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Synthesis and Electrochemical Properties of Binuclear Molybdenum Carbonyl Complexes with Bridging α,α′-Diimine Ligands

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Abstract

New binuclear molybdenum complexes with bridging ligands derived from 2-pyridinecarbaldehyde and the diamines such as hydrazine, *p*-phenylenediamine, *p*-xylylenediamine, and 4,4′-diaminobiphenyl were prepared, to elucidate the effect on the separated distance and π-conjugation between two metal centers. All the complexes exhibit the low lying metal-to-ligand charge transfer (MLCT) bands at *ca.* 500 nm. The cyclic voltammogram shows either a single broad two-electron wave, or two one-electron reduction waves, depending on the nature of the bridging ligand. The MLCT band and the reduction behavior are rationalized in terms of the interaction between LUMO orbitals of two molybdenum-α,α′-diimine moieties.

Introduction

Extensive studies have been carried out in regard to the optical and electrochemical properties of complexes of the type $M(CO)_4L$ (M = Cr, Mo, or W; L = 2,2′-bipyridine(bpy) or α,α′-diimine) [1]. The ligand 2,2′-bipyridine or α,α′-diimine has the energetically low-lying ligand π* orbitals which enable a back donation of electrons from filled d-metal orbitals to empty ligand orbitals. As a consequence, the complexes $M(CO)_4L$ exhibit the metal-to-ligand charge transfer (MLCT) transition and reversible reduction processes [1, 2].

Recently, binuclear and multinuclear complexes have been paid much attention because of the possibility of multielectron transfer and cooperative reactivity between metals [3]. In the present study we describe the synthesis of binuclear Mo complexes based on a ligand system which contains two α,α′-diimine moieties (Fig. 1). When considered with the accumulated electrochemical results of monomeric $M(CO)_4L$ [1d, 2], these binuclear complexes bridged by two α,α′-diimine moieties can be expected to have the potential to serve as multielectron transfer reagents. Until now, several papers about the synthesis and electrochemical behavior of binuclear Mo and W complexes with bridging ligands such as pyrazine [4], 2,2′-bipyrimidine [1g], *p*-benzoquinonediimine [5], and 4,4′-bipyridine [6] have appeared.

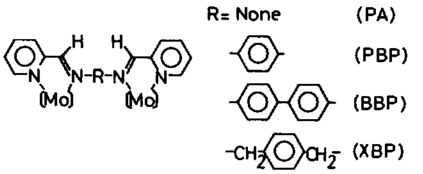

Fig. 1. Structure of the ligands and their abbreviations.

Experimental

Materials

$Mo(CO)_6$ (Strem Chem.) was of reagent grade and was used as supplied. Pyridinecarbaldehyde, *o*-phenylenediamine, *o*-xylylenediamine, benzidine-(4,4′-diaminobiphenyl), and hydrazine monohydrate were used without further purification. Tetrabutylammonium perchlorate (TBAP) was recrystallized from ethanol, and vacuum-dried. Benzene was dried over sodium, and distilled. Dimethylformamide (DMF) was distilled *in vacuo* prior to use.

Ligand Synthesis

2-Pyridine aldazine (PA) was synthesized as described in the literature [7].

p-Phenylenebis(picolinaldimine) (PBP)

2-Pyridinecarbaldehyde (10.0 g, 0.09 mol) was added dropwise to a stirred solution of *p*-phenylenediamine (5.1 g, 0.05 mol) in ethanol (70 ml) at 60 °C. The reaction mixture was refluxed for 2 h, during which time the color of the solution changed to red. The resulting solution was cooled to 0 °C. The yellow precipitate was filtered and recrystallized from ethanol, 66% yield, m.p. 152–153 °C. *Anal.* Calcd for $C_{18}H_{14}N_4$: C, 75.49; H, 4.94; N, 19.57. Found: C, 75.58; H, 4.80; N, 19.52%.

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p-Xylylenebis(picolinaldimine) (XBP) and p-biphenylenebis(picolinaldimine) (BBP)

These were similarly prepared by the reaction of 2-pyridinecarbaldehyde with an appropriate diamine, recrystallized from ethanol (60 and 70% yield, respectively). XBP: m.p. 122–123 °C. *Anal.* Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.28; H, 5.79; N, 17.72%. BBP: m.p. 176–178 °C. *Anal.* Calcd for $C_{24}H_{18}N_4$: C, 79.53; H, 5.01; N, 15.46. Found: C, 78.57; H, 4.92; N, 15.24%.

