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Electronic spectra of $RMn(CO)_3(\alpha\text{-diimine})$ ($R = H, CH_3$): a CASSCF/CCI comparative study of the lowest singlet excited states

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ABSTRACT AND CONTENTS

A theoretical study, based on CASSCF/CCI calculations of the lowest part of the electronic spectra of $RMn(CO)_3(\alpha\text{- diimine})$ ($R=H$, CH_3), is reported. These systems are a model for a rather general class of transition metal complexes with low-lying Metal-to-Ligand Charge Transfer (MLCT) states. The theoretical electronic spectrum of $HMn(CO)_3(\alpha\text{- diimine})$ is characterized by a high density of states below 35000 cm^{-1} (285 nm). The lowest $^1A'$ and $^1A''$ singlet states, directly accessible through allowed transitions from the $^1A'$ ground state, correspond to $d \rightarrow \pi^*$ excitations, between 17110 and 22300 cm^{-1}. These values are in excellent agreement with the vis-UV absorption spectra usually obtained for this family of molecules with a MLCT band at around 500 nm (20000 cm^{-1}). The next $^1A'$ and $^1A''$ states (above 27800 cm^{-1}) correspond to $d \rightarrow d$ excitations and should contribute to a shoulder on the absorption spectra at around 350 nm. The first excited $^1A'$ $\sigma \rightarrow \pi^*$ state, susceptible to play a role in the homolysis of the Metal-R bond, is calculated at 32150 cm^{-1}. This state is not directly acces-

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sible upon irradiation at 500 nm, but may interact with the lowest ^{1}MLCT states early on the reaction path corresponding to the homolysis of the Metal-R bond. In the light of these results, the photochemical behavior of other transition metal (α- diimine) complexes with low-lying MLCT excited states is discussed. The excitation energies for the lowest $^1A'$ states only slightly differ when going from the hydride to the alkyl complex.

A. INTRODUCTION

In later years many photochemists working on transition metal complexes changed their investigations from Ligand Field (LF) photochemistry to the photophysics and photochemistry of molecules with low-lying Metal-to-Ligand Charge Transfer (MLCT) states. Usually the MLCT states are poorly reactive and their long lifetime makes them very well suited for energy and electron transfer processes [1-6].

If the photochemistry of transition metal carbonyls is well documented experimentally [7-11] and theoretically [12-18], the density and the diversity of states which characterize the electronic spectrum of complexes with low-lying MLCT states, the position of which depends on the experimental conditions, is responsible for the incomplete understanding of their photochemical and photophysical behavior. Most of the time the futur of the molecule after irradiation is followed up either by emission measurement or by wavelength dependence of the quantum yield of the primary reactions [19]. A fundamental question does concern the role of the MLCT states in the observed photoreactivity of the molecule which does depend strongly on the metal center, the ligand providing the low π - acceptor orbital and the other ligands.

The MLCT states were mostly assumed to be unreactive [2-3,20-21] until recent experiments reported on $M(CO)_4(\alpha\text{-diimine})$ (M = Cr, Mo, W), $RM(CO)_3(\alpha\text{-diimine})$ (R = Me, Et, Benzyl; M = Mn, Re) and $XM(CO)_3(\alpha\text{-diimine})$ (X = halide, M = Mn, Re) [22-26]. According to these experiments, these complexes seem to indicate distinct MLCT and LF reactivities.

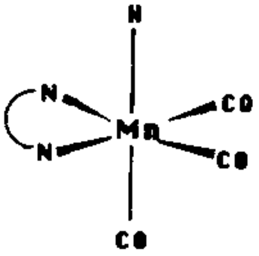
Indeed, excitations into the MLCT bands (between 380 and 500 nm) lead to radical formation whereas LF photochemistry is characterized by the dissociation of a carbonyl ligand. From recent experimental investigations reported for α-diimine Rhenium tricarbonyl complexes [27], it was concluded that mainly MLCT states are involved in absorption and emission of these complexes and that homolysis reactions take place from " close-lying" Ligand-to-Ligand Charge Transfer (LLCT) states ($\sigma \rightarrow \pi^*$). The relative position in the electronic spectra of the photodissociative states corresponding to $d \rightarrow d$, $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$ with respect to the MLCT states is probably the key of the photochemical behavior of this family of complexes.

