Preparation and Electronic Spectra of Dichlorobis(1,10-phenanthroline)-molybdenum(III) and Dichlorobis(2,2′-bipyridine)molybdenum(III) Ions

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A preparation method of pure crystalline salts, *cis*-$[MoCl_2(phen)_2]X$ (phen, 1,10-phenanthroline; X^-= Cl^-, Br^-, $CH_3C_6H_4SO_3^-$) and *cis*-$[MoCl_2(bpy)_2]Cl$ (bpy, 2,2′-bipyridine), has been established. They are stable in solid state under oxygen- and moisture-free conditions. They deteriorate within one hour in water at room temperature, but are much more stable in various organic solvents free from oxygen. In the visible region, two absorption peaks were observed in methanol at 21510 cm^{-1} (ε=2570 $dm^3\ mol^{-1}\ cm^{-1}$) and 26740 cm^{-1} (ε=4420 $dm^3\ mol^{-1}\ cm^{-1}$) for the phen complex, and one broad peak at 22820 cm^{-1} (ε=3630 $dm^3\ mol^{-1}\ cm^{-1}$) for the bpy complex, which are assigned to the metal-to-ligand d-π^* charge transfer transition.

The coordination chemistry of molybdenum(III) has been less known as compared with that of chromium(III). Particularly, there are very few well characterized monomeric molybdenum(III) complexes containing amino carboxylates or aliphatic amines.[1,2] While chromium(III) complexes are inert to the oxidation with common oxidants, molybdenum(III) complexes are easily oxidized by air and by a variety of mild oxidants.[1] Nevertheless molybdenum(III) complexes have drawn interest as a counterpart of the well studied chromium(III) chemistry.

2,2′-Bipyridine(bpy) and 1,10-phenanthroline(phen) provide a variety of stable complexes of transition elements in low oxidation states.[3,4] Several monomeric molybdenum(III) complexes have been reported,[5–10] containing one to three 2,2′-bipyridine or 1,10-phenanthroline. However, some of them were not well characterized, and chemical properties of the characterized species are uncertain. Particularly only a few electronic absorption data are available.

We have isolated pure dichlorobis(2,2′-bipyridine)- and dichlorobis(1,10-phenanthroline)molybdenum(III) complexes in crystalline state and observed their electronic absorption spectra in various solvents.

Experimental

Materials. 2,2′-Bipyridine, 1,10-phenanthroline, and *p*-toluenesulfonic acid (Wako pure chemical industries, Ltd.) were used without further purification. Ammonium pentachloroaquamolybdate(III), $(NH_4)_2[MoCl_5(H_2O)]$, was prepared by the known method.[11] Organic solvents except acetone for the spectrometry were dehydrated with Molecular Shieves 4A and used without distillation. Acetone (Dotite spectrosol) was used as received. The concentration of water in these solvents was $(2—20)\times10^{-3}$ mol dm^{-3}.

Preparation of the Complexes. The bis(bpy) and bis(phen) complexes were synthesized by substituting the aromatic ligands for the aqua and the chloro ligands in $[Mo^{III}Cl_5(H_2O)]^{2-}$.