Synthesis of Complexes

All experimental manipulations were performed under nitrogen using the typical Schlenk-type technique.

[p-Phenylenebis(picolinaldimine)] bis[tetracarbonylmolybdenum], [Mo(CO)4]2(PBP)

Solid PBP (1.0 g, 3.5 mmol) was added to $Mo(CO)_6$ (1.8 g, 7.0 mmol) in benzene (100 ml) at 60 °C. The reaction mixture was refluxed for 20 h, during which time gas was evolved and a crystalline precipitate was gradually formed. The resulting precipitate was collected by filtration, washed with benzene, and dried *in vacuo*. Yield, 2.4 g (96%). *Anal.* Calcd for $C_{26}H_{14}N_4O_8Mo_2$: C, 44.47; H, 2.01; N, 7.98. Found: C, 44.48; H, 2.13; N, 8.04%.

The other molybdenum complexes, $[Mo(CO)_4]_2(L^a)$ (L^a = BBP, XBP, and PA), were prepared as mentioned above; L^a = BBP: *Anal.* Calcd for $C_{32}H_{18}N_4O_8Mo_2$: C, 49.38; H, 2.33; N, 7.20. Found: C, 50.44; H, 2.67; N, 7.55%. L^a = XBP: *Anal.* Calcd for $C_{28}H_{18}N_4O_8Mo_2$: C, 46.05; H, 2.48; N, 7.67. Found: C, 46.03; H, 2.64; N, 7.75%. L^a = PA: *Anal.* Calcd for $C_{20}H_{10}N_4O_8Mo_2$: C, 38.37; H, 1.61; N, 8.95. Found: C, 38.25; H, 1.73; N, 8.98%.

Physical Measurements

Infrared spectra were recorded in Nujol mulls or DMF solution on a Shimadzu IR-420 Spectrophotometer. Electronic spectra were obtained on a Shimadzu UV-210A double-beam spectrophotometer equipped with a 1 cm quartz cell.

Cyclic voltammograms were obtained with a Hokuto Denko HA-301 potentiostat-galvanostat, a Hokuto Denko HF-201 function generator and a Yokogawa Model 3086 x–y recorder. The three-electrode measurements were carried out with a Beckman stationary platinum disk in conjunction with a Pt-flag auxiliary electrode and a silver quasi-reference electrode. The silver quasi-reference electrode was calibrated by adding small amounts of ferrocene to the test solution.

Results and Discussion

Synthesis and Characterization

The binuclear complexes $[Mo(CO)_4]_2(L^a)$ (L^a = PBP, BBP, XBP, and PA) were obtained in good yield from the reaction between $Mo(CO)_6$ and the appropriate ligand L^a in the molar ratio 2:1. Attempts to prepare the mononuclear complexes $Mo(CO)_4(L^a)$ were unsuccessful. These new binuclear complexes are soluble in DMF, and insoluble in methanol, dichloromethane, and benzene. The IR spectra of the complexes $[Mo(CO)_4]_2(L^a)$ show four carbonyl ν(CO) bands (2020–1800 cm^{-1}) (Table I), which are similar to that of $Mo(CO)_4$(bpy) [8] and $[Mo(CO)_4]_2$(bpym) [1g] (bpym = 2,2′-bipyrimidine). This indicates the complexes $[Mo(CO)_4]_2(L^a)$ contain both *cis*-disubstituted $Mo(CO)_4$ moieties. The assignment of the IR stretching mode was obtained by using the Cotton-Kraihanzel method [9]. For the complex $[Mo(CO)_4]_2$(PA), five carbonyl bands were observed which may suggest the presence of the conformational isomers.

Electronic Spectra

The electronic spectra of new binuclear complexes are shown in Fig. 2, and electronic spectroscopic data are listed in Table I. All of the spectra exhibit

TABLE I. Infrared and Electronic Absorption Spectral Data of the Molybdenum Complexes.

Complex	ν(CO), cm^{-1} [a]				λ_{max}, nm (ε)[b]
	A_1	A_2	B_1	B_2	
$Mo(CO)_4$(bpy)[c]	2017	1878	1909	1829	463
$Mo(CO)_4$(bpym)[d]	2014	1869	1912	1832	468, 368
$[Mo(CO)_4]_2$(bpym)[d]	2013	1896	1920	1837	574, 380
$[Mo(CO)_4]_2$(PA)	1999	1882	1908	1842, 1827	529(5800), 375(5900), 299(25400)
$[Mo(CO)_4]_2$(PBP)	2016	1863	1918	1805	507(8400),[e] 338(23300), 307(27300)
$[Mo(CO)_4]_2$(BBP)	2002	1861	1908	1800	505(9200), 361(31700), 301(31700)
$[Mo(CO)_4]_2$(XBP)	2002	1871	1892	1814	483(10400), 386(5700), 300sh

[a] Recorded on Nujol mulls. [b] In DMF. [c] From Ref. [1a]. [d] From Ref. [1g]. [e] λ_{max} = 530 nm in dimethoxyethane and λ_{max} = 546 nm in benzene/DMF (19:1 v/v).

