Solution Properties of [(CO)$_5$Mo(pz)] and [{(CO)$_5$Mo}$_2$(pz)]: Organometallic Analogues of [(NH$_3$)$_5$Ru(pz)]$^{2+}$ and [{(NH$_3$)$_5$Ru}$_2$(pz)]$^{4+}$ (pz = Pyrazine)

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Summary A comparison of the solution stabilities and spectral properties of [(CO)$_5$Mo(pz)] and [{(CO)$_5$Mo}$_2$(pz)] to the [(CN)$_5$Fe(pz)]$^{3-}$, [(NH$_3$)$_5$Ru(pz)]$^{2+}$, and [{(CN)$_5$Fe}$_2$(pz)]$^{6-}$, [{(NH$_3$)$_5$Ru}$_2$(pz)]$^{4+}$ systems is reported (pz = pyrazine).

THE complexes of formulation L_5Mpz and L_5MpzML_5 (pz = pyrazine; M = low spin Fe^{II} or Ru^{II}) and their one-electron, mixed-valence, oxidation products have been extensively studied in the past 10 years.[1–3] The $[(NH_3)_5Ru(pz)]^{2+}$ and $[(CN)_5Fe(pz)]^{3-}$ complexes are notable for metal-to-ligand charge-transfer (MLCT) bands (472 and 452 nm in $H_2O)^{4,5}$ and high formation constants ($>10^{10}$ and $9.0 \times 10^5 \,l\,mol^{-1}$, respectively)[6,7] in contrast to $[(H_2O)_5Ni(pz)]^{2+}$ with no MLCT visible band and a modest value of $10 \, l \, mol^{-1}$ [8] for its formation constant. On the basis of the radial extension of the t_{2g}^6 configuration and charge effects, the trend towards increasing affinities within an L_5M–pz or L_5Mpz–ML_5 series would be predicted as $Fe^{II} < Ru^{II} < Mo^0 < W^0$. The same order is expected for the location of the charge transfer (CT) band in wavelength. We have prepared $[Mo(CO)_5(pz)]$ and $[W(CO)_5(pz)]$ photochemically from $[Mo(CO)_6]$ and $[W(CO)_6]$. The observed order of increasing MLCT band wavelength and apparent affinities for pyrazine are found to be $[Mo(CO)_5] < [W(CO)_5] << [Fe(CN)_5]^{3-} < [Ru(NH_3)_5]^{2+}$.

Photolysis of $[Mo(CO)_6]$ and pyrazine (0.02M at 366nm in continually N_2-flushed benzene) gives a single maximum at 387 nm for $[Mo(CO)_5(pz)]$ for up to 45.0 min total photolysis time (450 W Hg lamp). Earlier work with substitution of other N donors was used to ensure that under these conditions only primary photolysis products were obtained. A similar result is obtained with 2-methylpyrazine $\{[(CO)_5Mo(2\text{-}Mepz)]; \lambda_{max} = 387 \, nm\}$. Removal of solvent and excess of pyrazine under reduced pressure at 35 °C or by passing N_2 leads to the reaction shown in equation (1). The resultant solid phase always darkens from yellow to brown.

$$2[(CO)_5Mo(pz)] \longrightarrow [\{(CO)_5Mo\}_2(pz)] + pz \quad (1)$$
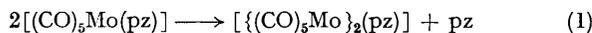
The solid mixture consists of $[(CO)_5Mo(pz)]$ and $[\{(CO)_5Mo\}_2(pz)]$ in an approximate ratio of 67:33. The presence of the binuclear complex is shown by appearance of a new band at 480 nm when the solid phase is redissolved in benzene. In the absence of scavenging ligands, $[\{Mo(CO)_5\}_2(pz)]$ dissociates irreversibly in benzene into $[(CO)_5Mo(pz)]$ and undefined soluble molybdenum carbonyl products {represented by '$[Mo(CO)_5)]_n$' in reactions (3), (5), and (6)}. However, if pyrazine is added to the dissolving solvent ($[Mo]_{tot}$: [pz], ca. 1:30), slow conversion of $[\{(CO)_5Mo\}_2(pz)]$ into the monomer species $[(CO)_5Mo(pz)]$ is indicated by appearance of a sharp isosbestic point at 419 nm, decay of the 480 nm band, and growth of the 387 nm band in the u.v. spectrum. The decay and growth rates are identical. The kinetic events are summarized in equations (2)—(5).

$$[(CO)_5Mo(pz)Mo(CO)_5] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{(CO)_5Mo(pz) \cdot Mo(CO)_5\}_{cage} \quad (2)$$
$$(I)$$

$$(I) + solvent \xrightarrow{k_2} [(CO)_5Mo(pz)] + 1/n'[Mo(CO)_5]_n' \quad (3)$$

$$(I) + pz \xrightarrow{k_3} 2[(CO)_5Mo(pz)] \quad (4)$$

$$[(CO)_5Mo(pz)] + solvent \xrightarrow{k_4} pz + 1/n \, '[Mo(CO)_5]_n' \quad (5)$$
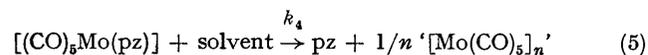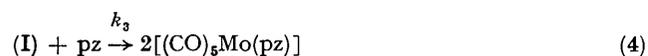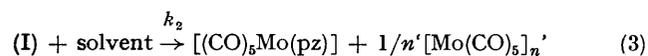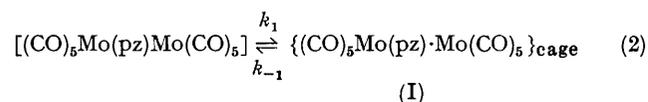
In benzene, without added pyrazine, the recombination of the dissociated cage complex is relatively efficient (i.e, $k_{-1} \gg k_2[solvent]$) in contrast to co-ordinating solvents

