_{(3)}L_{(4)}L_{(5)}L_{(6)}]$ (Fig. 1) may be written:

$$\begin{aligned} \sigma_{xy} &= \alpha(d_2 + d_3 + d_4 + d_5)/4, \\ \sigma_{yz} &= \alpha(d_1 + d_2 + d_4 + d_6)/4, \\ \sigma_{zx} &= \alpha(d_1 + d_3 + d_5 + d_6)/4, \end{aligned} \quad (1)$$

where $d_n$ ($n$=1,2,···6) is a parameter of the ligand $L_{(n)}$ previously defined[6] as $\delta$ and $\alpha$ a reduction parameter. Then it becomes,

$$\begin{aligned} \sigma &= (\sigma_{xy} + \sigma_{yz} + \sigma_{zx})/3 \\ &= \alpha(d_1 + d_2 + d_3 + d_4 + d_5 + d_6)/6, \end{aligned} \quad (2)$$

where $\sigma$ is a mean energy of the first d-d absorption band. When $\alpha$=1.00, Eqs. 1 and 2 reduce to the

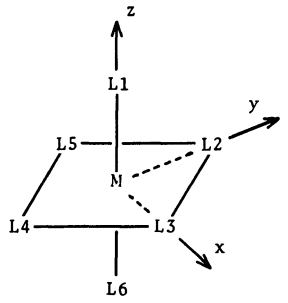


Fig. 1. An octahedral complex $[ML_{(1)}L_{(2)}L_{(3)}L_{(4)}L_{(5)}L_{(6)}]$.

Table 1. Empirical $\alpha$ Values for the Mixed Complexes [M $a_x b_{6-x}$] of Holohedrized $D_{4h}$ Symmetry[a,b]

| a[c] | b[c] | M=Fe(II) | Co(III) | Rh(III) | Ir(III) | Pd(IV) | Pt(IV) |
|---|---|---|---|---|---|---|---|
| $CN^-$ | P,As | — | 0.98[0.96] | — | — | — | — |
| $CN^-$ | N | 0.90 | 0.955[0.91] | 0.97 | 0.83 | — | — |
| $CN^-$ | O | — | 0.94[0.88] | 0.965 | 0.81 | — | — |
| $CN^-$ | $Cl^-$ | — | 0.935 | 0.95 | 0.80 | — | 0.67[0.64?] |
| $CN^-$ | $Br^-$ | — | 0.93 | 0.92 | 0.77 | — | — |
| $CN^-$ | $I^-$ | — | 0.92 | 0.87 | 0.74 | — | — |
| P,As | O | | 0.97[0.94] | — | — | — | — |
| P,As | $Cl^-$ | 0.90[0.80] | 0.95[0.90] | 0.94[0.88] | 0.92[0.84] | — | — |
| N | $Cl^-$ | — | 0.98[0.96] | 0.97[0.94] | 0.96[0.92] | 0.93[0.86] | 0.92[0.84] |
| N | $Br^-$ | — | 0.965[0.93] | 0.95[0.90] | 0.93[0.86] | 0.92[0.84] | 0.81[0.79?] |
| N | $I^-$ | — | 0.96[0.92] | 0.92[0.91?] | 0.86[0.84?] | — | 0.77 |
| O | $Cl^-$ | — | — | 0.98[0.96] | 0.98[0.96] | — | 0.95[0.90] |
| O | $Br^-$ | — | — | 0.95[0.90] | — | — | — |

a) The value in square brackets is for the complexes of *trans*-[M $a_4b_2$] and -[M $a_2b_4$] types. b) As to the carbonyl complexes $[M(CO)_xX_{6-x}]$(X=N, O, $Cl^-$, $Br^-$, or $I^-$), $\alpha$=0.86 for M=V(−I), 0.87 Cr(0), 0.94 Mo(0), 0.90 W(0), 0.95 Mn(I), 0.91 Re(I), 0.93 Ru(II), and 0.90 Os(II). c) An element symbol underlined shows a ligating atom.

Yamatera rule[3,6] and the rule of average environment,[7] respectively. Most of the N,O-mixed[6] and all of the non-mixed complexes of low-spin $d^6$ type obey Eqs. 1 and 2 with $\alpha$=1.00, but the other mixed complexes, for example the mixed cyano complexes seem to have $\alpha$ values smaller than 1.00 as shown in Table 1, where $\alpha$ values are estimated empirically from a compilation of absorption data of a variety of $d^6$ complexes.

