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Energy decomposition analysis of the metal-imine bond in $[(CO)_4M{-}SB]$ ($M = Cr, Mo, W$; SB: $RHC{=}N{-}CH_2CH_2{-}N{=}CHR$)

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ABSTRACT

The electronic and molecular structures of the metal-Schiff base complexes $[(CO)_4M{-}SB]$ (M: Cr, Mo, W; SB: $RHC{=}N{-}CH_2CH_2{-}N{=}CHR$, $R = C_6H_5$, C_6F_5, *Ortho-*, *Meta- and Para*-XC_6H_4 ($X = F, Cl, Br, CH_3$)) have been investigated at the DFT level using the exchange correlation functional BP86. The nature of the TM–Schiff base interactions was analyzed with charge and energy decomposition methods. The octahedral equilibrium geometries have C_{2v} symmetry. The $(CO)_4M{-}SB$ bond dissociation energies vary little for different substituents R. The calculated values indicate rather strong bonds which exhibit the trend for the different metals M = Mo (D_e = 59.8–65.4 kcal/mol) < Cr (D_e = 62.3–67.8 kcal/mol) < W (D_e = 69.9–75.8 kcal/mol). The energy decomposition analysis suggests that the $(CO)_4M{-}SB$ attractive interactions come mainly from electrostatic attraction which provide ~60% to ΔE_{int} while ~40% come from orbital interactions. The latter term arises mainly (~70%) through $(CO)_4M \leftarrow SB$ σ donation from the nitrogen lone-pair orbitals while a much smaller part (~20%) comes from $(CO)_4M \rightarrow SB$ π backdonation. The transition metals carry large negative partial charges between −2.3 e for M = Cr and −1.1e for M = W.

1. Introduction

Schiff bases (RR'C=NR") are an important class of ligands which are believed to be bonded via strong σ donation and π-back backdonation to metal ions [1–9]. Schiff bases can be synthesized by condensation of aldehydes or ketones with suitable amines ($R{-}NH_2$). Monodentate Schiff bases are not known to form stable complexes probably due to the insufficient donor strength of the imino nitrogen of the C=N group [1]. Multidentate Schiff bases with at least one donor atom near to the nitrogen atom stabilize the metal-nitrogen bond through formation of chelate rings [1]. The coordination chemistry of transition metal complexes with bidentate Schiff base (SB) complexes was fueled by the successful synthesis and characterization of numerous compounds $L_nM{-}SB$ [1–9]. Recently, Tripathi and his coworkers reported the isolation and characterization of the complexes $[(CO)_4M{-}SB]$ (M = Cr, Mo, SB: $R'RC{=}N{-}CH_2CH_2{-}N{=}CRR'$) (R = H, $R = C_6H_5$ or $C_6H_5(OCH_3)$; $R = CH_3$, $R' = C_6H_5$; $R = R' = C_6H_5$) [6]. They reported that the latter species exhibit four CO stretching bands which were assigned to the $2a_1 + b_1 + b_2$ modes in C_{2v} symmetry which is in agreement with cis configuration of the ligands. In contrast to the extended experimental work, there is no theoretical work about the bonding situation in Schiff base complexes which has been reported so far.

It has been shown in recent years that a quantitative estimate of the strength of TM ← L σ donation, TM → L π backdonation in transition metal complexes with a large variety of ligands can be made [10–12] with the help of the energy decomposition analysis (EDA), which was developed by Morokuma [13] and by Ziegler and Rauk [14]. The EDA extends the bonding analysis beyond the attractive orbital terms by including electrostatic interactions and the Pauli repulsion. The EDA has been used in systematic studies [15–44] of carbonyl complexes [15], phosphine complexes [16], carbene and carbyne complexes [16–18], group-13 diyl ER (E = B – Tl) complexes [19,20] alkene and alkyne complexes [21,22] sandwich complexes [23–26] dihydrogen complexes [27] and in other types of TM compounds [28–44]. The EDA is also very helpful for the quantitative analyses of chemical bonding in main-group compounds [45–53].

In our previous work [54], we reported about an energy decomposition analysis of metal–dioxime complexes $[Ni\{RC(NOH)C(NO)R\}_2]$ ($R = CH_3$ (dmgH), H, F, Cl, Br, Ph, CF_3). Here, we report about EDA studies of the metal-imine bond in the complexes $(CO)_4M{-}SB$ {M = Cr, Mo, W; SB: $RHC{=}N{-}CH_2CH_2{-}N{=}CHR$,

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R = C_6H_5, C_6F_5, *ortho*-, *meta*- and *para*-XC_6H_4 (X = F, Cl, Br, CH_3)} (Fig. 1). The study is the first theoretical investigation of the nature of the chemical bond in transition metal-SB complexes.

