

CHEMISTRY OF Mo(O), W(O) AND Cr(O) CARBONYLS

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New binuclear $[M(\text{CO})_4]_2$ ($L-L$) ($M = \text{Cr}, \text{W}$; ($L-L$) = *p*-phenylene bis(picolinaldehyde) or *p*-biphenylene bis(picolinaldehyde) compounds are synthesized. The reactions of the binuclear complexes of Mo and W, viz. $[M(\text{CO})_4]_2$ ($L-L$) [$M = \text{Mo}, \text{W}$; $L-L = \text{PBP}$ or BBP] were carried out with various π -acceptor ligands. The influences of basicity and bulkyness of EPh_3 ($E = \text{P}, \text{As}, \text{Sb}$) group on the stability of the complexes are discussed. Furthermore, the solvatochromic effect of M to L CT band is elaborated in detail.

Oxidative addition reactions of $[M(\text{CO})_4]_2$ ($L-L$) ($M = \text{Mo}, \text{W}$; ($L-L$) = PBP, BBP) with iodine and mercuric chloride were also carried out.

Key Words : Metal Carbonyls; Solvatochromic Effect; π -Acceptor Ligands; Binuclear Complexes; Redox Behavior

INTRODUCTION

BINUCLEAR transition metal complexes constitute one of the most important classes of compounds. These play a central role in the intramolecular redox processes by electronic interaction between the metal centres through a common binucleating ligand.¹⁻³ Recent studies have shown a great promise in this direction by binuclear metal carbonyl complexes with ligands having two $\alpha-\alpha'$ diimine moieties, particularly by the study of simple derivatives of $[\text{Mo}(\text{CO})_4]_2$ ($L-L$) ($L-L = \alpha-\alpha'$ diimine).⁴⁻⁶ Furthermore, an attempt has also been made to synthesize the analogous binuclear system with other group VI metals. These complexes show very intense solvatochromic charge transfer bands in the visible region which prompted us to make a little more detailed investigation regarding the bonding properties of $[M(\text{CO})_4]_2$ ($L-L$) [$M = \text{Mo}, \text{W}$; $L-L = \text{PBP}; \text{BBP}^*$] compounds where the metal centres are bridged through conjugated double bonds.

Furthermore, there is considerable current interest in the seven coordinated complexes of the type $[\text{MX}_2(\text{CO})_3 L_2]$ [$M = \text{Mo}, \text{W}$; $X = \text{Cl}, \text{Br}$; $L = \text{PPh}_3, \text{AsPh}_3$], which have recently been found to be good catalysts for the ring opening polymerization of norbornene and norbornadiene.^{7,8} Therefore, it will also be interesting if a study related to the oxidative elimination reactions of $[M(\text{CO})_4]_2$ ($L-L$) [$M = \text{Mo}, \text{W}$; ($L-L$) = PBP, BBP] be carried out. The results of such studies are reported herein.

*PBP = *p*-phenylene bis(picolinaldimine); BBP = *p*-biphenylene bis(picolinaldimine).

EXPERIMENTAL

All reagents used were of AnalAR grade. The metal carbonyls were purchased from Fluka Chemical Co. The ligands, PBP (*p*-phenylene bis(picolinaldimine) and BBP (*p*-phenylene bis(picolinaldimine) were prepared by the literature methods.⁶ Pyridine-2-carbaldehyde, phenylenediamine and benzidine were purchased from Merck. The solvents, benzene, dichloromethane, chloroform, tetrahydrofuran, acetone, acetonitrile, benzonitrile and propylene carbonate(PC) were of spectroscopic grade and were distilled prior to their use. Zn-Hg amalgam (2-3 per cent) was prepared as reported.⁹

The microanalytical, vibrational and the electronic spectral data were taken as described earlier.¹⁰ The EPR spectra in tetrahydrofuran were recorded on Varian 109E. X-band spectrometer at room temperature and liquid nitrogen temperature.

