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

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Chromium(0), molybdenum(0) and tungsten(0) complexes of $[M\cdot(CO)_4AA]^0$ type (AA= ethylenediamine (en), *l*-propylenediamine (*l*-pn), trimethylenediamine (tn), bipyridyl (bp), and phenanthroline (phen); *l*-pn and tn derivatives are new compounds) have been synthesized and their absorption spectra, rotatory dispersion (RD) and circular dichroism (CD) measured in methanol at room temperature. The nature of the absorption bands has been discussed by comparing them with one another and with those of hexacarbonyl- and piperidinepentacarbonyl complexes of these elements. The peaks in the region 23000 to 25000 cm^{-1} seem to be due to spin-allowed d–d transition. The bands at 30000 to 33000 cm^{-1} appears to correspond to the metal to carbonyl charge transfer band of hexacarbonyls at *ca.* 36000 cm^{-1}. Besides them, complexes of aromatic amines (bp and phen) show broad and strong bands at 21000 to 22000 cm^{-1} which seem to owe to metal to amine charge transfer.

Although many carbonyl compounds of VIB group elements of the periodic table have been studied,[1] little[2-5] is known of their optical properties except the infrared absorption spectra. Gray and Beach[2] measured the ultraviolet absorption spectra of hexacarbonyls of VIB group elements in the vapor state, and assigned the bands on a molecular orbital model. They gave thus several remarkable features of metal-carbonyl bonds. Strohmeier and Gerlach[4] measured the visible and ultraviolet absorption spectra of some mono- and diamine derivatives of metal carbonyls of group VIB elements and found that the patterns of spectra are all similar to one another. However, the character of each band was not made clear.

The bond between metal and carbon monoxide ligand has a significant π-character, whereas that between metal and amines is of almost pure σ-character. Hence studies of mixed complexes containing both kinds of ligand seem quite worthwhile. We have measured the absorption spectra of 15 kinds of mixed diamine carbonyls of the type $[M(CO)_4AA]$ ($M=Cr^0$, Mo^0, W^0; AA=ethylenediamine [en], *l*-propylenediamine [*l*-pn], trimethylenediamine [tn], bipyridyl [bp], phenanthroline [phen]) as well as their circular dichroism (CD) and rotatory dispersion (RD) and discussed the results in conjunction with those of hexacarbonyl complexes.

Experimental

Material. New compounds $[M(CO)_4\text{l-pn}]$ and $[M(CO)_4\text{tn}]$ were prepared by a similar method to Krainhanzel's,[6] which was useful for the preparation of $[M(CO)_4\text{en}]$. Bipyridyl and phenanthroline complexes, $[M(CO)_4\text{bp}]$ and $[M(CO)_4\text{phen}]$ were synthesized by Abel's method.[7] Each compound was identified by infrared spectra in the CO-stretching region and chemical analysis of carbon, hydrogen and nitrogen. The results of chemical analysis of the new compounds are shown in Table 1. Optically active *l*-pn was obtained by resolving commercial propylenediamine according to Dwyer.[8] The aqueous solution of *l*-isomer was acidified with hydrochloric acid and evaporated to dryness. Water was completely eliminated by adding ethanol and evaporating off ethanol together with water, twice. Anhydrous *l*-pn dihydrochloride was dissolved in absolute methanol containing an equivalent amount of sodium methylate, the sodium chloride decanted and the free *l*-pn distilled twice in the presence of metallic sodium. (yield after resolution, 26%) $[\alpha]_D^{25°}$ −34.3° (2% in benzene, by Dwyer's method.[8]) The solvent methanol was purified by the usual method in nitrogen atmosphere.

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[1] G. R. Dobson, I. W. Stoltz and R. K. Sheline, *Advances in Inorg. Chem. and Radiochem.*, **8**, 1 (1966).

[2] H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

[3] D. S. Alderdice, *J. Mol. Spectry.*, **15**, 509 (1965).

