Organometallic Heterocyclic Chemistry. III. Optical and Electrochemical Properties of Group VI Carbonyl Bridged Complexes of Pyrazine and Pyridazine

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There has been considerable recent interest in the optical, electrochemical, and chemical properties of group VI carbonyl derivatives of aromatic hetero-cyclic complexes of the type $M(CO)_5L$ (M = Cr, Mo, W; L = pyridine, pyrazine, pyridazine, and pyrimidine [2–4]). Following an initial study by Wrighton on the pyridine system [2], we have reported that the $W(CO)_5$ complexes of the isomeric diazine ligands possess ligand field electronic transitions that are unaffected by the ligand while the charge transfer (M → L) are dependent upon the ligand as would be expected [1]. We further indicated that the electrochemical properties of the complexes were such that oxidations occurred from a metal localized orbital. All such redox reactions were irreversible under the conditions employed; however, we also noted that complexes of the type $M(CO)_5–L–M(CO)_5$ exhibited very red shifted CT bands and reversible electrochemical reductions. We wish at this time to present our data on these new complexes which are illustrative of some very general new phenomena in zero oxidation state bridged metal complexes.

The complexes we have studied are of the general formula $(CO)_5M–L–MCO)_5$, L = pyrazine, M = Cr, Mo, W and $(CO)_3M–(L)_3–M(CO)_3$, L = pyridazine, M = Cr, Mo, W.

The bridged pyrazine complexes were prepared from the reaction of the pentacarbonyl complex with an equivalent of the corresponding $M(CO)_5THF$ complex prepared by photochemical irradiation of the hexacarbonyl in THF. The new complexes were purified by column chromatography and recrystallization from hexane/CH_2Cl_2 solutions. The pyridazine complexes were prepared by the method of Heberhold for the Cr complex [5]. Table I contains the infrared and analytical data on all the new complexes reported, and Table II the uv–vis and electrochemical data.

TABLE II. UV–Visible and Electrochemical Data.

Complex	E_{Red}[a]	Absorption Data[b]	
		$^1A_1{}^1E$	M–L (CT)
Pyrazine(Cr)$_2$	1.59	405(405)	520(482)
Pyrazine(Mo)$_2$	1.41	385(398)	494(470)
Pyrazine(W)$_2$	1.31	390(391)	518(475)
(Pyridaz)$_3$Cr)$_3$	1.07, 1.61, 2.00		544(548)
(Pyridaz)$_3$(Mo)$_3$	1.61, 2.15, 2.51		498(503)
(Pyridaz)$_3$(W)$_3$	1.25, 1.45, 1.88		518(523)

[a]Performed in CH_2Cl_2 solvent, 10^{-3} M in complex, 10^{-1} M in TBAP, scan rate 0.65v/s.
[b]Spectra obtained in CH_2Cl_2. Values in parenthesis obtained in THF.

All the complexes reported exhibit red shifted CT bands when compared to the nonbridged penta-carbonyl analogs, $M(CO)_5L$. In the case of the pyrazine complexes the ligand field $^1A_1 \rightarrow {}^1E^b$ transitions are almost identical with those reported for the non-bridged complexes we reported earlier (389 nm), indicating that little or no interaction between the two metal centres is taking place, *i.e.*, each metal centre behaves in exactly the same fashion regardless of the coordination properties of the other nitrogen atom. In the case of the pyrazine complexes the charge transfer band is solvent dependent as were those of the monometal pentacarbonyl complexes. The CT band for pyridazine complexes is not very

TABLE I. Infrared and Analytical Data.

Complex	ν(CO) cm^{-1}	Anal.[a]	
		Calcd	Found
Pyrazine(Cr)$_2$	2075, 1990, 1960, 1920	36.2, 0.9, 6.0	34.8, 0.8, 6.5
Pyrazine(Mo)$_2$	2080, 1980, 1955, 1910	30.4, 0.7, 5.1	29.7, 0.9, 5.4
Pyrazine(W)$_2$	2075, 1980, 1950, 1920	23.1, 0.5, 3.8	23.9, 0.7, 4.3
(Pyridaz)$_3$(Cr)$_3$	1920, 1815	Known Complex	
(Pyridaz)$_3$(Mo)$_3$	1925, 1815	36.0, 2.0, 14.0	35.7, 2.8, 11.5
(Pyridaz)$_3$(W)$_3$	1910, 1820	27.8, 1.5, 10.8	27.6, 2.2, 11.6

[a]Analyses performed by Galbraith Laboratories, Knoxville, Tenn.

solvent dependent as the data shows probably due to the greater steric constraints of solvent interaction with the triply bridging ligand system.

The electrochemical properties of the complexes also differ distinctly from those of the monometal complexes. For the pyridazine complexes three separate one electron reductions are observed, for the pyrazine only a single reduction. Clearly, the reduction process involves placing an electron directly into the orbital system of the ligands.

The reduction potential of the pyrazine changes progressively from > 3.0 for the free ligand to 2.18 for the $LW(CO)_5$ complex to a low value of 1.07 for the $[W(CO)_5]_2L$ complex, *i.e.*, increased coordination of the N lone pairs causes a progressive lowering of the reduction potential. The same applies to the other metals and ligands also. Another major aspect is that the reaction of the bridged complex is reversible under the conditions employed while that of the monometal complex is not.

All of the new data obtained points to a simple effect upon coordination of the pyrazine and pyridazine in terms of both the uv/vis and electrochemical results.

The lowering of the M—L CT bands coupled with the constant ligand field intrametal excitations; the lowering of the reduction potentials upon complexation and the increasing reversibility, suggest that the prime result of coordination is a progressive lowering of the energy levels of the π^* orbitals of the heterocyclic ligand. This may be understood in terms of a simple HMO analysis of the system. The LUMO orbital of the pyrazine ligand possesses the following configuration with nodes bisecting the N—C bonds [6].
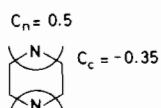
The change in energy of a particular orbital upon substitution of atoms or atom character is given by the expression $\delta E = C_n^2 \delta \alpha_n - 2C_n C_c \delta \beta$ using a first order perturbation treatment.

If we assume in a first order approximation that the resonance integral is unchanged upon substitution at N since the basic C=N bond distances and geometry remain unchanged, the major component in changing the energy of an orbital will be the change in the coulombic integral expression. Since complexation by the N lone pair is effectively removing electron

density from the N atom, there will automatically be a reduction in the energy level, $C_n^2 \delta \alpha_n$, of all orbitals that possess a non-zero coefficient at the N atoms. Thus, such reductions in CT band energy, reduction potentials, *etc.* as noted in the present work will be general if the LUMO possesses non-zero coefficients at the coordinating ligand.

Attempts to chemically reduce the complexes using Na mirrors in the presence of various crown ethers and cryptates to produce stabilized radical anions were unsuccessful since only the anion radical of the free ligand was obtained. The new bridged complexes of pyrazine are oxidatively stable in the solid form for prolonged time periods, but in solution tend to decompose yielding, *inter alia*, the non-bridged complexes $LM(CO)_5$.

The complexes reported here bear a formal similarity to those coordination complexes of the type $Ru^{II}(NH_3)_5 - L - Ru^{III}(NH_3)_5$ *etc.* [8]. However, no 'intravalence' bonds are expected in our systems since the two metal sites are equivalent. Our studies on these and related complexes are continuing.

Acknowledgment

References

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