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SYNTHESIS OF THE MONONUCLEAR $Mo(CO)_4(L)$ [L = 5,6-DIPHENYL-3-(2-PYRIDYL)-1,2,4-TRIAZINE (dppt) OR 3,5,6-TRI(2-PYRIDYL)-1,2,4-TRIAZINE (tpt)] COMPLEXES AND THE CHELATING ACTION OF THE $Mo(CO)_4(tpt)$ DERIVATIVE TOWARDS $M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn; hfac = HEXAFLUOROACETYLACETONATE ION)

J. GRANIFO

Departamento de Ciencias Químicas, Facultad de Ingeniería y Administración,
Universidad de La Frontera, Casilla 54-D Temuco, Chile

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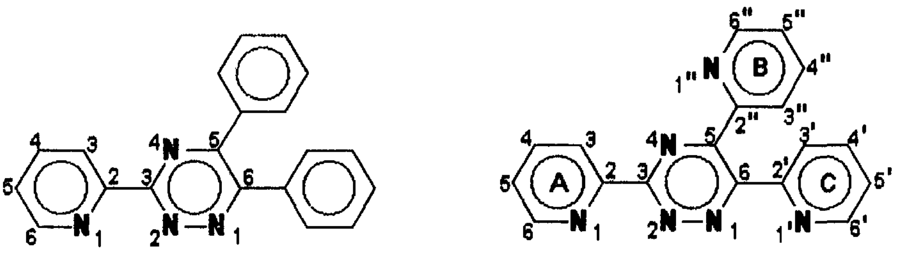
Abstract—The novel mononuclear tetracarbonyl complexes $Mo(CO)_4(L)$, where L is 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) or 3,5,6-tri(2-pyridyl)-1,2,4-triazine (tpt), have been synthesized and characterized. The ligands dppt and tpt seem to be coordinated to the metal centre via a pyridyl nitrogen and a triazine nitrogen. The tpt complex $Mo(CO)_4(tpt)$ is effective as a bidentate chelating system toward the acidic $M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) species producing the bimetallic $(CO)_4Mo(tpt)M(hfac)_2$ compounds. In these Mo–tpt–M products the ligating $Mo(CO)_4(tpt)$ complex is coordinated in an unusual mode involving only pyridyl nitrogen atoms. The new substances were characterized by IR, ^1H NMR, electronic spectroscopy, electrochemical and magnetic moment measurements.

Recent studies[1,2] have demonstrated that the mononuclear tetracarbonyl $Mo(CO)_4(L)$ [L = 2,3-bis(2-pyridyl)pyrazine (dpp) or 2,3-bis(2-pyridyl)quinoxaline (dpq)] complexes show a chelating activity toward the $M(hfac)_2$ (M = Co, Ni; hfac = hexafluoroacetylacetonate ion) species producing the heterobimetallic complexes $(CO)_4Mo(L)M(hfac)_2$ (L = dpp, M = Co, Ni; L = dpq, M = Co). In these polynuclear species, the coordination of the dpp and dpq ligands involves one pyrazine nitrogen and one pyridyl nitrogen atom. However, Escuer *et al.*[3–5] have reported that the direct reaction of these L ligands with the acidic $M(hfac)_2$ (M = Co, Ni, Cu) produces the mononuclear $M(L)(hfac)_2$ compounds, where the ligands show different chelating modes depending on the metal centre involved. So, while in the nickel(II) and copper(II) complexes the ligands present an uncommon coordination by using the nitrogen of their two pyridyl groups, in the corresponding cobalt(II) complexes the habitual coordination through the nitrogen atoms of the couple of pyrazine–pyridyl rings is observed.