Current understanding of excited states properties of transition metal coordination compounds is generally based on molecular orbital diagrams, coupled with an analysis in terms bonding and antibonding character [7]. This analysis, although conceptually appealing and certainly useful, has a number of drawbacks and may turn partly erroneous in some cases [18]. One way for getting insights in the nature of the photoexcited states involved in the photoreactivity of these molecules is to calculate the excitation energies to the lowest electronic states and to draw the state correlation diagrams which connect them to the ground and excited states of the primary products [28-29]. This approach constitutes the first step of a more complete study based on the calculation of the potential energy surfaces, followed by an investigation of the photodissociation dynamics. This method has been applied recently with success to mononuclear transition metal hydride carbonyls [30-32].

The aim of the present study is to analyze the remarkable complexity of the electronic spectrum of this family of molecules by investigating the nature of the lowest excited states and their corresponding excitation energies obtained from CASSCF/CCI calculations for $RMn(CO)_3(\alpha$- diimine) ($R = H$, CH_3). These systems will serve as a model for a rather general class of transition metal coordination compounds with low-lying MLCT states.

B. COMPUTATIONAL DETAILS

The calculations were carried out for $RMn(CO)_3$(α- diimine) (R = H, CH_3; α- diimine = 1,4-Diaza- 1,3-butadiene) with the conformations 1 (R = H) and 2 (R = CH_3) in the C_s symmetry.



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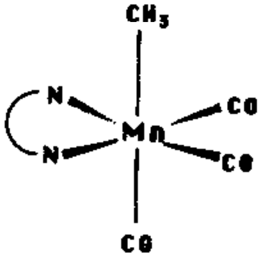

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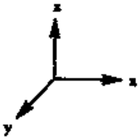

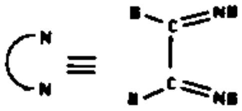

Idealized geometries were deduced from the structures of $Mn(CO)_3(dab)Cl$ [33] and of $HMn(CO)_5$ [34] with the following bond lengths:

- for both molecules: Mn-C_{CO} = 1.82 Å (for the carbonyl ligand trans to the R group) or 1.807 Å(for the other carbonyls ligands), Mn-N = 2.032 Å, N-C = 1.28 Å, C-C = 1.49 Å, C-H = 1.08 Å, N-H = 1.01 Å, C-O = 1.142 Å

- for $HMn(CO)_3$(α- diimine): Mn-H = 1.576 Å, for $CH_3Mn(CO)_3$(α- diimine) Mn-C = 2.19 Å, C-H = 1.09 Å.

and the angles θ = 96° and α = 117.5°.

The following Gaussian basis sets were used: for the manganese atom a (15,11,6) set contracted to [9,6,3] [35], for the first row atoms a (10,6) set contracted to [4,2] [38], for hydrogen either a (6,1) set contracted to [3,1] [39] (for the atom directly linked to the metal center), or a (4) set contracted [2] [38] for the other hydrogen atoms.

A detailed description of the method used to reproduce correctly the sequence and energetics of electronic states is reported elsewhere [40]. Complete Active Space SCF (CASSCF) calculations [41] were carried out to obtain wave functions which are used as references in the Contracted Configuration Interaction (CCI) calculations [42]. Our interest will center mostly on the lowest excited states corresponding to $d \rightarrow d$, $d \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ excitations. The rigorous way to calculate the excitation energies consists of carrying out for each electronic state a CASSCF calculation followed by a Multireference CI calculation. However, this procedure is too expensive for transition metal complexes, due to the size of the system and to the large number of low-lying states. In this application we use a more economical approach that consists in two steps i) we perform a CASSCF calculation for which the energy is averaged on the lowest states of same symmetry and same spin ii) this CASSCF wave function is used as reference in subsequent CI calculations of all the states of interest. In the CASSCF calculation, eight electrons are correlated (the 3d electrons and the two electrons involved in the Mn-R bond) in ten active orbitals corresponding to the 3d orbitals and the 4d orbitals which correlate them, the σ and σ^* orbitals (σ and σ^* denote the molecular orbitals that are respectively, bonding and antibonding with respect to the Mn-R bond) and the lowest π^* molecular orbital.

