reason, a complete structural study of 1,4-thiatellurane was not attempted; however, a study of the structure of a least one of the halogen addition compounds is planned.

Further evidence of isomorphism of thiatellurane and thiaselenane is found in the melting points of mixtures. These observations suggest continuous miscibility in the solid state.

Formation of Polymer.—In the first synthesis of 1,4-thiatellurane only 400 ml. of water was used and the mustard was not diluted with ethanol. The yield of thiatellurane in that case was 0.76 g. or only 1.2%. Along with this, 22 g. of a nonvolatile, insoluble material was recovered. This was presumed to be a linear polymer of the type $[-S-(CH_2)_2-Te-(CH_2)_2-]_n$ formed in competition with the cyclic monomer. The structure and properties of the polymer are under investigation.

Hydrolytic Loss of Mustard.—The yields of polymer and thiatellurane account for about 35% of the mustard. The remaining mustard was presumably lost through competitive reaction of the cyclic sulfonium ion intermediate with water.[4,5] Two variations in procedure were tried in an attempt to reduce the hydrolytic loss of mustard. In the first of these the water was replaced by 400 ml. of ethanol. The reaction of tellurium with rongalite was slow and incomplete and no thiatellurane was found in the distillate. In the second case, the reaction between tellurium and rongalite was carried out in 100 ml. of water, the mixture cooled, 300 ml. of ethanol added, and again refluxed while the mustard (dissolved in 100 ml. of ethanol) was added. About 0.2 g. of polymer was formed but no thiatellurane was isolated.

Although it might be possible to improve the per cent yield of thiatellurane by following the procedure used for 1,4-thiaselenane,[4] this would involve the synthetic sequence

$$Te \longrightarrow Al_2Te_3 \longrightarrow H_2Te \longrightarrow Na_2Te$$

followed by reaction of sodium telluride with mustard in absolute ethanol. This would be an unpleasant and time-consuming process and product isolation would be more difficult. For these reasons, further efforts to improve the yield of thiatellurane were confined to the simpler rongalite procedure.

Effect of Dilution on Yield of Monomer.—On the assumption that the production of the cyclic monomer would be favored over the polymer by increasing the volume of the system the effect of dilution was studied. An increase in the volume of water from 400 to 800 ml. increased the yield of thiatellurane to 2.0%. A still greater increase (to 6.6%) resulted when 800 ml. of water was used and the 38 ml. of mustard was diluted with 120 ml. of ethanol. It is probable that the per cent yield of 1,4-thiatellurane could be increased still further by going to higher dilutions. However, this would require the use of larger reaction flasks and equipment or starting with smaller quantities of the reactants. The former would make the synthesis more unwieldy, while the latter would reduce the actual yield. Increasing the volume of ethanol to 200 ml. (or more) might be beneficial but this would also increase losses in the solvent. Thus, it is believed that the described conditions are near optimum for a small-scale synthesis.

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Contribution from the Department of Chemistry,
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The Interaction of Dibenzenechromium with Lewis Acids

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Dibenzenechromium reacts with symmetrical trinitrobenzene, *p*-quinone, chloranil, and tetracyanoethylene in benzene solution to form deeply colored compounds containing one molecule of dibenzenechromium to one molecule of the Lewis acid. The ultraviolet, infrared, and electron spin resonance spectra of these compounds are discussed and suggest that the complexes are best described as dibenzenechromium salts of radical anions.

The structure of dibenzenechromium has recently received considerable attention with evidence being presented for delocalization[1] of the π-electron system in the benzene ring as well as for a localized system[2] in which each ring attains a Kekulé-like structure. Unlike ferrocene and its derivatives, bisarenechromium

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(1) F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Am. Chem. Soc.*, **85**, 1543 (1963).

(2) F. Jellinek, *Nature*, **187**, 871 (1960); *J. Organometal. Chem.*, **1**, 43 (1963).

compounds do not readily undergo the standard electrophilic ring substitution reactions characteristic of an aromatic nucleus,[3] the usual conditions for such reactions being sufficiently oxidizing to form the bisarenechromium cation. The ring systems in bisarenechromium compounds have not been successfully substituted under either free radical[3] or nucleophilic[3] conditions. We present evidence here that dibenzenechromium interacts with Lewis acids by electron transfer to form radical anions.

Experimental

Reagents.—Dibenzenechromium was synthesized by the reducing Friedel–Crafts method of Fischer and Hafner[4] and purified by sublimation at 150° under high vacuum. The benzene used as the solvent in the reactions described was the commercial thiophene-free product which was dried by refluxing over CaH_2, distilling, and saturating with dry nitrogen. All other reagents were commercial products which were recrystallized or sublimed to a constant melting point.