In the present work we report on the ligating properties of the closely related triazine ligands 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) and 3,5,6-tri(2-pyridyl)-1,2,4-triazine (tpt) (Fig. 1), first, when they form the precursor mononuclear complexes containing the tetracarbonyl $Mo(CO)_4$ fragments and second, when these precursors are attempted to be bound to the $M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) complexes. The results of this investigation suggest that in the new mononuclear $Mo(CO)_4(dppt)$ and $Mo(CO)_4(tpt)$ complexes the ligands are coordinated by the pyridyl N-1 and the triazine N-2 nitrogen atoms, and that the precursor complex $Mo(CO)_4(tpt)$ is coordinated to $M(hfac)_2$ by using no more than the two pyridyl nitrogens (N-1′ and N-1″). In the literature, only the mononuclear ruthenium(II)[6] and iron(II)[7] complexes with the chelating dppt and tpt ligands have been characterized.

EXPERIMENTAL

All the solvents used in preparing the complexes were reagent grade and were used without further



dppt

tpt

Fig. 1. Structural formulae of the ligands dpp and tpt.

purification. $Mn(hfac)_2 \cdot 3H_2O$, $Co(hfac)_2 \cdot 3H_2O$, $Ni(hfac)_2 \cdot 3H_2O$, and $Cu(hfac)_2 \cdot H_2O$ were purchased from the Aldrich Chemical Company. The compounds $Fe(hfac)_2$,[8] $Zn(hfac)_2 \cdot 2H_2O$,[9] Mo $(CO)_4(piperidine)_2$,[10] dppt[7] and tpt[7] were prepared by similar methods to those described in the literature. IR spectra were registered as solid KBr samples on a Bruker Model IFS-66V FTIR instrument. The electronic spectra were obtained on a Spectronic 3000 diode array spectrophotometer. ^1H NMR spectra were obtained using a Bruker AC-250 P instrument with CD_2Cl_2 as solvent. All peak positions are relative to TMS. The experimental conditions for the COSY were as follows: 128 FIDs of eight scans, every one data size 1 K, were collected. After digital filtering (sine bell window function), the FID was zero filled to 512 W in the F_1 dimension. Acquisition parameters were SW1 = 252.016 Hz, SW2 = 504.032 Hz; recycle time 1.0 s. Magnetic susceptibilities at room temperature were measured by the Faraday method using a Cahan RM-2 balance. Cyclic voltammograms were obtained in CH_2Cl_2 containing 0.10 M $TBAPF_6$ as supporting electrolyte. The three electrode measurements were carried out with a Wenking Potentioscan POS-73 and a X–Y recorder. A platinum-disk working electrode, a platinum wire auxiliary electrode and a AgCl/Ag reference electrode (with internal reference ferrocenium/ferrocene) were used in the cyclic voltammetry experiments.

Synthesis of $Mo(CO)_4(dppt)$ *and* $Mo(CO)_4(tpt)$

Both complexes were prepared following a similar method using fresh samples of $Mo(CO)_4$ $(piperidine)_2$ as starting material. The preparation below is typical.

$Mo(CO)_4(tpt)$. $Mo(CO)_4(piperidine)_2$ (0.660 g, 1.745 mmol) and tpt (0.545 g, 1.745 mmol) in MeOH (50 cm^3) were refluxed gently for 0.5 h. The dark purple precipitate was filtered and washed three times with 3 cm^3 portions of methanol and dried *in vacuo*, 0.640 g (70% yield) of the crystalline compound were obtained. The results of the elemental analyses are presented in Table 1.

Synthesis of $(CO)_4Mo(tpt)M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)

All these complexes were prepared by reaction of $Mo(CO)_4(tpt)$ with $M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) at room temperature in CH_2Cl_2; a typical reaction runs as follows.

$(CO)_4Mo(tpt)Zn(hfac)_2$. The complexes Mo $(CO)_4(tpt)$ (0.123 g, 0.236 mmol) and Zn $(hfac)_2 \cdot 2H_2O$ (0.122 g, 0.236 mmol) were dissolved in CH_2Cl_2 (25 cm^3) and the resulting mixture was stirred for 4 h. The blue solution was then filtered, benzene (10 cm^3) was added to this solution and the total volume was then reduced *in vacuo* to *ca* 7–8 cm^3. Dark blue needle like crystals precipitated upon standing for 1 h, which were washed with benzene (3 × 4 cm^3). Yield 0.180 g (80%). This complex, like the other binuclear tpt derivatives, could be recrystallized from CH_2Cl_2–benzene, if necessary, the compound precipitate on standing after volume reduction *in vacuo* to eliminate most of CH_2Cl_2. The elemental analyses are presented in Table 1.