[4] W. Strohmeier and Kl. Gerlach, *Z. Phys. Chem.*, *N. F.*, **27**, 439 (1961).

[5] S. Yamada, H. Yamazaki, H. Nishikawa and R. Tsuchida, This Bulletin, **33**, 481 (1960).

[6] C. S. Krainhanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

[7] E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, **1959**, 2323.

[8] F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Am. Chem. Soc.*, **81**, 292 (1959).

Table 1. Chemical analysis of the complexes

	C, %		H, %		N, %	
	Calcd	Obs	Calcd	Obs	Calcd	Obs
[M(CO)$_4$*l*-pn]						
$CrC_7H_{10}O_4N_2$	35.54	35.30	4.03	4.23	11.83	11.76
$MoC_7H_{10}O_4N_2$	29.63	29.81	3.38	3.57	10.00	9.93
$WC_7H_{10}O_4N_2$	23.01	22.72	2.54	2.72	7.77	7.57
[M(CO)$_4$tn]						
$CrC_7H_{10}O_4N_2$	36.19	35.30	4.40	4.23	11.14	11.76
$MoC_7H_{10}O_4N_2$	30.93	29.81	4.02	3.57	9.46	9.93
$WC_7H_{10}O_4N_2$	23.72	22.72	2.86	2.72	7.27	7.57

Measurements. Visible and ultraviolet absorption spectra were measured with Hitachi EPS-3 Automatic Recording Spectrophotometer in the region where log ε is greater than 2. RD and CD were recorded with JASCO ORD/CD-5 Recorder in the wave number region below 35000 cm^{-1}. The measurements were all made in freshly prepared absolute methanol solution at room temperature. The mixed complexes tend to decompose in this solution, especially in the presence of dissolved oxygen.

Results and Discussion

Absorption curves of the diamine complexes are shown in Figs. 1 to 5, and the numerical data summarized in Tables 2 and 3. From these figures it is seen that the spectra depend on the ligand more remarkably than on the central metal atom. Especially, as seen from Fig. 5, bipyridyl and phenanthroline complexes give quite a different feature from those of aliphatic diamine complexes including ethylenediamine and trimethylenediamine derivatives. Such a difference can be expected from the aromaticity of ligand.

Bands at 23000 to 25000 cm^{-1}. All the complexes give bands in this wave number region, although bipyridyl and phenanthroline complexes give only shoulders. The wave numbers of the

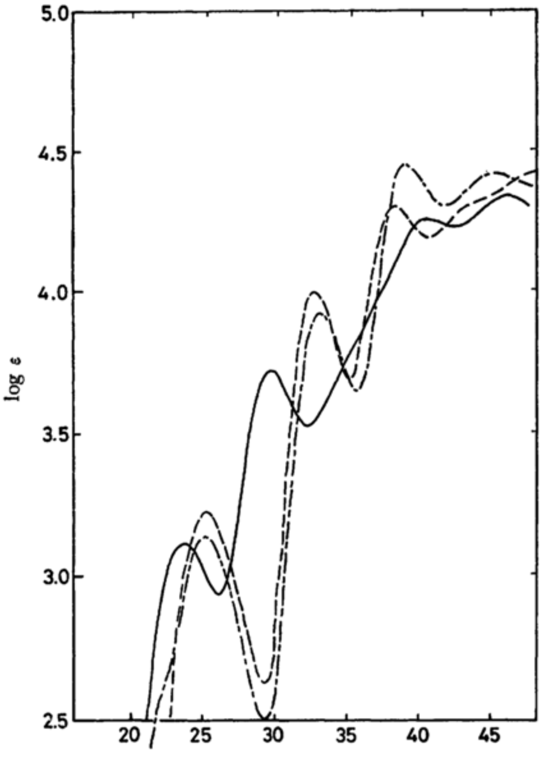

Fig. 1. Absorption spectra of [Cr(CO)$_4$en] (——), [Mo(CO)$_4$en] (----) and [W(CO)$_4$en] (-·-·) in methanol.