For each electronic state a multireference CCI calculation is performed including all the configurations which appear with a coefficient larger than 0.08 in the CASSCF calculation (the number of references may vary from 4 to 10 states in these CCI calculations depending on the state of interest). Single and double exranged from 250000 to 960000, but this number is reduced to at most a few thousands by the contraction. The integral calculations were carried out either with the system of programs ARGOS [43] or with the system of programs ASTERIX [44].

B. RESULTS

$HMn(CO)_3$(α- diimine) electronic spectrum. The calculated excitation energies to the lowest $^1A'$ and $^1A''$ excited states of $HMn(CO)_3$(α- diimine) are reported in Table 1.

TABLE 1

Calculated CASSCF/CCI excitation energies (in cm^{-1}) for the lowest singlet states of $HMn(CO)_3$(α- diimine).

	one-electron excitation in the main configuration	
a $^1A' \rightarrow$ a $^1A''$	$3d_{yz} \rightarrow \pi^*$	17110
a $^1A' \rightarrow$ b $^1A'$	$3d_{x^2-y^2} \rightarrow \pi^*$	17330
a $^1A' \rightarrow$ c $^1A'$	$3d_{xz} \rightarrow \pi^*$	22280
a $^1A' \rightarrow$ b $^1A''$	$3d_{x^2y^2} \rightarrow 3d_{xy}$	27800
a $^1A' \rightarrow$ c $^1A''$	$3d_{xz} \rightarrow 3d_{xy}$	30700
a $^1A' \rightarrow$ d $^1A'$	$\sigma \rightarrow \pi^*$	32150
a $^1A' \rightarrow$ e $^1A'$	$3d_{yz} \rightarrow 3d_{xy}$	34850
a $^1A' \rightarrow$ d $^1A''$	$3d_{yz} \rightarrow \sigma^*$	47500

The lowest part of the electronic spectrum (below 35000 cm^{-1}) is particularly crowded. The lowest states, accessible through allowed transitions $^1A' \rightarrow {}^1A'$ and $^1A' \rightarrow {}^1A''$ range between 17110 and 22280 cm^{-1} and correspond to $d \rightarrow \pi^*$ excitations, in excellent agreement with the main feature of the UV-vis absorption spectra obtained for this family of molecules, namely a large band around 500 nm assigned to MLCT states [22-27,45]. The corresponding triplet states lye between 16600 and 17000 cm^{-1} [40], being nearly degenerate with the corresponding singlet states, excepted for the $^1A'$ ($d_{xz} \rightarrow \pi^*$) which is calculated at a rather high energy (22280 cm^{-1}). Interestingly, the allowed transitions corresponding to $d \rightarrow d$ excitations are calculated at 27800 and 30700 cm^{-1} and cannot be populated upon excitation at 500 nm. They should appear on the absorption spectrum as a shoulder at around 350 nm in agreement with experimental data reported for $CH_3Mn(CO)_3$ (iPr-DAB) [45]. These excited states could be photoactive for the dissociation of a carbonyl ligand, primary reaction currently observed for this family of manganese complexes [22-27]. The first so-called LLCT $^1A'$ $\sigma \rightarrow \pi^*$ excited state is situated at 32150 cm^{-1}. From recent experiments reported on different molecules [27], this excited state could be responsible for the metal-R bond homolysis which characterizes the photochemical behavior of a series of complexes L_nR M′ $(CO)_3$(α- diimine) (R = Alkyl,M). From a preliminary calculation, the corresponding triplet state should range between 28000 and 31000 cm^{-1} [46]. The excited state corresponding to a $d \rightarrow \sigma^*$ excitation is calculated at 47500 cm^{-1} (Table 1). The excitation energy for corresponding triplet which has been found to be photoactive for the carbonyl loss in transition metal hydrides [14,17,31], is estimated at 32000 cm^{-1} [40]. The results reported in Table *1* are in excellent agreement with the values obtained for the lowest excited states of $HMn(CO)_5$ [17]. We may conclude that the perturbarion induced by the MLCT states on the lowest part of the electronic spectrum of transition metal hydrides is very small. The presence of these MLCT states will more probably operate on the early stage of the photodissociation. Indeed, avoided crossing between the usually dissociative states, corresponding to $d \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ excitations [14-17], and the non dissociative MLCT states will modify the potential energy surfaces which connect the excited states of the reactant to the ground states of the primary products (R + $Mn(CO)_3$(α- diimine) or $RMn(CO)_2$(α- diimine) + CO). Consequently, the dynamics of the corresponding primary reactions will be dramatically affected.

