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The Configurations of Yellow and Red Trichlorotris-(diethyl sulfide)-iridium(III)[1]

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Measurements of dipole moment, electrolytic conductance, electrophoresis, visible and ultraviolet absorption and reflectance spectra, and nuclear magnetic resonance spectra have shown the yellow form of $[Ir((C_2H_5)_2S)_3Cl_3]$[3] to be the *cis* (1,2,3) isomer and the red form to be an electrolytic "polymerization" isomer, *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$. In the course of establishing the structure of the red isomer, several new derivatives, salts of both the cation and anion, as well as a new iridium(IV) compound, believed to be *trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$, were prepared. As final proof of structure, the red isomer was metathetically synthesized from these derivatives.

Introduction

Chromatographic column experiments with nonaqueous solutions of several square-planar Pt(II) nonelectrolytic complexes have shown that the more polar *cis* isomers are more strongly adsorbed on polar adsorbents than are the less polar *trans* isomers.[4] An apparent exception to this behavior, encountered with the supposedly hexacoordinate octahedral complex $[Ir((C_2H_5)_2S)_3Cl_3]$,[5] suggested that the configurations assigned by the original investigators[6] merely on the basis of color might be incorrect. Further evidence for this possibility is the fact that the yellow ("*cis*") isomer is very soluble in both nonpolar and polar organic solvents, while the red ("*trans*") isomer, although soluble in chloroform and nitrobenzene, is insoluble in most nonpolar solvents. Also, the red ("*trans*") isomer forms an addition compound with chloroform,[7] a behavior that might be expected of the more polar *cis* isomer. Thus the present stereochemical study of these isomers by both physical and chemical methods was undertaken.

Experimental

(1) **Yellow and Red Isomers of $[Ir((C_2H_5)_2S)_3Cl_3]$.**[8]—An aqueous suspension of $(NH_4)_2IrCl_6$[9] was refluxed with a solution of $(C_2H_5)_2S$ in ethanol.[10] The yellow isomer (m.p. 131–132°) was extracted from the resulting crystalline precipitate with hot benzene. The red isomer (m.p. 165–166°) was extracted with chloroform as a flesh-colored to brick-red powder from the benzene-insoluble residue; it was crystallized by addition of benzene. The yellow isomer is insoluble in water, sparingly soluble in ethanol, and very soluble in benzene, chloroform, acetone, and most organic solvents. The red isomer is insoluble in water, sparingly soluble in benzene, ethanol, and acetone, soluble in nitrobenzene, and very soluble in chloroform.

Anal. Calcd. for $IrC_{12}H_{30}S_3Cl_3$: Ir, 33.88; C, 25.33; H, 5.31. Found: Ir, 33.37 (red); 34.12 (yellow); C, 25.53[11] (yellow); H, 5.36[11] (yellow).

(2) **Dipole Moments.**—Dielectric constants of solutions of the yellow and red isomers were measured at 25° by the resonance method at a frequency of 1040 kc.

Dipole moments (in e.s.u.-cm.) were calculated according to Guggenheim's formula[12]

$$\mu = 0.01282 \times 10^{-18} \sqrt{\frac{3T}{(\epsilon_1 + 2)^2} \frac{M_2}{d_1} \left(\frac{\Delta}{w}\right)_{w \to 0}}$$

where T = absolute temperature, ϵ_1 = dielectric constant of the solvent, M_2 = molecular weight of the solute (569), d_1 = density of the solvent, and

$$\left(\frac{\Delta}{w}\right)_{w \to 0} = \left(\frac{\epsilon - \epsilon_1}{w}\right)_{w \to 0} - \left(\frac{n^2 - n_1^2}{w}\right)_{w \to 0}$$

where ϵ and ϵ_1 = dielectric constants of solution and pure solvent, respectively, n and n_1 = refractive indices[13] of solution and pure solvent, respectively, and w = weight fraction of solute. The reagent grade solvents employed (benzene, carbon tetrachloride, carbon disulfide, and chloroform) were purified and dried by standard methods.[14] Dipole moments for chlorobenzene, *m*- and *p*-dichlorobenzene, and *m*-dinitrobenzene calculated by Guggenheim's formula from empirically determined dielectric constants showed excellent agreement with literature values.

(3) **Electrolytic Conductances.**—Molar conductances[15] at 25° of the yellow and red isomers in nitrobenzene and chloroform were obtained with a Freas-type cell which had previously been calibrated with aqueous potassium chloride solution. Resistances were measured with a Leeds and Northrup Type 4760 Wheatstone bridge equipped with a cathode-ray oscillograph for detecting the null point.

(4) **Electrophoresis Experiments.**—Chloroform and chloro-

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[3] The abbreviations R (alkyl) and py (pyridine) are used in this paper.

[4] G. B. Kauffman, R. P. Pinnell, and L. T. Takahashi, *Inorg. Chem.*, **1**, 544 (1962).

[5] The yellow isomer, supposedly *cis* (1,2,3), was readily eluted with chloroform from a silica gel column, while the red isomer, supposedly *trans* (1,2,6), required the more polar solvent ethanol for elution. Details of this and other chromatographic separations of nonelectrolytic hexacoordinate isomer pairs will form the basis of a subsequent article.