Preparation of Complexes.—All of the complexes were prepared by adding a benzene solution of the Lewis acid to a solution of dibenzenechromium in the same solvent. In a typical experiment, a benzene solution of 1,3,5-trinitrobenzene (0.748 g., 3.51×10^{-3} mole) was added dropwise and with good stirring to a benzene solution of dibenzenechromium (0.488 g., 2.34×10^{-3} mole). Immediately a brown-black precipitate formed, and, upon completion of the addition, the supernatant solution was colorless, indicating that all of the dibenzenechromium had reacted. The precipitate was filtered under nitrogen, washed with two 50-ml. portions of benzene, dried *in vacuo*, and stored in a helium-filled drybox; decomposition point (explosive) in a sealed evacuated capillary, 127°. The complex is stable in air, no noticeable decomposition occurring after several days in a closed flask. However, solutions of the complex fade rapidly in air and are best handled in an inert atmosphere. The complex is soluble in N,N-dimethylformamide and aqueous acetone, the latter yielding red basic solutions; aqueous acetic acid discharges the red color which may be regenerated by the addition of aqueous sodium hydroxide. The latter observations suggest that the trinitrobenzene radical anion is converted into an indicator-type species, probably by reaction with water.

Anal. Calcd. for $C_{18}H_{15}CrN_3O_6$: Cr, 12.36; N, 9.98. Found: Cr, 12.39; N, 9.77.

Complexes (1:1) of dibenzenechromium with *p*-quinone (brown; decomposition point 145–147°), chloranil (green; decomposition point 140–147°), and tetracyanoethylene (blue; decomposition point 80°) were prepared in quantitative yield using the general procedure outlined above.

Anal. Calcd. for $C_{18}H_{16}CrO_2$: Cr, 16.45. Found: Cr, 16.56.

Anal. Calcd. for $C_{18}H_{12}Cl_4CrO_2$: Cr, 11.44; Cl, 31.23. Found: Cr, 11.40; Cl, 31.89.

Anal. Calcd. for $C_{18}H_{12}CrN_4$: Cr, 15.47; N, 16.65. Found: Cr, 15.42; N, 16.22.

All efforts to obtain reproducible carbon analysis for these complexes using standard combustion techniques were unsuccessful. The hydrogen values were acceptable but the carbon values were about 2% below the theoretical values when solid oxidants (*e.g.*, tungstic oxide) were mixed with the samples prior to combustion.

Dibenzenechromium iodide was prepared by passing a stream of air through a benzene solution of dibenzenechromiume extracting the solid formed into a small volume of water, adding an equal volume of a saturated aqueous solution of potassium iodide, and chilling the mixture. The orange crystals of dibenzenechromium iodide were washed with ice water, ethyl alcohol, and ether and dried *in vacuo*.

Potassium tetracyanoethylenide was prepared by the reaction of tetracyanoethylene with potassium iodide in acetonitrile.[5]

Electron Spin Resonance Spectra.—A Strand Labs Model 601A spectrometer, consisting of a microwave bridge, a klystron power supply with frequency control and stabilization, a tuned narrow band width 6-kc. signal amplifier with phase sensitive detection, and a modulation amplifier was used to determine the electron spin spectra of the complexes reported here. A steady magnetic field was supplied by a Harvey Wells L-128 12-in. electromagnetic system, and the data were recorded with a Moseley Autograf Model 2D-2 *x–y* recorder. Magnetic field measurements were made with a proton nuclear magnetic resonance probe, containing a dilute aqueous $Cu(NO_3)_2$ solution, coupled to a marginal oscillator-type spectrometer with adjustable frequency. Sixty-cycle modulation was used, allowing display of the signal on an oscilloscope. The frequency of the marginal oscillator was monitored by mixing with a standard 10-Mc. signal and counting the beat frequency with a Hewlett-Packard Model 524-CD digital frequency counter.

The e.s.r. spectra of $(C_6H_6)_2Cr{\cdot}C_6Cl_4O_2$, $(C_6H_6)_2Cr{\cdot}C_2H_4O_2$, $(C_6H_6)_2Cr{\cdot}C_6H_3(NO_2)_3$, and $(C_6H_6)_2Cr{\cdot}C_2(CN)_4$ (Table I) were determined as acetonitrile solutions, prepared in an inert atmosphere, in sealed evacuated capillaries.