$CH_3Mn(CO)_3$(α- diimine) lowest $^1A'$ excited states. In order to follow the effect of the radical on the relative order of the lowest singlet states in this family of molecules, we did compare in Table 2 the excitation energies for the $^1A'$ excited states of $HMn(CO)_3$(α- diimine) and $CH_3Mn(CO)_3$(α- diimine).

TABLE 2

Calculated CASSCF/CCI excitation energies (in cm^{-1}) for the lowest $^1A'$ states of $RMn(CO)_3$(α- diimine): comparison for R = H (a) and R = CH_3 (b).

	one-electron excitation in the main configuration	(a)	(b)
a $^1A' \rightarrow$ b $^1A'$	$3d_{x^2-y^2}\rightarrow\pi^*$	17330	17570
a $^1A' \rightarrow$ c $^1A'$	$3d_{xz}\rightarrow\pi^*$	22280	21540
a $^1A' \rightarrow$ d $^1A'$	$\sigma\rightarrow\pi^*$	32150	34470
a $^1A' \rightarrow$ e $^1A'$	$3d_{yz}\rightarrow 3d_{xy}$	34850	33600

Apparently, the replacement of hydrogen by an alkyl group slightly affects the lowest part of the electronic spectrum. The detailed analysis of the CI coefficients in the final wavefunctions of the excited states does not show any significant difference between the two systems, apart from a little stronger interaction between the $^1A'$ ground state and the LLCT $^1A'$ $\sigma \rightarrow \pi^*$ excited state in the methyl complex than in the hydride. The results reported in Table 2 validate the use of $HMn(CO)_3$(α- diimine) as a model in futur investigations based on potential energy surfaces.

D. CONCLUSION

From the results reported above, it may be concluded that the presence of MLCT states affects only slightly the lowest part of the electronic spectrum of transition metal hydrides. These MLCT states will play an indirect role in the photoreactivity of these molecules through their interaction with dissociative states at the early stage of the photodissociation. Consequently the mechanism of photodissociation will be extremely complicated leading to a quite confusing photochemical behavior. The replacement of hydrogen by an alkyl group does not modify quantitatively the excitation energies calculated for the lowest singlet excited states corresponding to $d \rightarrow d$, $d \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ excitations.

The theoretical results, based on CASSCF/CCI calculations, agree with the main features of the absorption spectra usually produced for this family of molecules i) an intense band at around 500 nm corresponding to MLCT states ii) a shoulder around 350 nm which could be assigned to excited states corresponding to $d \rightarrow d$ and $\sigma \rightarrow \pi^*$ excitations.

Mapping of potential energy surfaces for selected electronic states will constitute the next step of the present study. Indeed, on the basis of the calculated excitation energies any conclusion about the photoactive states responsible for the primary reactions currently observed in this family of molecules (loss of a carbonyl ligand vs. homolysis of a bond originating at the metal center) would be speculative.

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REFERENCES

1. K. Kalyanasundaram, Coord. Chem. Rev., 46 (1982) 159.
2. T.J. Meyer, Pure Apll.Chem., 58 (1986) 1193.
3. T. J. Meyer, Acc. Chem. Res., 22 (1989) 163.
4. V. Balzani, F. Bolletta, F. Scandola, R. Ballardini, Pure Appl. Chem., 51 (1979) 299.
5. F. Scandola, C. A. Bignozzi, C. Chiorboli, M. T. Indelli, M. A. Rampi, Coord. Chem. Rev., 97 (1990) 299.
6. V. Balzani, L. de Cola, L. Prodi, F. Scandola, Pure Appl. Chem., 62 (1990) 1457.
7. G. L. Geoffroy, M. S. Wrighton, Organometallic Photochemistry, Academic Press, New-York, 1979.
8. V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds; Academic, London, 1970.
9. M. S. Wrighton, Chem. Rev., 74 (1974) 401.
10. E. Koerner von Gustorf, F. W. Grevels, Fortschr. Chem. Forsch., 13 (1969) 366.
11. J. J. Turner, Angew. Chem. Int. Ed. Engl., 14 (1975) 304.
12. C. Daniel, M. Bénard, A. Dedieu, R. Wiest, A. Veillard, J. Phys. Chem., 88 (1984) 4805.

