Inorganica Chimica Acta, 32 (1979) 113–116
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He(I) Photoelectron Spectra of Pentacarbonyl(selenocarbonyl)chromium(0) and Related Complexes

A. M. ENGLISH, K. R. PLOWMAN, I. S. BUTLER

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

E. DIEMANN and A. MÜLLER

Fakultät für Chemie, Universität Bielefeld, Postfach 8640, 4800 Bielefeld 1, F.R.G.

Received May 31, 1978

The He(I) p.e. spectrum of $Cr(CO)_5(CSe)$ has been measured and all the ionization potentials are slightly lower than those reported earlier for the related thiocarbonyl derivative. The bands associated with the σ-donor and π-acceptor levels of the CSe ligand are well separated from the other bands and appear in the 10–11.5 eV range, i.e., *in between the bands for the metal 3d and the carbonyl ligands. The decrease in binding energies on replacement of a CO group in $Cr(CO)_6$ by CSe is at variance with the known physical and chemical properties of this and other selenocarbonyl complexes and is most probably due to a destabilization of the metal orbitals similar to that suggested for metal thiocarbonyl complexes. The first ionization potentials of $BzCr(CO)_2(CX)$ ($Bz = \eta^6$-C_6H_6; X = O, S, Se) were also measured and comparison of these values with those for the corresponding $Cr(CO)_5(CX)$ species indicates that there is a significant transfer of electron density from the benzene ring to the chromium atom in each case.*

Introduction

Unlike CO and CS, the isoelectronic carbon monoselenide species, CSe, has never been isolated even at very low temperatures [1]. While comparisons of the physicochemical properties of the three free ligands themselves are therefore not possible, the recent discovery of several transition metal selenocarbonyl complexes does allow comparisons of the properties of the coordinated ligands since the analogous carbonyl and thiocarbonyl complexes are also known [2]. Although the photoelectron spectra of some metal carbonyls and thiocarbonyls have been investigated, as yet no p.e. spectra have been reported for metal selenocarbonyls. We present here the He(I) p.e. spectra of $Cr(CO)_5(CSe)$ and $BzCr(CO)_2(CX)$ ($Bz = \eta^6$-C_6H_6; X = S, Se) and compare the observed ionization potentials with those measured previously for the related complexes, $Cr(CO)_6$ [3], $Cr(CO)_5(CS)$ [4], and $BzCr(CO)_3$ [5, 6].

Experimental

The $BzCr(CO)_2(CX)$ (X = S, Se) complexes were prepared by displacement of *cis*-cyclooctene from $BzCr(CO)_2(C_8H_{14})$ with CX_2/PPh_3 [7, 8]. The $Cr(CO)_5(CSe)$ complex was prepared by the literature method [9]. The p.e. spectra were recorded on a Vacuum Generators UVG3 electron spectrometer with He(I) excitation. The samples were introduced into the spectrometer *via* a variable temperature inlet system. The measurements were made at or slightly above room temperature. For the benzenechromium(0) complexes, only the first ionization potentials are reported because the compounds decomposed under the typical operating conditions of the spectrometer (the only identifiable products being CO and benzene). The measured ionization potentials are considered accurate to ±0.04 eV.

Results and Discussion

The He(I) p.e. spectrum of $Cr(CO)_5(CSe)$ is shown in Fig. 1. The H_2O impurity in the sample was used as a calibrant. Table I lists the observed ionization potentials for $Cr(CO)_5(CSe)$ and the first ionization potentials for the benzenechromium(0) complexes. The value quoted for $BzCr(CO)_3$ is from our own study on this particular complex. We have included ionization data from the literature for $Cr(CO)_6$ [3] and $Cr(CO)_5(CS)$ [4] in Table I for ready comparison.

$Cr(CO)_5(CSe)$

The most striking result is the similarity of the p.e. spectrum of $Cr(CO)_5(CSe)$ to that of $Cr(CO)_5(CS)$. Except for small shifts to lower binding energies in the case of the selenocarbonyl complex, the spectra in regions A, B, and C are identical. The differences in region D are more difficult to discern because of the broad, overlapping bands appearing in this region.

