A Tandem Mass Spectrometry Study of the Gas Phase $\text{RSC}_6\text{H}_5\text{Cr}^+\text{L}$ ($\text{R} = \text{H}, \text{C}_6\text{H}_5$; $\text{L} = \text{arene}$) and $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ Ions

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Ion-molecule reactions of chromium containing ions with arylsulfides have been studied in the gas phase and their products have been characterized by tandem mass spectrometry. $\text{C}_6\text{H}_5\text{SH}$ and $(\text{C}_6\text{H}_5)_2\text{S}$ react as typical aromatic compounds and give rise to $\text{Cr}^+\text{C}_6\text{H}_5\text{SR}'$ and $\text{RC}_6\text{H}_5\text{Cr}^+\text{C}_6\text{H}_5\text{SR}'$ [$\text{R} = \text{H}, \text{CH}_3, \text{CH}(\text{CH}_3)_2$; $\text{R}' = \text{H}, \text{C}_6\text{H}_5$] ions. Metastable ion mass spectra of the latter species show that the metal is more strongly bound to diphenylsulfide than to alkylbenzenes. $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ reacts with chromium-containing ions to form only $\text{Cr}^+(\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5)$. The decomposition characteristics of this ion and, in particular, the presence of a recovery signal in the neutralization-reionization mass spectrum are in keeping with the formation of a 1,2-dithia[2]cyclophane complex ion, which rearranges into a structure(s) that contains Cr—S bond(s). No evidence was found for metal atom insertion into S—S, C—S, or S—H bonds. (*J Am Soc Mass Spectrom* 1994, 5, 928–934)

Gas-phase ion-molecule reactions of the ligated L_nM^+ or "bare" transition metal ions ($n = 0$) with aromatic compounds (arene) have been extensively studied [1, 2]. Formation of a new metal-ligand bond $\text{M}^+\text{--arene}$ by addition or substitution reactions has been observed. Sandwich-like complexes $\text{LM}^+(\text{arene})$ where L is a π -ligand, have been produced by ion-molecule reactions of ligated metal ions with the corresponding arenes [2]. An interesting type of complex is a cyclophane-like structure, in which the same ligand is connected via two separate sites to the central metal atom. Formation of such species has been observed as a result of unimolecular decomposition of some transition metal π -complexes [3]. For example, loss of three CO molecules from the molecular ion of **1** ($\text{X} = [\text{CH}_2]_2$ or $[\text{CH}_2]_4$) resulted in rearrangement into the ion **2**⁺, which was indicated by its reactivity in NH_3 chemical ionization conditions [3a]: unlike other (arene)- Cr^+ ions, they did not form ammonia adducts (Scheme I).

In the present study, ion-molecule reactions of some aromatic sulfides, namely, thiophenol, diphenylsulfide, and diphenyldisulfide, with chromium-containing ions are described. These ligands have been chosen as models for the investigation of complex formation in polyphenylenesulfide polymers doped by metal atoms. A study of the reaction products between chromium

atom vapors and polyphenylenesulfides by other physicochemical methods [4] has not provided much evidence for the formation of π -complexes and in particular, "sandwich" complexes between polyphenylenesulfide layers and chromium atom(s). For this purpose, $\text{C}_6\text{H}_5\text{SH}$ and $\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$ were chosen for the possible generation of the above species. It should be noted that complexes of diphenylsulfide with the chromium tricarbonyl group [5], as well as chromium tricarbonyl complexes with other thiophenol derivatives, have been already synthesized [6]. Diphenyldisulfide was considered to be a potential chelating ligand, able to form cyclophane complexes in which two aromatic rings of the organic molecule are bound to the metal ion. Similar chromium complexes, which contain two carbon (Structure 3; $\text{X} = \text{CH}_2\text{CH}_2$ [7]) or silicon (Structures 2 and 3; $\text{X} = (\text{CH}_3)_2\text{Si}$

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$(\text{CH}_3)_2$ [8, 7]) atoms in the bridge between two η^6 aromatic ligands, have been previously synthesized.