RESULTS AND DISCUSSION

Mononuclear complexes

Treatment of the piperidine complexes Mo $(CO)_4(piperidine)_2$ with an equimolar amount of the ligands L (dppt, tpt) in hot methanol affords red–purple solutions, from which the new mononuclear tetracarbonyl complexes $Mo(CO)_4(L)$ were precipitated. These compounds are air stable and soluble in solvents such as dichloromethane, chloroform and acetone, slightly soluble in meth-

Table 1. Analytical data, IR spectra and magnetic moments for the complexes $Mo(CO)_4(dppt)$, $Mo(CO)_4(tpt)$ and $(CO)_4Mo(tpt)M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)

Compound	Analysis (%)[a]			IR (cm^{-1})[b]	μ_{eff}
	C	H	N	$\nu(CO)$	(B.M.)
$[Mo(CO)_4(dppt)]$	55.4(55.6)	2.8(2.7)	10.8(10.8)	2016, 1919, 1878, 1840	
$[Mo(CO)_4(tpt)]$	50.9(50.8)	2.4(2.3)	16.3(16.2)	2008, 1915, 1877, 1840	
$[(CO)_4Mo(tpt)Mn(hfac)_2]$	39.1(38.9)	1.3(1.4)	8.2(8.5)	2020, 1922, 1895, 1850	6.0
$[(CO)_4Mo(tpt)Fe(hfac)_2]$	39.2(38.8)	1.5(1.4)	8.3(8.5)	2020, 1920, 1895, 1850	5.4
$[(CO)_4Mo(tpt)Co(hfac)_2]$	38.9(38.7)	1.6(1.4)	8.6(8.5)	2019, 1924, 1900, 1850	4.9
$[(CO)_4Mo(tpt)Ni(hfac)_2]$	38.7(38.7)	1.5(1.4)	8.4(8.5)	2020, 1924, 1895, 1851	3.2
$[(CO)_4Mo(tpt)Cu(hfac)_2]$	38.8(38.5)	1.4(1.4)	8.2(8.4)	2022, 1911, 1895, 1840	2.0
$[(CO)_4Mo(tpt)Zn(hfac)_2]$	38.7(38.4)	1.6(1.4)	8.3(8.4)	2019, 1928,[c] 1852	

[a] Required values are given in parentheses.
[b] KBr discs, all bands are strong.
[c] Broad.

anol and insoluble in light petroleum. The carbonyl stretching frequencies of the new dppt and tpt complexes are characteristic of the *cis*-$Mo(CO)_4$(NN-donor) species.[11]

In Table 2 ^1H NMR spectra in CD_2Cl_2 of the complexes $Mo(CO)_4(L)$ are presented together with those of the uncoordinated ligands L. The assignments are made by analogy with related systems[12] and the numbered labels are indicated in Fig. 1. The A ring pyridyl protons of the free ligands dppt and tpt suffer a clear downfield shift on coordination; the strongest shift corresponds to the H-6 proton [0.27 ppm (dppt) and 0.29 ppm (tpt)]. The remaining resonances of the complexes assigned to the phenyl protons (dppt) and the pyridyl protons (tpt; rings B and C) of the ligands are not shifted significantly from those of the uncomplexed ligands. So, the coordination of the ligands must involve the nitrogen atoms of the pyridyl ring A and either N-2 or N-4 of the triazine ring. In dppt and tpt complexes of ruthenium(II) and iron(II) it has been suggested[6,7] that the coordination mode of the pyridyltriazine ligands occurs through the N-2 atoms, since in this case the steric hindrance between the phenyl (dppt) or the uncoordinated pyridyl (tpt) groups and the other ligands next to them is small.

