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Spectroscopic Studies of Mixed Amine Carbonyl Complexes of d^6 Structure. II. Solvent Effect on the Ultraviolet and Visible Absorption Spectra of Diamine-tetracarbonyl Complexes of Chromium(0), Molybdenum(0) and Tungsten(0)

Hide SAITO, Junnosuke FUJITA and Kazuo SAITO

Chemistry Department, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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Absorption bands, especially metal to amine charge transfer bands of bipyridyl- and phenanthroline-tetracarbonyl chromium(0), molybdenum(0) and tungsten(0) are shifted in various solvents by less than 4500 cm^{-1}. The shift is discussed in accordance with McRae's equation, which was derived with the point-dipole approximation. The solvents can be classified into two groups, the alcohol and the ester group. When three constants corresponding to (1) the interaction between induced dipoles of the solute and of the solvent, (2) the interaction between permanent dipole of the solute and induced dipole of the solvent, and (3) the interaction between permanent dipoles of the solute and of the solvent, are duely chosen for the two groups of solvent individually, the experimental values are satisfactorily accounted for. Short range interactions, such as hydrogen bonding can be ignored.

Many studies have been made of the solvent effect (frequency shift) on visible and ultraviolet absorption spectra of π-conjugate organic compounds, and theoretical interpretation on the basis of simple electrostatic model, among them, seems quite successful.[1-5] On the other hand, little information is available concerning the solvent effect on absorption spectra of coordination compounds. Nakamoto *et al.* studied the absorption spectra of tervalent chromium and cobalt complexes in water, methanol and acetic acid.[6] The *d-d* transition bands exhibited red shift by less than 200 cm^{-1} and the extent increased in the order given. The intraligand transition bands, however, did not always give such a shift with a definite tendency. Alderdice[7] reported that the charge transfer band ($M\rightarrow\pi^*_{CO}$ ${}^{(1)}$C.T.)[*1] of hexacarbonyltungsten(0) showed small blue shift in water and cyclohexane. Behrens and Harder[8] described that bisbipyridyl- and bisphenanthrolinedicarbonyl molybdenum(0) and tungsten(0) changed their colors according to the solvent and temperature.

We have found that several absorption bands of diamine-tetracarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) are shifted in various solvents. Especially the shift of the metal to diamine transition bands in the visible region is remarkable, *e. g.* shift by 3800 to 4500 cm^{-1} in acetonitrile and cyclohexane. In this paper the frequency shift of absorption bands of diamine-tetracarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) has been described and discussed on the basis of McRae's equation for solvent effect, which was derived with the point-dipole approximation.

Experimental

Preparation of the compounds was described elsewhere.[9] The solvents were carefully purified by the usual methods from commercial extra pure grade products. The absorption spectra were measured with Hitachi EPS-3 Automatic Recording Spectrophotometer at 20 to 25°C, with a slow scanning speed, (6 min 700—340 mμ, 360—210 mμ) and 1 cm quartz cells. Sparingly soluble compounds in *e. g.* cyclohexane, *n*-butyl ether and carbon tetrachloride were measured with 2, 5 or 10 cm quartz cells. The solution was filtered through a glass filter of G4 texture, whenever necessary.

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[*1] The abbreviations are the same as mentioned in Part I. (This Bulletin).

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Results

The absorption curves are shown in Figs. 1 to 5 and the numerical data for the bands showing distinct shifts are summarized in Tables 1 to 4. The constancy of integrated intensities and the small change in shapes of the absorption band indicate that no substantial change occurs in the complexes themselves. The tungsten(0) compound $[W(CO)_4en]^0$ decomposed rapidly and its spectrum was not measured.

The bands generally show blue shifts to various extents according to the dielectric constant of solvents, and it appears reasonable to classify the solvents into two groups, the alcohol (solvents Nos. 1 to 7 in Tables 1 to 4) and the ester group (Nos. 8 to 13), because the correlation seems better within one particular group.

Application of McRae's Equation I. McRae[2)] gave a theoretical equation for solvent effects on absorption spectra. His theory is based on a simple electrostatic model in which the solvent-solute interaction is only long-range dipole interaction. (Onsager's approximation) The equation in a simplified form[4)] is as follows:

$$\tilde{\nu} = \tilde{\nu}_{\text{gas}} + (A + B)\frac{n^2 - 1}{2n^2 + 1} + C\left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right) \quad (1)$$

where $\tilde{\nu}$ is the wave number of bands in a given solution, and D and n are static dielectric constant, and refractive index of the solvent, respectively.

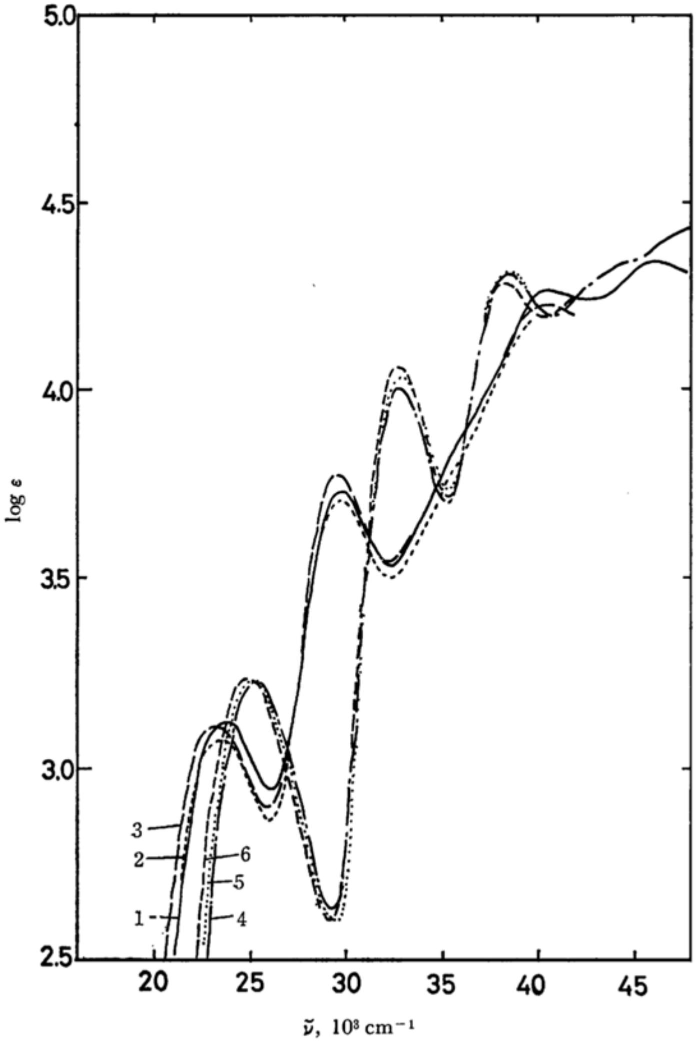

Fig. 1. Absorption spectra of ethylenediamine-tetracarbonyl chromium(0) and molybdenum(0) in some solvents:
$[Cr(CO)_4en]$ 1 —— in methanol, 2 ---- in methylacetate, 3 —— —— in *p*-dioxane;
$[Mo(CO)_4en]$ 4 — — — in methanol, 5 ······ in methylacetate, 6 — — in *p*-dioxane.