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Some cyclophane sulfur-containing π -complexes, for example, 1,2,3-trithia[3]ferrocenophane [9], also have been produced, but similar complexes of chromium that contain bridging sulfur atom(s) are not known. Gladysz et al. [10] attempted to produce a chromium complex of dibenzylsulfide by condensation with Cr atom vapors, but the reaction failed because of major desulfurization processes. The formation of metal sulfides also has been observed in the unimolecular decomposition of chromium complexes with sulfur-containing ligands [11] and in gas-phase ion-molecule reactions between metal-containing ions and organic sulfides [12]. For example, the reaction of FeS_n^+ ($n = 0-2$) with $\text{C}_6\text{H}_5\text{SH}$ resulted in FeS_{n+1}^+ ions and a benzene molecule [2s].

Benzenechromiumtricarbonyl, its alkyl derivatives, $\text{Cr}(\text{CO})_6$ and $(\text{C}_5\text{H}_5)_2\text{Cr}$ were used in the present study as sources for the chromium-containing ions that reacted with aromatic sulfides, benzene, toluene, and dimethyldisulfide.

Experimental

Mass spectra were recorded using Kratos MS30 (Kratos Analytical, Ramsey, NJ) and modified VG ZAB-2F (VG Analytical Ltd., Manchester, UK) [13] mass spectrometers. Ionizing electron energies varied from 6 to 70 V; the ion source temperature was 180–250 °C. To observe ion-molecule reactions, organometallic and organic compounds were evaporated simultaneously into the ion source by using the solid probe inlet systems. For volatile compounds (CH_3SSCH_3 , C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$), the gas inlet systems were used.

Metastable ion (MI), collision-induced decomposition (CID), collision-induced dissociative ionization (CIDI), and neutralization-reionization (NR) mass spectra were recorded on a three-sector (BEE) VG ZAB-2F mass spectrometer. In the CID and CIDI experiments, oxygen was used as the collision gas; its pressure in the second collision cell of the second field-free region (2FFR) was adjusted to give a main ion beam transmission of 85–90%. In triple mass spectrometry experiments fragment ions of interest were produced in the 2FFR from mass-selected precursor ions; they were then energy-selected by the first electric sector and collisionally activated (He, 70% transmission) in

the 3FFR. The resulting CID mass spectrum was recorded by scanning the second electric sector voltage. In the NR experiments Xe was used for neutralization and oxygen was used for reionization. Their respective pressures in the first and second collision cells of the 2FFR were adjusted to provide 15% reduction of the main ion beam.

Results and Discussion

Ion Formation

Mass spectra from the ion source mixtures of organometallic compounds and aromatic sulfides displayed molecular and fragment ions of each component as well as ion-molecule reaction products. Some of the latter originated from reactions of the metal-containing ions with the parent organometallic compound; such reactions have been reported elsewhere [14]. The mass spectra of some mixtures also showed ions in which the transition metal atom was bound to a new ligand (L), the most common species was $\text{Cr}^+\text{C}_6\text{H}_5\text{R}$ (Table 1). In the mass spectra of mixtures of the metal complexes with aromatic sulfides these ions were observed at (nominal) ionizing electron energies lower than the ionization energy of $\text{C}_6\text{H}_5\text{SR}$, which indicates their possible formation by reactions of the metal-containing ions with a neutral arylsulfide.

Thiophenol and diphenylsulfide react with arene- $\text{Cr}(\text{CO})_n^+$ like other aromatic compounds (see Table 1 and ref 2j) to produce bis-arene complexes $[\text{arene}-\text{Cr}(\text{C}_6\text{H}_5\text{SR})^+]$ that contain the initial arene and a new sulfur-containing ligand. $(\text{C}_6\text{H}_5\text{SR})\text{Cr}^+$ ions were also observed. All these species can originate from substitution of the carbonyl or arene ligands by L at the central metal atom. However, adduct formation between arene- Cr^+ or Cr^+ ions and the aromatic (sulfide) molecule cannot be excluded. If such an adduct is formed it is probably stabilized by secondary collisions in the ion source.