Dichlorobis(1,10-phenanthroline)molybdenum(III) Chloride Tetrahydrate, $[MoCl_2(phen)_2]Cl\cdot4H_2O$: A three-necked round-bottomed flask (1 dm^3) was connected to a dropping funnel and a reflux condenser,[12] the top of which was connected to a manifold for vacuum and nitrogen gas. Aqueous ethanol (40% v/v, 200 cm^3) containing 16 g of 1,10-phenanthroline and 5 g of *p*-toluenesulfonic acid was placed in the flask and the content was stirred with a teflon-coated bar. The whole system was evacuated and nitrogen gas was introduced. The purge cycle was repeated more than ten times. A solution of $(NH_4)_2[MoCl_5(H_2O)]$ (4.3 g) in 1.0 mol dm^{-3} hydrochloric acid (100 cm^3) was prepared in a 300 cm^3 round-bottomed Schlenk tube filled with nitrogen, transfered to the dropping funnel through a transfer tube, and added dropwise (6 h) to the phen solution at 50 °C with stirring. The red mixture was refluxed in an oil bath (*ca.* 100 °C) for 24 h. The color turned deep violet and then dark orange. The solution was allowed to cool slowly and kept in a refrigerator for 24 h. Yellowish orange needles appeared during storage, which were filtered off with a fritted funnel under nitrogen atmosphere, dried under a stream of nitrogen, dried *in vacuo*, and recrystallized from methanol. The deep orange prismatic crystals were washed with diethyl ether and dried *in vacuo*. Yield 2.2 g (35% from $(NH_4)_2[MoCl_5(H_2O)]$). Found: C, 45.94; H, 3.55; N, 8.85; Cl, 16.79%. Calcd for $C_{24}H_{24}N_4O_4Cl_3Mo$: C, 45.41; H, 3.81; N, 8.83; Cl. 16.76%. $[MoCl_2(phen)_2]Cl\cdot4H_2O$ is soluble in water, propylene carbonate, acetonitrile, *N,N*-dimethylformamide, methanol, ethanol, acetone and dichloromethane, slightly soluble in acetic acid, and insoluble in diethyl ether and 1,4-dioxane. The magnetic moment of the solid was 3.20 BM (292 K).

Dichlorobis(1,10-phenanthroline)molybdenum(III) p-Toluenesulfonate Sesquihydrate, $[MoCl_2(phen)_2](CH_3C_6H_4SO_3)\cdot1.5H_2O$: This was prepared similarly to the chloride salt by use of 20 g (instead of 5 g) of *p*-toluenesulfonic acid in aqueous ethanol to obtain large dark orange prismatic crystals. Yield 4.6 g (50% from $(NH_4)_2[MoCl_5(H_2O)]$). Found: C, 51.31; H, 3.65; N, 7.77; Cl, 9.72; S, 4.48%. Calcd for $C_{31}H_{26}N_4O_{4.5}Cl_2SMo$: C, 51.32; H, 3.61; N, 7.72; Cl, 9.77; S, 4.42%.

Dichlorobis(1,10-phenanthroline)molybdenum(III) Bromide Tetrahydrate, $[MoCl_2(phen)_2]Br\cdot4H_2O$: The preparation method was similar to that of the chloride salt except using 1.0 mol dm^{-3} hydrobromic acid in place of 1.0 mol dm^{-3} hydrochloric acid. The solution of $(NH_4)_2[MoCl_5(H_2O)]$ in 1.0 mol dm^{-3} hydrobromic acid (100 cm^3) was stirred for 24 h, and then added to the phen solution. Yield of orange powder, 15%. Found: C, 41.54; H, 2.90; N, 8.94; Cl, 10.32; Br, 11.62%. Calcd for $C_{24}H_{24}N_4O_4BrCl_2Mo$: C, 42.44; H, 3.56; N, 8.25; Cl, 10.44; Br, 11.76%.

Dichlorobis(2,2′-bipyridine)molybdenum(III) Chloride Dihydrate, $[MoCl_2(bpy)_2]Cl\cdot2H_2O$: This was made by a method similar to that for the phen complex chloride. Yield 2.3 g (31% from $(NH_4)_2[MoCl_5(H_2O)]$). Found: C, 43.65; H, 3.56; N, 10.16; Cl, 18.67%. Calcd for $C_{20}H_{20}N_4O_2Cl_3Mo$: C, 43.62; H, 3.66; N, 10.17; Cl, 19.31%. The orange crystals of $[MoCl_2(bpy)_2]Cl\cdot2H_2O$ are soluble in the same solvents as mentioned for $[MoCl_2(phen)_2]Cl\cdot4H_2O$.

Stability of the Complexes. The complex solids are stable under nitrogen atmosphere or *in vacuo* for at least one month, and relatively stable in dry air for at least two

days at room temperature. Their solutions in organic solvents free from oxygen are stable for at least 1 h at room temperature. Aqueous solutions (pH $\approx$7) are very unstable at room temperature even in the absence of oxygen.