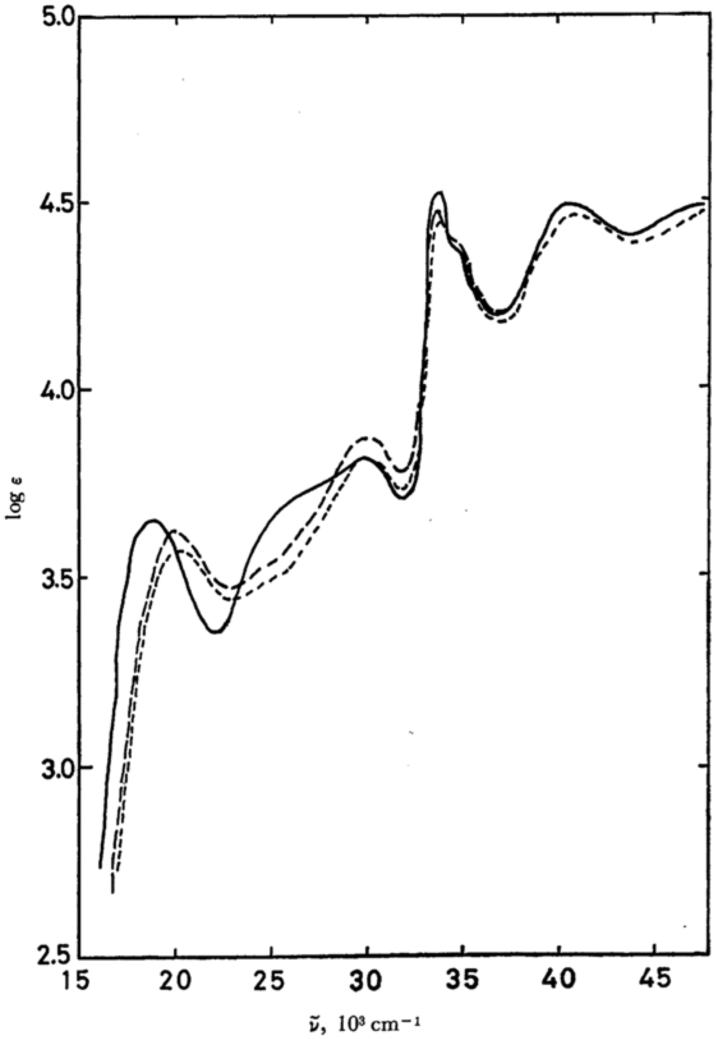

Fig. 2. Absorption spectra of bipyridyl-tetracarbonyl chromium(0) in some solvents: - - - - in methanol, — — in methylacetate, —— in ethylether.

$\tilde{\nu}_{gas}$ denotes the wave number of bands of the compound in "vapor state," which is not subject to solvent effect. The term $A\cdot(n^2-1)/(2n^2+1)$ represents the induced dipole-induced dipole interaction (dispersion force). The term $B\cdot(n^2-1)/(2n^2+1)$ indicates the interaction between permanent dipole of the solute and induced dipole of the solvent (induced force). The last term shows interaction between permanent dipoles of the solute and the solvent (orientation force). Equation (1) ignores any short range interaction including hydrogen bonding, π-π interaction and short range dipole interaction, as if the cavity radius, a, of Onsager's approximation were equal in all solvents in an ideal case. The equation also excludes the interaction between permanent dipole of the solvent and induced dipole of the solute.

McRae gave different values to the "weighted mean wavelength" L_0, which is expressed by $A=-2.14\times10^{-14}\ fL_0/\tilde{\nu}a^3$ as the first approximation (f, integrated intensity, a, cavity radius) and involves the influence of all transitions of both solvent and solute. However, this value L_0 was assumed to be constant by several workers[3,4] and we have applied Eq. (1) to the $M\rightarrow\pi^*_{AA}$C.T. bands of diamine-tetracarbonyl chromium(0) complexes, assuming that L_0 is constant for all solvents. The cavity radius, a, is also assumed to be constant. The constants n and D were taken from Landolt-Börnstein's tables. The values for n are those for Na-D line at 20°C and those of D at 20°C. The constants, $\tilde{\nu}_{gas}$, $(A+B)$ and C in Eq. (1) were determined by the least square method for the solvents Nos. 1 to 13 in Table 5. Then the expected wave number $\tilde{\nu}_{calcd}$ obtained from these values, should coincide with the observed value $\tilde{\nu}_{obs}$ if the shifts