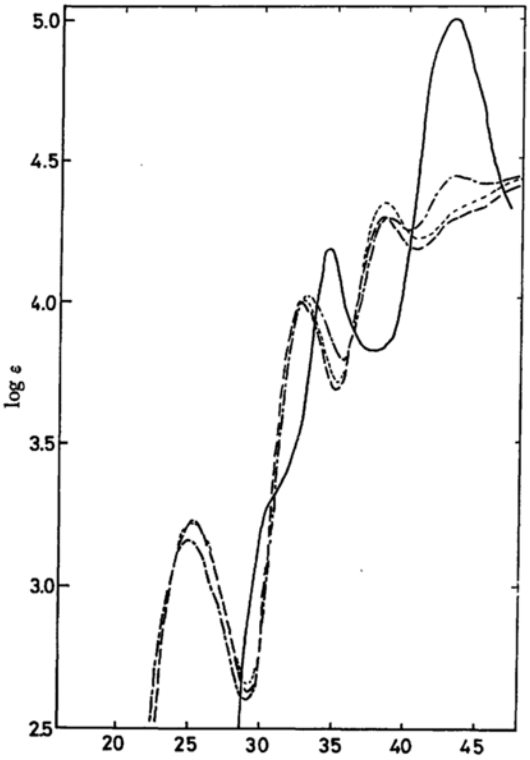

Fig. 2. Absorption spectra of [Mo(CO)$_6$] (——), [Mo(CO)$_4$en] (----), [Mo(CO)$_4$ *l*-pn] (····) and [Mo(CO)$_4$tn] (-·-·) in methanol.

TABLE 2. ABSORPTION MAXIMA OF THE COMPLEXES [M(CO)$_4$AA] (AA=en, *l*-pn, tn) IN METHANOL

Complex	Tentative assignment[2]					
	d-d		M → π_{CO}*(1)	uncertain	M → π_{CO}*(2)	uncertain
[Cr(CO)$_4$en]	—	23.6(3.12)	29.7(7.73)	35.5(sh 3.8)	40.3(4.26)	46.2(4.34)
[Mo(CO)$_4$en]	—	25.3(3.23)	32.7(4.00)	—	38.4(4.30)	43.4(sh 4.3)
[W(CO)$_4$en]	22.2(sh 2.6)	25.2(3.15)	33.2(3.92)	—	39.2(4.45)	45.0(4.42)
[Cr(CO)$_4$*l*-pn]	—	23.6(3.13)	29.7(3.74)	35.0(sh 3.8)	40.3(4.28)	45.9(4.32)
[Mo(CO)$_4$*l*-pn]	—	25.3(3.22)	32.8(4.02)	—	38.5(4.35)	43.4(sh 4.3)
[W(CO)$_4$*l*-pn]	22.2(sh 2.6)	25.2(3.14)	33.2(3.84)	—	39.2(4.38)	45.8(4.38)
[Cr(CO)$_4$tn]	—	<23.6	29.7	—	40.6	<46.2
[Mo(CO)$_4$tn]	—	25.0(3.18)	33.1(4.05)	—	38.7(4.33)	43.5(4.48)
[W(CO)$_4$tn]	22.2(sh 2.7)	24.7(3.14)	33.6(4.02)	—	39.5(4.48)	45.5(4.48)

The frequencies are given in 10^3cm^{-1}, and the intensity by log ε in parentheses.
sh: shoulder