2. Computational methods

The geometries of the molecules were optimized at the gradient-corrected DFT level using the functional BP86 [55,56]. Triple-zeta-quality basis sets were used, which are augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. This level of theory is denoted as BP86/TZ2P+. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [57]. Scalar relativistic effects were considered using the zero-order regular approximation (ZORA) [58–60]. Structures were optimized with C_{2v} symmetry constraints. The nature of stationary points as minima has been confirmed by calculation of the Hessian matrices. All investigated structures and most of the fragments are singlet species. The calculations were performed with the program package ADF 2009.01.2 [61].

Table 1
Most important bond lengths [å] and angles [°] at BP86/TZ2P+ of $[(CO)_4M{-}SB]$[a] (M = Cr, Mo, W; SB = RHC=N–CH_2CH_2–N=HCR; R = C_6H_5, C_6F_5, *para*-XC_6H_4.

R	M	Bond angle	Bond lengths		
		N–M–N	M–N	M–C(*cis*)	M–C(*trans*)
C_6H_5	Cr	80.4	2.099	1.841	1.901
	Mo	76.8	2.235	1.978	2.050
	W	76. 8	2.219	1.983	2.048
$CH_3C_6H_4$– *para*	Cr	80.3	2.102	1.840	1.900
	Mo	76.7	2.238	1.977	2.049
	W	76.6	2.221	1.982	2.047
FC_6H_4– *para*	Cr	80.3	2.099	1.841	1.901
	Mo	76.8	2.234	1.978	2.050
	W	76.7	2.219	1.982	2.048
ClC_6H_4– *para*	Cr	80.4	2.097	1.842	1.901
	Mo	76.9	2.232	1.979	2.051
	W	76.8	2.217	1.983	2.048
BrC_6H_4– *para*	Cr	80.4	2.097	1.842	1.901
	Mo	76.9	2.232	1.979	2.051
	W	76.8	2.217	1.983	2.048
C_6F_5	Cr	81.3	2.092	1.847	1.905
	Mo	77.8	2.227	1.983	2.054
	W	77.6	2.213	1.988	2.052

EDA calculations were carried out in order to analyze the nature of the bonding. In the EDA, bond formation between the interacting fragments is divided into three steps, which can be interpreted in a plausible way. In the first step, the fragments, which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation to yield the quasiclassical

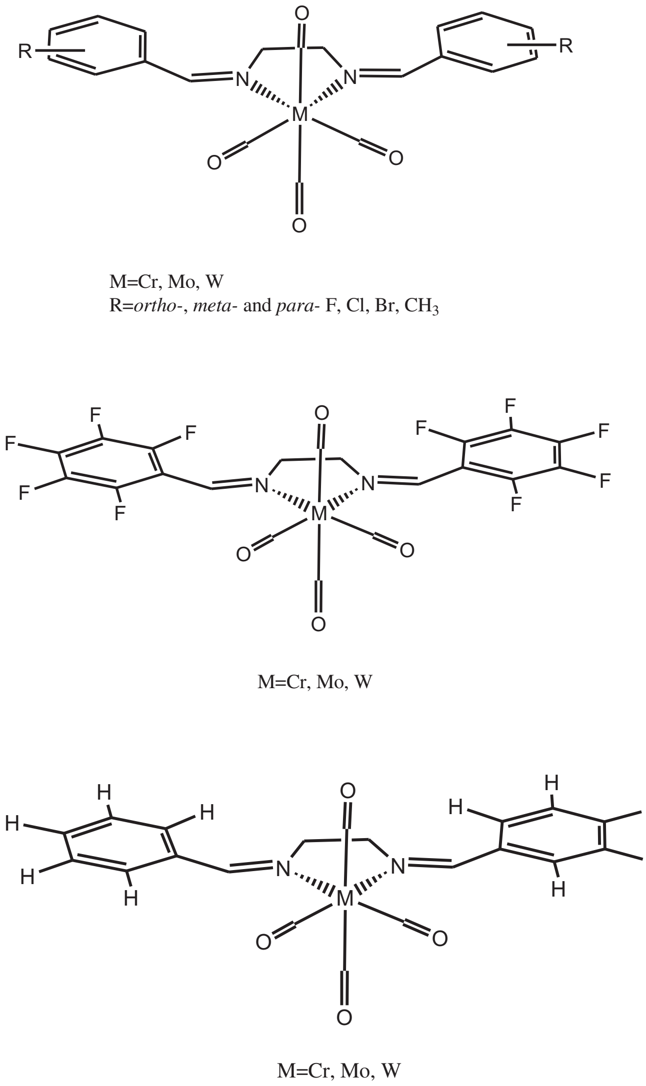

Fig. 1. Schematic representation of the investigated complexes $[(CO)_4M{-}SB]$.