It has been found that only three different $\alpha$ values are sufficient for prediction of the first d-d band energies of a series of mixed complexes [M $a_xb_{6-x}$] ($x$=1—5) except for *mer*-[M $a_3b_3$]: one is for [M $a_5b$], *cis*-[M $a_4b_2$], *cis*-[M $a_2b_4$], and [M $ab_5$], amounting to $1.00-\beta$ ($0 \leqq \beta \leqq 0.4$), and the second is for *trans*-[M $a_4b_2$] and -[M $a_2b_4$], amounting to $1.00-2\beta$, and the third is for *fac*-[M $a_3b_3$], remaining to be 1.00. This fact means that the reduction parameter $\alpha$ is related to the order of lowering (from $O_h$ to $D_{4h}$) of the holohedrized symmetry[8] of a given complex. It is remarkable that all tris-chelate complexes have $\alpha$=1.00 regardless of the ligating atoms.

The $d$ value (in $10^3$ $cm^{-1}$) of each ligand for different complexes of a given metal can be evaluated from the observed data of mean $\sigma$ or its components $\sigma_{xy}$, $\sigma_{yz}$, or $\sigma_{zx}$ using Eqs. 1 and 2. Of course the position of the first d-d band of a [M $a_6$]-type is equal to the $d$ value of the ligand a for that metal, because $\alpha$=1.00 in this case. For a bidentate ligand A~B, the $d$ value can be defined as,

$$d\langle \mathrm{A}\sim\mathrm{B}\rangle^n = (d\langle -\mathrm{A}\rangle^n + d\langle -\mathrm{B}\rangle^n)/2, \quad (3)$$

where $n$ means chelate ring size, for example $n$=7 for $d\langle NH_2CH_2CH_2CH_2CH_2NH_2\rangle^7 = d\langle -CH_2NH_2\rangle^7$, and $n$=6 for $d\langle\beta\text{-ala}\rangle^6 = d\langle NH_2CH_2CH_2CO_2^-\rangle^6 = (d\langle -CH_2NH_2\rangle^6 + d\langle -CO_2^-\rangle^6)/2$. Besides the $d$ values for different unidentate ligands, those of such chelate ends are also arranged in Table 2.

Table 2 gives $d_{Co}$ values obtained for 100 ligands (or chelate ends) of cobalt(III) complexes, ranging from the highest value 35.0 for CO to the lowest value 7.0 for $\langle -CH_2Se^-\rangle^5$, which is selenolato end of a bidentate ligand forming 5-membered chelate ring. In Table 3, $\sigma_{obs}$ of the typical mixed cobalt(III) complexes are compared to $\sigma_{calc}$ obtained from the $d$ values in Table 2 by applying Eq. 1 or 2. The deviation $\Delta$ is generally within ±2%.

**Spectrochemical Series of Metals.** For the metals (M) other than cobalt(III), a series of $d_M$ can be obtained from the existing data. A plot of $d_M$ versus $d_{Co}$ makes a straight line passing the origin (Fig. 2):

$$d_M = m d_{Co}, \quad (4)$$

where $m$ is the spectrochemical parameter for the metal M. The $m$ values obtained from Eq. 4 are tabulated in Table 4. The $m$ value can be correlated to the Jørgensen's $g$ (central ion) value[9] (Fig. 3), while $d_{Co}$ (and $d_M$ also) to the Jørgensen's $f$ (ligand) value[9] (Fig. 4).