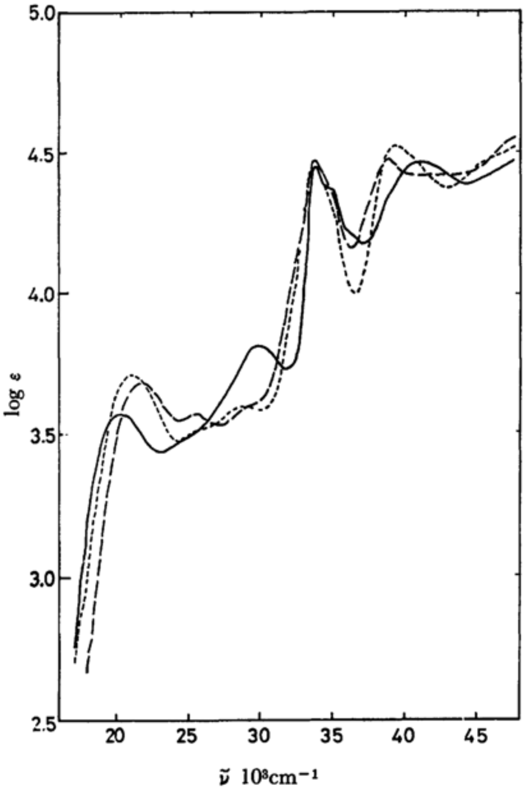

Fig. 3. Absorption spectra of [Cr(CO)$_4$bp] (——), [Mo(CO)$_4$bp] (----) and [W(CO)$_4$bp] (····) in methanol.

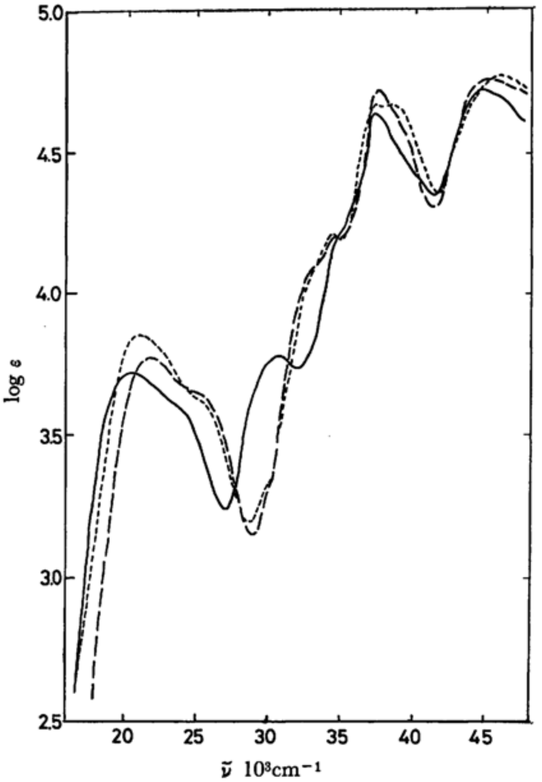

Fig. 4. Absorption spectra of [Cr(CO)$_4$phen] (——), [Mo(CO)$_4$phen] (----) and [W(CO)$_4$phen] (····) in methanol.

peak of molybdenum and tungsten complexes are similar to each other and significantly greater than those of the chromium complex. The molar extinction coefficient ε increases slightly in the sequence chromium, tungsten and molybdenum. The absorption spectra of ethylenediamine and *l*-propylenediamine complexes are almost identical and their absorption maxima are at a higher wave number than those of trimethylenediamine complexes by *ca.* 500 cm^{-1}. Such a tendency is seen only for the bands in this region, and coincides with that expected from the spectrochemical series. Hence these bands are regarded to be mainly due to the spin-allowed d–d transition. The d-d transition of the cobalt(III) complexes, [Co(CN)$_4$en)]$^-$, and [Co(CN)$_4$tn]$^-$, which are isoelectronic with the mixed diamine carbonyls of chromium(0), shows the same trend.