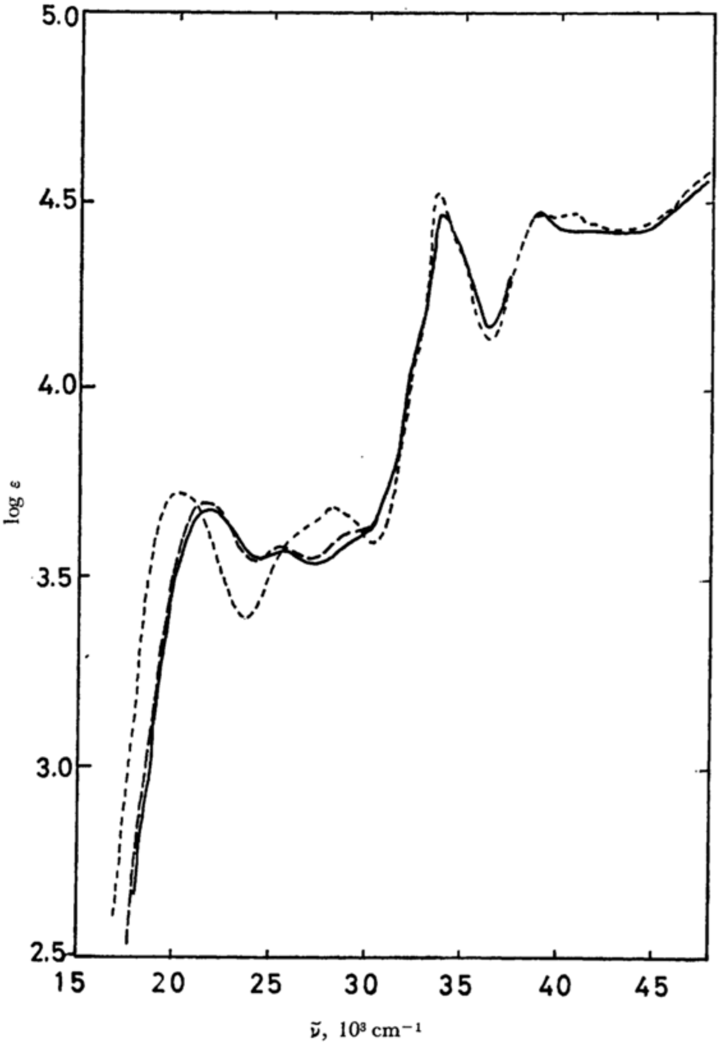

Fig 3. Absorption spectra of bipyridyl-tetracarbonyl molybdenum(0) in some solvents: —— in methanol, — — in methylacetate, - - - - in ethylether.

were accounted for by Eq. (1). The results are listed in Table 5 (analysis 1). The difference in wave number between the calculated and the observed, $\tilde{\nu}_{\rm calcd}-\tilde{\nu}_{\rm obs}$ amounts to 200 to 700 cm^{-1} (5 to 20 mμ), and it appears as if Eq. (1) cannot be applied to the present bands in its original form.

Application of McRae's Equation II. The difference $\tilde{\nu}_{\rm calcd}-\tilde{\nu}_{\rm obs}$ is, however, always positive for the alcohols, and always negative for the esters. Such a tendency suggests that different factors are operating in each solvent. The $\tilde{\nu}_{\rm gas}$ of a given compound should be always the same, but A, B, and C can represent the terms operating differently according to the kind of solvent. These values are generally expressed as A', B' and C' henceforth and particular terms operating in the given solvent groups as A_a, B_a, C_a and A_e, B_e, and C_e, for the alcohol and the ester group, respectively. Thus Eq. (1) is modified as Eq. (2).

$$\tilde{\nu}=\tilde{\nu}_{\rm gas}+(A'+B')\left(\frac{n^2-1}{2n^2+1}\right)+C'\left(\frac{D-1}{D+2}-\frac{n^2-1}{n^2+2}\right) \qquad (2)$$

The results for $M\rightarrow\pi^*_{AA}$ (C. T. band of bipyridyl- and phenanthroline-tetracarbonyl chromium(0) are shown in Table 5 (analysis 2). The difference $|\tilde{\nu}_{\rm calcd}-\tilde{\nu}_{\rm obs}|$ in the alcohol and in the ester group are less than 60 and 100 cm^{-1}, respectively. All the $|\tilde{\nu}_{\rm calcd}-\tilde{\nu}_{\rm obs}|$ values obtained by this treatment for metal to amine charge transfer bands are less than 120 cm^{-1} (3 mμ) for molybdenum(0) complexes and less than 140 cm^{-1} (3.5 mμ) for tungsten(0) complexes. The reliability of the values $\tilde{\nu}_{\rm gas}$ (A_a+B_a), (A_e+B_e), C_a and C_e is 80

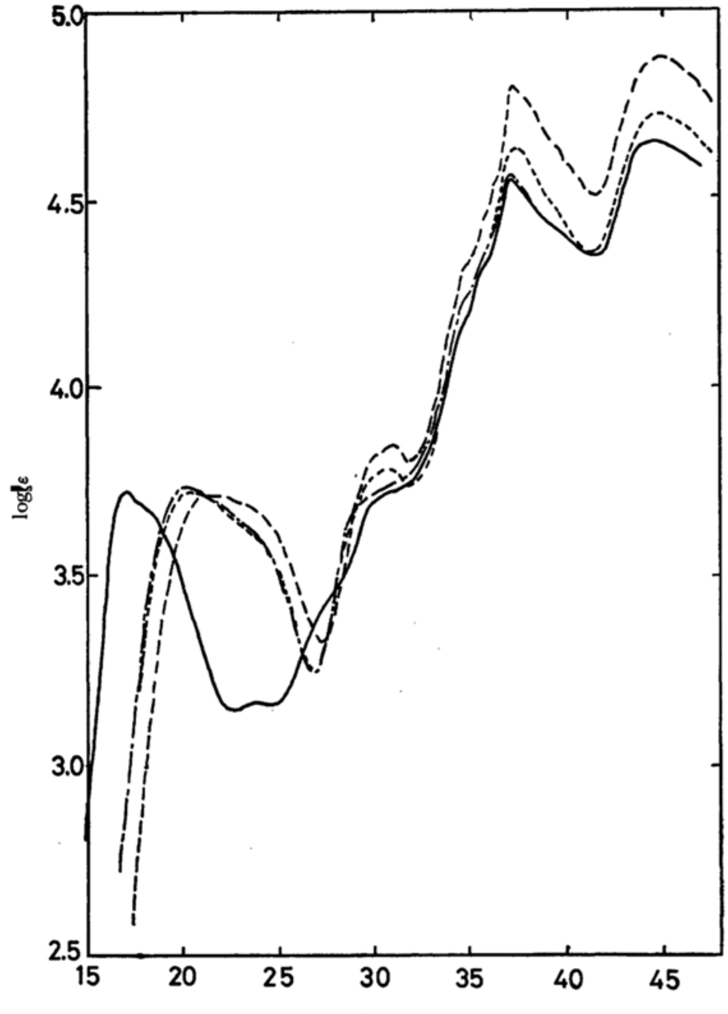

Fig. 4. Absorption spectra of phenanthroline-tetracarbonyl chromium(0) in some solvents: —— in cyclohexane, ---- in methanol, — — — in methylacetate, — — in acetonitrile (arbitrary scale intensity).

to 110 cm^{-1}. These constants are summarized in Table 7 and their meanings will be discussed in the following.