Synthesis of $[M(CO)_4]_2 (L-L)$ ($M = Cr, W$; $(L-L) = PBP, BBP$)

Metal hexacarbonyl and the ligand in the mole ratio of 2 : 1 were refluxed in 10ml toluene under nitrogen for 20h whereby the colour of the solution changed to dark green. The insoluble chromium compound (dark brown) was separated from the solution which was washed with benzene and petroleum ether. In the case of tungsten, a reddish brown compound was precipitated from the refluxed solution by the addition of petroleum ether which was recrystallized from dichloromethane/petroleum ether, and washed successively with petroleum ether. The compounds were then dried *in vacuo* and analyzed (yield, 60 per cent).

Synthesis of $[(M(CO)_3 Y)_2 (L-L)]$ ($M = Mo, W$; $(L-L) = PBP, BBP$; $Y = PPh_3, AsPh_3, SbPh_3, Py, Diphos$)

To a solution of $[M(CO)_4]_2 (L-L)$ (.25mmol) in 20ml of tetrahydrofuran ($M = Mo$)/toluene ($M = W$), an excess of the ligand Y (1mmol) was added. The mixture was refluxed under nitrogen for 20h. The dark green solution thus obtained was filtered* and petroleum ether was added to the filtrate, where upon a green compound was obtained. It was recrystallized** from dichloromethane/petroleum ether, washed successively with petroleum ether and dried under vacuo (yield, 70 per cent).

Synthesis of $[M(CO)_3 I_2]_2 (L-L)$ ($M = Mo, W$; $(L-L) = PBP, BBP$)

To the suspension of $[(M(CO)_4]_2 (L-L)]$ (.25mmol) in 25ml of tetrahydrofuran, iodine (.3mmol) was added and the solution was stirred for 4h, whereby the colour of the solution changed to orange brown. The resulting solution was filtered and the filtrate was concentrated to 5ml under reduced pressure. Excess petroleum ether was added to the concentrate whereupon orange brown microcrystalline compound was obtained. It was separated and recrystallized from

*When $Y = AsPh_3, SbPh_3$, the solution was filtered and worked up under N_2 atmosphere.

**For $Y = AsPh_3, SbPh_3$, a little exposure to air during recrystallization decomposed the compounds. The order of decomposition rate was $AsPh_3 < SbPh_3$.

tetrahydrofuran/petroleum ether, washed with petroleum ether and dried under vacuo (yield, 40 per cent).

Synthesis of $[(M(CO)_3(HgCl)(Cl))_2(L-L)]$ ($M = Mo, W$; $(L-L) = PBP, BBP$)

To the suspension of $[M(CO)_4]_2(L-L)$, (0.25mmol) in 20ml tetrahydrofuran, stoichiometric amount of mercuric chloride was added and the solution was stirred for 4.5h whereby the colour of the solution changed to bright orange-red. The solution was filtered and its volume was reduced to 5ml, at reduced pressure. Petroleum ether was added to the concentrate, whereby an orange compound separated out. It was filtered, recrystallized from tetrahydrofuran/petroleum ether, washed with petroleum ether and dried under vacuo (yield, 50 per cent).

Redox Reaction of $[Mo(CO)_4]_2(L-L)$ ($(L-L) = PBP, BBP$)

The suspension of $[Mo(CO)_4]_2(L-L)$ (.25mmol) in 20ml of tetrahydrofuran was stirred with excess of 2-3 per cent ZnHg amalgam under N_2 atmosphere for 24h. The solution was filtered to remove ZnMg amalgam and other insoluble materials. The colour of the filtrate changed from violet to blood red. The red solution was concentrated and light petroleum was added to the concentrate. The red coloured compound, thus obtained, was recrystallized from dichloromethane/petroleum ether, washed with petroleum ether and dried under vacuo (yield, 60 per cent).

RESULTS AND DISCUSSION

The reaction of $\alpha-\alpha'$ diimine ligands, PBP and BBP with metal hexacarbonyls in 1 : 2 molar ratio yielded stable dinuclear complexes of the form $[M(CO)_4]_2(L-L)$. They all have low solubility in common organic solvents. The microanalytical data matched well with the proposed formulation (Table I). Their reactions with π -acceptor ligands like triphenylphosphine, etc. yielded complexes in which one of the carbonyl groups is substituted with the incoming ligand. The compounds $[(M(CO)_3Y)_2(L-L)]$ [$M = Mo, W$; $(L-L) = PBP, BBP$; $Y = AsPh_3, SbPh_3, Py$] were highly unstable and on exposure to air decomposed to brown insoluble solids.