Measurements. Ultraviolet and visible absorption spectra were recorded on a Hitachi 330 spectrophotometer under nitrogen atmosphere by the syringe technique.[12] Air was eliminated and nitrogen or argon was introduced into the solvents before measurement. Infrared spectra were recorded on a JASCO IRA-1 and a Hitachi 215 infrared spectrophotometer in KBr disks. The magnetic susceptibility was measured by the Faraday method in the Physics Department of this University at room temperature.

The concentration of water in organic solvents was determined by the Karl Fischer method with a Metrohm Karl Fischer-Automat E547, equipped with a Multi-Dosimat E415 and a Multi-Bürette E485.

Results and Discussion

Preparation. Bis(2,2'-bipyridine) and Bis(1,10-phenanthroline) Complexes: $[MoCl_2(phen)_2]Cl$ was prepared by Du Bois *et al.* from $[Mo^{III}Cl_3(py)_3]$ (py= pyridine) and phen in xylene.[9] The complexes, $[Mo^{III}I_2L_2]X$ (L=bpy, phen; $X^-=I^-$, $B(C_6H_5)_4^-$) were prepared by Westland and Muriithi,[10] by treating MoI_3 and the ligands in tetralin at 160—170 °C for 24 h. When MoI_3 and phen were mixed in benzonitrile at 180 °C for 3 d, $[Mo^{II}I_2(phen)_2]$ was claimed to be formed.[10] The products were reported to be powder, and the formulations were based on analytical data of Mo, and Cl or I alone. No electronic absorption spectrum was reported.

The elemental analysis of the present complexes are consistent with the given formulae. The magnetic moment of $[MoCl_2(phen)_2]Cl\cdot 4H_2O$ (3.20 BM) is similar to those of other monomeric molybdenum(III) complexes.[1] Three salts of the bis(phen) complexes gave almost identical absorption spectra in the visible region in methanol, indicating that all the samples contain the same complex cation. $[MoCl_2(phen)_2]Cl\cdot 4H_2O$ and $[MoCl_2(bpy)_2]Cl\cdot 2H_2O$ gave infrared absorption bands at 325 cm^{-1} and 323 cm^{-1}, respectively, which are assigned to $M^{III}o$–Cl stretching frequency (*cf.* Mo^{III}–Cl stretching frequency at 305 cm^{-1} in $K_3[MoCl_6]$[13,14]).

The bis-chelate complexes were successfully synthesized by the dilution method; *i.e.* $[Mo^{III}Cl_5(H_2O)]^{2-}$ in 1.0 mol dm^{-3} hydrochloric acid slowly added to the ligand solution. The ligand solution contains *p*-toluenesulfonic acid as 'inert' acid (perchloric acid is known to oxidize Mo(III)[11]) to keep reaction mixture acidic and low chloride concentration. The initial red reaction mixture turned violet within twenty minutes and then dark orange within 1 h. The violet color may indicate the formation of an intermediate $[MoCl_4L]^-$ (L=bpy, phen).[8] When the solutions of the ligand and of $[Mo^{III}Cl_5(H_2O)]^{2-}$ were rapidly mixed, a red-violet precipitate was formed, which was first assigned to $[MoL_3]Cl_3$ (L=bpy, phen) by Steele,[5] but later claimed to be $[MoCl_2L_2][MoCl_4L]$, $(LH)[MoCl_4L]$ or their mixture by Marzilli and Buckingham.[8] Our results of elemental analysis (C, H, N, Cl) of the red-violet precipitate fell between the calculated values for the last two formulations. Carmichael *et al.* reported that a similar insoluble salt was obtained by the reaction of molybdenum(III) trichloride or potassium hexachloromolybdate(III) with molten bipyridine.[7] It seems that under the reaction conditions where substantial amounts of $[MoCl_4L]^-$ and $[MoCl_2L_2]^+$ (or LH^+) are present, an insoluble salt between these two ions precipitated.