There would be no big difference among the physical properties of diamine-tetracarbonyl complexes with varying metals and amines except for the molecular radii, so that the interaction between a given solvent and a complex molecule would be very similar. Hence the difference in wave number of absorption maximum between any two complexes in a given solvent would be almost constant and equal to that in "vapor state." In Table 6 the mean differences in wave number among complexes in both groups of solvents and in "vapor state" are listed. They coincide well with one another.

The changes in values $A'+B'$, and C' in different solvent groups have similar trend for complexes with different central metals. The C_e value is always larger than the C_a but the difference is less than 30% relative corresponding to a shift less than 530 cm^{-1}. The absolute value for (A_a+B_a) is always larger than the (A_e+B_e), but the difference is even smaller (less than 15% relative).

Thus Eq. (2) seems to be applicable to the metal to amine charge transfer bands. The *d-d* transition, metal to carbonyl charge transfer ($M \rightarrow \pi^*{}_{CO}{}^{(1)}$ C. T.) and intraligand transition bands are shifted to a smaller extent in various solvents, but calculation has disclosed that Eq. (2) is more appropriately applied to all these bands than Eq. (1) is. The values $|\tilde{\nu}_{calcd}-\tilde{\nu}_{obs}|$ are less than 70, 100 and 50 cm^{-1}, for the *d-d* transition, the intra ligand transition and the metal to carbonyl charge transfer

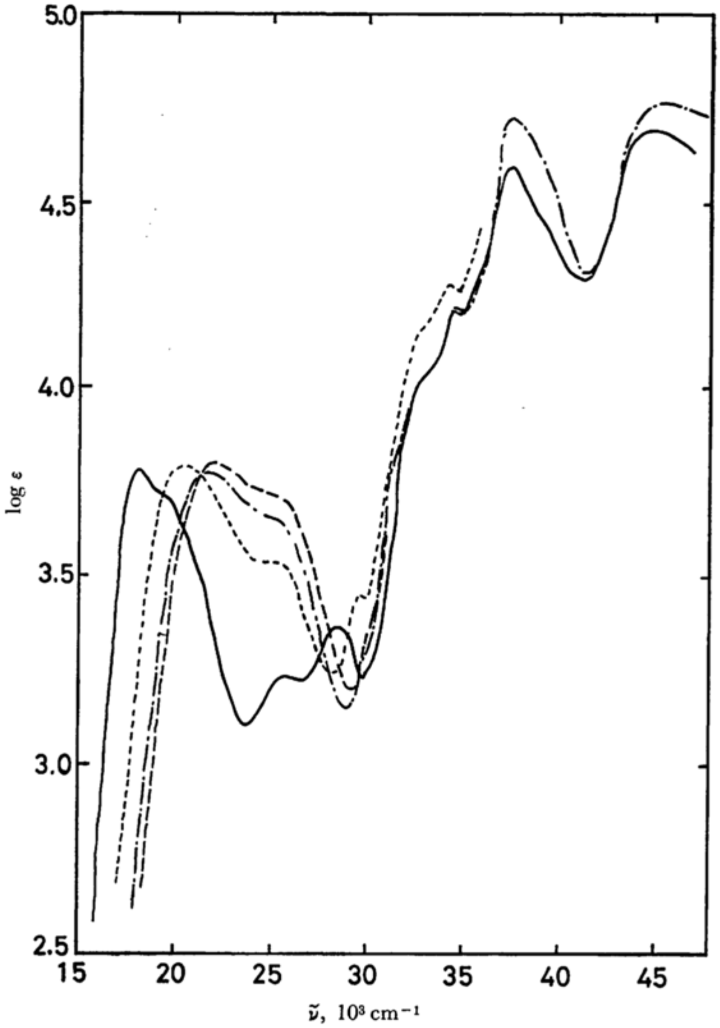

Fig. 5. Absorption spectra of phenanthroline-tetracarbonyl molybdenum(0) in some solvents: —— in cyclohexane (arbitrary scale intensity), - - - - in benzene, —-— in methanol, — — in acetone.

bands, respectively. The constants, $\tilde{\nu}_{\text{gas}}$ (A_a+B_a), C_a, (A_e+B_e), and C_e are listed in Table 7.

Discussion

It has been made clear that the shifts of the bands of these compounds are reasonably expressed by McRae's model of a simple electrostatic interaction in such solvents as alcohols, esters, ethers, acetonitrile and acetone. From the data in Tables obtained by Eq. (1) the solvents are arranged in the order of increasing $\tilde{\nu}_{\text{calcd}}-\tilde{\nu}_{\text{obs}}$ values as follows:

toluene ≃ benzene ≃ *p*-dioxane < chloroform ≤
acetic acid ≃ the "esters" < carbon tetrachloride ≃
the "alcohols" < cyclohexane

In carbon tetrachloride and cyclohexane solution, split components are observed in the metal to amine charge transfer bands, but the mean absorption maximum of phenanthroline-tetracarbonyl chromium(0) in cyclohexane is estimated to be about 17400 cm^{-1}. This value is compared to 17530 and 18180 cm^{-1} expected from A_a+B_a and C_a and A_e+B_e and C_e, respectively. On the other hand, the split components in carbon tetrachloride are less obvious, so that the splitting can be neglected. A similar result is also seen for molybdenum(0) and tungsten(0) complexes. Hence these two solvents can be regarded as belonging to the alcohol group.

The anomaly given in benzene and toluene solution would be due to π interaction between the aromatic diamine in the ligand sphere and the solvent molecule. Such an interaction has been known in *e. g.* pyridine *N*-oxide solution.[4] *p*-Dioxane has strong local dipole moments which are compensated in the whole molecule and does not

TABLE 1. NUMERICAL DATA OF ETHYLENEDIAMINE-TETRACARBONYL CHROMIUM(0) AND MOLYBDENUM(0) IN VARIOUS SOLVENTS
(maximum absorption, 10^3 cm^{-1}; molar extinction coeff. in parentheses, log ε)