IR Spectra

The infrared spectra of the tetracarbonyl compounds exhibited in the region 2100-1800 cm^{-1} , characteristic infrared spectral pattern of $[M(CO)_4]$ group and those of tricarbonyl complexes, characteristic band pattern of $M(CO)_3$ group having C_s symmetry, similar to those observed for $[Mo(CO)_4bipy]$ and $[Mo(CO)_3bipyPPh_3]$ respectively.¹¹ The spectra of $[M(CO)_3Y]_2(L-L)$ is analogous to $[Mo(CO)_3bipyPPh_3]$ in the region of ν_{CO} having the infrared active modes A' & B , where E mode is in general split into A' and A'' .¹² This also suggests that the substitution of CO by the π -acceptor ligand takes place at a *cis*-position with respect to $(L-L)$, thereby causing lowering of ν_{CO} .

TABLE I
 Microanalytical and infrared spectral data of compounds

S. No.	Compound	Col-our	C	H	N	M	ν_{CO} (cm ⁻¹)	δ_{M-C-O}	ν_{C-N}
1	2	3	4	5	6	7	8	9	10
1.	[Mo(CO) ₄] ₂ PBP] ^r	R	44.6 (44.5)	2.0 (2.01)	8.1 (8.0)	26.8 (27.4)	2010, 1865, 1910, 1820	610, 590, 550	1604
2.	[(Mo(CO) ₄] ₂ BBP] ^r	R	49.1 (49.4)	2.4 (2.3)	7.4 (7.2)	23.7 (24.6)	2000, 1870, 1900, 1830	610, 585, 540	1604
3.	[Cr(CO) ₄] ₂ PBP]	BB	50.2 (50.8)	3.1 (2.3)	8.9 (9.1)	16.5 (16.9)	2000, 1870, 1900, 1830	640, 550	1602
4.	[(Cr(CO) ₄] ₂ BBP]	BB	55.8 (55.6)	3.2 (2.6)	7.8 (8.1)	14.7 (15.0)	2010, 1860, 1910, 1835	640, 550	1602
5.	[W(CO) ₄] ₂ PBP]	RB	35.2 (35.6)	2.5 (1.6)	6.1 (6.4)	41.2 (42.0)	2000, 1860, 1900, 1820	635, 540	1608
6.	[W(CO) ₄] ₂ BBP]	RB	39.8 (40.2)	2.5 (1.9)	5.2 (5.9)	39.1 (38.6)	2000, 1860, 1900, 1830	640, 545	1608
7.	[Mo(CO) ₃ PPPh ₃] ₂ PBB]	G	60.9 (61.6)	4.5 (3.8)	4.2 (4.8)	16.0 (16.4)	1920, 1800, 1832	630, 600, 510	1590
8.	[Mo(CO) ₃ PPh ₃] ₂ BBP]	G	57.2 (57.7)	4.3 (3.8)	3.9 (4.5)	15.2 (15.4)	1930, 1810, 1840	635, 595, 515	1590
9.	[W(CO) ₃ PPPh ₃] ₂ PBP]	G	54.1 (53.5)	4.1 (3.3)	3.9 (4.2)	26.8 (27.3)	1920, 1800, 1830	625, 590, 510	1595
10.	[W(CO) ₃ PPh ₃] ₂ BBP]	G	55.1 (55.7)	4.2 (3.4)	3.5 (3.9)	25.1 (25.9)	1925, 1800, 1830	625, 590, 510	1595
*11.	[Mo(CO) ₃ AsPh ₃] ₂ PBP]	G							
*12.	[Mo(CO) ₃ AsPh ₃] ₂ BBP]	G							
*13.	[W(CO) ₃ AsPh ₃] ₂ PBP]	G							
*14.	[W(CO) ₃ AsPh ₃] ₂ BBP]	G							
*15.	[Mo(CO) ₃ SbPh ₃] ₂ PBP]	G							
*16.	[Mo(CO) ₃ SbPh ₃] ₂ BBP]	G							
*17.	[W(CO) ₃ SbPh ₃] ₂ PBP]	G							
*18.	[W(CO) ₃ SbPh ₃] ₂ BBP]	G							
19.	[Mo(CO) ₃ Diphos] ₃ PBP]	G	62.9 (63.2)	4.5 (4.3)	3.5 (3.9)	13.1 (13.3)	1920, 1800, 1840	630, 600, 500	1590