Table 2. Spectrochemical Series of Ligands:[a,b] $d_{Co}$ Values in $10^3$ $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | 35.0 | $\langle NH_2C_6H_4NH_2\rangle^5$ | 20.9 | $\langle -CH_2OH\rangle^5$ | 16.4 | $F^-$ | 14.8 |
| $CN^-$ | 32.1 | $\langle$bgH$\rangle^5$ | 20.9 | $\langle NO_3^-\rangle^4$ | 16.4 | $\langle R_2NCSe_2^-\rangle^4$ | 14.4 |
| $P(OMe)_3$ | 29.4 | py | 20.8 | $NCS^-$ | 16.3 | $\langle -CH_2O^-\rangle^5$ | 14.4 |
| $\langle -CH_2SO_2^-\rangle^5$ | 27.6 | $NH_2CHO$ | 20.7 | $OCOCF_3^-$ | 16.3 | $OP(OR)_3$ | 14.2 |
| $\langle Me_2PC_6H_4PMe_2\rangle^5$ | 27.6 | $\langle -CH_2NH_2\rangle^6$, tn | 20.4 | $CH_3OH$ | 16.2 | $OSMe_2$ | 14.0 |
| $\langle -CH_2PMe_2\rangle^5$ | 26.0 | $\langle -CH_2SO^-\rangle^5$ | 20.2 | $\langle EtOCS_2^-\rangle^4$ | 16.2 | $OCMe_2$ | 14.0 |
| $\langle Ph_2PC_6H_4PPh_2\rangle^5$ | 25.6 | $NCNH_2$ | 20.2 | $OCOCHRNH_3$ | 16.1 | $CH_3SO_3^-$ | 14.0 |
| $PMe_3$ | 25.6 | $\langle -CH_2NHMe\rangle^5$ | 20.0 | $\langle CS_3^{2-}\rangle^4$ | 16.0 | $N_3^-$ | 13.9 |
| $SO_3^{2-}$ | 25.6 | $NH_2Me$ | 20.0 | $OCOCCl_3^-$ | 16.0 | $\langle PO_4^{3-}\rangle^4$ | 13.9 |
| $NO_2^-$ | 25.3 | $\langle -CH_2NH_2\rangle^7$ | 19.9 | $\langle -CH_2SeMe\rangle^5$ | 15.8 | $P_2O_7^{4-}$ | 13.8 |
| $\langle -CH_2PMe_2\rangle^6$ | 25.3 | $\langle -C_6H_4NH_2\rangle^7$ | 19.3 | $NCO^-$ | 15.8 | $OSeO_2^{2-}$ | 13.8 |
| $PhSO_2^-$ | 24.1 | $ONO^-$ | 18.2 | $\langle P_2O_7^{4-}\rangle^6$ | 15.7 | $\langle (RO)_2PS_2^-\rangle^4$ | 13.55 |
| $\langle Me_2AsC_6H_4AsMe_2\rangle^5$ | 23.6 | $\langle -CH_2SH\rangle^5$ | 17.9 | $\langle R_2NCS_2^-\rangle^4$ | 15.6 | $CF_3SO_3^-$ | 13.5 |
| NCMe | 23.5 | $\langle -CH_2SMe\rangle^5$ | 17.7 | $O_2^-$ | 15.6 | $PO_4^{3-}$ | 13.2 |
| $PPh_3$ | 23.2 | $\langle -CH_2SeO^-\rangle^5$ | 17.6 | $\langle CO_3^{2-}\rangle^4$ | 15.5 | $ReO_4^-$ | 13.2 |
| $\langle =CHPPh_2\rangle^5$ | 23.0 | $\langle -CH_2NHPh\rangle^5$ | 17.6 | $OCOMe^-$ | 15.5 | $SCN^-$ | 13.0 |
| $\langle -CH_2AsMe_2\rangle^5$ | 23.0 | $\langle O_2^{2-}\rangle^3$ | 17.0 | $OH^-$ | 15.4 | $\langle Me_2PS_2^-\rangle^4$ | 12.75 |
| $NH_2OH$ | 22.8 | $\langle RCS_2^-\rangle^4$ | 16.95 | $OCO_2^{2-}$ | 15.4 | $Cl^-$ | 12.5 |
| $\langle =CHAsMe_2\rangle^5$ | 22.7 | $\langle$acac$^-\rangle^6$ | 16.9 | $OCOCO_2^{2-}$ | 15.4 | $SSO_3^{2-}$ | 12.0 |
| $\langle -CH_2AsMe_2\rangle^6$ | 22.4 | $\langle -CH_2NMe_2\rangle^5$ | 16.8 | $OCONH_2^-$ | 15.4 | $SeCN^-$ | 11.8 |
| $\langle$bpy$\rangle^5$ | 22.2 | $NCSe^-$ | 16.8 | $OCHNMe_2$ | 15.3 | $Br^-$ | 11.7 |
| $\langle$phen$\rangle^5$ | 22.0 | $\langle -CO_2^-\rangle^5$, ox | 16.6 | $NO_3^-$ | 15.2 | $CrO_4^{2-}$ | 11.1 |
| $\langle -CH_2NH_2\rangle^5$, en | 21.4 | $H_2O$ | 16.5 | $OC(NH_2)_2$ | 15.15 | $I^-$ | 9.0 |
| imH | 21.2 | $\langle TeO_6H_4^{2-}\rangle^4$ | 16.5 | $\langle SO_4^{2-}\rangle^4$ | 15.0 | $\langle -CH_2S^-\rangle^5$ | 9.3—7.5[c] |
| $NH_3$ | 21.0 | $\langle -CO_2^-\rangle^6$, mal | 16.45 | $SO_4^{2-}$ | 15.0 | $\langle -CH_2Se^-\rangle^5$ | 7.0 |