A large excess of the ligand (more than 8 times of the molybdenum) was also required to obtain the bis complex in high yield. When only 2.5 molar excess of the ligand was used, a red-violet precipitate was formed, which can be $[MoCl_2L_2][MoCl_4L]$. Substantial amount of $[MoCl_2L_2]Cl$ was also obtained from the filtrate.

Attempts to Prepare the Tris-chelate Complexes, $[Mo(bpy)_3]^{3+}$ and $[Mo(phen)_3]^{3+}$: Various attempts by the ligand substitution method were unsuccessful. Prolonged refluxing (1—10 d) of the reaction mixture used for the preparation of the bis-chelate complexes (*vide supra*) always resulted in exclusive formation of the bis-chelate complexes. We thought that the third bpy or phen would not coordinate to molybdenum(III) in a strongly acid medium. Addition of a small amount of 0.5 mol dm^{-3} sodium hydroxide solution free from oxygen to the reaction mixture gave a blue solution even at a pH less than unity. This solution was evaporated to dryness to leave a purple-gray residue which gave an infrared absorption band at 950 cm^{-1}, suggesting the presence of Mo=O bond.[1] When $[MoCl_2(phen)_2]Cl\cdot 4H_2O$ and phen were mixed in ethanol free from oxygen in the Schlenk tube, the color also turned blue within 1 h. When this complex was dissolved in ethanol without phen, the color remained orange for 1 h even in the presence of oxygen. This solution turned black, and then almost colorless after 1 d. No attempt was made for clarifying the oxidation process of the molybdenum(III).

Preparation of $[MoL_3]X_3$ (L=bpy, phen; $X^-=Cl^-$, Br^-, I^-) was reported previously by Steele[5] and Carmichael *et al.*[7] We repeated Carmichael's method,[7] *i.e.* MoI_3 was treated with molten bipyridine, and obtained a black-brown powder, of which the elemental analysis (C, H, N, I) was closer to $[MoI_2(bpy)_2]I$ rather than to $[Mo(bpy)_3]I_3$. Further attempts to obtain crystals of $[MoI_2(bpy)_2]I$ or $[Mo(bpy)_3]I_3$ from the powder were unsuccessful. Thus the hitherto reported "tris-chelate complexes" deserve further experimental evidence for the formulation.

Tris(bpy) and tris(phen) complexes of chromium(III) have not been prepared by the ligand substitution,[15,16] but obtained by the oxidation of the tris-chelate complexes of chromium(II).[16,17] Such an oxidation method cannot be applied to the molybdenum(III) complexes since the corresponding uninuclear molybdenum(II) complexes are not known.

Geometrical Structure. The present complexes, $[MoCl_2L_2]^+$ can occur in *cis* and *trans* forms. The shape of crystals (orange prismatic crystals in the case of $[MoCl_2(phen)_2]Cl\cdot 4H_2O$) of the complex salts and their absorption patterns in solution did not change on further recrystallization from methanol, ethanol or acetonitrile, suggesting no change in the

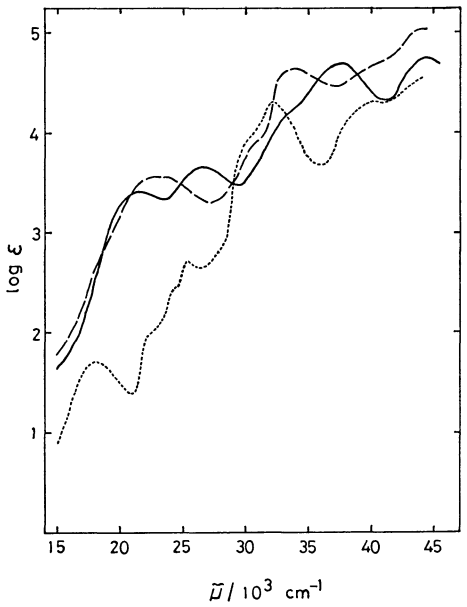

Fig. 1. Absorption spectra of $[MoCl_2(bpy)_2]Cl \cdot 2H_2O$ in methanol (— —), *cis*-$[MoCl_2(phen)_2]Cl \cdot 4H_2O$ in methanol (——) (under nitrogen atmosphere) and *cis*-$[CrCl_2(bpy)_2]Cl$[19] in 1:1 aqueous methanol (----).