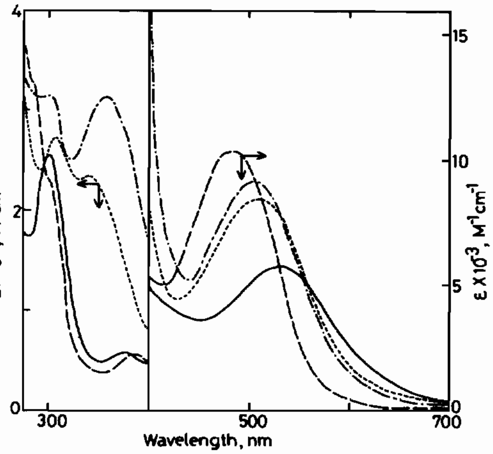

Fig. 2. Electronic absorption spectra of $[Mo(CO)_4]_2(L^a)$ in DMF; L^a = PA (———), PBP (-------), BBP (—-—-—), and XBP (— — —).

absorption maxima at *ca.* 500 nm. These intense low-energy absorption bands are remarkably similar to those of mononuclear $Mo(CO)_4L$ (L = bpy, bpym, and N-methylpicolinaldimine) [1]. In the mononuclear complexes $Mo(CO)_4L$ the low-energy band is markedly solvent dependent, and has been assigned to a metal-to-ligand charge transfer (MLCT) transition [1]. The observed absorption band shifts here to lower energy in less polar solvents such as dimethoxyethane and benzene/DMF (19:1 v/v) (Table I). Thus, these bands in binuclear complexes can also be assigned to MLCT transitions. The MLCT transition energy of $[Mo(CO)_4]_2(L^a)$ decreases in the order of L^a = XBP > BBP ⩾ PBP > PA, which suggests that the LUMO energy of the binuclear complexes (mainly π^* orbital energy of α,α'-diimine moieties in the ligand L^a) decreases in that order. The absorption bands below 400 nm may be composed of a second MLCT, ligand field, or intraligand transitions. However, these bands have not been assigned because of their overlapping. The similarity of the absorption spectra in the low-energy regions of binuclear $[Mo(CO)_4]_2(L^a)$ to that of mononuclear $Mo(CO)_4L$ complexes suggests that the electronic structure of the binuclear complexes can be treated by considering the perturbation interaction of two monomeric Mo-α,α'-diimine complexes.

Electrochemistry

The cyclic voltammograms of ligands in DMF exhibit one or two reduction processes, which are all irreversible except for the first reduction process of PA (Table II). When the ligand is incorporated into a complex, the reduction processes increase the reversibility and the reduction potentials of complexes are 0.6 ~ 0.8 V more positive than those of free ligands. The electrochemical behavior of $[Mo(CO)_4]_2(L^a)$ can be classified into two types; the typical cyclic voltammograms of L^a = PA and BBP complexes in DMF are illustrated in Fig. 3. The PA complex shows two well-separated waves (Fig. 3a). Both are quasi-reversible one-electron reductions when judged by the separation between the anodic and the cathodic peak potentials and the ratio of the cathodic to the anodic peak currents [10]. On the other hand, the cyclic voltammograms of the BBP complex gives a single broad wave (Fig. 3b), which consists of the two-electron reduction process confirmed by coulometry. The electrochemical data for all the ligands and complexes obtained here in DMF solution are summarized in Table II. No reversible oxidation processes are observed for all the complexes.

In the reduction steps the electron will be added to the LUMO orbital mainly composed of ligand π^* orbital, by comparing with the redox behaviors of

TABLE II. Electrochemical Data for Ligand L^a and their Binuclear Molybdenum Complexes.

