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CHROMIUM PENTACARBONYL COMPLEXES OF SOME DIHYDRO- AND TETRAHYDRO-THIOPHENE DERIVATIVES: DETERMINATION OF THE TYPE OF BONDING OF CHROMIUM TO A SULFOXIDE MOIETY

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Summary

Chromium pentacarbonyl complexes of some dihydro- and tetrahydro-thiophenes and their sulfoxides have been prepared. In the sulfide derivatives the chromium is readily seen to be attached to the sulfur atom. The sulfoxide functionality also acts as a ligand for chromium, and by means of IR and mass spectra and the ESCA technique it was tentatively concluded that chromium is bonded to the sulfur atom of the sulfoxide. This assignment was confirmed by an X-ray analysis of 2,5-dihydrothiophene-1-oxide chromium pentacarbonyl.

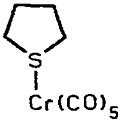
Introduction

During our study of the interaction of metal carbonyls with thiophene derivatives [1,2] the chromium pentacarbonyl complexes of these compounds were examined. From ^1H and ^{13}C NMR spectra it was obvious that the chromium metal was bound to the sulfur atom in sulfide derivatives or to the sulfoxide moiety in sulfoxide derivatives. In the latter case, however, nuclear magnetic resonance spectra provide no information whether the chromium is bonded to the sulfur atom or to the oxygen atom (a more esoteric possibility, for which no precedent exists, is bonding of the metal to the sulfur—oxygen double bond). In the chromium pentacarbonyl complexes investigated, recourse was taken in other techniques, i.e., IR, mass, ESCA and X-ray methods, for solution of this structural problem.

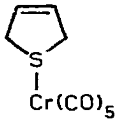
Results and discussion

Irradiation of the sulfur-containing ligands with chromium hexacarbonyl in benzene gave the metal pentacarbonyl complexes of tetrahydrothiophene (I)

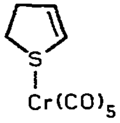
[3], 2,5-dihydrothiophene (II) [4], 2,3-dihydrothiophene (III) and their corresponding sulfoxides (IV, V and VI, respectively). From the ^{1}H and ^{13}C NMR



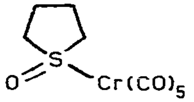
(I)



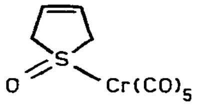
(II)



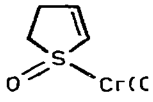
(III)



(IV)



(V)

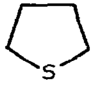
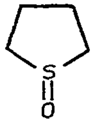
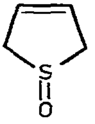
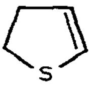
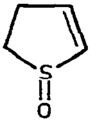


(VI)

spectra it was evident that the double bond in II, III, V and VI was not affecte (see Table 1). The electrons of the ligands necessary for the coordination by a metal pentacarbonyl group must thus come from the sulfur atoms in I, II and III and from the sulfoxide moieties in IV, V and VI. As already mentioned the

TABLE 1

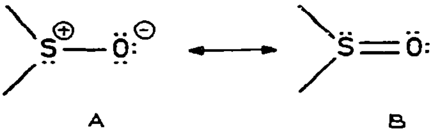
NMR DATA FOR THIOPHENE DERIVATIVES AND THEIR CHROMIUM PENTACARBONYL COMPLEXES IN CD_3COCD_3 (unless otherwise stated; 30°C, δ (in ppm) relative to TMS)

L	Free ligand (PMR)[a]	$Cr(CO)_5L$(PMR)[a]	$Cr(CO)_5L$ (^{13}C NMR)
	2.92—2.60 2.10—1.75	3.20—2.87 [b] 2.28—1.92	
	3.03—2.70 ($CDCl_3$) 2.70—1.80	3.57—3.19 [b] 2.52—2.19	
	5.83(s) 3.67(s)	6.01(s) 3.94(s)	222.0(s): 215.3(s) 128.2(d, *J* 168 Hz); 49.4 (t, *J* 146 Hz)
	6.02(s) 3.58(dd, *J* 17 Hz)	6.16(s) 4.18(s)	220.8(s): 213.8(s) 127.0(d, *J* 175 Hz); 69.1(t, *J* 144 Hz)
	6.31—6.08 5.75—5.50 3.45—3.08 2.95—2.50	6.32—6.18 6.12—5.94 3.56—3.32 3.12—2.85	222.4(s): 215.4(s); 129.7(d, *J* 176 Hz) 126.7(d, *J* 179 Hz); 40.3(t, *J* 144 Hz) 35.0(t, *J* 140 Hz)
	7.02—6.55 3.73—2.48	7.34—7.02 6.94—6.70 3.96—2.78	221.2(s), 213.8(s), 140.7(d, *J* 168 Hz) 138.7(d, *J* 189 Hz), 61.8(t, *J* 143 Hz) 33.4(t, *J* 137 Hz)

[a] Virtually all absorptions were multiplets except those mentioned. [b] See ref. 3.

are two potential sites of bonding to the sulfoxide making the structural problem more involved for the complexes of IV—VI.