geometrical structure of molybdenum complex cation. The X-Ray diffraction method disclosed *cis* structure for $[MoCl_2(phen)_2]Cl \cdot 4H_2O$.[18] No such information is available for the salts of $[MoCl_2(bpy)_2]^+$.

Electronic and infrared absorption spectra did not give straightforward evidence for their geometrical isomerism. Absorption spectral patterns of the two complex cations in the visible region are apparently different from each other (Fig. 1); two peaks for the phen complex and one broad band for the bpy complex in the region from 20000 to 30000 cm^{-1}. However, such a difference cannot be taken as an evidence for different geometrical isomerism of these two complex cations, since the nature of the absorption bands are of charge-transfer type (*vide infra*) and their relation to the geometrical isomers would not be simple. Since all the known geometrical structures of dihalobis(2,2'-bipyridine) type complexes with various metal ions are *cis*,[19-25] we tend to consider that the bpy complex is also of the *cis* form.

Absorption Spectra. The absorption spectra in all the solvents except water changed only very slightly over 100 min at room temperature. Whenever the spectrum (patterns and/or intensity) changed, it was measured for 100 min at ten minutes intervals and the original pattern was estimated by the extrapolation to zero time. The spectrum changed so rapidly in water (pH $\approx$7) that the zero-time spectrum was not obtained. The complex solution in 0.1 mol dm^{-3} hydrochloric acid was relatively stable, and the original absorption spectrum was estimated.

General Features: The absorption curves of the 2,2'-bipyridine and 1,10-phenanthroline complexes are shown in Fig. 1, together with that of *cis*-$[CrCl_2(bpy)_2]^+$.[19] In the visible region (<30000 cm^{-1}), the bpy and the phen complexes of molybdenum(III) have one broad and two distinct peaks, respectively,

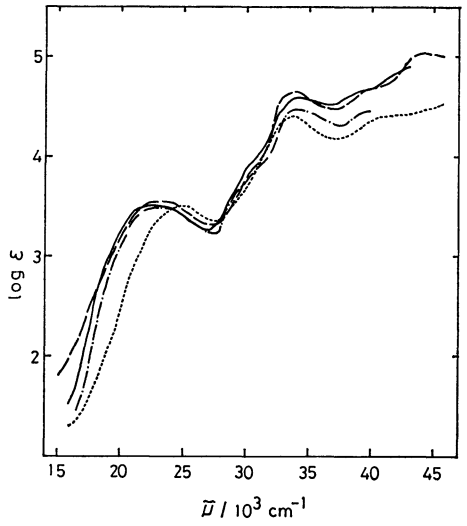

Fig. 2. Absorption spectra of $[MoCl_2(bpy)_2]Cl \cdot 2H_2O$ in dichloromethane (——), in acetonitrile (— —), in methanol (—·—) and 0.1 mol dm^{-3} hydrochloric acid (----) (under nitrogen atmosphere).

with extinction coefficients between 2000 and 4000 $dm^3\ mol^{-1}\ cm^{-1}$. Two or three much stronger absorption peaks ($\log \varepsilon > 4$) are observed in the ultraviolet region (>30000 cm^{-1}). Some of the peaks shift in different solvents, but the overall pattern remains almost unchanged, and the nature of absorption bands is discussed on the basis of the spectra in methanol (Fig. 1, *vide infra*).