a) Abbreviations of ligands: acac, acetylacetonate $CH_3COCHCOCH_3^-$; bgH, biguanide $NHC(NH_2)NHC(NH_2)NH$; bpy, 2,2′-bipyridine $C_{10}H_8N_2$; en, ethylenediamine $NH_2CH_2CH_2NH_2$; imH, imidazole $C_3H_4N_2$; mal, malonate $CH_2(CO_2)_2^{2-}$; ox, oxalate $C_2O_4^{2-}$; phen, 1,10-phenanthroline $C_{12}H_8N_2$; py, pyridine $C_5H_5N$; tn, trimethylenediamine $NH_2CH_2CH_2CH_2NH_2$. For some frequently appearing ligands such as en, tn, ox, mal etc., the angle bracket with chelate ring size, $\langle\ \rangle^n$, are omitted for convenience. b) An element symbol underlined shows a ligating atom. c) The $d$ value of thiolato chelate end $\langle -CH_2S^-\rangle^5$ is subject to some variation from complex to another (see Table 6).

Table 3. Observed and Calculated First d-d Band Positions ($10^3\,cm^{-1}$) of the Typical Cobalt(III) Complexes

| No. | Complex | $\sigma_{obs}$ | $\sigma_{calc}$[a] | Eq. | $\alpha$ | $\Delta$/%[b] | $d$[c] | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | $[Co(CO)(CN)_5]^{2-}$ | 32.6 | 32.58 | (2) | 1.00 | −0.1 | CO 35.0; $CN^-$ 32.1 | 10) |
| 2 | $[Co(CN)(NH_3)_5]^{2+}$ | 22.7 | 22.71 | (1) | 0.955 | +0.0 | $CN^-$ 32.1; $NH_3$ 21.0 | 11) |
| 3 | *fac*-$[Co(NH_2CH_2CH_2PMe_2)_3]^{3+}$ | 23.70 | 23.70 | (2) | 1.00 | 0.0 | $<-CH_2PMe_2>^5$ 26.0[d] | 12) |
| 4 | *fac*-$[Co(NH_2CH_2CH_2CO_2)_3]$ | 18.7 | 18.43 | (2) | 1.00 | −1.4 | tn 20.4; mal 16.45 | 13) |
| 5 | $[Co(en)_2(CO_3)]^+$ | 19.5 | 19.43 | (2) | 1.00 | −0.4 | $<CO_3^{2-}>^4$ 15.5 | 14) |
| 6 | $[CoCl(NH_3)_5]^{2+}$ | 18.65 | 18.50 | (1) | 0.98 | −0.8 | $Cl^-$ 12.5; $NH_3$ 21.0 | 15) |
| 7 | *trans*-$[CoCl_2(en)_2]^+$ | 16.3 | 16.27 | (1) | 0.96 | −0.2 | $Cl^-$ 12.5 | 16) |
| 8 | *cis*-$[CoCl_2(en)_2]^+$ | 18.7 | 18.79 | (1) | 0.98 | +0.5 | $Cl^-$ 12.5 | 17) |
| 9 | $[CoBr(CN)_5]^{3-}$ | 25.2 | 25.11 | (1) | 0.93 | −0.4 | $Br^-$ 11.7; $CN^-$ 32.1 | 18) |
| 10 | *trans*-$[CoI_2(en)_2]^+$ | 14.0 | 13.98 | (1) | 0.92 | −0.1 | $I^-$ 9.0 | 19) |

a) The position from Eq. 1 refers to the doubly degenerate component. b) $\Delta=100(\sigma_{calc}-\sigma_{obs})/\sigma_{obs}$. c) $d<en>^5=d<-CH_2NH_2>^5=21.4$. d) $d<NH_2CH_2CH_2PMe_2>^5=(d<-CH_2NH_2>^5+d<-CH_2PMe_2>^5)/2=(21.4+26.0)/2=23.7$.

