Complexes of metals with aromatic systems

XC*. Charge-transfer complexes of arenechromium tricarbonyls

*Preparative results***

In continuing our work on arene–metal complexes we have found that arenechromium tricarbonyls form charge-transfer complexes with various organic acceptors in solution. Only in three cases have we been able to isolate solid compounds on which we report here.

Toluenechromium tricarbonyl and the corresponding anisole and dimethylaniline complexes all form red solids when powdered with trinitrobenzene. The same products are obtained when these components are sublimed together in a vacuum, or when they are fused together. The best way to obtain crystalline products is to evaporate slowly an equimolar chloroform solution of the components.

By taking a melting-point diagram in the case of the toluenechromium tricarbonyl trinitrobenzene compound it has been confirmed that the red substance is a 1:1 molecular compound of trinitrobenzene and the chromium complex. This stoichiometry is also indicated by elementary analysis of all three substances.

Because of the apparently low formation constant of the complexes in solution and because of the high extinction of the π-complexes themselves, the visible and ultraviolet spectra of the addition compounds could not be determined in solution. Reflectance spectra of the solids show a much increased absorption in the long wavelength region as compared with the free chromium complexes, and also a shoulder appearing at about 480 mμ for all three compounds. The infrared spectra are approximately additive with respect to the spectra of the components. Table 1 gives the positions of some bands of the charge-transfer complexes and the components as well.

TABLE 1

INFRARED FREQUENCIES IN CM^{-1}

TNB = 1,3,5-$(NO_2)_3C_6H_3$; s = strong; m = medium; w = weak.
For column headings see text.

	1	*2*	*3*	*4*	*5*	*6*
$CH_3C_6H_5Cr(CO)_3$	1959 s		816 w			665 m
$CH_3C_6H_5Cr(CO)_3 \cdot TNB$	1962 s	1345 s	823 w	732 s	717 s	669 m
$CH_3OC_6H_5Cr(CO)_3$	1961 s		815 w			666 m
$CH_3OC_6H_5Cr(CO)_3 \cdot TNB$	1962 s	1346 s	822 w	731 s	718 s	666 m
$(CH_3)_2NC_6H_5Cr(CO)_3$	1935 s		802 w			674 m
$(CH_3)_2NC_6H_5Cr(CO)_3 \cdot TNB$	1959 s	1344 s	813 w	731 s	717 s	681 m
TNB		1345 s		732 s	715 s	

It is found that the trinitrobenzene absorptions are not notably shifted on complex formation (columns 2, 4, 5). This behaviour is in contrast to the observations made on addition compounds of trinitrobenzene with dibenzenechromium[2] or dicyclopentadienylcobalt[3]. In both cases the authors report a remarkable shift of the trinitro-

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* Part LXXXIX see ref. 1.

** By the German group.

benzene absorptions on complex formation. This difference may be attributed to the more ionic character of these compounds, corresponding to the tendency of the π-complexes to form cations. Nevertheless frequency shifts are observed in the arenechromium tricarbonyl absorptions as shown in Table 1 (columns 1, 3, 6). The symmetrical CO valence frequency (column 1) which is known to be very sensitive to electronic effects, is shifted to shorter wavelengths, as would be expected if charge is withdrawn from the metal by charge-transfer complex formation. A shift in the same direction is observed with the metal–CO bending vibration (column 6), where the same explanation may apply. The high-frequency shift of the symmetrical carbon–hydrogen bending vibration of the π-bound benzene rings (column 3) may be attributed to an enhancement of this bending mode by the steric vicinity of the trinitrobenzene molecules. This explanation is confirmed by the structural investigations shown in the next section.

*X-ray investigation of tricarbonylchromiumanisole-1,3,5-trinitrobenzene**

The tricarbonylchromiumanisole-1,3,5-trinitrobenzene complex crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.10$, $b = 13.42$, $c = 13.87$ Å, $\beta = 101°45'$, $Z = 4$. The crystal structure was elucidated by the heavy-atom method[4] and the atomic parameters were refined by Fourier and least-squares calculations using three-dimensional X-ray data. At the end of the analysis the value of R, the average discrepancy between measured and calculated structure amplitudes, is 13.7 % over 2028 independent reflexions. The arrangement of molecules in the crystal as seen in projection along the a axis is shown in Fig. 1 and the conformation of the tricarbonylchromiumanisole molecule as viewed perpendicular to the benzene plane is shown in Fig. 2.

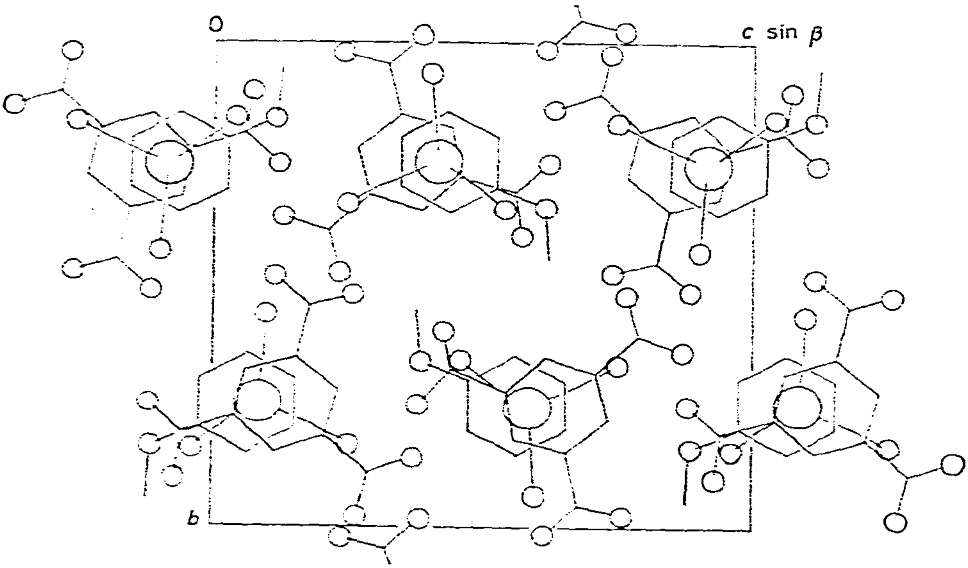

Fig. 1. Arrangement of molecules in the crystal as viewed along the a axis.