The approach most often used for determining the type of chromium—sulfoxide bonding is analysis of the infrared spectra, especially in the region of the S—O absorptions [5]. The S—O bond is usually regarded as having considerable double bond character [6], i.e. as being a resonance hybrid of structures A and B. Bonding of a metal, or any other electron deficient species, to the oxygen atom of the sulfoxide should lower the bond order of the S—O bond, as implied in resonance structure A, and lead to a decrease of ν(SO). Bonding of a metal to the sulfur atom of a sulfoxide leads to an increase in the S—O bond order, i.e. a shift towards resonance structure B and hence an increase of ν(SO). The principle is very simple, but in practice the determination of the type of bonding meets with a number of complications. Although the S—O stretching mode generally gives rise to an intense peak, on complexation some extra absorptions can appear in the S—O region, which sometimes makes the identification of this stretching frequency difficult; also ν(SO) in solution depends on the nature of the solvent, the concentration and the state of aggregation [5]. From analyses of the shift of the S—O stretching frequencies in metal—sulfoxide complexes either metal—sulfur [3] or metal—oxygen [7] bonding has been concluded.



Correlation of infrared and crystallographic studies reveals that second and third row transition metal—dialkyl sulfoxide complexes contain metal—sulfur rather than metal—oxygen bonds (see Table 2). Metals belonging to the first transition series favor oxygen bonding on complexation [5,8].

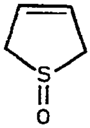
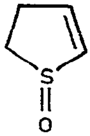
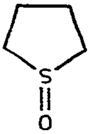
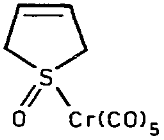
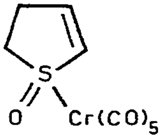
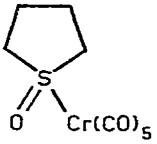
The S—O stretching frequencies in the IR spectra of the free ligands tetrahydrothiophene-1-oxide, 2,5- and 2,3-dihydrothiophene-1-oxide are found at 1020 cm^{-1}, whereas the S—O absorptions of compounds IV, V, VI are found at about 1070 cm^{-1}. These shifts to higher frequencies indicate metal—sulfur bonding in these complexes.

Further indications for metal—sulfur bonding for IV—VI are found in the mass spectra of these complexes. In the fragmentation pattern of these compounds peaks arising from $(M - O)^+$ fragments are observed (see Table 3). The loss of an oxygen from a carbon monoxide ligand has never been reported, and is extremely unlikely. Therefore it must be the sulfoxide functionality that loses its oxygen atom, a phenomenon which has been observed in non-complexed sulfoxides [16]. This loss in the complexes IV—VI can be most easily rationalized by invoking metal—sulfur bonding.

ESCA (electron spectroscopy for chemical analysis) is a new and important method that might also be used for resolution of such structural questions. Su and Faller [17] applied the ESCA technique to determine the type of bonding of a metal atom to a sulfoxide moiety. They postulated that the difference between the O1*s* and S2$p_{3/2}$ ionization potentials of the complexed sulfoxide will reveal the type of bonding. For metal—S bonding this difference was found to be 365.0 (±0.3 eV), whereas for metal—O bonding 365.8 (±0.3) eV.

TABLE 2

SO STRETCHING FREQUENCIES OF METAL SULFOXIDE COMPLEXES AND THE RESULTS OF X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS

Formula		ν(SO) (cm^{-1})	Mode of bonding [a]	Ref.
DMSO	b	1046		9
$FeCl_3.(DMSO)_2$	c	933, 988	Fe—O	10, 11
$PdCl_2.(DMSO)_2$	c	1118	Pd—S	12, 13
$Pd(NO_3)_2.(DMSO)_2$	c	1136, 1157	Pd—S	14
$(C_{15}H_{13}O)IrCl_2(DMSO)_2$	c	d	Ir—S	15
	b	1020		
	b	1020		
	b	1022		
 (V)	c	1071		
 (VI)	c	1074, 1070		
 (IV)	c	1068		3

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[a] Determination by X-ray crystallography. [b] Liquid phase. [c] KBr pellets. [d] Citation of the authors: "spectroscopic evidence (IR and NMR) is consistent with the proposed structure (Ir—S bond)".