No.	Solvent	$[Cr(CO)_4en]$			$[Mo(CO)_4en]$		
		$d\rightarrow d$	$M\rightarrow\pi^*_{CO}$	C.T.	$d\rightarrow d$	$M\rightarrow\pi^*_{CO}$	C.T.
1	Methanol	23.63 (3.12)	29.70 (3.73)	40.54 (4.26)	25.30 (3.23)	32.73 (4.00)	38.39 (4.30)
3	Isopropanol	23.50	29.52	40.52	25.27	32.66	38.43
4	*n*-Butanol	23.36	29.43	40.40	25.13	32.57	38.28
6	Ethylether	22.82	29.31	40.49	24.78	32.68	38.61
8	Acetonitrile	23.76	29.73	40.27	25.38	32.81	38.43
10	Methylacetate	23.30 (3.08)	29.67 (3.70)		25.06 (3.13)	32.79 (4.02)	38.43 (4.30)
11	Ethylacetate	23.18 (3.10)	29.57		24.98 (3.23)	32.75	
12	*n*-Butylacetate	23.11 (3.11)	29.54		24.87 (3.23)	32.69	
13	Isoamylacetate	23.09	29.50		24.83	32.66	
16	*p*-Dioxane	23.09 (3.11)	29.51 (3.77)	40.32 (4.22)	24.83 (3.23)	32.68 (4.06)	38.24 (4.28)

fit the point-dipole approximation. Chloroform is said[10] to form π-hydrogen bonding with benzene from NMR studies and such an interaction might also occur with diamine-tetracarbonyl complexes to result in anomaly in band shift.

Short Range Dipole Interaction. Solvents of the alcohol and the ester group obey McRae's formula with differing constants. The difference does not seem to come from any special interaction other than electrostatic. One of such special interactions could be hydrogen bonding, but this force cannot play a role, because ethers, cyclohexane and carbon tetrachloride belong to the alcohol group, whereas acetic acid having a greater acidity than alcohols belong to the other ester group.

The nature of interaction represented by C' in Eq. (2) might involve a kind of short range dipole interaction, which has similar factors to those of long range dipole interaction, but is subject to significant steric influence. The dipole moments of solvent molecules belonging to the "ester" and the "alcohol" group are 1.8 to 4 and less than 1.8 debyes, respectively. In the former group, the dipole moment originates mainly from the functional group $\rangle C{=}O$ or $-C{\equiv}N$. On the other hand, dipole distribution of diamine-tetracarbonyl complexes is considered as shown in Fig. 6. Although the contribution of the metal amine bond is quite big, that of the metal carbonyl bond is also appreciable owing to the metal to carbonyl back donation.[11,12] The latter bonding is formally similar to the functional groups, $\rangle C{=}O$, and $-C{\equiv}M$, so that the symmetry of dipoles M–CO corresponds well to that of R_1R_2CO and R–CN. When such a part of the molecule (M–CO) interacts with the solvent molecule by a simple short range dipole-dipole interaction, anti-parallel orientation would be far preferable to parallel both energetically and

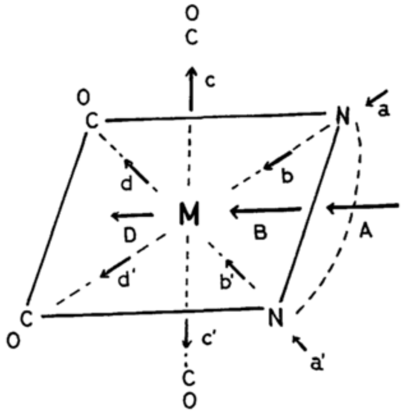

Fig. 6. Distribution of dipoles in metal diamine-tetracarbonyl complexes.

$\vec{a}, \vec{a}'$: Dipole moment of the ligand

$\vec{A} = \vec{a} + \vec{a}'$; en, $\simeq 2.0$; py_2, bp, phen $\simeq 3.6$ Debyes

$\vec{b}, \vec{b}'$: nitrogen to metal $(\overrightarrow{N\text{–}M})$

$\vec{B} = \vec{b} + \vec{b}'$; 5 to 6.2 Debyes

$\vec{c}, \vec{c}'$; metal to carbonyl (*trans*) $(\overrightarrow{M\text{–}CO})$

$|\vec{c}| = |\vec{c}'|$; 0.5 to 0.8 Debyes,

$\vec{d}, \vec{d}'$: metal to carbonyl (*cis*) $(\overrightarrow{M\text{–}CO})$

$\vec{D} = \vec{d} + \vec{d}'$; 0.7 to 1.1 Debyes (for estimations, *cf.* Refs. 11, 12)

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TABLE 2. NUMERICAL DATA OF METAL TO AMINE CHARGE TRANSFER BANDS OF BIPYRIDYL- AND PHENANTHROLINE-TETRACARBONYL COMPLEXES IN VARIOUS SOLVENTS
(maximum absorption, 10^3 cm^{-1}; molar extinction coeff. in round brackets, log ε; integrated intensity in square brackets $f \times 10^2$)

No.	Solvent	[Cr(CO)$_4$bp]	[Mo(CO)$_4$bp]	[W(CO)$_4$bp]	[Cr(CO)$_4$phen]	[Mo(CO)$_4$phen]	[W(CO)$_4$phen]
1	Methanol	(3.57) 20.11 [6.62]	(3.68) 21.60 [8.99]	(3.71) 20.98 [8.86]	(3.72) 20.37 [10.58]	(3.77) 21.68 [11.74]	(3.85) 21.01 [14.53]
2	Ethanol	(3.58) 19.68 [5.89]	(3.68) 21.14 [8.13]	20.49	(3.69) 19.90 [8.99]	(3.78) 21.22 [11.22]	(3.79) 20.48 [11.52]
3	Isopropanol	19.38	20.83	20.30	19.68	21.05	20.24
4	*n*-Butanol	19.18	20.67	19.97	19.50	20.76	20.06
5	Isopentanol	19.10	20.56	—	19.34	20.64	—
6	Ethylether	(3.65) 18.73 [6.79]	(3.72) 20.11 [8.69]	19.33	(3.72) 18.90 [9.37]	(3.81) 20.16 [10.23]	(3.85) 19.36 [12.21]
7	*n*-Butylketone	18.02	19.32	18.56	18.25	19.38	18.71
8	Acetonitrile	21.00 [6.97]*	22.47 [9.42]*	21.90	21.37 [9.46]*	22.63 [12.21]*	21.98 [14.79]*
9	Acetone	(3.60) 20.53 [6.32]	(3.69) 21.99 [8.04]	(3.71) 21.43	(3.73) 20.84 [10.06]	(3.79) 22.10 [11.57]	(3.85) 21.37 [13.98]
10	Methylacetate	(3.61) 19.97 [7.05]	(3.69) 21.42 [8.47]	(3.76) 20.74 [10.10]	(3.73) 20.25 [10.66]	(3.79) 21.50 [11.65]	(3.86) 20.76 [13.59]
11	Ethylacetate	(3.62) 19.69 [7.00]	(3.71) 21.11 [9.12]	(3.75) 20.39 [10.84]	(3.75) 19.98 [11.27]	(3.81) 21.22 [12.47]	(3.87) 20.44 [15.62]
12	*n*-Butylacetate	(3.61) 19.30 [6.28]	(3.70) 20.71 [8.17]	19.98	(3.74) 19.54 [9.76]	(3.79) 20.83 [11.87]	(3.88) 20.01 [14.32]
13	Isoamylacetate	19.12	20.55	19.75	(3.74) 19.45 [10.15]	(3.78) 20.67 [11.27]	(3.89) 19.88 [14.36]
14	Benzene	(3.62) 18.83 [6.62]	(3.69) 20.16 [8.05]	(3.75) 19.41 [9.29]	(3.72) 19.08 [8.94]	(3.79) 20.27 [10.49]	(3.91) 19.51 [14.10]
15	Toluene	(3.62) 18.66 [6.19]	(3.73) 19.99 [8.73]	19.22	(3.72) 18.93 [8.90]	(3.82) 20.11 [11.01]	(3.90) 19.36 [13.50]
16	*p*-Dioxane	19.26	20.65	19.92	(3.71) 19.58	20.84	20.07
17	Chloroform	(3.63) 19.08 [6.84]	(3.72) 20.41 [8.56]	(3.78) 19.69 [10.02]	19.42	20.60	19.84
18	CCl_4	17.21 [6.67]*	18.45 [7.87]*	—	17.49 [8.64]*	18.57 [10.79]*	18.13
19	Cyclohexane	—	—	—	16.95 [8.51]	18.10 [10.06]	17.64
20	Acetic acid	19.81	21.31	20.68	20.08	21.46	20.79