The electronic spectra in the visible region of the tetracarbonyl complexes $Mo(CO)_4(L)$ shows an intense and broad solvatochromic band (Table 3). This band presents similar solvent dependent characteristics with results previously published on related complexes.[2,13] More specifically, an extensive blue shift (Table 4) of the absorption occurs when the polarity of the solvent increases, i.e. negative solvatochromism.[14] Hence, the absorption band of lowest energy of the $Mo(CO)_4(L)$ complexes can be assigned to an MLCT transition $L(\pi^*) \leftarrow Mo(4d)$. Furthermore the evaluation of the solvatochromic behaviour of the $Mo(CO)_4(L)$ complexes by plotting the MLCT absorption energies ($\bar{\nu}_{MLCT}$, cm^{-1}) vs the E^*_{MLCT} parameter[15] (Table 4) gives a linear relationship according to the equation $\bar{\nu}_{MLCT} = A + B \cdot E^*_{MLCT}$ (dppt: $A = 16{,}217$, $B = 3449$ cm^{-1}, $r = 0.982$; tpt: $A = 15{,}991$, $B = 2819$ cm^{-1}, $r = 0.969$). The tpt complex $Mo(CO)_4(tpt)$ exhibits the lower value of the slope B, i.e. the sensitivity toward solvent changes, in comparison with the $Mo(CO)_4(dppt)$ complex. Indeed, this result is expected considering that the MCLT transition $dppt(\pi^*) \leftarrow Mo(4d)$ of the $Mo(CO)_4(dppt)$ complex lies at an energy higher than that of $Mo(CO)_4(tpt)$ (Table 3), then a lower $tpt(\pi^*)/Mo(4d)$ gap for the tpt complex should exist; in this way the MCLT $tpt(\pi^*) \leftarrow Mo(4d)$ transition decreases their charge transfer character and the negative solvatochromism is reduced. The electrochemical results are more informative about the nature of this fact. The one-electron anodic potentials of the $Mo(CO)_4(L)$ complexes are almost identical and are observed as an irreversible oxidation wave (around 0.27 V) of the metal centre (0/+1). On reduction, every complex displays a ligand centred first reduction reversible one-electron process with different $E_{1/2}$ values (dppt: −1.61 V; tpt: −1.50 V). This result suggests that the LUMO of the $Mo(CO)_4(tpt)$ complex must be stabilized with respect to that of the dppt complex $Mo(CO)_4(dppt)$, indicating the better electron-withdrawing capacity of the free pyridyl groups of the tpt ligand than the phenyl groups of the dppt ligand.

Table 2. ^{1}H NMR chemical shifts,[a] in CD_2Cl_2, of the ligands L (dppt, tpt) and the complexes $Mo(CO)_4(L)$ and $(CO)_4Mo(tpt)Zn(hfac)_2$

Compound	Chemical shift							
	H-6	H-5	H-4	H-3	H-6′, H-6″	H-5′, H-5″	H-4′, H-4″	H-3′, H-3″
dppt[b]	8.87 dd	7.47 m	7.92 td	8.65 dd				
tpt	8.87 dd	7.49 m	7.94 m	8.67 dd	8.33 dd (2 H)	7.31 m (2 H)	7.89 m (2 H)	8.16 cm (2 H)
$[Mo(CO)_4(dppt)]$[c]	9.14 dd	7.57 m	8.06 td	8.73 dd				
$[Mo(CO)_4(tpt)]$	9.16 dd	7.60 m	8.07 td	8.76 dd	8.35 d (2 H)	7.36 m (2 H)	7.94 m (2 H)	8.20 dd (2 H)
$[(CO)_4Mo(tpt)Zn(hfac)_2]$[d]	9.19 d	7.62 t	8.07 t	8.70 d	8.87 d (1 H) 8.72 d (1 H)	7.72 m (1 H) 7.72 m (1 H)	8.18-8.13 m (1 H) 7.95 d (1 H)	8.21-8.16 m (1 H) 8.18-8.11 m (1 H)

[a] Shifts are in ppm from TMS.
[b] Phenyl protons (10 H) : 7.70–7.32 ppm.
[c] Phenyl protons (10 H) : 7.71–7.37 ppm.
[d] The protons of the hfac anion (2 H) appear at 5.93 ppm as a singlet.