TABLE I (Continued)

1	2	3	4	5	6	7	8	9	10	11
20.	[(MO(CO) ₂ Diphos) ₂ BBP] G	G	64.2 (64.8)	4.7 (4.3)	3.2 (3.7)	12.0 (12.6)		1920, 1810, 1840	630, 600, 510	1590
21.	[(W(CO) ₂ Diphos) ₂ PBP] G	G	55.8 (56.4)	4.2 (3.8)	3.2 (3.5)	21.9 (22.7)		1922, 1802, 1840	620, 585, 500	1595
22.	[(W(CO) ₂ Diphos) ₂ BBP] G	G	57.5 (58.0)	4.3 (3.9)	3.0 (3.3)	21.2 (21.7)		1920, 1805, 1840	620, 580, 500	1595
*23.	[(MO(CO) ₂ Py) ₂ PBP]	G								
*24.	[(MO(CO) ₂ Py) ₂ BBP]	G								
*25.	[(W(CO) ₂ Py) ₂ PBP]	G								
*26.	[(W(CO) ₂ Py) ₂ BBP]	G								
27.	[(Mo(CO) ₂ I ₂) ₂ PBP]	OB	25.1 (24.9)	1.8 (1.2)	4.5 (4.9)	44.2 (44.0)	15.9 (16.6)	2010, 1970, 1915	600	1600
28.	[(Mo(CO) ₂ I ₂) ₂ BBP]	OB	28.8 (29.2)	1.9 (1.5)	4.2 (4.6)	41.1 (41.3)	15.3 (15.6)	2030, 1975, 1935	595	1600
29.	[(W(CO) ₂ I ₂) ₂ PBP]	OB	22.2 (21.6)	1.3 (1.0)	3.9 (4.2)	37.9 (38.2)	27.2 (27.7)	2030, 1970, 1920	595	1600
30.	[(W(CO) ₂ I ₂) ₂ BBP]	OB	25.1 (25.6)	1.8 (1.3)	3.8 (4.0)	35.8 (36.1)	26.8 (26.2)	2025, 1975, 1925	590	1600
31.	[(Mo(CO) ₂ (HgCl)Cl) ₂ PBP] O	O	23.8 (24.2)	1.6 (1.2)	4.2 (4.7)	11.8 (12.0)	15.9 (16.1)	1980, 1880 (br)	590	1610
32.	[(Mo(CO) ₂ (HgCl) ₂ BBP] O	O	28.1 (28.5)	1.7 (1.4)	4.2 (4.4)	10.8 (11.2)	15.0 (15.2)	1985, 1880 (br)	585	1610
33.	[(W(CO) ₂ (HgCl)Cl) ₂ PBP] O	O	20.9 (21.1)	1.7 (1.0)	4.1 (4.1)	10.1 (10.4)	27.1 (27.0)	1980, 1875 (br) 1820 (sh)	590	1595
34.	[(W(CO) ₂ (HgCl)Cl) ₂ BBP] O	O	24.7 (25.0)	1.9 (1.3)	3.7 (3.9)	10.2 (9.8)	25.2 (25.5)	1980, 1880 (br) 1820 (sh)	580	1595

r = Reduced

R = Red, BB = Brown Black, RB = Reddish Brown, G = Green, OB = Orange Brown, O = Orange.

* = Compounds were highly unstable so they were characterized by electronic spectra only.

br = broad, sh = shoulder.

In all the complexes the coordination of the diimine ligand to the metal causes lowering of ν_{C-N} . The effect on the back bonding from metal to diimine by substituting a CO group by π -acceptor ligand, is nicely shown by the shifts towards lower energy side in the positions of ν_{C-N} of the ligand.