Table 4. Spectrochemical Series of Central Metals: Values of $m$ Obtained from Eq. 4

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| V(−I) | 0.715 | Cr(0) | 0.890 | Mn(I) | 0.945 | Fe(II) | 0.965 | Co(III) | 1.00 | Ni(IV) | 1.28 |
| Nb(−I) | 0.695 | Mo(0) | 0.875 | Tc(I) | — | Ru(II) | 1.22 | Rh(III) | 1.56 | Pd(IV) | 1.70 |
| Ta(−I) | 0.705 | W(0) | 0.910 | Re(I) | 1.16 | Os(II) | 1.43 | Ir(III) | 1.90 | Pt(IV) | 2.10 |

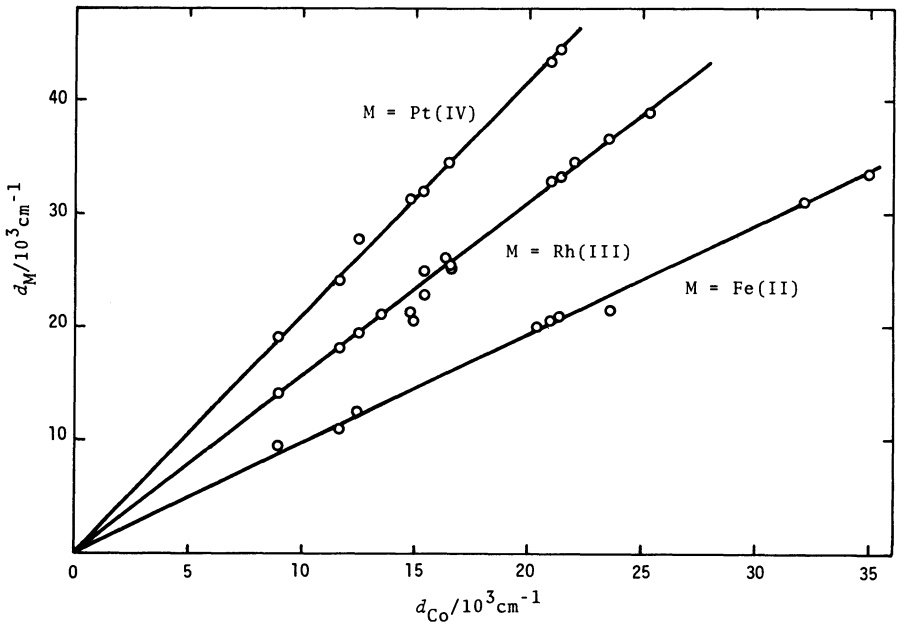


Fig. 2. Plots of $d_M$ versus $d_{Co}$: $d_M=md_{Co}$ for M=Fe(II), Rh(III), and Pt(IV).

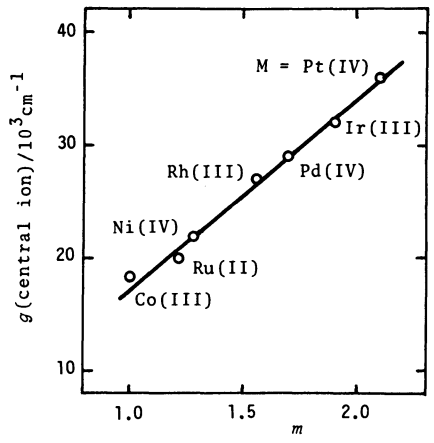


Fig. 3. A plot of $m$ versus $g$ (central ion).

In Table 5, $\sigma_{obs}$ of the typical $d^6$ complexes are compared with $\sigma_{calc}$ obtained from the $d_{Co}$ and $m$ values. The deviation $\Delta$ is generally within ±3%.

**S- or Se-Ligands.** As is seen in Table 2, the sulfur-donor (or selenium-donor) ligands distribute widely along the spectrochemical series, where the thiolato (or selenolato) ligands being on the weakest end. Houlding et al.[34] pointed out a striking characteristic of such thiolato (or selenolato) complexes of cobalt(III), i.e., that these have an extra shoulder band on the low-energy side of the first d-d absorption band. In Table 6, the splitting of the first d-d band of the thiolato (or selenolato), and the related S- (or Se-) ligands such as $SCN^-$ and $SSO_3^{2-}$ is interpreted by an assumption of anisotropy of the antibonding contribu-