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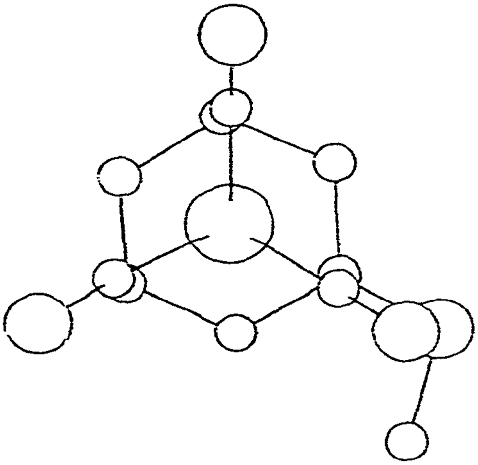

Fig. 2. Conformation of tricarbonylchromiumanisole.

The structure of the complex is similar to that of other charge-transfer complexes involving aromatic molecules[5] (*e.g.* azulene 1,3,5-trinitrobenzene[6], indole 1,3,5-trinitrobenzene[7]) with the planes of the benzene rings of the two components approximately parallel. However, in the other complexes the distances between adjacent molecules are about 3.3 Å, whereas in the tricarbonylchromiumanisole-1,3,5-trinitrobenzene complex the perpendicular distances from the carbon atoms of the anisole molecule to the plane of the trinitrobenzene molecule are 3.34–3.50 Å (average, 3.41 Å). The increased separation indicates that the charge-transfer interaction is weaker than in the other complexes and this can presumably be attributed to the strong electron withdrawing capacity of the tricarbonylchromium group decreasing the π-electron-donor capacity of the anisole molecule.

Tricarbonylchromiumbenzene[8] and tricarbonylchromiumhexamethylbenzene[9] both exhibit the staggered conformation (I) in the solid state. Our results (see Fig. 2) demonstrate that tricarbonylchromiumanisole deviates only very slightly from the eclipsed conformation (II). If we picture the chromium atom as having six octahedrally directed bonds, then the three directed towards the benzene ring point at the carbon atoms *ortho* and *para* to the methoxyl substituent, *i.e.* those atoms whose electron densities are enhanced by the electron-releasing character of the methoxyl group.

General procedure

The chromium complex (2.00 mmole) is powdered together with 2.00 mmole of 1,3,5-trinitrobenzene. Dry oxygen-free chloroform (5 ml) is added and the solution filtered. The dark-red solution is slowly evaporated by a slight reduction in pressure and the resulting crystals are removed by filtration. They are washed with a few drops of cold chloroform and dried under vacuum. The yield of pure dark red crystals is about 50 % by this method. When the mother liquor is evaporated a less pure product is obtained (yield *ca.* 50 %). The compounds are strongly dissociated in solution so that the red concentrated solutions turn yellow on dilution and *vice versa*. The solid complexes are stable in air but solutions must be handled under oxygen-free dry nitrogen.

Toluenechromium tricarbonyl trinitrobenzene: red crystals; m.p. 81–83°. (Found: C, 43.64; H, 2.51; Cr, 11.4; N, 9.95. $C_{16}H_{11}CrN_3O_9$ calcd.: C, 43.60; H, 2.52; Cr, 11.8; N, 9.54%.)

Anisolchromium tricarbonyl trinitrobenzene: red crystals; m.p. 88–90°. (Found: C, 41.99; H, 2.67; Cr, 11.14; N, 9.29. $C_{16}H_{11}CrN_3O_{10}$ calcd.: C, 42.03; H, 2.43; Cr, 11.38; N, 9.19%.)

Dimethylanilinechromium tricarbonyl trinitrobenzene: dark-red crystals; m.p. 95° (decomposition). (Found: C, 43.66; H, 3.19; Cr, 10.86; N, 11.91. $C_{17}H_{14}CrN_4O_9$ calcd.: C, 43.43; H, 3.00; Cr, 11.06; N, 12.19%.)

Infrared spectra (KBr discs) were obtained using a Perkin–Elmer Model 21 spectrometer with a LiF prism in the short-wavelength region and a NaCl prism otherwise. Visible and ultraviolet spectra of the solid substances were measured on a Zeiss PMQ2 spectrophotometer with a 45° reflectance–unit attached.

Acknowledgements

We are indebted to the Deutsche Forschungsgemeinschaft and to the U.S. National Science Foundation for their support of this work.

Summary

The preparations of crystalline 1:1 charge-transfer adducts of 1,3,5-trinitrobenzene with anisolechromium tricarbonyl, toluenechromium tricarbonyl and dimethylanilinechromium tricarbonyl are reported. Infrared, visible and ultraviolet spectra are discussed briefly. An X-ray structure investigation on the anisole complex reveals the structure of this type of compound.

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Received December 14th, 1965