TABLE 3. ABSORPTION MAXIMA OF THE COMPLEXES $[M(CO)_4AA]$ (AA=bp, phen) IN METHANOL

Complex											
$[Cr(CO)_4bp]$	20.11 (3.57)	24.75 (sh 3.5)	—	—	30.00 (3.84)	—	33.78 (4.44)	34.72 (sh 4.4)	40.88 (4.46)	—	—
$[Mo(CO)_4bp]$	21.60 (3.68)	25.45 (3.57)	29.07 (sh 3.6)	—	32.6 (sh ca. 4)	—	33.85 (4.46)	34.97 (sh 4.4)	38.91 (4.46)	40.65 (4.41)	42.37 (4.41)
$[W(CO)_4bp]$	20.98 (3.71)	25.84 (sh 3.5)	28.94 (3.60)	—	32.5 (sh ca. 4)	—	33.68 (4.44)	34.72 (sh 4.4)	39.31 (4.52)	40.62 (sh 4.5)	45.87 (sh 4.5)
$[Cr(CO)_4phen]$	20.37 (3.72)	23.53 (sh 3.6)	—	29.67 (sh 3.7)	30.75 (3.78)	34.72 (sh 4.2) 35.71 (sh 4.3)	37.37 (4.67)	—	44.72 (4.74)	—	—
$[Mo(CO)_4phen]$	21.68 (3.77)	25.25 (3.64)	—	29.94 (sh 3.3)	32.68 (sh 4.1)	34.51 (4.20)	37.47 (4.72)	—	45.15 (4.75)	—	—
$[W(CO)_4phen]$	21.01 (3.85)	25.25 (sh 3.6)	—	29.90 (sh 3.3)	32.68 (sh 4.1)	34.39 (4.23)	37.38 (4.69) 38.46 (4.69)	—	45.87 (4.79)	—	—

The frequencies are given in $10^3 cm^{-1}$, and the intensity by log ε in parentheses.
sh: shoulder

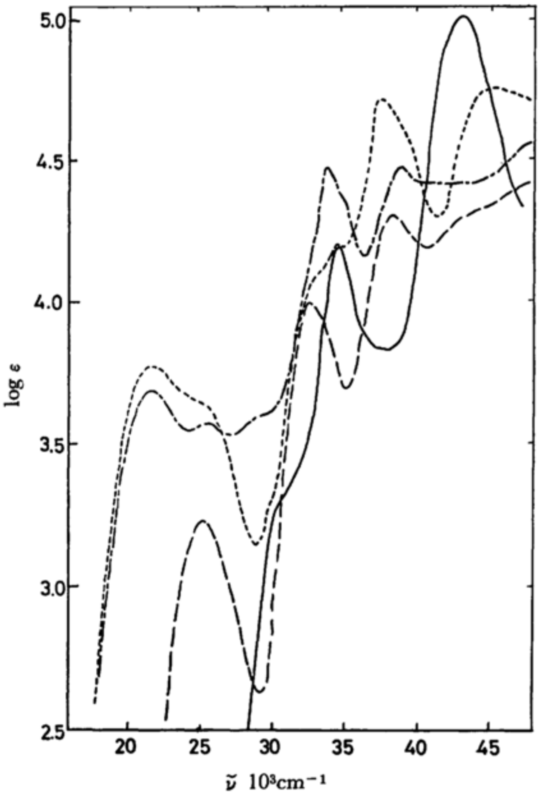

Fig. 5. Absorption spectra of $[Mo(CO)_6]$ (——), $[Mo(CO)_4en]$ (----), $[Mo(CO)_4bp]$ (-·-·) and $[Mo(CO)_4phen]$ (····) in methanol.