Table 3. Long wavelength absorption maxima of the complexes $Mo(CO)_4(L)$ (L = dppt, tpt, dpp, dpq)[a] and $(CO)_4Mo(L)M(hfac)_2$ (L = tpt, M = Mn, Fe, Co, Ni, Cu, Zn; L = dpp, M = Co, Ni; L = dpq, M = Co) in CH_2Cl_2

Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\Delta\bar{\nu}_{max}$ (cm^{-1})[b]
$[Mo(CO)_4(dppt)]$	548	12 200	—
$[Mo(CO)_4(tpt)]$	563	10 200	—
$[(CO)_4Mo(tpt)Mn(hfac)_2]$	594	12 800	927
$[(CO)_4Mo(tpt)Fe(hfac)_2]$	590	12 400	813
$[(CO)_4Mo(tpt)Co(hfac)_2]$	590	11 000	813
$[(CO)_4Mo(tpt)Ni(hfac)_2]$	593	13 000	899
$[(CO)_4Mo(tpt)Cu(hfac)_2]$	600	13 100	1095
$[(CO)_4Mo(tpt)Zn(hfac)_2]$	597	12 800	1012
$[Mo(CO)_4(dpp)]$[c]	510	6300	—
$[(CO)_4Mo(dpp)Co(hfac)_2]$[d]	579	8500	2337
$[(CO)_4Mo(dpp)Ni(hfac)_2]$[d]	579	8410	2337
$[Mo(CO)_4(dpq)]$[e]	562	4886	—
$[(CO)_4Mo(dpq)Co(hfac)_2]$[e]	643	6760	2242

[a] dpp = 2,3-bis(2-pyridyl)pyrazine; dpq = 2,3-bis(2-pyridyl)quinoxaline.
[b] $\Delta\bar{\nu}_{max} = \bar{\nu}_{max}[Mo(CO)_4(L)] - \bar{\nu}_{max}(CO)_4MO(L)(L)M(hfac)_2\}$.
[c] Ref. 13.
[d] Ref. 1.
[e] Ref. 2.

Table 4. Low energy visible absorption maxima (cm^{-1}) of the complexes $Mo(CO)_4(dppt)$ and $Mo(CO)_4(tpt)$ in several solvents

Solvent (E^*_{MLCT})[a]	$Mo(CO)_4(dppt)$	$Mo(CO)_4(tpt)$
CCl_4 (0.12)	16 530	16 290
Mesitylene (0.25)	17 150	16 860
Benzene (0.34)	17 510	17 120
$CHCl_3$ (0.42)	17 760	17 150
2-Propanol (0.46)	17 830	17 210
1-Butanol (0.55)	17 790	17 120
THF (0.59)	18 420	17 830
CH_2Cl_2 (0.67)	18 250	17 760
MeOH (0.73)	18 830	17 950
Acetone (0.82)	19 190	18 480
MeCN (0.98)	19 570	18 830

[a] Solvent parameters (E^*_{MLCT}) from Ref. 15.

Heterobinuclear complexes

The addition of the $M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) compounds to a red–purple dichloromethane solution of the potential chelating complex $Mo(CO)_4(tpt)$ gives blue solutions, from which the heterobinuclear products $(CO)_4Mo(tpt)M(hfac)_2$ are precipitated by addition of benzene. This kind of interaction is not manifested by the related $Mo(CO)_4(dppt)$ complex. The novel bimetallic products $(CO)_4Mo(tpt)M(hfac)_2$ are soluble in CH_2Cl_2 and slightly soluble in benzene; nevertheless, in polar solvents such as acetone they undergo dissociation to give the starting mononuclear species $Mo(CO)_4(tpt)$ and M(hfac), as shown by the electronic spectra. The infrared spectra of the mixed-metal systems $(CO)_4Mo(tpt)M(hfac)_2$ display in the ν(CO) region (Table 1) the same pattern as its mononuclear tetracarbonyl parent complex $Mo(CO)_4(tpt)$.