TABLE I

ELECTRON SPIN RESONANCE RESULTS

Compound	g_1[a]	g_2
$(C_6H_6)_2Cr{\cdot}C_2(CN)_4$	1.991 ± 0.003	2.006 ± 0.003
$(C_6H_6)_2Cr{\cdot}C_6H_4O_2$	1.986 ± 0.003	2.000 ± 0.003
$(C_6H_6)_2Cr{\cdot}C_6Cl_4O_2$	1.984 ± 0.003	. . .
$(C_6H_6)_2Cr{\cdot}C_6H_3(NO_2)_3$	1.989 ± 0.003	. . .
$(C_6H_6)_2CrI$	1.989 ± 0.003	. . .
$K^+C_2(CN)_4^-$	. . .	2.006 ± 0.003

[a] g_1, attributed to $(C_6H_6)_2Cr^+$; g_2, attributed to a radical anion.

TABLE II

ELECTRONIC SPECTRA OF COMPOUNDS FORMED BETWEEN DIBENZENECHROMIUM AND VARIOUS LEWIS ACIDS

Complex	Solvent	λ_{max}, mμ (log ε)
$(C_6H_6)_2Cr{\cdot}C_6H_4O_2$	H_2O	227 (3.67), 272 (3.74), 333 (3.70)
	Nujol	380 (1.0)[a]
$(C_6H_6)_2Cr{\cdot}C_6Cl_4O_2$	CH_3CN	278 (4.24), 286 (4.22), 327 (4.31), 421 (3.92), 440[b] (4.00), 448 (4.09)
	Nujol	340 (1.00), 420[b] (0.72), 456[b] (0.58), 760 (0.73)
$(C_6H_6)_2Cr{\cdot}C_6H_3(NO_2)_3$	$(CH_3)_2NCHO$	272 (4.15), 337 (3.91), 446 (4.31), 513 (4.10), 528[b] (4.10)
	Nujol	338 (1.00), 490 (0.95)
$(C_6H_6)_2Cr{\cdot}C_2(CN)_4$	CH_3CN	228 (3.76), 264 (3.84), 272[b] (3.79), 325 (3.92), 376 (3.59), 374 (3.60), 388 (3.62), 398 (3.78), 408 (3.79), 416 (3.79), 426 (3.76), 437 (3.71), 446 (3.63), 458 (3.56), 467 (3.45)
	Nujol	420 (1.00), 665 (0.97)

[a] The relative intensity rather than log ε is given for spectra determined as Nujol mulls. [b] Shoulder.

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(3) H. P. Fritz and E. O. Fischer, *Z. Naturforsch.*, **12b**, 67 (1957).

(4) E. O. Fischer and W. Hafner, *ibid.*, **10b**, 665 (1955).

(5) O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

Visible and Ultraviolet Spectra.—Visible and ultraviolet spectra were recorded for all of the complexes on a Cary Model 14 recording spectrophotometer. The spectra of $(C_6H_6)_2Cr \cdot C_6Cl_4O_2$ and $(C_6H_6)_2Cr \cdot C_2(CN)_4$ were determined in acetonitrile solutions, prepared in an inert atmosphere; the spectrum of $(C_6H_6)_2Cr \cdot C_6H_3(NO_2)_3$ was determined in N,N-dimethylformamide while that of $(C_6H_6)_2Cr \cdot C_6H_4O_2$ was determined in water. The results are summarized in Table II.

Since solutions of the compounds formed from chloranil, tetracyanoethylene, and trinitrobenzene are colored differently from the corresponding solids, the spectra of these compounds as Nujol mulls were determined in the visible region (Table II). The spectra were determined on quartz plates fitted with 0.1-mm. lead spacers; a Nujol blank was used in the reference beam.

Infrared spectra (Table III) of the complexes were determined on a Beckman IR-7 infrared spectrophotometer as Nujol mulls.