The infrared spectra of the brown insoluble compounds obtained after the decomposition of the $[M(CO)_3 Y]_2 (L-L)$ showed no bands arising due to carbonyl and coordinated ligands ($AsPh_3$, $SbPh_3$ etc). New intense bands however appear at 950 and 890cm^{-1} which can be assigned to $\nu_{M=O}$. On the basis of microanalytical data and the vibrational spectral features, the compounds were tentatively assigned the formulae $[MO_3]_2 (L-L)$. Due to its insolubility in most of the common organic solvents further study could not be carried out.

The $M(II)$ iodo complex shows i.r. spectral bands at around 2020, 1970 & 1920cm^{-1} characteristic of the other group VI iodo complexes having seven coordination.¹³ The spectra of the $M(II)$ mercurous chloride complex showed bands due to ν_{CO} at around 1980, 1880 and 1829cm^{-1} typical of the mercurous chloride $M(II)$ carbonyl complexes.¹⁴ In the reactions of mercuric chloride it is assumed that mercuric chloride attacks the metal centre as $HgCl$ and Cl .

Electronic Spectra

The electronic spectra of $M(O)$ complexes showed intense bands in the visible region at around 500nm in the case of tetracarbonyl complexes and at around 600nm in the tricarbonyl metal complexes. These have been assigned to metal to ligand charge transfer transition.^{6,11,15} In the ultraviolet region most of the bands have been the intra ligand bands. In going from the complexes of the ligand PBP to the ligand BBP, the bands are slightly blue shifted. On the basis of increased conjugation in BBP (due to two phenyl rings) one expected a red shift. The observed blue shift of the band positions shows that the two phenyl rings in BBP are not coplanar and are either prependicular or at some angle to each others. This nonplanarity of the ring because of the hindrance in the free rotation around C-C bond, will reduce the conjugation in BBP which will destabilize the π^* orbitals of the ligand causing a blue shift in the MLCT band position.

Substitution of CO by π -acceptor ligands in $[M(CO)_3 Y]_2 (L-L)$ has a large influence on the position of MLCT transition. Introduction of such a group destabilizes the metal d -orbitals.¹¹ The bands are therefore shifted to lower energy.

MLCT bands exhibited strong solvatochromic effect. Its position is blue shifted in all the polar solvents. Assigning C_{2v} geometry to $[(M(CO)_4)_2 (L-L)]$ molecule (*vide infra*) the ground state dipole lies along the z-axis with the negative charge built up in the carbonyl region. As the MLCT excitation is from metal to diimine, this transition is in opposition to the ground state dipole thereby shifting the MLCT transition to the blue in more polar solvents.

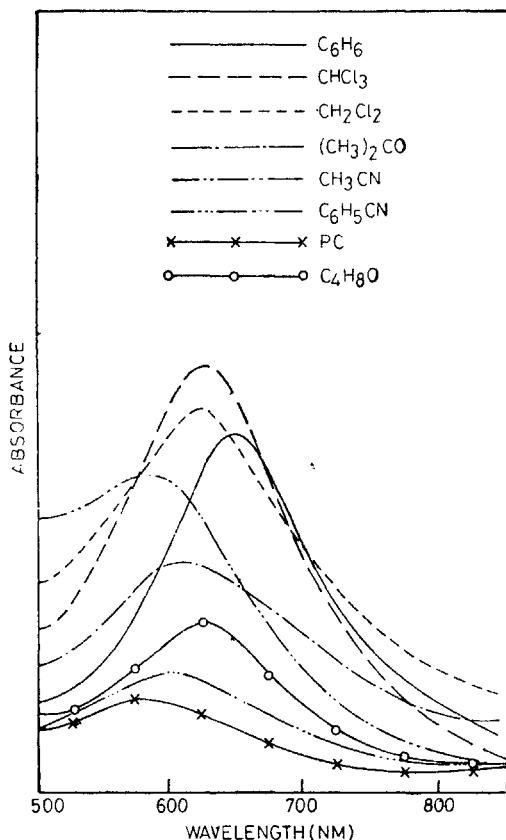


FIG 1 Spectra (*Abs Vs.* $\lambda_{(nm)}$) plots of $[\text{Mo}(\text{CO})_3\text{PPh}_3]_2$ (PBP) in various solvents, showing solvent dependence of MLCT band