The possible formation of stable adducts is clearly indicated by the mass spectrum of the chromocene-toluene mixture, which displays $\text{C}_5\text{H}_5\text{Cr}^+\text{C}_6\text{H}_5\text{CH}_3$ and $\text{Cr}^+\text{C}_6\text{H}_5\text{CH}_3$ ions in $\approx 1:6$ abundance ratio. The metal-cyclopentadienyl bond is one of the strongest metal- π -ligand bonds; for example, the energy required for removal of the C_5H_5 ligand from

Table 1. Relative abundances of arene- Cr^+L and arene- Cr^+ ions in the mass spectra of some arene- $\text{Cr}(\text{CO})_3/\text{L}$ mixtures

Arene	L	[arene- Cr^+]/[LCr^+]
C_6H_6	$\text{C}_6\text{H}_5\text{CH}_3$	0.17
C_6H_6	$\text{C}_6\text{H}_5\text{SH}$	0.20
C_6H_6	$\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$	$\ll 0.01$
C_6H_6	CH_3SSCH_3	0.14
$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$	0.11
$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$	0.07
$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$	$\ll 0.01$

(C_5H_5) $_2Cr^+$ and $C_5H_5Cr^+$ ions is 6.55 [15] and 4.6 eV [16], respectively, whereas that for the $C_6H_6-Cr^+$ bond cleavage is less than about 3 eV [16, 17]. Differences in $C_6H_6-Cr^+$ and $C_5H_5-Cr^+$ bond strengths can be illustrated by the behavior of $C_5H_5Cr^+C_6H_6$ ions, for which arene loss is the dominant reaction [16]. Note also, that substitution of the cyclopentadienyl ligand at the transition metal atom (M) on benzene or its derivatives has not been observed in the gas phase (C_5H_5) $_2M^+$ or $C_5H_5M^+$ ions [2h, 2p]. Therefore, in the present experiments, the formation of ions that have a Cr-arene bond likely resulted from the addition of arene to the corresponding metal-containing ions.

The mass spectra of mixtures of arenechromiumtricarbonyls with CH_3SSCH_3 displayed arene- $Cr^+CH_3SSCH_3$ and $Cr^+CH_3SSCH_3$ ion peaks. In all these experiments the arene- Cr^+L/Cr^+L ion abundance ratios varied in a relatively narrow range (0.07-0.20) independent of the substituent in the aromatic ring of the organometallic complex and the nature of the new organic ligand.

Diphenyldisulfide behaved differently from the other organic molecules studied. The mass spectra of its mixtures with arenechromiumtricarbonyl derivatives contained no signals that correspond to arene- $Cr^+(C_6H_5SSC_6H_5)$, which shows the $Cr^+(C_6H_5SSC_6H_5)$ ion as the only ion-molecule reaction product having a new metal-ligand bond. Note that the latter species also were formed in the electron ionization (EI) mass spectrum of the diphenyldisulfide mixture with $Cr(CO)_6$, whereas mixtures of the latter with other substituted benzenes [C_6H_5R ($R = CH_3$, SH , SC_6H_5 , or CH_3SSCH_3)] did not show Cr^+L ions. From the above observations it can be proposed that diphenyldisulfide forms a special complex with chromium ions. Possible structures of this complex (Structures 4-10), are shown below. Structure 4 is the least likely candidate because if the $C_6H_5SSC_6H_5$ molecule is coordinated to a Cr atom as a typical π -aromatic ligand, its behavior should be similar to that of other aromatic compounds.

Metastable and Collision-Induced Dissociation

To characterize the $C_6H_5SSC_6H_5Cr^+$ ion structure, its decomposition was studied and compared with that of the other chromium-containing ions and the metal-free diphenyldisulfide molecular ion.