The relevant spectral ESCA data for the chromium complexes we prepared are presented in Table 4, together with data for some noncomplexed organosulfur compounds for comparison.

The sp^3C, CH_3 segment in complex VII was used as the reference at a value of 285.0 eV. The value thereby obtained for the $Cr2p_{3/2}$ ionization potential of

TABLE 3

RELATIVE ABUNDANCES IN FRAGMENTATION SPECTRA OF II, III, V AND VI (Spectra recorded at 60°C (II), 50°C (III), 80°C (V) and 70°C (VI))

m/e	Ion	II	III	m/e	Ion	V	VI
278	M^+	11	1	294	M^+	1	2
250	$(M-\mathrm{CO})^+$	1	1	278	$(M-\mathrm{O})^+$	6	3
222	$(M-2\mathrm{CO})^+$	5	~0	266	$(M-\mathrm{CO})^+$	1	3
194	$(M-3\mathrm{CO})^+$	7	~0	250	$(M-\mathrm{O}-\mathrm{CO})^+$	1	1
166	$(M-4\mathrm{CO})^+$	19	1	238	$(M-2\mathrm{CO})^+$	1	1
138	$(M-5\mathrm{CO})^+$	51	4	210	$(M-3\mathrm{CO})^+$	1	1
86	$(\mathrm{C_4H_6S})^+$	100	100	194	$(M-\mathrm{O}-3\mathrm{CO})^+$	4	1
				182	$(M-4\mathrm{CO})^+$	6	9
				166	$(M-\mathrm{O}-4\mathrm{CO})^+$	1	6
				154	$(M-5\mathrm{CO})^+$	16	27
				138	$(M-\mathrm{O}-5\mathrm{CO})^+$	32	16
				102	$\mathrm{C_4H_6SO^+}$	10	4
				86	$\mathrm{C_4H_6S^+}$	100	100

575.2 eV was assigned to all Cr$2p_{3/2}$ lines for calibration.

The emissions for the carbon atoms of the ligand and the carbonyl groups as well as those for the oxygen atoms of the sulfoxide moiety and the carbonyls are not well separated. For this reason all the ESCA spectra (narrow scan spectra for every atom) for each compound were simulated, using the simulation program written by Sawatzky and coworkers [19]. This program first makes a background and X-ray satellite correction and then adapts the value of the ionization potentials and the intensities of the programmed number of peaks of the measured and corrected ESCA spectrum in a least square fitting routine. In this way the ESCA emission is divided into the desired number of peaks for which the ionization potentials, intensities, and areas are known. Simulation of measured ESCA spectra is the most accurate and unbiased way for separating complex emissions into the component peaks. The relative peak areas for the C1*s* and O1*s* ionization potentials are not completely in agreement with those expected, probably owing to sublimation of some traces of residual carbon and/or water on the sample holder, or to some free ligand disengaged from the complex by irradiation with X-rays.

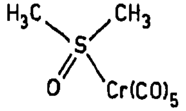
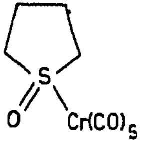
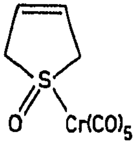
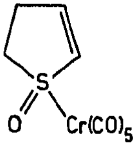
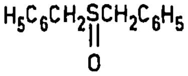
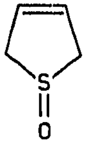
That the ESCA measurements do refer to the complexes and not to the free ligands is concluded from the presence of satellite peaks in the narrow scan spectra for the C1*s* and O1*s* emissions of the carbon monoxide functionalities in these complexes; a phenomenon which is characteristic of metal carbonyls [20]. The satellite peaks, found at 5.4 eV and 5.5 eV (averaged) higher binding energies for the O1*s* and C1*s* emissions, respectively, are referred to as shake-up peaks and have been described theoretically by Barber and coworkers [21]. Furthermore the position and intensities of the satellite peaks confirm the assignment of the observed ionization potentials (vide infra) to the C1*s* and O1*s* emissions of the carbon monoxide groups and the ligands, respectively.