This conclusion is further supported by the fact that the location and extinction coefficient seem to be compared to those of the d–d transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) of hexacarbonyls at 31000 to 33000 cm^{-1}, which are regarded to be spin-allowed.2) The apparent differences in transition energy between diamine-tetracarbonyl and hexacarbonyl complexes (in cyclohexane) are estimated to be 7800, 6100 and 7400 cm^{-1} for the chromium, the molybdenum and the tungsten complex, respectively. These bands are subject to significant solvent effect. The estimation should be modified to be 9000 and 6900 cm^{-1} for the chromium and the molydbenum complexes in cyclohexane, respectively, when McRae's theoretical equation is applied.9) Contribution of the solvent effect cannot be appropriately estimated for the tungsten complex. The difference is only 3800 cm^{-1} for the corresponding hexa- and tetracyano cobalt(III) complexes. Such a remarkable difference between the carbonyl and the cyano complexes can be regarded as due to the greater destabilization of d_π levels on replacement of two carbonyls by diamine, as compared in case of the cyano cobalt(III) complexes. Such a view is also supported by infrared studies.6,10)

Strohmeier4) measured the absorption spectra of piperidinepentacarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) in cyclohexane and found that they also have absorption bands at 23000 to 26000 cm^{-1}. Their characteristics are very similar to those of the diamine-tetracarbonyl complexes given above, except for intensity. These bands are also considered to be mainly due to spin-allowed d–d transition.

Since these bands are considered to be a split component of d–d transitions which are triply degenerate in the hexacarbonyl complexes, it seems worthwhile, to examine whether their

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9) H. Saito, J. Fujita and K. Saito, This Bulletin, **41**, No. 4 (1968).
10) H. Sugi, Thesis, Tohoku Univ. (1964).

Table 4. Shift of the first band due to replacement of ligands by Yamatera's theory

Electronic transition	$[MA_6]$		$[MA_5B]$		*cis*-$[MA_4B_2]$	
$d_{xy} \rightarrow d_{x^2-y^2}$	0	T_{1g}	0	A_2	$1/2\,\delta$	B_1
$d_{yz} \rightarrow d_{y^2-z^2}$	0		$1/4\,\delta$	E	$1/4\,\delta$	A_1 and B_2
$d_{zx} \rightarrow d_{z^2-x^2}$	0		$1/4\,\delta$		$1/4\,\delta$	
mean	0		$1/6\,\delta$		$1/3\,\delta$	

δ, $(=\delta_\pi+\delta_\sigma)$ energy difference of the first band between $[MA_6]$ and $[MB_6]$.
The maximum frequency of the first band of $[Cr(CO)_6]$ is taken as zero.

locations are in accord with Yamatera's theory.[11] A similar trial was successful for the corresponding cyano complexes.[12] Ethylenediamine-tetracarbonylchromium(0) is insoluble in cyclohexane, but the location of maximum of d–d transition in cyclohexane is estimated to be at about 22170 cm^{-1} from the solvent effect.[9] The transition of piperidinepentacarbonylchromium(0) is observed at 23800 cm^{-1} in cyclohexane. We can estimate the wave numbers of the spin-allowed d-d transition of $[Cr(CO)_6]^0$, $[Cr(CO)_5pip]^0$ and $[Cr(CO)_4en]^0$ to be 31300, 23800, and 22170 cm^{-1}, respectively in cyclohexane. The ratio (31300—23800)/(31300—22170) is 3.3/4. According to Yamatera's theory, the expected shift of split componenets of the first bands of two mixed carbonyl complexes, $[MA_5B]$ and *cis*-$[MA_4B_2]$ type, are shown in Table 4. If the observed first bands of the two mixed carbonyl complexes were regarded as due to the three components averaged simply, the expected ratio mentioned above should be $(1/6\delta)/(1/3\delta)=1/2$, which is much smaller than the observed value. However, it would be possible to assign the observed band of $[Cr(CO)_5pip]$ as the E component of the first band, since the magnitude of shift seems to be extraordinarily remarkable, and further the theoretically forbidden A_2 component would have weaker intensity than the allowed E component has. The observed band of $[Cr(CO)_4en]$ shows no indication of splitting, on the other hand, and might consist of the three components mixed one another. Thus the magnitude of shift is $1/4\ \delta$ for $[Cr(CO)_5pip]$ and $1/3\delta$ for $[Cr(CO)_4en]$ and the ratio is 3/4. This value equals nearly to the observed value. However, the present case will be the first example, where Yamatera's theory applied to the band shifts of mixed carbonyl complexes involving low oxidation state metal and π-character ligand. More detailed study would be needed to elucidate the applicability of this theory to such complexes.