The MI mass spectra of diphenyldisulfide and its complex with Cr^+ are shown in Figure 1. Two common decompositions, namely, C_6H_6 and S_2 loss, were observed. Fragmentation of ionized diphenyldisulfide also involves the loss of H^+ , HS^+ and $C_6H_5S^+$ radicals to yield even-electron ions. $C_6H_5S^+$ loss becomes the most abundant process in the CID mass spectrum. In contrast, coordinated diphenyldisulfide decomposes only with the loss of *even-electron* neutral species, to form metal-containing ions. Differences in fragmenta-

Figure 1. MI mass spectra of (a) the ionized diphenyldisulfide and (b) $Cr^+C_6H_5SSC_6H_5$ ion.

tion of the metal-free and metal-coordinated aromatic compounds have been observed before [18] and were explained by charge localization on the central metal atom [19], whose ionization energy ($\text{IE}(\text{Cr}) = 6.77 \text{ eV}$ [20]) is substantially lower than that of most benzene derivatives [20]. $\text{C}_6\text{H}_5\text{S}^\cdot$ loss also was not observed from collisionally activated $\text{Cr}^+\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ ions, which makes the ions 6-8, in which the chromium atom is surrounded by two ligands, unattractive structure proposals.

Dissociations of metastable $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ ions can be divided usefully into two types. The first involves interaction between a metal and sulfur atom(s) and results in chromium sulfide ions. The CIDI mass spectrum of $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ shows signals at m/z 186 and 154, which show that formation of CrS^+ and CrS_2^+ is accompanied by $\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{C}_6\text{H}_5$ loss, respectively. Collisional activation of $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ also results in CrS^+ ion formation. CrS^+ and CrS_2^+ ions are present in the MI and CID mass spectra of $\text{RC}_6\text{H}_5\text{Cr}^+(\text{CH}_3\text{SSCH}_3)$ and $\text{Cr}^+(\text{CH}_3\text{SSCH}_3)$ ions in which the only possible type of coordination of dimethyldisulfide to the metal atom is by one or two Cr—S bonds. Therefore, formation of chromium sulfide ions can be associated with structures 9 or 10.

The second type of $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ ion decomposition involves reactions in which the metal atom is formally a spectator. These are hydrogen and skeletal rearrangements that result in H_2S , C_6H_6 , or $\text{C}_6\text{H}_5\text{SH}$ loss, which may originate from the isomers 9 and 10 that contain Cr—S bond(s). Formation of benzene and thiophenol as neutrals is indicated by the CIDI mass spectrum (see Experimental), which contains their molecular ion peaks at m/z 78 and 110, respectively. Collisional activation of $\text{C}_6\text{H}_4\text{S}_2\text{Cr}^+$ and $\text{C}_6\text{H}_4\text{SCr}^+$ ions that originate from metastable $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ by C_6H_6 and $\text{C}_6\text{H}_5\text{SH}$ loss, respectively, showed a significant signal due only to Cr^+ , which indicates no metal atom insertion into the C—S bond; ions 11 and 12 are likely structures for these species.

The MI mass spectrum of $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ (Figure 1b) also displayed a very small peak due to Cr^+ . This ion was not present in the MI mass spectra of sandwich-type ions [$(\text{arene})_2\text{Cr}^+$, $\text{C}_5\text{H}_5\text{Cr}^+-\text{arene}$, $(\text{C}_5\text{H}_5)_2\text{Cr}^+$], which leads us to suggest that 5, 6, 7, and 8 are unlikely structures for this ion. Production of Cr^+ can occur from structures 9 or 10; this is supported by, for example, the presence of Cr^+ in the MI mass spectrum of $\text{Cr}^+(\text{CH}_3\text{SSCH}_3)$.

Collisional activation of $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ ions by using oxygen as a target (a good charge stripping target [21]) resulted in formation of doubly charged species. Dibenzene chromium and its substituted analogs behaved similarly, whereas $\text{Cr}^+(\text{CH}_3\text{SSCH}_3)$ ions did not undergo further ionization under the same conditions.