Bands in the Ultraviolet Region: The phen complex shows two distinct bands at 44250 cm^{-1} and 37840 cm^{-1}, which are assigned to the intraligand transitions corresponding to the two bands of free 1,10-phenanthroline at 44440 cm^{-1} and 37880 cm^{-1} in methanol. Similarly, bands of the bpy complex at 40000 cm^{-1} and 33900 cm^{-1}, are of intraligand transition nature corresponding to the two bands of free 2,2'-bipyridine at 42550 cm^{-1} and 35570 cm^{-1}. The peaks of free ligand shift to lower energy on coordination to the metal ion, as reported for other metal complexes.[26,27]

Bands in the Visible Region: The bpy complex in methanol gives apparently one very broad maximum at 22800 cm^{-1}, which seems to involve two or more transitions as indicated by the spectra in different solvents (Fig. 2); *i.e.* the bpy complex gives a maximum at 24770 cm^{-1} and no shoulder is appreciable in 0.1 mol dm^{-3} hydrochloric acid, but a prominent shoulder is observed at a lower wave number in a less polar solvent. The phen complex gives two bands at 26740 cm^{-1} and 21510 cm^{-1} in methanol. The shape of the two bands of $[MoCl_2(phen)_2]^+$ did not change in different solvents (Fig. 3).

All these bands have extinction coefficients between 2000 and 4000 $dm^3\ mol^{-1}\ cm^{-1}$, too strong to be assigned to the d-d transition. The spectral data of the other metal complexes having the same ligand environment are shown in Table 1. The extinction coefficients of the complexes of chromium(III),[19] cobalt(III),[20,21] and rhodium(III)[22,28] are different from those of the complexes of iridium(III),[23,28] iron-

TABLE 1. SPECTRAL DATA OF (a) *cis*-DICHLOROBIS(DIIMINE)TYPE COMPLEXES AND (b) MOLYBDENUM(III) COMPLEXES CONTAINING bpy OR phen IN THE VISIBLE REGION

	Complex	$\tilde{\nu}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})	Assignment	Solvent	Reference
(a)	$[MoCl_2(bpy)_2]^+$	22820 (3630)	d-π*	CH_3OH	This work
	$[MoCl_2(phen)_2]^+$	21510 (2570) 26740 (4420)	d-π*	CH_3OH	This work
	$[CrCl_2(bpy)_2]^+$	18020 (46) 22400^{sh} (100)	d-d	H_2O-CH_3OH (1 : 1)	19
	$[FeCl_2(bpy)_2]$	18870 (1540) 27780 (2700)	d-π*	CH_2Cl_2	24
	$[RuCl_2(bpy)_2]$	18020 (9200) 26460 (9170)	d-π*	CH_2Cl_2	24, 25
	$[OsCl_2(bpy)_2]$	17910 (12000) 26110 (11500)	d-π*	CH_2Cl_2	24, 25
	$[CoCl_2(bpy)_2]^+$	17100 (100) 18300 (125)	d-d	H_2O	21
	$[CoCl_2(phen)_2]^+$	19230 (60) 21650 ($\approx$100)	d-d	H_2O	20
	$[RhCl_2(bpy)_2]^+$	25800^{sh} (110)	d-d	H_2O	22, 28
	$[RhCl_2(phen)_2]^+$	26100^{sh} (110)	d-d	H_2O	22, 28
	$[IrCl_2(bpy)_2]^+$	28570 (2400)	d-π*	H_2O	28, 30
	$[IrCl_2(phen)_2]^+$	27780 (3300)	d-π*	H_2O	23, 31
(b)	$[MoCl_4(bpy)]^-$	18380 (1210)	d-π*	$(CH_3)_2NCHO$	8
	$[MoCl_4(phen)]^-$	18690 (2720)	d-π*	$(CH_3)_2NCHO$	8
	$[MoCl_3(py)(bpy)]$	20330 (1275)	d-π*	$(CH_3)_2NCHO$	8