Bands at 21000 to 22000 cm^{-1}. Broad and strong bands are observed in this region only in the spectra of aromatic diamine tetracarbonyl complexes. Their characteristics are different from those of the spin-allowed d–d bands mentioned above. The wave number of the absorption maximum increases with almost equal differences (700 cm^{-1}) in the order chromium, molybdenum and tungsten, and the extinction co-efficient in the same order for a given diamine. Two low-spin d^6 type complexes $[Fe(bp)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$, have metal to ligand charge transfer bands at about 20000 cm^{-1} [13] and these seem to correspond to those of diamine-tetracarbonyl complexes in question.

Bands in Other Regions. The bands of diamine-tetracarbonylchromium(0) at 30000 and those of molybdenum and tungsten complex at 33000 cm^{-1} (shoulders for aromatic diamine complexes) would be metal to carbonyl charge transfer bands, because their extinction coefficients are very great and they would possibly correspond to the bands of hexacarbonyl complexes at 35000 cm^{-1} ($^1A_{1g}$ to $^1T_{1u}$[1] charge transfer).[2] The remaining bands of aliphatic diamine complexes at 40000 cm^{-1} appear to correspond to those of hexacarbonyl complexes at 44000 cm^{-1}, which are assigned to metal to carbonyl transition band in molecular orbital sense[2] (see Fig. 6).

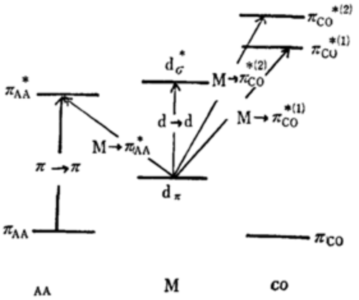

Fig. 6. Schematic energy level diagram for mixed carbonyls.

The sharp bands of bipyridyl-tetracarbonyl complexes at *ca.* 34000 cm^{-1} are little affected by the central metal and accompanied by shoulders

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[11] H. Yamatera, This Bulletin, **31**, 95 (1958).
[12] K. Ohkawa, J. Fujita and Y. Shimura, *ibid.*, **38**, 66 (1965).

[13] S. F. Mason, A. J. McCaffery and B. J. Norman, *Proc. Chem. Soc.*, **1964**, 259.

at a higher wave number by about 1000 cm^{-1}. They are likely due to intra-ligand transition (π-π^*), as exemplified by many bipyridyl complexes. The bands of phenanthroline-tetracarbonyl complexes at 37000 cm^{-1} seem also to be mainly due to the intra-ligand transition.

d$_\pi$-Levels. As seen from Figs. 3 and 4, the intra-ligand π-π^* transition energy of the bipyridyl and the phenanthroline complexes is rather constant regardless of the kind of central metal. Hence the energy level of π_{AA}^* does not change significantly by complex formation with different metal atoms. Thus the shift of metal-to-diamine charge transfer bands would reflect the energy of metal d$_\pi$ levels. This level is destabilized by 700 cm^{-1} each in going from molybdenum to tungsten and from tungsten to chromium.

On the other hand, the location of d-d band is rather independent of the kind of diamine for complexes of a given metal. The differences in d-d transition energies are estimated from the absorption spectra of ethylenediaminetetracarbonyl complexes of these metals: *i. e.* 1700 cm^{-1} between chromium and molybdenum, and 1600 cm^{-1} between chromium and tungsten complex. From these values and the d$_\pi$ levels mentioned above, it is seen that the d$_\sigma$* levels are destabilized in the order, chromium, molybdenum and tungsten, and the difference is 300 cm^{-1} between chromium and molybdenum, and 900 cm^{-1} between chromium and tungsten.