Table 5. Observed and Calculated First d-d Band Positions ($10^3$ cm$^{-1}$) of the $d^6$ Metals except for Cobalt(III)

| No. | Complex | $\sigma_{obs}$[a] | $\sigma_{calc}$[b] | Eq. | $\alpha$ | $\Delta$/%[c] | $d_M$ from Eq. 4 | Ref. |
|---|---|---|---|---|---|---|---|---|
| 11 | $[V(CO)_5(NH_3)]^-$ | 19.5 | 19.35 | (1) | 0.86 | −0.8 | CO 25.0; $NH_3$ 15.0 | 20) |
| 12 | $[Cr(CO)_4(en)]$ | 23.6 | 23.61 | (2) | 0.87 | +0.0 | CO 31.2; en 19.0 | 21) |
| 13 | $[Cr(CO)_5F]^-$ | 23.0 | 23.23 | (1) | 0.87 | +0.8 | CO 31.2; $F^-$ 13.2 | 22) |
| 14 | $[Mo(CO)_5(NH_3)]$ | 25.6 | 25.90 | (1) | 0.94 | +1.0 | CO 30.6; $NH_3$ 18.4 | 23) |
| 15 | $[W(CO)_5(OH)]^-$ | 24.0 | 24.68 | (1) | 0.90 | +2.7 | CO 31.9; $OH^-$ 14.0 | 22) |
| 16 | $[Mn(CO)_5Cl]$ | 26.5 | 26.39 | (1) | 0.95 | −0.5 | CO 33.1; $Cl^-$ 11.8 | 23) |
| 17 | $[Re(CO)_5Cl]$ | 31.1 | 30.85 | (1) | 0.91 | −0.7 | CO 40.4; $Cl^-$ 14.4 | 23) |
| 18 | $[Fe(CO)(CN)_5]^{3-}$ | 31.4 | 31.47 | (2) | 1.00 | +0.2 | CO 33.8; $CN^-$ 31.0 | 24) |
| 19 | $[Fe(CN)_4(en)]^{2-}$ | 25.6 | 25.58 | (1) | 0.90 | −0.1 | $CN^-$ 31.0; en 20.7 | 25) |
| 20 | $[Ru(NH_3)_5(H_2O)]^{2+}$ | 24.1 | 24.23 | (1) | 1.00 | +0.5 | $NH_3$ 25.6; $H_2O$ 20.1 | 26) |
| 21 | $[Os(CO)(NH_3)_5]^{2+}$ | 31.6 | 31.52 | (1) | 0.90 | −0.3 | CO 50.1; $NH_3$ 30.0 | 27) |
| 22 | *trans*-$[Rh(N_3)_2(en)_2]^+$ | 26.7 | 27.45 | (1) | 1.00 | +2.8 | en 33.3; $N_3^-$ 21.6 | 28) |
| 23 | *trans*-$[RhCl_2(en)_2]^+$ | 24.6 | 24.77 | (1) | 0.94 | +0.7 | en 33.3; $Cl^-$ 19.4 | 5) |
| 24 | *cis*-$[RhCl_2(en)_2]^+$ | 28.4 | 28.93 | (1) | 0.97 | +1.9 | en 33.3; $Cl^-$ 19.4 | 5) |
| 25 | *trans*-$[IrCl_2(ox)_2]^{3-}$ | 27.2sh | 26.50 | (1) | 0.96 | −2.8 | $ox^{2-}$ 31.5; $Cl^-$ 23.7 | 29) |
| 26 | *cis*-$[IrCl_2(ox)_2]^{3-}$ | 27.8sh | 28.32 | (2) | 0.98 | +1.9 | $ox^{2-}$ 31.5; $Cl^-$ 23.7 | 29) |
| 27 | $[IrCl_5(H_2O)]^{2-}$ | 24.7 | 24.47 | (2) | 0.98 | −0.9 | $H_2O$ 31.3; $Cl^-$ 23.7 | 29) |
| 28 | *trans*-$[PdCl_2(en)_2]^{2+}$ | 24.6sh | 24.81 | (1) | 0.86 | +0.9 | en 36.4; $Cl^-$ 21.3 | 30) |
| 29 | $[PtCl(NH_3)_5]^{3+}$ | 35.4 | 36.48 | (1) | 0.92 | +3.1 | $NH_3$ 44.1; $Cl^-$ 26.3 | 31) |
| 30 | *trans*-$[PtCl_2(NH_3)_4]^{2+}$ | 29.9 | 29.57 | (1) | 0.84 | −1.1 | $NH_3$ 44.1; $Cl^-$ 26.3 | 31) |
| 31 | *trans*-$[PtCl_4(NH_3)_2]$ | 29.4 | 29.57 | (1) | 0.84 | +0.6 | $NH_3$ 44.1; $Cl^-$ 26.3 | 32) |
| 32 | $[PtCl_5(NH_3)]^-$ | 29.1 | 28.29 | (1) | 0.92 | −2.8 | $NH_3$ 44.1; $Cl^-$ 26.3 | 33) |

a) sh=shoulder band. b) The position from Eq. 1 refers to the doubly degenerate component. c) $\Delta=100(\sigma_{calc}-\sigma_{obs})/\sigma_{obs}$.