Table 2
EDA results BP86/TZ2P+ of complexes $[CrCO_4\text{-}SB]$[a] the interacting fragments are $CrCO_4$ and the ligand SB in the singlet ground state.

R	C_6H_5	$CH_3C_6H_4$			FC_6H_4		
		Ortho	Meta	Para	Ortho	Meta	Para
ΔE_{int}	−70.2	−70.7	−70.7	−70.8	−69.4	−69.3	−69.7
ΔE_{Pauli}	119.6	118.9	118.6	118.6	119.4	120.3	119.6
ΔE_{elstat}[b]	−114.3	−114.	−114.3	−114.5	−113.4	−113.3	−113.8
	60.2	*60.5*	*60.4*	*60.4*	*60.1*	*59.8*	*60.2*
ΔE_{orb}[b]	−75.5	−74.9	−75.0	−74.9	−75.5	−76.2	−75.4
	39.8	*39.5*	*39.6*	*39.6*	*39.9*	*40.2*	*39.8*
$\Delta E\ a_1$[c]	−24.4	−24.7	−24.4	−24.4	−24.5	−24.3	−24.4
	32.3	*33.0*	*32.5*	*32.6*	*32.5*	*31.8*	*32.4*
$\Delta E\ a_2$[c]	−7.9	−7.7	−7.8	−7.8	−7.8	−8.1	−7.8
	10.4	*10.2*	*10.4*	*10.3*	*10.4*	*10.6*	*10.4*
$\Delta E\ b_1$[c]	−29.2	−29.2	−29.1	−29.1	−29.2	−29.2	−29.1
	38.6	*39.0*	*38.8*	*38.8*	*38.5*	*38.2*	*38.6*
$\Delta E\ b_2$[c]	−14.1	−13.3	−13.8	−13.7	−14.0	−14.7	−14.1
	18.7	*17.8*	*18.4*	*18.3*	*18.6*	*19.3*	*18.7*
ΔE_{prep}	3.1	3.1	3.1	3.0	3.6	3.3	3.1
$\Delta E = -De$	−67.1	−67.6	−67.6	−67.8	−65.8	−66.0	−66.6

R	C_6F_5	ClC_6H_4			BrC_6H_4		
ΔE_{int}	−67.1	−68.9	−69.0	−69.7	−68.5	−68.9	−69.6
ΔE_{Pauli}	122.5	120.4	120.3	120.2	120.1	120.1	120.2
ΔE_{elstat}[b]	−111.2	−112.6	−113.0	−113.9	−112.2	−112.8	−113.8
	58.6	*59.5*	*59.7*	*60.0*	*59.5*	*59.7*	*60.0*
ΔE_{orb}[b]	−78.4	−76.7	−76.3	−76.0	−76.5	−76.2	−76.0
	41.4	*40.5*	*40.3*	*40.0*	*40.5*	*40.3*	*40.0*
$\Delta E\ a_1$[c]	−24.2	−24.1	−24.2	−24.4	−24.0	−24.2	−24.3
	30.9	*31.4*	*31.8*	*32.0*	*31.4*	*31.8*	*32.0*
$\Delta E\ a_2$[c]	−8.8	−8.5	−8.1	−8.0	−8.4	−8.1	−8.0
	11.2	*11.0*	*10.6*	*10.6*	*11.0*	*10.6*	*10.6*
$\Delta E\ b_1$[c]	−29.1	−28.9	−29.1	−29.2	−28.8	−29.1	−29.2
	37.2	*37.7*	*38.2*	*38.4*	*37.7*	*38.2*	*38.3*
$\Delta E\ b_2$[c]	−16.3	−15.2	−14.8	−14.5	−15.1	−14.8	−14.5
	20.8	*19.9*	*19.4*	*19.0*	*19.8*	*19.4*	*19.1*
ΔE_{prep}	4.8	3.7	3.3	3.2	3.8	3.3	3.2
$\Delta E = -De$	−62.3	−65.2	−65.7	−66.5	−64.7	−65.6	−66.4

[a] SB: RHC=N–CH_2CH_2–N=CHR.

[b] The value in Italic gives the percentage contribution to the total interactions ΔE_{int}.

[c] The value in Italic gives the percentage contribution to the total orbital interactions ΔE_{orb}.