Compound	$E^{1/2}$, V *vs.* SCE[a]		K[b]
	E^1	E^2	
PA	−1.49(70),	−1.98(irr)	
PBP	−1.57(irr),	−2.04(irr)	
BBP	−1.82(irr)		
XBP	−2.08(irr)		
$[Mo(CO)_4]_2(PA)$	−0.66(70),	−1.17(85)	4.8 X 10^8
$[Mo(CO)_4]_2(PBP)$	−0.94(65),	−1.17(87)	7.8 X 10^3
$[Mo(CO)_4]_2(BBP)$	−1.10(138)		~15
$[Mo(CO)_4]_2(XBP)$	−1.36(110)		~5

[a] Half-wave potentials are measured in DMF solution containing 0.1 M TBAP as a supporting electrolyte at scan rate of 100 mV/s. The values in parentheses are differences in anodic and cathodic peak potentials; irr = irreversible. [b] Calculated values of coproportionation constant.

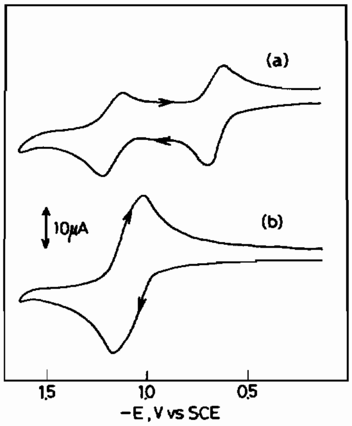

Fig. 3. Cyclic voltammograms of 1 mM $[Mo(CO)_4]_2(L^a)$ (L^a = PA(a) and BBP(b)) in 0.1 M TBAP/DMF; scan rate 100 mV/s.

of mononuclear $\mathrm{Mo(CO)_4(bpy)}$ [1d, 2]. The first reduction potentials of the complexes $[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})$ move anodically in the order of $\mathrm{L^a}$ = PA < PBP < BBP < XBP, which reflects the lowering of LUMO energy of the ligand $\mathrm{L^a}$. The reduced forms of ligands in the complexes are more stabilized by ligation than are those of free ligands, and the degree of stabilization can be estimated roughly as 0.6 ~ 0.8 V.

For molecules that contain two chemically equivalent and reversible redox sites, the difference in potential between the half-reactions of the successive electron transfers can depend on the extent of interaction between the sites; larger potential difference indicates stronger interaction [10, 11]. The difference ΔE (= $E^1 - E^2$) is related to the conproportionation constant K as follows:

$$[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a}) + \mathrm{e^-} \rightleftharpoons [\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})^- \qquad E^1$$

$$[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})^- + \mathrm{e}- \rightleftharpoons [\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})^{2-} \qquad E^2$$

$$[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a}) + [\mathrm{Mo(CO)_4}]_2(\mathrm{L_a})^{2-} \overset{K}{\rightleftharpoons} 2\,[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})^-$$

$$\Delta E = E^1 - E^2 = 0.0591 \log K \text{ (at 25 °C)}.$$

Since the value of K (Table II) for the binuclear complexes $[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})$ decreases in the order of $\mathrm{L^a}$ = PA > PBP > BBP > XBP, the extent of interaction between Mo–α,α'-diimine moieties decreases in that order. This decreasing trend results from the extent of π-conjugation of ligand $\mathrm{L^a}$ in $[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})$. As the XBP ligand is unconjugated beyond the α,α'-diimines, the interaction between two Mo–α,α'-diimine moieties is weak, and therefore a single broad two-electron reduction wave is observed as a result of the small potential difference. On the other hand, the PA ligand has a high degree of π-conjugation and can closely bind two $\mathrm{Mo(CO)_4}$ moieties. The interaction between two Mo moieties in $[\mathrm{Mo(CO)_4}]_2(\mathrm{PA})$ is relatively strong and two one-electron reduction processes are observed. The energy repulsion between a pair of electrons on the highest occupied antibonding orbital of $[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})^{2-}$ will also be responsible for the potential difference ΔE, as discussed for the organic systems previously [12]. The distance between Mo–α,α'-diimine moieties in the PBP complex is shorter than that in the BBP complex, which means the reduced form of PBP complex has larger repulsion energy between electrons and a larger potential difference than that of BBP complex.

It is of interest to examine whether there exists a relationship between the first reduction potential E^1 and the MLCT transition energies. Plots of E^1 *vs.* transition energies, $\nu_{\max}$ (MLCT), are almost linear; the complex with lower reduction potential exhibits the higher transition energies. This result indicates that the relative LUMO energy level of the binuclear complexes $[\mathrm{Mo(CO)_4}]_2(\mathrm{L^a})$ decreases by increasing the interaction between Mo–α,α'-diimine moieties.

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