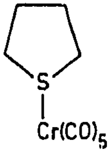
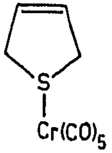
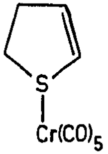
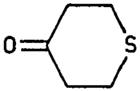
The assignment of the measured C1*s* and O1*s* ionization potentials, respectively, to the carbon and oxygen atoms of the organic ligand and of the carbon monoxide groups is in accord with the resonance forms $^{-}\mathrm{Cr{-}C{\equiv}O^{+}} \longleftrightarrow \mathrm{Cr{=}C{=}O}$. This resonance leads to a strong bonding: therefore higher ionization potentials

(Continued on p. 368)

TABLE 4

IONIZATION POTENTIALS IN eV

	$C1s(sp^2 + sp^3)$	$C1s(CO)$	$O1s(CO)$	$O1s(SO)$	$S2p_{1/2}$	$Cr2p_{1/2}$	$Cr2p_{3/2}$ [a]
 (VII) [b]	285.0	286.6	533.0	531.3	166.7	583.9	575.2
 (IV) [b]	284.9	286.6	532.9	531.1	166.2	583.9	575.2
 (V)	285.1	286.8	533.0	531.3	166.1	584.1	575.2
 (VI)	284.9	286.7	532.9	530.9	166.2	584.0	575.2
 $H_5C_6CH_2S(=O)CH_2C_6H_5$ [c]				531.5	166.1		
	285.1	286.6	532.9	531.3	166.0		

	(I)	b	285.0	286.4	532.8	164.2	584.0	575.2
	(II)		284.9	286.5	532.8	164.0	584.0	575.2
	(III)		284.9			164.2	583.9	575.2
		c				164.0		
$HOOCCH_2SCH_2COOH$		c				163.9		

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[a] The $Cr2p_{3/2}$ ionization potential is used as an internal reference to correlate the spectra of all chromium pentacarbonyl complexes. [b] See ref. 3. [c] ESCA values published in the literature (ref. 18) with the sp^3C, CH_3 value of 285.0 eV as calibration.

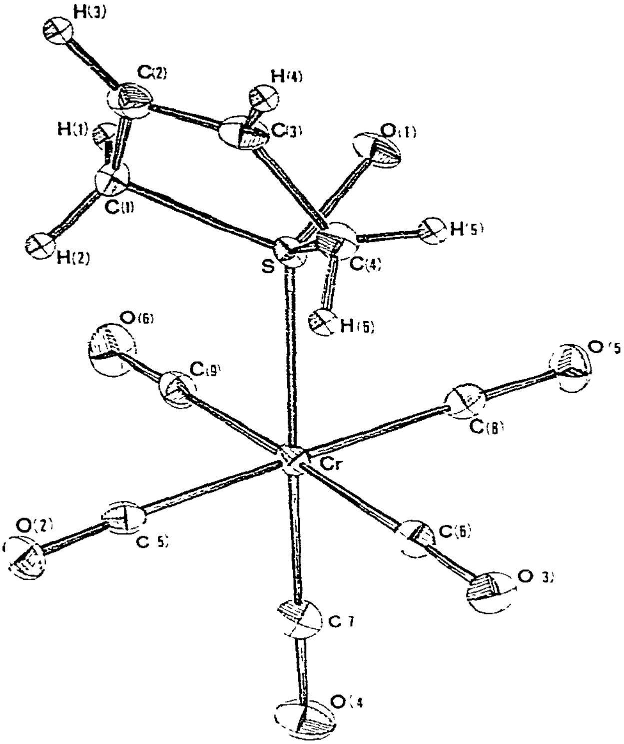

Fig. 1. Structure of complex V.

are expected for the C1*s* and O1*s* electrons of the carbon monoxide moieties relative to those of the $sp^2 + sp^3$C atoms and the sulfoxide O atoms. The relative intensities of the measured C1*s* and O1*s* ionization potentials are also in accord with this assignment. The same approach to assignment has been used in respect to the ESCA emissions of iron tricarbonyl complexes [2]. For the various complexes the variation for the C1*s* and O1*s* emissions is minimal, which means that the $Cr(CO)_5$ moieties are electronically similar in all complexes and indeed can be used for calibration.

It is noteworthy that from the ESCA spectral data (Table 4) no shifts are

TABLE 5

CRYSTAL DATA FOR COMPLEX V (Monocyclic crystals, space group $P2_1/c$, $Z = 4$)