We propose that $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ ions can originate from the addition of Cr^+ to diphenyldisulfide. Arene- Cr^+ ions also are able to form adducts, but they are unstable and easily undergo intramolecular ligand substitution, which results in a loss of an arene ligand originally bound to a metal atom. At the moment of formation $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5\text{Cr}^+$ ions well may have the cyclophane structure 5, which can be responsible for S_2 loss. Further, it can isomerize to structures (9 or 10) with Cr—S bond(s), which gives rise to the major metastable and collisional-induced decompositions.

Neutralization-Reionization

Additional support for the cyclophane structure 5 for the $\text{Cr}^+\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ ion is provided by neutralization-reionization experiments [22], which previously have been used to aid the characterization of transition metal-containing species [23]. The NR mass spectrum of this ion and those of $(\text{C}_6\text{H}_6)_2\text{Cr}^+$, $(\text{C}_5\text{H}_5)_2\text{Cr}^+$, and $(\text{CH}_3\text{SSCH}_3)\text{Cr}^+$ ions (chosen as model ions) are shown in Figures 2-5. As the most abundant species, all the spectra display metal-free organic ions that originate from different reactions discussed elsewhere [23d, g, and i]. The similar relative abundances of the organic ions in the NR and CIDI mass spectra of these ions indicate that (dissociative) ionization of neutrals produced in metastable and collision-induced dissociation of the parent ions is a major source for their formation.

The survival ion and other metal containing ions in the NR mass spectrum of dibenzenechromium are of extremely low abundance (Figure 2), which shows that two separate arene ligands are easily lost on neutralization or following reionization. That the ligand loss may be a two step process is indicated by the absence

Figure 2. NR mass spectrum (Xe, 90% T/O_2 , 85% T) of $(\text{C}_6\text{H}_6)_2\text{Cr}^+$ ion.

Figure 3. NR mass spectrum (Xe, 90% T/O₂, 85% T) of (C₅H₅)₂Cr⁺ ion.

of recovery signals in the NR mass spectra of C₆H₅Cr⁺, C₆H₅CH₃Cr⁺, and C₆H₅CH(CH₃)₂Cr⁺ ions, which shows a probable low stability for neutral arene-Cr species. Note that the C₆H₅Fe⁺ ion also shows no recovery signal in its NR mass spectrum [23g].

The NR mass spectrum of (C₅H₅)₂Cr⁺ (Figure 3) is similar to that of other metallocenes [23i]; it is dominated by hydrocarbon ions, but it also contains a recovery signal. The latter indicates a higher stability for Cr-C₅H₅ relative to Cr-C₆H₆ in keeping with previous experimental results [17].

No recovery signal was found in the NR mass spectrum (Figure 4) of Cr⁺(CH₃SSCH₃) under any experimental conditions. The most abundant peaks correspond to metal-free ions. Some metal-containing ions, particularly CrS⁺ and CrS₂⁺, were observed. These also were present in the CID mass spectrum of Cr⁺(CH₃SSCH₃), and so in the NR experiment stable neutral Cr(CH₃SSCH₃) was probably formed, but decomposed following reionization. This may also account for the presence of a ligand ion, CH₃SSCH₃⁺, in the NR mass spectrum.

The NR mass spectrum of Cr⁺C₆H₅SSC₆H₅ (Figure 5) displays a significant recovery signal, as does chromocenium, which shows that the corresponding neu-

Figure 4. NR mass spectrum (Xe, 90% T/O₂, 85% T) of Cr⁺CH₃SSCH₃ ion.

Figure 5. NR mass spectrum (Xe, 90% T/O₂, 85% T) of Cr⁺C₆H₅SSC₆H₅ ion.

trals are stable under the given experimental conditions. Their structure is unlikely to be 4, 9, or 10, whose analogues, RC₆H₅Cr⁺ and Cr⁺(CH₃SSCH₃), do not show recovery peaks in NR experiments. A quantitative comparison of the NR mass spectra of different ions is quite difficult because of uncertainties of ion production. Intuitively, the stability of Cr⁺C₆H₅SSC₆H₅ in the NR experiments seems to be higher than that of dibenzenechromium, but lower than that of chromocenium. Also, from the fragmentation data for these ions, it is clear that a part of them isomerize into "open" structure(s), 9 or 10, species that are unlikely to be stable under NR conditions. Thus the NR mass spectrum of a "pure" ion 5 would be expected to show a recovery signal of higher abundance than Cr⁺C₆H₅SSC₆H₅ ions produced in our experiments.