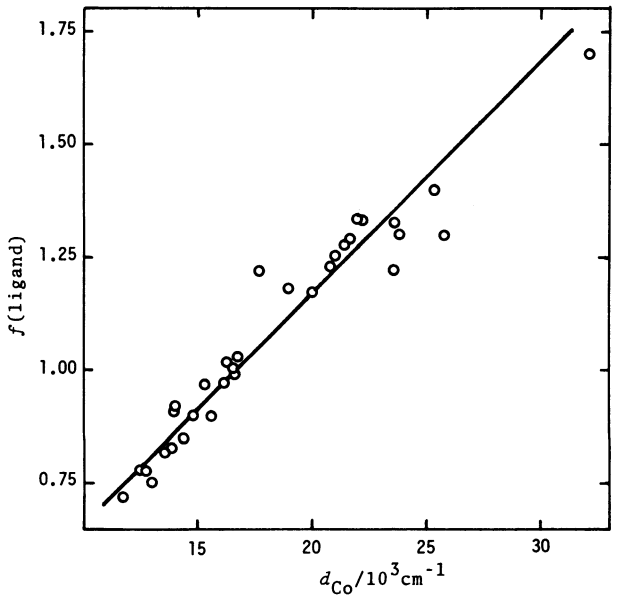


Fig. 4. A plot of $d_{Co}$ versus $f$ (ligand).

tion of S (or Se) donor atoms, and then the $d_{(S)}$ parameter is written as:

$$d_{(S)} = (d_{(S)//} + d_{(S)\perp})/2. \quad (5)$$

Thus, in a $CoN_5S$-type complex containing the thiolato-like S atom, the three $\sigma$ components are expressed by $\alpha d_{(N)}$, $\alpha(3d_{(N)}+d_{(S)//})/4$, and $\alpha(3d_{(N)}+d_{(S)\perp})/4$. If the S atom is no more anisotropic, the latter two components combine to give a degenerate one $\alpha(3d_{(N)}+d_{(S)})/4$. In the case of complexes Nos. 35—37, the component at longer wavelength is observed as a shoulder, and the next peak observed is an overlap of the two components at shorter wavelength.

**Mixed Cyano Complexes.** An empirical rule of Shimura,[39,40] which states that, for the first d-d bands of cis and trans isomers of [M $a_4b_2$] of a $d^6$ metal M, $\Delta\sigma=\sigma(cis)-\sigma(trans)<0$ if b is ahead of a in the spectrochemical series, while $\Delta\sigma>0$ if b is behind a, suffers from a few exceptions. An example is the isomers of $[Co(CN)_2(NH_3)_4]^+$ which show $\Delta\sigma_{obs}=+1.4$. By the present introduction of reduction parameter $\alpha$, however, most of the exceptions can be explained reasonably because the different $\alpha$ values are assigned to the geometrical isomers (Table 7).

The introduction of the parameter $\alpha$ has also improved the predicted values of $\sigma$ for a variety of mixed cyano complexes, which were heretofore regarded as serious exception of the Yamatera rule[4] (see complexes Nos. 2, 9, 19, and 38—43 in Tables 3, 5, and 7). Fujinami et al.[41] proposed an angular overlap treatment taking into account of (i) mixing of 3d orbitals with 4s and 4p by the lowering of symmetry in the mixed complexes and (ii) a configuration interaction between excited states, these factors being probably in line with the present introduction of empirical parameter $\alpha$.