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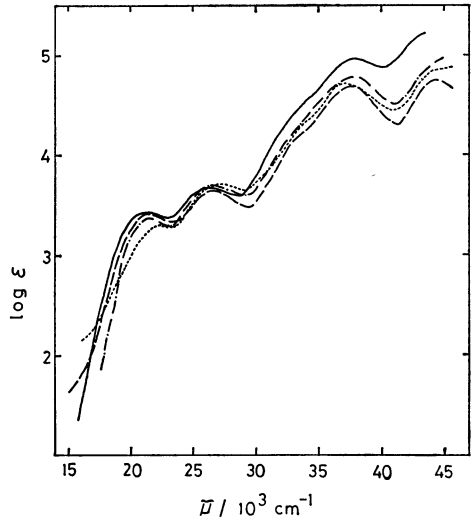

Fig. 3. Absorption spectra of *cis*-$[MoCl_2(phen)_2]Cl \cdot 4H_2O$ in dichloromethane (——), in acetonitrile (— —), in methanol (—·—), and in 0.1 mol dm^{-3} hydrochloric acid (----) (under nitrogen atmosphere).

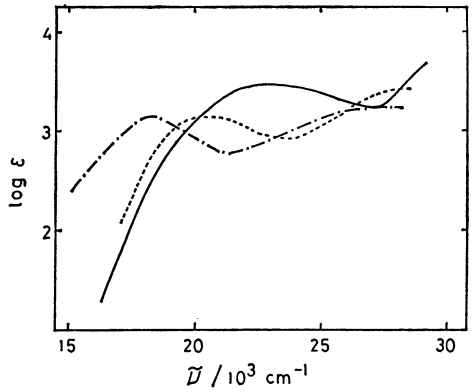

Fig. 4. Absorption spectra in *N*,*N*-dimethylformamide of $[MoCl_2(bpy)_2]^+$ (——), $[MoCl_3(bpy)(py)]$[8] (----), and $[MoCl_4(bpy)]^-$[8] (—·—) (under nitrogen atmosphere).

(II),[24] ruthenium(II),[24,25] and osmium(II).[24,25] The absorption bands of the former and the latter group of complexes have been assigned to the d-d transitions, and the metal-to-ligand charge transfer (d-π*) transitions, respectively. The extinction coefficient, as well as the ease of oxidation of molybdenum(III) state, suggest that the bands of *cis*-$[MoCl_2(phen)_2]^+$ and $[MoCl_2(bpy)_2]^+$ in the visible region are of the d-π* charge transfer type.

The difference in spectral pattern of d-π* transitions between the bpy and the phen complexes is found in the complexes of other metal ions. The d-π* transitions (near 23000 cm^{-1}) appear as a sharp maximum and a prominent shoulder for $[Ru^{II}(bpy)_3]^{2+}$ and two distinct peaks for $[Ru^{II}(phen)_3]^{2+}$.[29] *cis*-$[Ir^{III}Cl_2(bpy)_2]^+$ shows one maximum near 28000 cm^{-1},[28,30] while *cis*-$[Ir^{III}Cl_2(phen)_2]^+$ shows one maximum and a prominent shoulder.[23,31] Also an appreciable difference is observed between the tris(bpy) and the tris(phen) complexes of iron(II)[32] as well as osmium(II).[33] On the other hand, the difference is very small between *cis*-$[Fe^{II}Cl_2(bpy)_2]$ and *cis*-$[Fe^{II}Cl_2(phen)_2]$.[24,25,34]

Thus the d-π* spectral pattern is not necessarily similar between the bpy and the phen complexes. The difference of the spectral patterns of the present complexes does not contradict our assignment of the d-π* charge transfer transitions.

Comparison with Analogous Molybdenum(III) Complexes in the Visible Region: The absorption bands of (bpyH)-[$MoCl_4$(bpy)] and [$MoCl_3$(bpy)py] in the visible region[8] (Fig. 4) must be of charge-transfer type as judged from their intensity. The absorption peaks give blue shift with decrease in number of chloride ligand. This fact implies that these bands involve the transition from d-orbitals of molybdenum(III) to the ligand π^*-orbital. The increase in number of nitrogen (the decrease in number of chloride) causes the increase in the degree of d-orbital splitting which would increase the gap between the occupied d-orbitals and the ligand π^*-orbitals. The change in overall charge of the complexes can be also responsible for the band shift.[35]

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