f values with * marks are estimated on the assumed log ε values
[Cr(CO)$_4$bp], 3.60; [Mo(CO)$_4$bp], [Cr(CO)$_4$phen], 3.70; [Mo(CO)$_4$phen], 3.80; [W(CO)$_4$phen], 3.85.

TABLE 3. NUMERICAL DATA OF THE INTRA-LIGAND π-π ABSORPTION OF BIPYRIDYL- AND PHENANTHROLINE-TETRACARBONYL COMPLEXES IN VARIOUS SOLVENTS
(maximum absorption, $10^3\,\mathrm{cm}^{-1}$; molar extinction coeff. in parentheses, log ε)

No.	Solvent	$[Cr(CO)_4by]$	$[Mo(CO)_4bp]$	$[W(CO)_4bp]$	$[Cr(CO)_4phen]$	$[Mo(CO)_4phen]$	$[W(CO)_4phen]$
1	Methanol	33.78 (4.44)	33.85 (4.46)	33.68 (4.44)	37.37 (4.67)	37.47 (4.72)	37.38 (4.69)
2	Ethanol	33.67	33.77 (4.47)	33.52	37.27 (4.69)	37.43 (4.75)	37.24 (4.63)
3	Isopropanol	33.61	33.68	33.48	37.29	37.34	37.19
4	*n*-Butanol	33.52	33.57	33.41	37.24	37.34	37.16
5	Isopentanol	33.52	33.56	—	37.20	37.29	—
6	Ethylether	33.58 (4.50)	33.61 (4.53)	33.41	37.13 (4.63)	37.31 (4.70)	37.31 (4.63)
7	*n*-Butylether	33.36	33.44	33.24	37.23	37.29	37.12
8	Acetonitrile	33.90	33.98	33.81	37.38	37.61	37.52
10	Methylacetate	33.72 (4.48)	33.78 (4.50)	33.60 (4.52)	37.34 (4.69)	37.52 (4.74)	37.31 (4.70)
11	Ethylacetate	33.67 (4.48)	33.73 (4.54)	33.53 (4.51)	37.31 (4.68)	37.44 (4.72)	37.27 (4.69)
12	*n*-Butylacetate	33.59 (4.46)	33.64 (4.55)	33.44	37.30 (4.65)	37.33 (4.70)	37.23 (4.64)
13	Isoamylacetate	33.56	33.60	33.41	37.29 (4.69)		37.23 (4.69)
14	Benzene	33.20 (4.44)	33.20 (4.51)	33.00 (4.51)			
15	Toluene	33.17 (4.43)	33.13 (4.53)	32.92			
16	*p*-Dioxane	33.50	33.51	33.32	37.17 (4.65)	37.27	37.24
17	Chloroform	33.49	33.90	33.33 (4.52)	37.19		37.02
18	CCl_4	33.34	33.28	—	37.16	37.19	37.02
19	Cyclohexane	—	—	—	37.22	37.31	37.05

TABLE 4. NUMERICAL DATA OF METAL TO CARBONYL CHARGE TRANSFER BANDS OF BIPYRIDYL- AND PHENANTHROLINE-TETRACARBONYL CHROMIUM(0) IN VARIOUS SOLVENTS
(maximum absorption $10^3\,\mathrm{cm}^{-1}$; sh, shoulder; molar extinction coeff. in parentheses log ε)

No.	Solvent	$[Cr(CO)_4bp]$	$[Cr(CO)_4phen]$
1	Methanol	30.00 (3.84)	30.75 (3.78)
2	Ethanol	29.94	30.59 (3.72)
3	Isopropanol	29.90	30.63
4	*n*-Butanol	29.90	30.51
5	Isopentanol	29.90	30.58
6	Ethylether	29.90 (3.81)	30.45 (3.75)
7	*n*-Butylether	29.89	—
8	Acetonitrile	30.18	30.96
9	Acetone	30.03 (3.86)	—
10	Methylacetate	30.00 (3.86)	30.70 (3.82)
11	Ethylacetate	29.99 (3.86)	30.64 (3.83)
12	*n*-Butylacetate	29.89 (3.82)	30.53 (3.82)
13	Isoamylacetate	29.85	30.49 (3.81)
14	Benzene	29.94 (3.84)	30.44 (3.82)
15	Toluene	30.00 (3.84)	30.49 (3.81)
16	*p*-Dioxane	29.94	30.58 (3.80)
17	Chloroform	29.85	30.77
18	CCl_4	31.0 (sh)	30.0 (sh) 31.3 (sh)
19	Cyclohexane		27.0 (sh) 30.8 (sh)

sterically. (Here the term "energetic" represents the contribution of such an interaction where no steric effect is taken into consideration.) Such short range interactions could be expressed by $(\alpha+\beta+\gamma)$ so that the last term of Eq. (2) is multipled by $(1+\alpha+\beta+\gamma)$ (Fig. 6). The first term, α represents the effect around the two metal-carbonyl bonds on M–NN plane, the second, β, that around the two metal-carbonyl bonds across M–NN plane and the last, γ, that around the metal-amine bonds. γ does not seem to involve big steric effect. From the values of dipole moments of the solvent, it could be estimated that $\gamma_e > \gamma_a > 0$, for phenanthroline- and bipyridyl-tetracarbonyl complexes and $\gamma_e \geq \gamma_a \geq 0$ for ethylenediamine-tetracarbonyl complexes. Suffixes *e* and *a* stand for values for the ester and the alcohol group, respectively.