The p.e. spectrum of $Cr(CO)_6$ has been the subject of numerous studies [3] and has now been assigned

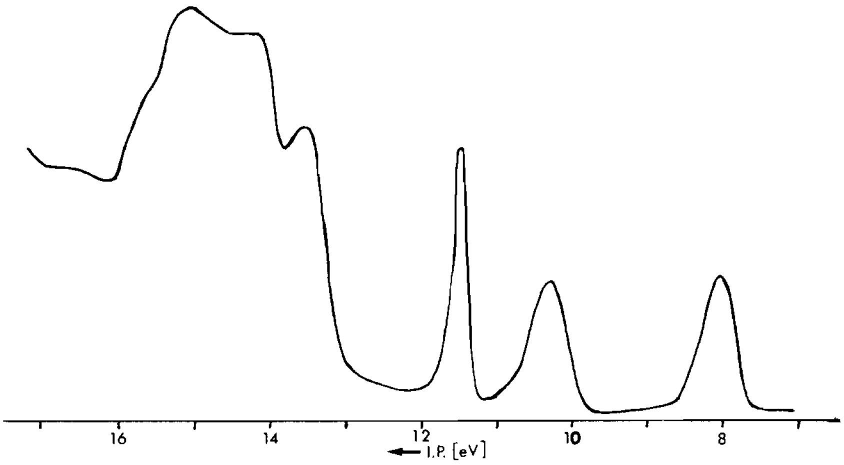

Figure 1. He(I) p.e. spectrum of $Cr(CO)_5(CSe)$ in the 7.0–16.5 eV range (sample pressure, 3.2×10^{-5} torr; scan time, 1×10^{-3} sec).

TABLE I. Ionization Potentials of $Cr(CO)_6$ [3], $Cr(CO)_5(CS)$ [4], and $Cr(CO)_5(CSe)$ and the First Ionization Potentials of the $BzCr(CO)_2(CX)$ (X = O, S, Se) Derivatives (eV).

Region	$Cr(CO)_6$	$Cr(CO)_5(CS)$[a]	$Cr(CO)_5(CSe)$
A	8.40 ($2t_{2g}$; 3d, π^*)	8.16 ($2b_2 + 7e$; 3d, π^*)	8.03 ($b_2 + e$; 3d, π^*)
B		10.93 (7σ, CS)	10.26 (9σ, CSe)
C		11.88 12.08 (2π, CS) 12.17	11.42 (3π, CSe)
D	13.38 ($8t_{1u}$) (5σ, CO) 14.21 ($1t_{1g}$) 14.40 ($1t_{2u}$) 15.12 ($7t_{1u}$)		13.46 (5σ, CO) 14.12 CO core 15.04
	$BzCr(CO)_3$	$BzCr(CO)_2(CS)$	$BzCr(CO)_2(CSe)$
A	7.29 ($17a_1 + 17e$; 3d, π^*)[b]	7.32 (3d, π^*)	7.36 (3d, π^*)

[a] A set of broad, overlapping peaks was observed for this complex above 13 eV but the peak maxima were not reported. [b] Literature value: 7.40 eV [5, 6]. The barycentre of this asymmetric peak in the present study is situated at 7.36 eV; the tabulated value refers to the peak maximum.

satisfactorily by means of an *ab initio* molecular orbital calculation [10]. The band in region A is attributed to a t_{2g} level which has a large portion of metal 3d character. The bands in region D and at higher binding energies are attributed to molecular orbitals derived mainly from the CO 5σ and 1π orbitals and deeper-lying molecular orbitals. Substitution of one CO group in $Cr(CO)_6$ by another two-electron ligand (L) lowers the molecular symmetry from O_h to C_{4v} and so the original t_{2g} level would be expected to split into a $b_2 + e$ set. For $Cr(CO)_5(CSe)$, however, no such splitting occurs for the band in region A. This is also true for the related thiocarbonyl complex [4] but not for the C_{4v} symmetry halopentacarbonylmanganese(I) complexes, $Mn(CO)_5L$ (L = Cl, Br, I), for which the band exhibits a splitting of about 0.7 eV [11].

The bands in regions B and C for $Cr(CO)_5(CSe)$ are assigned by analogy with those reported for $Cr(CO)_5(CS)$ [4] because of their similar intensities and shapes. Therefore, the observed bands are attributed to the M.O.'s which are associated primarily with the highest filled σ and π orbitals, respectively, of CSe. Relative to the intensity of the band in region A, replacement of S in $Cr(CO)_5(CS)$ by Se produces no significant changes in the intensities of the bands in regions B and C. This means that there is apparently no "heavy atom effect" similar to that which results in a doubling in intensity of the t_{2g} band on descending the metal hexacarbonyl series

[3]. However, this is really not too suprising as M.O. calculations on CO and CS [4] show that the 5σ and 7σ orbitals (the highest filled M.O.'s in CO and CS, respectively) are the lone pair orbitals centred on the carbon atoms. These calculations also indicate that the 2π (π*CO) and 3π (π*CS) orbitals, which are unoccupied in the free ligands, are again located chiefly on the carbon atoms.