TABLE III

INFRARED SPECTRA (CM.$^{-1}$) OF COMPOUNDS FORMED BETWEEN DIBENZENECHROMIUM AND VARIOUS LEWIS ACIDS

$(C_6H_6)_2Cr \cdot C_6H_4O_2$	660 (w), 675 (w), 692 (w), 722 (vw), 758 (vw), 779 (s),[a] 792 (s),[a] 830 (m), 861 (m), 871 (sh), 879 (sh), 889 (vw), 930 (vw), 953 (s), 969 (w), 981 (w), 996 (vw) (doublet), 1003 (sh), 1008 (m), 1081 (w), 1088 (w), 1119 (sh), 1127 (m), 1132 (sh), 1149 (w), 1228 (w), 1260 (w), 1293 (vw), 1356 (s), 1400 (vw), 1430 (s),[a] 1500 (vs), 1550 (vw), 3040 (w), 3080 (w)
$(C_6H_6)_2 \cdot C_6Cl_4O_2$	692 (m), 721 (s), 789 (s),[a] 909 (s), 990 (s),[a] 1133 (s), 1167 (w), 1194 (w), 1232 (vw), 1402 (m), 1430 (vs),[a] 1478 (vs), 1539 (vs), 1557 (sh), 1584 (vw), 1676 (m), 3060 (m), 3350 (w)
$(C_6H_6)_2Cr \cdot C_6H_3(NO_2)_3$	665 (vw), 675 (w), 715 (sh), 732 (s), 743 (w), 755 (vw), 781 (w), 796 (s),[a] 815 (w), 864 (w), 879 (vw), 922 (m), 939 (sh), 972 (m),[a] 1006 (m),[a] 1029 (sh), 1048 (s), 1075 (vw),[a] 1142 (m), 1166 (w), 1222, 1237 (vs) (doublet), 1308 (w), 1347 (m), 1367 (vw), 1397 (w), 1437,[a] 1492 (m), 1534, 1547 (s) (doublet), 1607 (s), 1623 (sh), 2730 (w), 3090 (w)
$(C_6H_6)_2Cr \cdot C_2(CN)_4$	690 (m), 785 (s),[a] 793 (sh), 802 (sh), 971 (m),[a] 1005 (m),[a] 1150 (vw),[a] 1365 (s), 1435 (s),[a] 1480 (m), 1597 (m), 2162 (s), 2169 (s), 2190 (s), 3090 (m)

[a] Dibenzenechromium cation.

Discussion

Two possible sites on the dibenzenechromium molecule exist for the formation of complexes with π-acceptor molecules. Charge-transfer complexes could theoretically occur either through the ring system or through the metal atom, which, in the case of arenechromiumtricarbonyls, has been shown to have a relatively high electron density.[6] In addition, electron-transfer reactions similar to that reported[7,8] between Lewis acids and bases could occur. For example, N,N,N′,N′-tetramethyl-*p*-phenylenediamine has been observed to give a series of complexes with electron acceptors which range from the covalent molecular complexes commonly described as charge-transfer complexes to compounds resulting from complete electron transfer which are best described as salts. The course of this reaction is influenced by the dielectric constant of the solvent, that is, molecular complexes are favored in low dielectric media, and electron transfer is favored in high dielectric media.[8]

The results of our experiments indicate that dibenzenechromium and a variety of π-acceptors, *i.e.*, tetracyanoethylene, *p*-benzoquinone, chloranil, and *sym*-trinitrobenzene, interact in a 1:1 mole ratio to give compounds resulting from electron transfer from dibenzenechromium to the acceptor molecule. This result was not totally unexpected since the reaction of dibenzenechromium with strong acids liberates hydrogen,[6] a process which probably occurs by a one-electron transfer. The interaction of metallocenes with π-acceptors had also recently been reported to give analogous compounds.[9]

The electron spin resonance studies on these systems (Table II) clearly show that dibenzenechromium(I) is formed and that the resulting compounds are best described as salts of the dibenzenechromium cation. In the case of the compounds formed from the interaction of dibenzenechromium and either *p*-benzoquinone or tetracyanoethylene, the electron spin resonance spectra showed the presence of another radical, which is presumably the corresponding radical anion. The signal attributed to the radical anions $C_2(CN)_4^{\cdot -}$ and $C_6H_4O_2^{\cdot -}$ exhibited no fine structure; however, the *g* factor in the former case was the same as that for an authentic sample containing this species, and failure to observe fine structure was probably due to instrumental difficulties. An authentic sample of potassium tetracyanoethylenide was shown to have the same *g* value as that for the anionic species found in the dibenzenechromium–tetracyanoethylene system. The radical anions of trinitrobenzene and chloranil were not observed, which might be attributed to instrumental difficulties, dimerization, or disproportionation in solution with the equilibrium favoring the dianion. The last two named alternatives seem unlikely in view of the spectral evidence presented below.

The visible–ultraviolet spectra of these compounds also indicate that in each case oxidation has occurred to form dibenzenechromium(I). In the case of the solid complexes of tetracyanoethylene and chloranil a new band was observed in the red region of the spectrum, which presumably arises from the interaction of the cation and the anion in the solid state. It should be noted that the bands at 420 and 448 mμ in the visible spectrum of the chloranil complex are essentially the same as those attributed to the sodium salt of the chloranil radical anion at 423 and 448 mμ.[8] In addition, the product formed by the interaction of chloranil and cobaltocene, which has been formulated as arising from an electron-transfer process, exhibits absorption bands at 421 and 448 mμ.[9]

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(7) C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, **16**, 1043 (1962).