For $\alpha+\beta$, the steric effect seems to be quite

TABLE 5. ANALYSIS OF THE ABSORPTION DATA OF METAL TO AMINE CHARGE TRANSFER BANDS OF BIPYRIDYL- AND PHENANTHROLINE-TETRACARBONYL CHROMIUM(0) IN VARIOUS SOLVENTS BY EQ. (1) AND EQ. (2)
(The values are $\nu_{\text{calcd}}-\nu_{\text{obs}}$ in cm^{-1})

No.	Solvent	Analysis 1 (Eq. (1))		Analysis 2 (Eq. (2))*	
		$[Cr(CO)_4bp]$	$[Cr(CO)_4phen]$	$[Cr(CO)_4bp]$	$[Cr(CO)_4phen]$
1	Methanol	+440	+490	−10	−30
2	Ethanol	+360	+450	−10	+50
3	Isopropanol	+290	+380	+50	0
4	*n*-Butanol	+290	+280	+20	−10
5	Isopentanol	+200	+260	−60	−20
6	Ethylether	+490	+670	+50	+80
7	*n*-Butylether	+430	+440	−20	−50
8	Acetonitrile	−610	−600	−40	−70
9	Acetone	−490	−510	+80	+120
10	Methylacetate	−480	−490	−100	−90
11	Ethylacetate	−390	−420	−10	−20
12	*n*-Butylacetate	−380	−380	+20	+60
13	Isoamylacetate	−400	−450	+40	+10
14	Benzene	−1820	−1840	−2050 −1310	−2060 −1330
15	Toluene	−1570	−1600	−1800 −1060	−1820 −1100
16	*p*-Dioxane	−1350	−1460	−1790 −1130	−1930 −1250
17	Chloroform	−830	−920	−1100 −250	−1190 −300
18	CCl_4	+240	+180	−100 +600	−160 +550
19	Cyclohexane	—	+1040	—	+580 +1230
20	Acetic acid	−490	−500	−940 −100	−970 +90

* Analysis 2: For solvents Nos. 1 to 7, A_a, B_a and C_a values are used, whereas for Nos. 8 to 13, A_e, B_e and C_e are used. For Nos. 14 to 20, the upper values are calcd. with A_a, B_a and C_a and lower with A_e, B_e and C_e.

TABLE 6. DIFFERENCE IN WAVE NUMBER OF $\tilde{\nu}_{\text{obs}}$ AND CALCULATED $\tilde{\nu}_{\text{gas}}$ OF THE METAL TO AMINE CHARGE TRANSFER BANDS BETWEEN CHROMIUM(0) MOLYBDENUM(0) AND TUNGSTEN(0) COMPLEX
(analysed by "analysis 2 in Table 5)

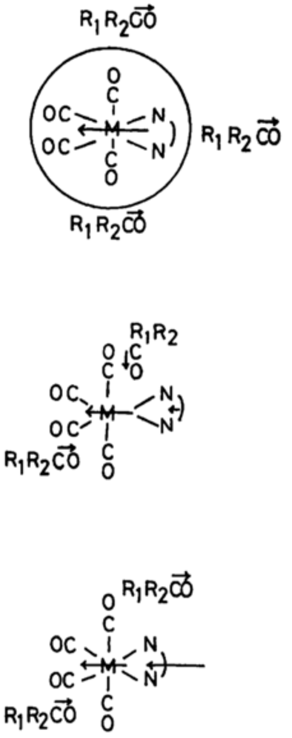
		Mo–Cr	Mo–W	W–Cr
$[M(CO)_4bp]$	ν_{obs}	1280	650	630
	ν_{gas}	1430	680	760
$[M(CO)_4phen]$	ν_{obs}	1180	420	760
	ν_{gas}	1270	730	520

important, but the energetic effect would be less so, because the absolute value of local dipole moment is rather small. Figure 7a illustrates the statistical dipole arrangement for the alcohol group solvent, where Onsager's approximation is applicable, *i. e.* $\alpha=\beta=0$. Figure 7b and 7c represent the cases where steric conditions are appreciable and short range interactions significant. A probable explanation is as follows.

The solvent molecules can orientate statistically as required by the overall dipole moment of the complex near the carbonyl ligands on the M–NN plane. On the other hand, such an orientation is hindered near those carbonyl groups in the plane across M–NN. Hence α is always positive, and β negative. The contribution of α would be slightly smaller in the case represented by Fig. 7b, than in the case represented by Fig. 7c, because the dipole moment of the whole complex is greater in the latter case, where the dipole of the amine ligand operates additive. By the same reason, the influence of β would be greater in the case Fig. 7b. Depending on whether the dipole moment of the whole complex molecule is greater or smaller than a certain value, $\alpha+\beta+\gamma$ has plus or minus sign. This value should be different for each central atom, because the cavity radius a and the dipole moment of M–CO are not expected to be equal in all the complexes. Ethylenediamine-, and bipyridyl- (or phenanthroline-) tetracarbonyl complex have dipole moments 8 to 10, and 9 to 11

TABLE 7. THE VALUES ν_{gas}, $A'+B'$ AND C' OBTAINED BY MODIFIED MCRAE'S EQUATION (cm^{-1})