The 2D-COSY ^1H–^1H spectrum of the diamagnetic complex $(CO)_4Mo(tpt)Zn(hfac)_2$ in CD_2Cl_2 is shown in Fig. 2 and the assignments of the peaks appear in Table 2. The study of the COSY spectrum allows the identification of the resonances associated with each pyridyl ring. Three separate spin systems (rings A, B and C), each one containing four spins, can be detected. The downfield doublet at 9.19 (H-6) ppm and its associate protons at 7.62 (H-5), 8.07 (H-4) and 8.70 (H-3) ppm are assigned to the ring A by the similarity in chemical shifts with those of the parent $Mo(CO)_4(tpt)$ complex. The two remaining sets of spins can thus be attributed to the rings B and C. In contrast to those of the ring A, the resonances of the protons of rings B and C are markedly affected on passing from the mononuclear Mo-tpt complex to the binuclear Mo-tpt-Zn compound. For instance, the nearest protons to the nitrogen atoms (H6′, H6″ and H5′, H5″) of the pyridyl rings B and C are notably displaced toward the lower field on formation of the binuclear Mo–tpt–Zn complex, reaching positions close to the analogous protons

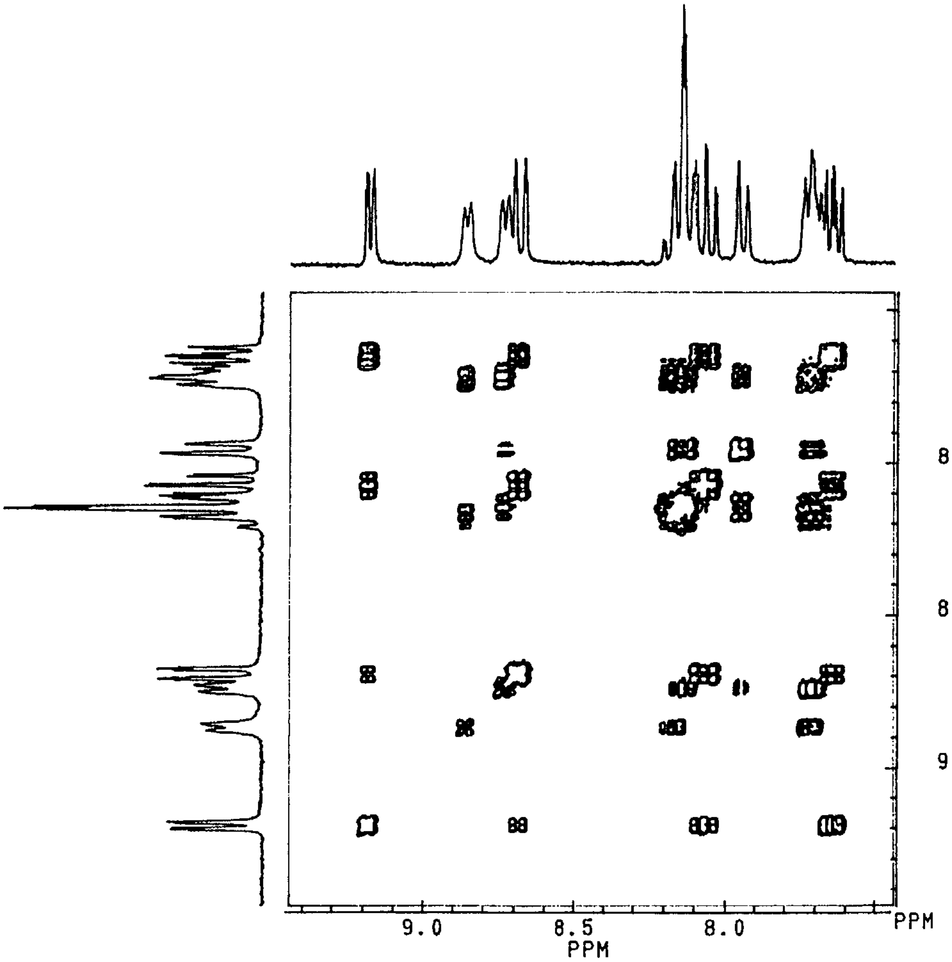


Fig. 2. 2D COSY ^1H–^1H spectrum of $(CO)_4Mo(tpt)Zn(hfac)_2$ in CD_2Cl_2.