(8) R. Foster and T. J. Thompson, *Trans. Faraday Soc.*, **58**, 860 (1962).

(9) J. C. Goan, E. Berg, and H. E. Podall, *J. Org. Chem.*, **29**, 975 (1964).

The infrared spectra of the complexes, tabulated in Table III, also show that $(C_6H_6)_2Cr^+$ has been formed during the course of the reaction as well as marked changes in the position of the bands associated with the Lewis acids. In particular it should be noted that the asymmetric stretching frequency of the nitro group, which occurs at 1567 cm.$^{-1}$ in trinitrobenzene, is shifted and split to give a doublet at 1547 and 1534 cm.$^{-1}$. The splitting of the $-NO_2$ frequency suggests that the ring and the $-NO_2$ group are no longer coplanar, which could arise because of either lattice-packing effects or the dimerization of the trinitrobenzene radical ions.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Properties of Metal-to-Oxygen Multiple Bonds, Especially Molybdenum-to-Oxygen Bonds[1]

BY F. A. COTTON AND R. M. WING

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Principally on the basis of structural and infrared data for Mo–O bonds, derived from recent studies in this laboratory, several aspects of multiple bonds from oxygen to transition metals have been examined. It is found that for MO_n groups, where $n > 1$, a positive M–O to M–O stretching interaction constant in the range 0.2–0.7 mdyne/Å. is generally necessary to account for the observed M–O stretching frequencies, although the actinyl ions are exceptions. Assignments of M–O stretching frequencies in a number of compounds are proposed, and with these assignments force constants are computed. For Mo–O bonds it is shown that the force constants are related to the bond distances and to estimated bond orders by smooth curves which have physically reasonable shapes.

1. Introduction

Several years ago, Barraclough, Lewis, and Nyholm[2] pointed out that complexes containing metal-to-oxygen multiple bonds seemed generally to have strong infrared absorption bands in the region of 900–1100 cm.$^{-1}$ and proposed that these bands be assigned to the metal–oxygen stretching frequencies. Since then, such bands have been observed and so assigned in some other molecules, but no further attempts appear to have been made to elaborate the general analysis and understanding of the M–O stretching modes. In particular, the problems of (1) interaction between two or more such M–O oscillators, either equivalent or not, and (2) the interdependence of metal–oxygen force constants, bond lengths, and bond orders seem to merit investigation. This report will deal first with the interaction problem and stretching force constants will be calculated for some relatively simple metal–oxygen compounds. The interesting cases in which one oxygen atom is present as a bridging group in a linear M–O–M system will be briefly discussed, and the infrared spectra of some more complex compounds, which contain a variety of metal–oxygen bond types, will be interpreted. Finally, relationships between the force constants, lengths, and orders of Mo–O bonds will be presented.

2. The Normal Coordinate Analyses and Stretch–Stretch Interactions

In order to interpret the spectra of molecules having two or more M–O oscillators with a common metal atom, it is necessary to consider the manner in which the vibration in one oscillator interacts with the vibration(s) in the other(s). Metal–oxygen π bonding can presumably be attributed to the overlap of the filled $p\pi$ orbitals of oxygen with empty $d\pi$ orbitals on the metal and each of the latter will, in general, be expected to be available to two or more of the oxygen atoms. Thus as one M–O bond stretches, lessening the involvement of some of the $d\pi$ orbitals in π bonding to that oxygen atom, these same $d\pi$ orbitals will become more available for π bonding to the other oxygen atoms, and the π bonding to them will become stronger. Consequently, the stretch–stretch interaction constants should be positive.

Using available data for several isoelectronic tetrahedral MO_4^{n-} species, force constants have been computed using simplified F matrices[3,4] in which only the M–O stretching constant and the stretch–stretch inter-

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[1] Supported in part by the National Institutes of Health and the National Science Foundation.

[2] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

[3] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

[4] The effect of omitting the bend and the bend–stretch interaction constants from the F_2 factored block on the stretch and stretch–stretch interaction constants was checked and found to be insignificant. Also due to the large difference in frequencies very little mixing of the stretching and bending modes occurred. This is fortunate because for most of the cases to be considered here the necessary data for including the bend–stretch interaction are not available.