The profound difference that solvent can play on CT band energies in $M(\text{O})$ diimine complexes is illustrated in Fig. 1 for $[(\text{Mo}(\text{CO})_3\text{PPh}_3)_2\text{PBP}]$, where the spread in band energy difference as a function of solvent is *ca* 1800cm^{-1} . Table II gives the λ_{max} (in nm) for all the complexes in various solvents.

The series of polar, aprotic solvents used in this study provide interesting data in context of empirical solvent scales.¹⁶ Fig 2 shows plot of a representative complex for λ_{max} (MLCT) *vs* the donor number parameter, DN.¹⁷ It is quite clear from the plot that correlations with donor number are quite successful except for the position of the λ_{max} value in benzene which is quite off the line. This is justified, as compared to the other solvents used [Benzene has almost zero (.001) donor number]. The points for dichloromethane and chloroform could not be included due to the non-availability of their donor-number parameters. However, we believe the values of their donor number to be near zero and so we have not considered these solvents in the plot.

TABLE II

S. No.	Compound	C ₆ H ₆	CHCl ₃	C ₄ H ₈ O (THF)	CH ₂ Cl ₂	(CH ₃) ₂ O	C ₆ H ₅ CN	CH ₃ CN	PC
1.	[(Mo(CO) ₄) ₂ PBP]†	540	535	525	525	515	a	510	a
2.	[(Mo(CO) ₄) ₂ BBP]†	540	545	527	528	508	a	495	a
3.	[(W(CO) ₄) ₂ PBP]	570	560	560	550	520	a	500	a
4.	[(W(CO) ₄) ₂ BBP]	570	565	560	555	525	a	515	a
5.	[(Mo(CO) ₃ PPh ₃) ₂ PBP]	640	625	620	620	605	605	585	580
6.	[(Mo(CO) ₃ PPh ₃) ₂ BBP]	650	630	625	625	610	610	580	580
7.	[(W(CO) ₃ PPh ₃) ₂ PBP]	650	625	a	620	605	605	585	580
8.	[(W(CO) ₃ PPh ₃) ₂ BBP]	640	625	a	620	605	605	590	585
9.	[(Mo(CO) ₃ AsPh ₃) ₂ PBP]	650	a	a	630	a	a	a	a
10.	[(Mo(CO) ₃ AsPh ₃) ₂ BBP]	650	a	a	635	a	a	a	a
11.	[(W(CO) ₃ AsPh ₃) ₂ PBP]	655	a	a	635	610	a	a	a
12.	[(W(CO) ₃ AsPh ₃) ₂ BBP]	655	a	a	640	a	a	a	a
13.	[(Mo(CO) ₃ SbPh ₃) ₂ PBP]	655	a	a	a	a	a	a	a
14.	[(Mo(CO) ₃ SbPh ₃) ₂ BBP]	655	a	a	a	a	a	a	a
15.	[(W(CO) ₃ SbPh ₃) ₂ PBP]	660	a	a	a	a	a	a	a
16.	[(W(CO) ₃ SbPh ₃) ₂ BBP]	660	a	a	660	a	a	a	a
17.	[(Mo(CO) ₃ Py) ₂ PBP]	720	a	a	665	a	a	580	a
18.	[(Mo(CO) ₃ Py) ₂ BBP]	725	a	a	665	a	a	585	a
19.	[(W(CO) ₃ Py) ₂ PBP]	720	a	a	660	a	a	a	a
20.	[(W(CO) ₃ Py) ₂ BBP]	720	a	a	a	a	a	a	a