$[Me_2CO, CHCl_3,$ tetrahydrofuran (THF)] which promote dissociation of the binuclear complex during the time of mixing. Dissociation of the monomer $[(CO)_5Mo(pz)]$ in these solvents (rate k_4) is slower by one order of magnitude. The following trend is observed at 25 ± 1 °C in the decay constant: benzene, $9.7 \times 10^{-5} \, mol \, l^{-1} \, s^{-1} \ll$ acetone, $2.2 \times 10^{-4} \leqslant CHCl_3$, $2.8 \times 10^{-4} < THF$, $2.3 \times 10^{-3} \, s^{-1}$. With pyrazine present in benzene, scavenging of the caged intermediate (I) is rate-limited by k_1 with elimination of the side reactions k_2 and k_4. The limiting rate k_1 is $5.65 \times 10^{-4} \, s^{-1}$ $(C_6H_6; \, 25 \, °C)$. The equilibrium constant for formation of the $[\{(CO)_5Mo\}_2(pz)]$ complex must be small since it is achieved only under forcing conditions, equation (1). The intensity of the 480 nm band is considerably reduced when the 2-methylpyrazine complex $[(CO)_5Mo(2\text{-}Mepz)]$ is isolated by an identical procedure. This is expected from the steric effect on formation of the binuclear species. Formation of the binuclear complex is blocked by 2-methylpyrazine in the case of $[(CN)_5Fe(2\text{-}Mepz)]^{3-}$.[9] It may be inferred that the stability constant for the formation of the monomer $[(CO)_5Mo(pz)]$ is also small since it dissociates at a moderate rate in co-ordinating solvents and can be displaced by a second $[(CO)_5Mo(pz)]$ as a ligand upon formation of the binuclear complex with solvent removal. The equilibrium constant for formation of $[(CO)_5Mo(pz)]$ is substantially less than that of $[(CN)_5Fe(pz)]^{3-}$. In an aqueous acetone solvent mixture, necessary to solubilize both $[(CO)_5Mo(pz)]$ and $[(CN)_5Fe(H_2O)]^{3-}$, transfer of the pyrazine group to the Fe^{II} centre occurs within 5.0 min manipulation time after mixing equation (6). The absorption maximum of $[(CN)_5Fe(pz)]^{3-}$ occurs at 480 nm in acetone–H_2O.(70:30). {Note that the 480 nm band of the binuclear Mo species is completely destroyed by acetone prior to combination with $[(CN)_5Fe(H_2O)]^{3-}$}. Displacement of pyrazine and transfer to $[(CN)_5Fe]^{3-}$ also occurs in MeCN. The ion $[CN)_5Fe(pz)]^{3-}$ was identified in MeCN by its cyclic voltammetric wave $(-0.55 \, V).$[5] At least one component of the pyrazine transfer reaction proceeds through a $[(CO)_5Mo(pz)Fe(CN)_5]^{3-}$ intermediate which exhibits a maximum at 510 nm.

$$[Mo(CO)_5(pz)] + [(CN)_5Fe(H_2O)]^{3-}$$
$$\longrightarrow [(CN)_5Fe(pz)]^{3-} + 1/n \, '[Mo(CO)_5]_n$$
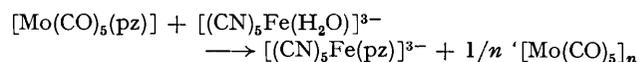
MLCT band maxima for complexes prepared in this work are as follows: [complex, $\lambda(nm)$, solvents] $[(CO)_5Mo(pz)]$: 387, C_6H_6; $[(CO)_5W(pz)]$: 396, C_6H_6; and $[\{(CO)_5Mo\}_2(pz)]$: 480, C_6H_6; 508, $CHCl_3$; and 532, n-C_6H_{14}. Spectra of related binuclear ions[2] exhibit the following maxima: $[\{(CN)_5Fe\}_2(pz)]^{6-}$: 505, H_2O; $[CN)_5Fe(pz)Ru(NH_3)_5]^{-}$: 523, KBr; and $[\{(NH_3)_5Ru\}_2(pz)]^{4+}$: 547, H_2O.

The 'spectator ligands' in the $L_5M(pz)$ and $[L_5M]_2(pz)$ complexes have a dominant role in the affinities and properties of t_{2g}^6 low-spin complexes for pyrazine. CO as the best π acceptor in the series $CO > pz > CN^- \gg NH_3$ is observed to invert the order of affinities and position of MLCT maxima. There are no comparisons between metal centres within a constant ligand environment and solvent system in the literature. The trends for the group relationships would seem to be obeyed on the basis of the MLCT band for $[Mo(CO)_5(pz)]$ at higher energy than $[W(CO)_5(pz)]$. The work reported here emphasizes the fact that the observations with $[(NH_3)_5Ru(pz)]^{2+}$ and $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{n+}$ ($n = 4$, 5, or 6) are unique. The ability of Ru^{II} and Ru^{III} to co-ordinate NH_3 provides this metal centre with the

ability to maximize its π-bonding interaction with pyrazine. The Mo⁰ centre, which requires π-bonding ligands for its stability, has its π-bonding capacity towards pyrazine quenched. The resultant affinity for pyrazine of $[Mo(CO)_5]$ is not much different from that of a high-spin first row ion species such as $[Ni(H_2O)_5]^{2+}$.

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