The difference of energy of $\pi_{CO}^{*(2)}$ levels can be also calculated from the data in Table 3 and the relative height of the d$_\pi$ levels. They are destabilized in the order, molybdenum, tungsten and chromium, and the difference is 100 cm^{-1} between molybdenum and tungsten, and 500 cm^{-1} between molybdenum and chromium. The order is the same as that for the d$_\pi$ levels, to indicate that the antibonding levels of carbon monoxide in these complexes are stabilized as the d$_\pi$ levels of the central metals are stabilized.

Rotatory Dispersion and Circular Dichroism of *l*-Propylenediaminetetracarbonyl Complexes. The curves are shown in Fig. 7. For the spin-allowed d-d transition of [Cr(CO)$_4$*l*-pn], negative and positive Cotton effect are observed from the lower wave number region. The RD curve has two inflection points, whose wave number coincides with the peaks of CD curve. *l*-Propylenediamine-tetracyanocobaltate(III) [Co(CN)$_4$*l*-pn]$^-$, isoelectronic to the chromium complex, also has such a CD pattern on the first d-d transition.[14] Although cyanide ions have weaker π-bonding character than carbonyl ligands has, the common pattern seems to support the assignment.

The splitting of d-d transition peak is not very great. The CD and the RD of molybdenum and tungsten complexes are very similar. They give only positive Cotton effect with large $\Delta\varepsilon$ values at the absorption maxima, and this feature is obviously different from that of the chromium complex. However, the reason cannot be appropriately accounted for at the present stage. Another positive Cotton effect seems to be in the M→$\pi^*_{CO}$$^{(1)}$ C. T. region, but its detailed discussion cannot be made because of the difficulty in accurate measurement.

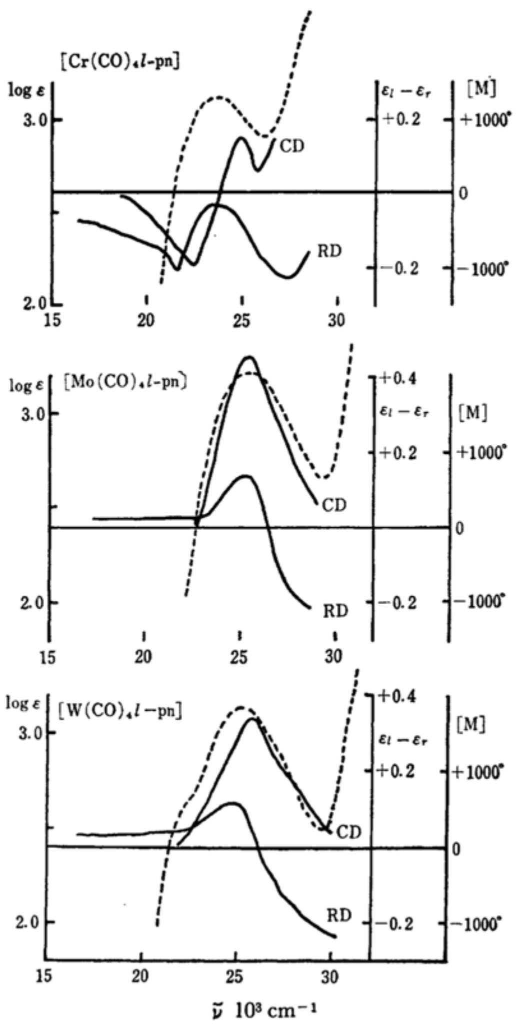

Fig. 7. Absorption spectra (····), CD and RD of the complexes [Mo(CO)$_4$ *l*-pn] (M=Cr, Mo, W) in methanol.

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[14] J. Fujita, to be published