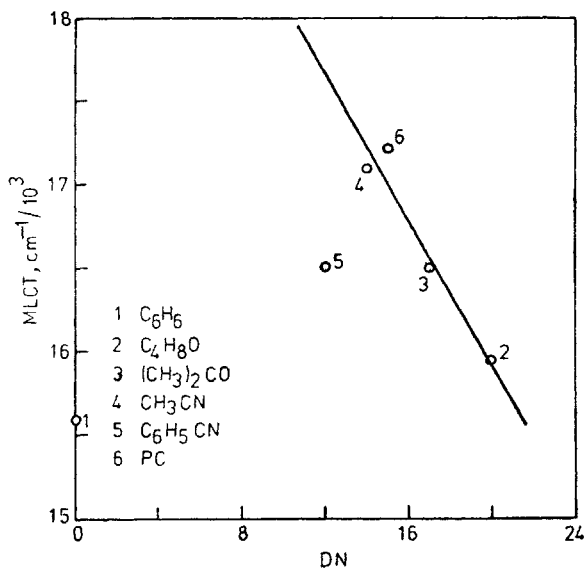
 †[(Mo(CO)₄)₂ PBP] 538

 ‡[(Mo(CO)₄)₂ BBP] 545

r = Reduced

C₆H₆ = Benzene; CHCl₃ = Chloroform; C₄H₈O = Tetrahydrofuran; CH₂Cl₂ = Dichloromethane; (CH₃)₂O Acetone; C₆H₅CN = Benzonitrile; CH₃CN = Acetonitrile; PC = Propylene Carbonate.

a = decomposed.


 FIG 2 λ_{\max} (MLCT) in cm^{-1} vs donor number (DN) for [(Mo(CO)₃PPh₃)₂ (PBP)]

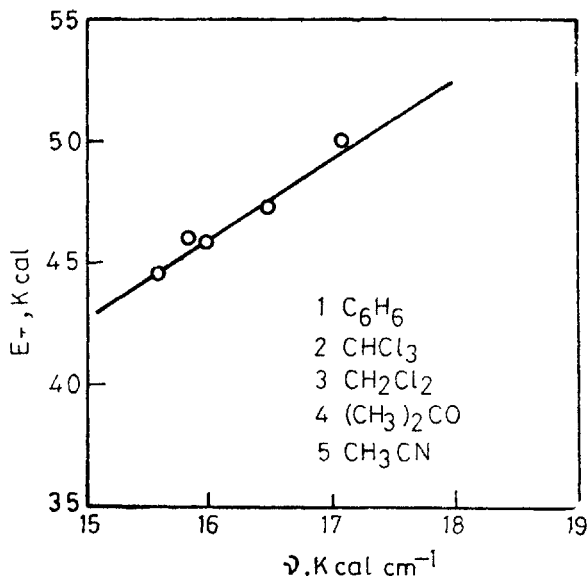


FIG 3 λ_{\max} (MLCT) in kcal cm⁻¹ vs E_T (kcal) for [(Mo(CO)₃PPh₃)₂(PBP)]

The intercept of the plot is a measure of the energy of the optical transition in 1,2 dichloroethane, which in the representative plot is 20300cm⁻¹. The slope of the plot provided a measure of relative sensitivity to variations in the solvent, the energy of the MLCT transition and the extent of electron pair donation to SbCl₅. It is notable that for MLCT bands $M(d\pi) \longrightarrow \pi^*(L)$, the plot of (MLCT) and DN has negative slope showing that the energy of the transition decreases as the electron donor ability of the solvent increases.

The second correlation was drawn between the λ_{\max} (MLCT) and Reichardt and Dismoroth scale.¹⁶ The plot of $\lambda_{\max}(\text{MLCT})$ vs E_T shows a straight line with all the points matching very well (Fig. 3).

It is possible that a charge transfer transition may be treated theoretically much like an intervalance transition whose solvatochromic behaviour has been utilized to calculate various parameters.¹⁸ However, the work in this direction is under progress and will be presented separately.

Apart from the strong MLCT transition the spectra of the compounds exhibited other features at around 380nm and 260nm. These bands are not influenced by the solvents and are assigned ligand field and/or intra ligand transition respectively. The band at 380nm may also have the contributions from the second MLCT and intraligand transition besides LF transition.