belonging to the ring A. Therefore, it seems logical to suggest that in the chelating coordination the $Mo(CO)_4(tpt)$ complex uses the nitrogen atoms of its two uncoordinated pyridyl rings (Fig. 3).

The data, in CH_2Cl_2, concerning the positions of the MLCT transitions tpt(π^*) ← Mo(4*d*) of the complexes $(CO)_4Mo(tpt)M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) are displayed in Table 3. The comparable energies and behaviour of all these absorptions suggest that the bis-chelating situation of the tpt ligand observed in the $(CO)_4Mo(tpt)Zn(hfac)_2$ complex (Fig. 3) is applicable to all the members of the series of Mo–tpt–M complexes. Indeed, the MLCT transitions tpt(π^*) ← Mo(4*d*) of the bridged species $(CO)_4Mo(tpt)M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) are displaced toward low energy relative to the position of the monometallic component $Mo(CO)_4(tpt)$ (Table 3). Displacements such as these have been observed in the related systems $(CO)_4Mo(L)M(hfac)_2$ [L = 2,3-bis(2-pyridyl) pyrazine (dpp), M = Co, Ni; L = 2,3-bis(2-pyridyl) quinoxaline (dpq), M = Co][1,2] and have been attributed to a stabilization of the π^* L orbitals of the monometallic species $Mo(CO)_4(L)$ upon coordination of the second metal centre. The energy of all these shifts is presented in Table 3 in terms of the difference between the wavelength absorption maxima, $\Delta\bar{\nu}_{max}$, in going from mononuclear to binuclear complexes. The complexes with the tpt ligand $(CO)_4Mo(tpt)M(hfac)_2$ present values of $\Delta\bar{\nu}_{max}$ ranging from 813 to 1095 cm^{-1}, which are approximately less than one half lower in mag-

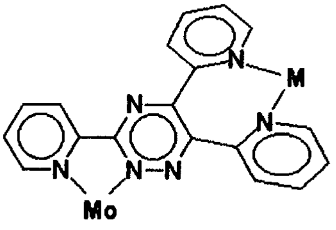


Fig. 3. Schematic representation of the proposed coordination of the bridging ligand tpt.

nitude than the analogous complexes with dpp and dpq (2337 and 2242 cm^{-1}, respectively). Presumably, this very dissimilar lowering of energy of the bridging ligand π^* LUMO of the binuclear tpt complexes vs the dpp and dpq comes principally as a consequence of the different way that the bridging ligands are connected with the metal fragments. In the dpp and dpq complexes the two metals are bound to different pyridyl units, but are sharing the same pyrazine ring. For the tpt-bridge complexes, only the molybdenum atom interacts directly with the central triazine ring; with the $M(hfac)_2$ groups such interaction appears as remote (Fig. 3). Then, in the tpt complexes the additional stabilization of the LUMO π^* level, provided by the acidic $M(hfac)_2$ fragments, should be expected to be weaker than that of the dpp and dpq complexes.

The magnetic moments for the bimetallic complexes $(CO)_4Mo(tpt)M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu,) are summarized in Table 1. The values agree with a six coordination environment for the M^{II} centres and with high-spin Mn^{II}, Fe^{II} and Co^{II} species.[16] However, since the visible region is dominated by the strong MLCT $\mathrm{tpt}(\pi^*) \leftarrow \mathrm{Mo}(4d)$ transitions, the expected ligand field (*d–d*) absorptions of the M^{II} species suffer the overlap of these MLCT transitions impeding their detection.

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