Bond distances	(Å)	Angles (°)	
Cr—S	2.331	Cr—S—O	114.6
S—O	1.486	Cr—S—C(1)	116.4
Cr—C(7)	1.858	Cr—S—C(4)	117.6
Cr—C(5)	1.917	S—Cr—C(8)	86.1
S—C(1)	1.811	S—Cr—C(7)	175.4
C(2)—C(3)	1.327	C(1)—S—O	106.2
C(9)—O(6)	1.144		

observed for the O1s and S2$p_{3/2}$ ionization potentials in the chromium pentacarbonyl complexes relative to the free ligands; this is the case not only for the sulfoxide complexes but also for the sulfide complexes. Relative differences between the O1s and S2$p_{3/2}$ ionization potentials of the complexed sulfoxides of 364.6, 364.9, 365.2 and 364.7 eV are found for IV—VII, respectively. Application of the Su and Faller criteria to IV—VII leads to the conclusion that chromium is bonded to sulfur in these complexes. However we have previously shown that the Su and Faller criteria cannot be extrapolated to all sulfoxide complexes (e.g. 2,5-dihydrothiophene-1-oxide iron tricarbonyl, iron bonded not only to the sulfoxide moiety but also to a double bond [2]) an X-ray structural determination was deemed necessary to confirm the assignment of a metal—sulfur bond in the sulfoxide complexes beyond doubt. The crystal structure of complex V establishes the metal—sulfur bond (Fig. 1). Note that the metal atom assumes a pseudo axial position.

Some crystallographic data are listed in Table 5; the dihydrothiophene ring has an envelope structure with a dihedral angle of 22.5°. Other details of the structure have appeared elsewhere [22]. Because of similar spectral behavior in relation to V we assign also a chromium—sulfur bond to the sulfoxide complexes IV, VI and VII *.

Experimental

General remarks

Microanalyses were performed in the Microanalytical Department of this laboratory by Mr. H. Draayer, Mr. J. Ebels, Mr. A.F. Hamminga, Mr. J. Hommes, Mr. A. Meetsma and Mr. J.E. Vos. Infrared spectra were recorded on a Perkin—Elmer 257, a Perkin—Elmer 125 or a Hitachi EPI-G spectrophotometer and calibrated relative to polystyrene. Mass spectra were obtained on an AEI MS-902 by Mr. A. Kiewiet. The magnetic resonance spectra were recorded on a Varian A-60 D or a Perkin—Elmer R-24 B spectrometer with TMS (δ 0 ppm) as an internal reference. A Varian XL-100 was used for the carbon-13 spectra. These spectra were recorded by and discussed with Ir. P.B.J. Driessen, Drs. H. Hiemstra, Drs. W.A. Mellink and Drs. O. Possel. Commercial chromium hexacarbonyl was used without purification. Solvents were purified by standard methods.

Some parts of this work were performed in close collaboration with Drs. E. Klei. We thank Ir. A. Heeres for recording the ESCA spectra.

General procedure for the preparation of the chromium pentacarbonyl complexes

1 mmol of the ligand and 1.1 mmol of $Cr(CO)_6$ were irradiated in benzene under dry nitrogen atmosphere with a Hanau S81 quartz lamp for about 20 h. After filtration and evaporation of the solvent the product was purified by sublimation. The compounds were characterized by ^1H NMR, ^{13}C NMR, IR and mass spectroscopic measurements and microanalytical data. Compounds I, IV and VII (ref. 3) and II (ref. 4) have been described in the literature. Analyses: III.

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* A base-induced electrocyclic ring-opening is observed in the reaction of V with NaH in DME; a similar reaction has been reported in the case of 2,5-dihydrothiophene and its 1,1-dioxide with KNH_2 in NH_3 [23].

Found: C, 38.78; H, 2.20; S, 11.16; Cr, 18.66. $C_9H_6O_5SCr$ calcd.: C, 38.86; H, 2.17; S, 11.52; Cr, 18.69%. V. Found: C, 38.00; H, 2.12; S, 10.83; Cr, 17.37. $C_9H_6O_6SCr$ calcd.: C, 36.74; H, 2.06; S, 10.90; Cr, 17.67%. VI. Found: C, 36.81; H, 2.07; S, 10.91, Cr, 17.60. $C_9H_6O_6SCr$ calcd.: C, 36.74; H, 2.06; S, 10.90, Cr, 17.67%.

ESCA measurements

The experiments were performed using an AEI ES 200 spectrometer with a PDP 8 data handling facility. The sample chamber of the spectrometer was modified to accept a liquid nitrogen cooled cryopump of a capacity such that the vacuum in the vicinity of the sample is even better than the measured vacuum, which was in most cases 10^{-9} Torr during a measurement. The cryopum also allowed working with cooled samples without serious problems from either water or hydrocarbon build-up on the surface. All samples were sublimed on to a cooled sample holder (—100°C) in the sample chamber of the spectrometer, usin either the AEI sample holder for materials of low volatility or the holder for volatile materials. During sublimation the pressure rose to about 2—3 × 10^{-8} Torr. All charging-up effects were corrected by taking the Cr2$p_{3/2}$ binding energy as calibration as described.

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