13. C. Daniel, I. Hyla-Kryspin, J. Demuynck, A. Veillard, Nouv. J. Chim., 9 (1985) 581.
14. A. Veillard, A. Strich, J. Am. Chem. Soc., 110 (1988) 3793.
15. C. Daniel, Coord. Chem. Rev., 97 (1990) 141.
16. C. Daniel, J. Phys. Chem., 95 (1991) 2394.
17. C. Daniel, J. Am. Chem. Soc., 114 (1992) 1625.
18. C. Daniel, A. Veillard in " Transition Metal Hydrides", A. Dedieu ed., Verlag Chemie, New-York, 1991.
19. A. J. Lees, Chem. Rev., 87 (1987) 711 and references therein.
20. A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev., 84 (1988) 85.
21. P.C. Ford, D. Wink, J. DiBenedetto, Prog. Inorg. Chem., 30 (1983) 213.
22. D. J. Stufkens, Coord. Chem. Rev., 104 (1990) 39.
23. M. W. Kokkes, T. L. Snoeck, D. J. Stufkens, A. Oskam, M. Christophensen, C. H. Stam, J. Mol. Struct., 131 (1985) 11.
24. R. W. Balk, T. L. Snoeck, D. J. Stufkens, A. Oskam, Inorg. Chem., 19 (1980) 3015.
25. H. V. van Dijk, D. J. Stufkens, A. Oskam, J. Am. Chem. Soc., 111 (1989) 541.
26. P. C. Servaas, D. J. Stufkens, A. Oskam, Inorg. Chem., 28 (1989) 1780.
27. D. J. Stufkens, Comments Inorg. Chem., Vol. 13 N°6 (1992) 359.
28. A. Veillard, Nouv. J. Chim., 5 (1981) 599.
29. C. Daniel, A. Veillard, Nouv. J. Chim., 10 (1986) 83.
30. C. Daniel, M. C. Heitz, L. Lehr, T. Schröder, B. Warmuth, Int. J. Quantum Chem., in press.
31. C. Daniel, E. Kolba, L. Lehr, T. Schröder, J. Manz, J. Am. Chem. Soc., submitted for publication.
32. C. Daniel, M. C. Heitz, L. Lehr, T. Schröder, J. Manz, J. Phys. Chem., submitted for publication.
33. G. S. Schmidt, H. Paulus, R. Van Eldick, H. Elias, Inorg. Chem., 27 (1988) 3211.

34. E.A. Mc Neill, F. R. Scholer, J. Am. Chem. Soc., 991 (1977) 6243.

35. This basis set is made from the (14,9,5) basis of Wachters [36] by adding an additional s function (exponent 0.3218), two diffuse p functions, and one diffuse d function. All exponents were chosen according to the even-tempered criterion of Raffenetti [37]

36. A. J. H. Wachters, J. Chem. Phys., 52 (1970) 1033.

37. R. L. Raffenetti, R. D. Bardo, K. Ruedenberg, in "Energy Structure and Reactivity", Smith D. W., Mc Rae W. B. Eds, Wiley, New-York (1973).

38. S. Huzinaga, "Approximate Atomic Functions" Technical Report, University of Alberta, Edmonton (1971).

39. S. Huzinaga, J. Chem. Phys., 42 (1965) 1293.

40. C. Daniel, T. Matsubara, to be published.

41. P. E. M. Siegbahn, J. Almlof, A. Heiberg, B. O. Roos, J. Chem. Phys, 74 (1981) 2384.

42. P. E. M. Siegbahn, Int. J. Quantum Chem., 23 (1983) 1869.

43. R. Ernenwein, M.M. Rohmer, M. Bénard, Comput. Phys. Commun., 58 (1990) 305. M. M. Rohmer, J. Demuynck, M. Bénard, R. Wiest, C. Bachmann, C. Henriet, R. Ernenwein, Comput. Phys. Commun., 60 (1990) 127. R. Wiest, J. Demuynck, M. Bénard, M. M. Rohmer, R. Ernenwein, Comput. Phys. Commun., 62 (1991) 107.

44. R. M. Pitzer, J. Chem. Phys., 58 (1973) 3111.

45. B. Rossenaar, D. J. Stufkens, private communication.

46. C. Daniel, unpublished results.