Effect of Sulfur Containing Substituent on Dissociation of Bisbenzenechromium Ions

The absence of RC₆H₅Cr⁺C₆H₅SSC₆H₅ in the mass spectra of arenechromiumtricarboxyl mixtures with diphenyldisulfide does not allow any estimate to be made for the bond strength between a C₆H₅Cr⁺ ion and η⁶-C₆H₅SSC₆H₅, relative to other RC₆H₅Cr⁺-ligand bonds. However, it was possible to do so for RC₆H₅Cr⁺C₆H₅R' cations, where R' = SH or SC₆H₅ and for this purpose the MI mass spectra were recorded for these species produced by ion-molecule reactions in mixtures of the corresponding arenechromiumtricarboxyls with aromatic compounds. According to ref 24a-d, the abundances of peaks that correspond to competitive ligand loss from di- and polyligated metal ions can be related to the order of ligand binding energies. The MI mass spectra of dibenzenechromium derivatives are very simple and display only two peaks related to arene ligand loss. Their relative abundances are listed in Table 2. According to the above criterion, alkyl substitution increases metal-arene bond strength, which, in agreement with previous results for the arene-Cr⁺ ions [17e, g], also increases as the size and number of alkyl groups rises. Thiophenol is more

Table 2. Relative abundances of arene ligand loss from the metastable $\text{RC}_6\text{H}_5\text{Cr}^+ \text{C}_6\text{H}_5\text{R}'$ ions

R	R'	$[\text{RC}_6\text{H}_5\text{Cr}^+]/[\text{R}'\text{C}_6\text{H}_5\text{Cr}^+]$
H	CH_3	0.17
H	HS	1.8
CH_3	HS	5.6
$\text{CH}_3\text{CH}_2\text{CH}_2$	CH_3	4.7
$(\text{CH}_3)_2\text{CH}$	CH_3	4.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$	CH_3	11.3
$(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}$	CH_3	9.5
$\text{C}_6\text{H}_5\text{S}$	CH_3	68
$\text{C}_6\text{H}_5\text{S}$	$(\text{CH}_3)_2\text{CH}$	26

weakly bound to chromium ion than benzene and its alkyl derivatives (Table 2).

The addition of a $\text{C}_6\text{H}_5\text{S}$ group to the benzene ring results in a larger increase in metal-ligand bond strength than does alkyl substitution. Such an effect may originate from the large number of vibrational degrees of freedom of the phenylthio group, which has been found to be the most important factor that affects dissociation of arene- Cr^+ ions [25]. A detailed analysis of the substituent effect on arene-chromium bond rupture in dibenzenechromium ions is in progress.

Conclusion

Stable dibenzenechromium derivatives with sulfur-containing substituents can easily be produced by ion molecule reactions in the gas phase. Thiophenol derivatives show comparable or even higher binding energies to Cr^+ relative to those of other benzene derivatives. The formation of cyclophane structure 5 that contains sulfur atoms in a bridge between two aromatic ligands is indicated by the dissociation characteristics of the $\text{Cr}^+(\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5)$ ion, whose stable neutral counterpart can be produced in neutralization-reionization experiments. Species that contain a chromium ion coordinated directly to sulfur atom(s), for example, 9 or 10, were also identified. All these types of chromium atom coordination to arylsulfides are expected to exist in polyphenylenesulfide or similar polymers doped with metal atoms. It can be predicted that such materials will be oxidized easily without destruction of their structure. No evidence was found for metal insertion into S-S, S-C, or S-H bonds.

Acknowledgments

JLH thanks the Natural Science and Engineering Research Council of Canada for continuing financial support, and DVZ acknowledges valuable discussions with Dr. V. Nedel'kin.

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