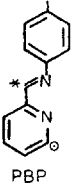
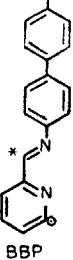
The electronic spectra of $M(\text{II})$ iodo complexes exhibited no bands in the visible region. However, those of mercurous chloride $M(\text{II})$ compounds showed a broad envelope having maxima around 400 nm. This may be assigned as Metal to Metal charge transfer band, (MMCT transition). The other bands below 400nm

are the same as those observed in $M(O)$ compounds and can be similarly assigned.

Proton NMR

The 1H NMR spectral details of the complexes and the free ligand are presented in Table III. Owing to the insolubility or very little solubility of $[(M(CO)_4)_2(L-L)]$ in common organic solvents, their NMR spectra could not be obtained. However, the NMR spectra of the reduced $[(M(CO)_4)_2(L-L)]$ could be taken. The ligand and the reduced ligand (ligand after Zn-Hg amalgam treatment) did not show any change in the spectral pattern in the range 7-9ppm, though a new hump appeared between 5-6ppm (*vide supra*) assignable to N-H proton which disappeared after deuteration.

TABLE III

Proton NMR Data (ppm) for the free Ligand and the Complexes			
Ligand	$[Mo(CO)_4]_2(L-L)$	$[Mo(CO)_3PPh_3]_2L-L$	
 PBP	* 8.35	8.45	8.40
	o 8.79	9.20	8.75
			9.20
 BBP	* 8.30	8.49	8.42
	o 8.78	9.22	8.70
			9.20

The reduced $[(Mo(CO)_4)(L-L)]$ presents the same features except that the peak at $\delta 8.7$ in PBP and reduced PBP and $\delta 8.7$ in BBP and reduced BBP shifts upfield at $\delta 9.2$ showing the coordination of the ligand through pyridine nitrogen.

The NMR spectra of $[M(CO)_3PPh_3]_2(L-L)$ showed similar features as those of $[(Mo(CO)_4)_2(L-L)]$ except that there appeared resonance due to triphenylphosphine protons.

Such type of compounds are also known to exhibit solvent dependent NMR¹⁹ but in our case due to the low solubility of compounds in solvents, no efforts have been made in this direction.

Redox Behaviour

The redox chemistry of $[(\text{Mo}(\text{CO})_4)_2(L-L)]$ showed very interesting results. Although the colour of the compounds after treatment with Zn-Hg amalgam changed to blood red and the products obtained had much increased solubility, the microanalytical data and the spectral features (IR, UV-VIS, NMR) did not show any difference. The chemical reactivity of the reduced complex was also enhanced and their reaction with various ligands (PPh_3 , AsPh_3 etc.) were complete in 4-5h. On this basis and on the basis of earlier results^{4,20} on the similar systems, it is postulated that the ligand is reduced and the formation of $[(M(\text{CO})_4)_2(L-L)]^{2-}$, which makes one CO group very labile.²¹ Moreover, the electrochemistry of the ligand and the complex $[(\text{Mo}(\text{CO})_4)_2(L-L)]^6$ showed $2e$ reduction of the ligands. We assume the same postulation in our cases also. The efforts to obtain the EPR signal for the $(L-L)^-$ radical at room temperature as well as at liquid N_2 temperature failed. However, reduction of the ligand with Zn-Hg amalgam in THF also gave small percentage of a compound having $-\text{NH}-$ group. As the NMR signal due to CH_2 proton could not be observed, we are not in a position to comment on the reduction of $-\text{HC} = \text{N}-$ group by Zn/Hg couple. Since in this type of reduction one requires hydrogen which is difficult to be obtained from THF, it is difficult to postulate the reduction of $\text{CH} = \text{N}-$ group. However, the presence of a little water in THF might give on reduction CH_2-NH group which we have observed in NMR and IR spectra. But its percentage is too small to make it a generalization. This peculiar redox reactivity in these systems is under further investigation.

CONCLUSION

On the basis of the foregoing discussion and the various spectroscopic results, it is seen that the ligands PBP and BBP have coordination properties similar to other diimines. Moreover, they have the potential to undergo reduction which can provide an interesting feature on metal-metal interaction.

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