	ν_{gas}	Alcohol group		Ester group	
		A_a+B_a	C_a	A_e+B_e	C_e
Metal to amine charge transfer					
[Cr(CO)$_4$bp]	22160	−23690	+2714	−20490	+3301
[Mo(CO)$_4$bp]	23440	−23840	+3063	−20040	+3479
[W(CO)$_4$bp]	22790	−24810	+3348	−21350	+3918
[Cr(CO)$_4$phen]	21980	−21840	+2874	−18670	+3627
[Mo(CO)$_4$phen]	23160	−22170	+3182	−18290	+3626
[W(CO)$_4$phen]	22740	−23720	+3130	−20650	+3858
d-d Transition					
[Cr(CO)$_4$en]	22440	−1364	+2017	+414	+1755
[Mo(CO)$_4$en]	24480	−585	+1326	−105	+1301
Intra ligand π-π transition					
[Cr(CO)$_4$bp]	34910	−8221	+378	−7607	+445
[Mo(CO)$_4$bp]	35070	−8766	+386	−8316	+509
[W(CO)$_4$bp]	34650	−7686	+466	−7315	+628
Metal to CO charge transfer					
[Cr(CO)$_4$en]	30300	−6972	+818	−4382	+289
[Cr(CO)$_4$phen]	31320	−5974	+628	−5492	+850



(a) Onsager's approximation

(b) Small dipole of ligand diamine

(c) Large dipole of ligand diamine

Fig. 7. Schematic representation of the orientation of organic carbonyl radical around polar metal carbonyl (M-CO) bonds.

Debyes, respectively.[12] From the values of C_a and C_e in Table 5, it might be concluded that Fig. 7b and 7c represent the cases of the ethylenediamine and the bipyridyl (or phenanthroline) complex respectively. Regardless of the nature of absorption bands, C_e is always greater than C_a for phenanthroline- and bipyridyl-tetracarbonyl complexes, whereas the reverse is true for ethylenediamine complexes.

The short range dipole interaction can induce the change of $A'+B'$ values expected from Onsager's approximation. The $-(A_a+B_a)$ value for the alcohol group is larger than $-(A_e+B_e)$ values for the ester group in all the absorption bands. The maximum value of $-A_a$ and $-A_e$ can be estimated from (A_a+B_a) and (A_e+B_e), respectively, by use of the following relationship,

$$B' = \frac{1}{\boldsymbol{h}\boldsymbol{c}a^3}(M_g{}^2 - M_e{}^2) \leqq \frac{2M_g}{\boldsymbol{h}\boldsymbol{c}a^3}(M_g - M_e) = C', \ (M_g,\ M_e > 0) \qquad (3)$$

where $\boldsymbol{h}$ stands for Planck's constant, $\boldsymbol{c}$ the light velocity, a the cavity radius, M_g the dipole moment of the ground state and M_e that of the excited Franck-Condon state for the transition in question.

When $-A$ value is to be approximated by $2.14 \times 10^{-14} fL_0/\tilde{\nu}a^3$, the ratio of the L_0 values for the alcohol and the ester group solvents could be calculated from the estimated A_a and A_e values, and measured $\tilde{\nu}$, on the assumption that f is equal for these two group solvents. The value L_0 (alcohol)/L_0 (ester) is 1.2. Generally L_0 is regarded to be independent of the solvent; McRae's consideration[2] suggests that ester group would have greater L_0, because esters themselves have strong absorption bands in low frequency region. Such discrepancies seem to suggest that the short range interaction is significant in the dispersion and the induced force, too. Such an interaction might be a kind of π-π interaction, although not necessarily due to orientation. Bauer and Nicol5) reported on the solvent effect for the ${}^1L_a$ transition of naphthacene, which is due to the dispersion force and the Stark effect of solvent. In this case varying solvents behave differently (difference, $\simeq 100\ \mathrm{cm}^{-1}$). This fact also suggests that the dispersion effect can differ from one solvent group to another.

Consideration on Individual Bands. The metal to amine charge transfer bands show red shift by 2000 to 4000 cm^{-1} as compared with $\tilde{\nu}_{\mathrm{gas}}$, owing to the big contribution of dispersion force. On the other hand, *d-d* transition bands of ethylenediamine-tetracarbonyl chromium(0) $[\mathrm{Cr(CO)_4en}]$ show a blue shift by 400 to 1000 cm^{-1}, owing to big contribution of orientation force. It appears as if the influence of dispersion force is quite significant for most organic compounds. It seems that the extinction coefficient is small for the *d-d* transition of $[\mathrm{Cr(CO)_4en}]$ and the electrons move in the interior molecule behind polarizable ligands to give only little influence upon the solvent molecule.

The large C values for the *d-d* band of $[\mathrm{Cr(CO)_4en}]$ could be attributed to the facts that the difference of permanent dipole moment between the ground and the excited Franck-Condon state is large and that the a values are rather small. The large difference in $M_g - M_e$ could be accounted for by considering that the d_π electron is polarized to the carbonyl ligand in the ground states, but the extent is decreased by transition to the $d_\sigma{}^*$ level. In this level the electrons would be localized appreciably on the central metal and the state of σ-bonding in CO ligand would remain unchanged. This view seems to be further supported by infrared and dipole moment studies.12,13) The dipole moment of the excited Franck-Condon state is estimated from the C values as shown in Table 8. The M_g is indirectly estimated from Strohmeier's data12) by simple addition of vectors. The cavity radii are estimated by adding 1 to 2 Å to the molecular radii calculated from the bond distance of diethylenetriaminetetracarbonyl chromium(0).14) The values in Table 8 seem reasonable.

TABLE 8. DIPOLE MOMENTS IN THE EXCITED FRANCK-CONDON STATE ESTIMATED FROM C VALUES (in Debye units)

	Assumed cavity radius		
	M_g	a(Å)	M_e
$[\mathrm{Cr(CO)_4en}]$			
$d \rightarrow d$	8.3	4	2.4—2.7
		5	3.0—3.7
$[\mathrm{Cr(CO)_4bq}]$			
$\mathrm{Cr} \rightarrow \pi^*{}_{\mathrm{bp}}$C.T.	9.3	5	1.6—3.0
		6	4.9—5.7
$\pi_{\mathrm{bp}} \rightarrow \pi^*{}_{\mathrm{bp}}$	9.3	5	8.3
		6	7.6
$[\mathrm{Cr(CO)_4phen}]$			
$\mathrm{Cr} \rightarrow \pi^*{}_{\mathrm{phen}}$C.T.	9.3	5	1.0—2.6
		6	4.4—5.4

The change of the electron distribution would occur in same directions but to different extents, for the metal to amine charge transfer and for the intra-ligand transition. Hence we can compare the values in Table 8 directly. The big change of dipole moments between the ground and the excited Franck-Condon state agrees with the assignment.9)

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13) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

14) F. A. Cotton and D. C. Richardson, *ibid.*, **5**, 1851 (1966).