The bands for $Cr(CO)_5(CSe)$ appearing in region D are attributed to the highest occupied σ and π levels of the carbonyl ligands by comparison with the spectra of $Cr(CO)_6$ and $Cr(CO)_5(CS)$. Finally, the similarities in the p.e. spectra of all three complexes suggest that the generalized M.O. diagram shown in Fig. 2 is applicable to this series of complexes.

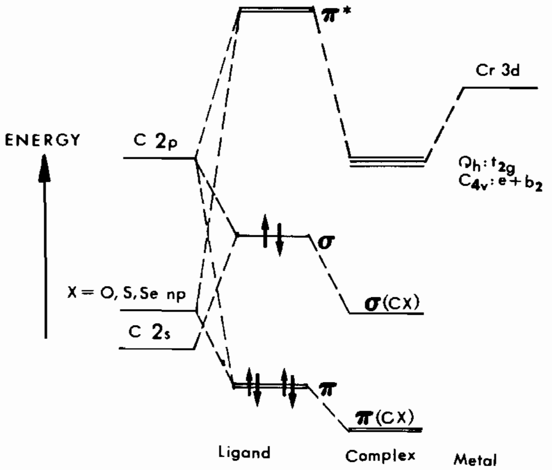

Figure 2. Generalized M. O. diagram for the three chalcocarbonyl complexes, $Cr(CO)_5(CX)$ (X = O, S, Se).

The shifts to lower binding energies on successive replacement of a CO group in $Cr(CO)_6$ by first CS and then CSe seem to be inconsistent with the physicochemical properties observed to date for transition methal thio- and selenocarbonyl complexes [2]. For example, recent ^{13}C and ^{17}O nmr studies on $Cr(CO)_5(CX)$ (X = S, Se) [12] together with complete normal coordinate calculations on the same species [8, 13] clearly indicate the greater electron withdrawing capacities of CS and CSe compared to CO. Also, the reactions of $Cr(CO)_5(CS)$ [14] and $Cr(CO)_5(CSe)$ [15] with monodentate ligands show that CS and CSe are much more inert with respect to substitution than is CO. From these experimental observations, the binding energies of the (3d, π*) levels would be expected to increase in the order $Cr(CO)_6 < Cr(CO)_5(CS) < Cr(CO)_5(CSe)$. From their SCF M.O. calculations on $Cr(CO)_5(CS)$, Lichtenberger and Fenske [4] showed, however, that this level should be destabilized by about 0.1–0.2 eV (0.24 eV observed) on substitution of a CS group into $Cr(CO)_6$. Therefore, although CS accepts a greater amount of charge, the increased electron density on the CS carbon atom (due to the lower electronegativity of sulfur) together with an increased percentage from the ligand result in a destabilization of the last occupied orbitals. Presumably, a somewhat similar situation will be operative in the analogous $Cr(CO)_5$-(CSe) complex. It is expected that M.O. calculations on CSe itself and some of its complexes will shed more light on the electronic behaviour of this interesting ligand in the future.

BzCr(CO)$_2$(CX) (X = S, Se)

Contrary to the pentacarbonyl complexes discussed above and on going from $CpMn(CO)_3$ to $CpMn(CO)_2(CS)$ (Cp = η^5-C_5H_5) [4], there is an increase in the first ionization potential on descending the benzenechromium(0) series. However, in the absence of more complete p.e. data and calculations on either the thio- or the selenocarbonyl derivative, a detailed discussion on the electronic structure and bonding in this series of complexes is unwarranted. Again, however, there is no strong splitting on lowering the local symmetry of the $Cr(CO)_3$ moiety from C_{3v} to C_s as the (3d, π*) level (a_1 + e) gives only an asymmetric signal in the p.e. spectra of the thio- and selenocarbonyl derivatives. On comparison of the binding energies for the bands in region A of the $BzCr(CO)_2(CX)$ series with those of the corresponding $Cr(CO)_5(CX)$ (X = O, S, Se) compound, it is clear that there is a decrease in binding energy of about 1 eV in each case. This decrease in binding energy indicates a drift of negative charge from the arene ring to the central metal atom. That the metal atom transfers some of this negative charge to the metal carbonyl moiety is illustrated by the decrease in the C–O stretching force constant on going from $Cr(CO)_6$ [16] to $BzCr(CO)_3$ [17], *viz.*, 17.04 to 14.8 mdyn/Å, respectively.

Acknowledgements

This research was generously supported by the National Research Council of Canada and the Quebec Department of Education. One of us (A.M.E.) thanks McGill University and the National Research Council of Canada for the award of graduate scholarships. A travel grant to I.S.B. by the Deutscher Akademischer Austauschdienst (DAAD) is gratefully acknowledged.

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