**Mixed Halogeno Complexes.** Ogino and Bailar[5] pointed out that there were big discrepancies between the predicted and the observed $\sigma$ values of mixed halogeno complexes of rhodium(III) and iridium(III), when the predicted value was calculated from the $d$ values obtained from the observed $\sigma$ value of non-mixed halogeno complexes. Such discrepancies,

Table 6. Anisotropic $d$ Parameters of the Thiolato-Like S- or Se-Ligands

| No. | Complex | $\sigma_{obs}$[a] | $\sigma_{calc}$ | Eq. | $\alpha$ | $\Delta$/%[b] | $d$(S or Se) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 33 | $[Co(SCN)(NH_3)_5]^{2+}$ | 17.8sh | 17.76[c] | (1) | 0.98 | −0.2 | 9.5 | 35) |
| | | 19.5 | 19.48[d] | (1) | 0.98 | −0.1 | 16.5 } $SCN^+$ 13.0 | |
| 34 | $[Co(SSO_3)(NH_3)_5]^+$ | 17sh | 17.03[c] | (1) | 0.98 | +0.2 | 6.5 | 36) |
| | | 19.6 | 19.72[d] | (1) | 0.98 | +0.6 | 17.5 } $SSO_3^{2-}$ 12.0 | |
| 35 | $[Co(SCH_2CH_2NH_2)(en)_2]^{2+}$ | 16.7sh | 16.70[c] | (1) | 1.00 | 0.0 | 2.6 | 37) |
| | | 20.72 | 20.73[d] | (1) | 1.00 | +0.0 | 16.0 } <-$CH_2S$->[5] 9.3 | |
| 36 | $[Co(SCH_2CO_2)(en)_2]^+$ | 16.2sh | 16.20[c] | (1) | 1.00 | 0.0 | 5.4 | 37) |
| | | 19.3 | 19.33[d] | (1) | 1.00 | 0.0 | 9.6 } <-$CH_2S$->[5] 7.5 | |
| 37 | $[Co(SeCH_2CH_2NH_2)(en)_2]^{2+}$ | 16.5sh | 16.45[c] | (1) | 1.00 | −0.3 | 1.6 | 38) |
| | | 20.4 | 20.28[d] | (1) | 1.00 | −0.3 | 12.4 } <-$CH_2Se$->[5] 7.0 | |

a) sh=shoulder band. b) $\Delta=100(\sigma_{calc}-\sigma_{obs})/\sigma_{obs}$. c) The non-degenerate component. d) A mean of the two shorter wavelength components.

Table 7. Geometrical Isomers of the Mixed Cyano Complexes

| No. | Complex | $\sigma_{obs}$ | $\sigma_{calc}$ | Eq. | $\alpha$ | $\Delta$/%[a] | $\Delta\sigma_{obs}$[b] | $\Delta\sigma_{calc}$[b] | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 38 | *cis*-$[Co(CN)_4(NH_3)_2]^-$ | 28.0 | 28.01 | (1) | 0.955 | +0.0 | +3.8 | +3.85 | 11) |
| 39 | *trans*-$[Co(CN)_4(NH_3)_2]^-$ | 24.2 | 24.16 | (1) | 0.91 | −0.2 | | | |
| 40 | *cis*-$[Co(CN)_2(NH_3)_4]^+$ | 25.3 | 25.36[c] | (1) | 0.955 | +0.2 | +1.4 | +1.2 | 4) |
| 41 | *trans*-$[Co(CN)_2(NH_3)_4]^+$ | 23.9 | 24.16 | (1) | 0.91 | +1.1 | | | |
| 42 | *cis*-$[Co(CN)_2(en)_2]^+$ | 24.7 | 25.55[c] | (1) | 0.955 | +3.4 | +0.3 | +1.2 | 4) |
| 43 | *trans*-$[Co(CN)_2(en)_2]^+$ | 24.4 | 24.34 | (1) | 0.91 | −0.2 | | | |

a) $\Delta=100(\sigma_{calc}-\sigma_{obs})/\sigma_{obs}$. b) $\Delta\sigma=\sigma$(cis)$-\sigma$(trans). c) The shorter wavelength non-degenerate component.

however, have disappeared in the present treatment with $\alpha$, as is seen in complexes Nos. 23—27 in Table 5.

For the halogeno rhodium(III), iridium(III), and platinum(IV) complexes of the trans type, some irregularities were found in the empirical $\alpha$ values in Table 1. The $\alpha$ value for the trans isomer (in bracket in Table 1) is nearly equal to or only a little smaller than that for the cis isomer in the case of $[Rh(\underline{N})_xI_{6-x}]$-, $[Ir(\underline{N})_xI_{6-x}]$-, $[Pt(CN)_xCl_{6-x}]$-, and $[Pt(\underline{N})_xBr_{6-x}]$-type of complexes. The reason may be found in the strong spin-orbit coupling in such complexes.

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