[6] P. C. Rây, N. Adhikari, and R. Ghosh, *J. Indian Chem. Soc.*, **10**, 275 (1933). These authors stated that "by his exhaustive works on isomerism in iridium complexes, Delépine has established that the *cis* compound is always orange and the *trans*, red." M. Delépine himself, however (private communication, Sept. 5, 1960), cites exceptions to this general rule.

[7] P. C. Rây and N. N. Ghosh, *ibid.*, **13**, 138 (1936).

[8] G. B. Kauffman, *Inorg. Syn.*, **7**, 224 (1963).

[9] G. B. Kauffman and L. A. Teter, *ibid.*, **8**, in press.

[10] Because of the photochemical "dimerization" of the yellow isomer in solution (G. B. Kauffman, J. H. Tsai, and R. C. Fay, in preparation), the reaction is probably best carried out in the dark.

[11] The authors are indebted to Dr. J. W. Hogarth and the late Prof. F. P. Dwyer, Australian National University, for the C and H analyses which they performed in the course of checking the synthesis.

[12] E. A. Guggenheim, *Trans. Faraday Soc.*, **47**, 573 (1951).

[13] Refractive indices were measured with a Zeiss Abbé-type refractometer.

[14] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents: Physical Properties and Methods of Purification," Interscience Publishers, Inc., New York, N. Y., 1955.

[15] Molecular weights of 569 (yellow isomer) and 1138 (red isomer) were used in calculating conductances.

form–benzene solutions of the red isomer, both with and without addition of sodium perchlorate to increase the conductance, were subjected to filter paper electrophoresis using a potential of 90 volts d.c. The light orange anion became bright violet on reaching the anode, while the light yellow cation underwent no color change at the cathode.[16] Similar solutions of the yellow isomer showed no migration, in agreement with its formulation as a nonelectrolyte.

Addition of concentrated nitric acid to chloroform solutions of the red isomer produced the bright violet color observed during electrophoresis. Solutions of the yellow isomer gave no color changes with nitric acid.

(5) **Preparation of Derivatives of the Red Isomer.**—**$[Ir((C_2H_5)_2S)_2Cl_4]$**.—An ethanol solution of $AgNO_3$ was added in slight excess to a chloroform solution of the red isomer. The resulting light orange precipitate of $Ag[Ir((C_2H_5)_2S)_2Cl_4]$ was separated from the yellow filtrate (A), washed with ethanol and chloroform, suspended in water, and the silver removed as Ag_2S by saturating the suspension with H_2S. The orange filtrate containing $H[Ir((C_2H_5)_2S)_2Cl_4]$ was evaporated under reduced pressure, and the blackish violet residue was recrystallized from chloroform by addition of ethanol. The crystals of $[Ir((C_2H_5)_2S)_2Cl_4]$ were washed with iced ethanol and air-dried. The compound melts at 130°, is insoluble in water, slightly soluble in ethanol, and very soluble in chloroform. In ethanol solution, black-violet $[Ir((C_2H_5)_2S)_2Cl_4]$ is slowly reduced to orange $H[Ir((C_2H_5)_2S)_2Cl_4]$. The oxidation of $H[Ir((C_2H_5)_2S)_2Cl_4]$ to $[Ir((C_2H_5)_2S_2)Cl_4]$ appears analogous to the change of $pyH[Ir(py)_2Cl_4]$ to $[Ir(py)_2Cl_4]$.[17]

Anal.[18] Calcd. for $IrC_8H_{20}S_2Cl_4$: Ir, 37.39; C, 18.68; H, 3.92; S, 12.46; Cl, 27.59. Found: Ir, 37.55; C, 18.41; H, 3.97; S, 12.19; Cl, 27.50.

Although it is difficult to distinguish between $[Ir^{IV}((C_2H_5)_2S)_2Cl_4]$ and the expected compound $H[Ir^{III}((C_2H_5)_2S)_2Cl_4]$ (or $[Ir^{V}H((C_2H_5)_2S)_2Cl_4]$) on the basis of chemical analysis alone, the absorption and n.m.r. spectra shown below clearly indicate the presence of Ir(IV). Moreover, the magnetic moment of 1.77 ± 0.02 B.M. found by Dr. Lauri Vaska of the Mellon Institute, a value very close to the theoretical μ_{eff} of 1.73 B.M. for one unpaired electron, definitely shows that the purple solid contains Ir(IV) (d^5 nonbonding configuration) and eliminates Ir(III) and Ir(V). Infrared spectra of the violet solid as well as of chloroform and ethanol solutions of the reduced substance showed no bands due to Ir–H bonding. Our spectral findings were corroborated by Dr. Klaus Noack of Cyanamid European Research Institute and by Dr. Vaska.

$[Ir((C_2H_5)_2S)_4Cl_2]NO_3$.—Filtrate A from the preceding preparation was treated with a slight excess of NaCl solution, the resulting precipitate of AgCl removed, and the yellow filtrate evaporated at room temperature. The residue was freed of NaCl by recrystallization from ethanol by adding water and cooling in an ice bath. The yellow crystals of $[Ir((C_2H_5)_2S)_4Cl_2]NO_3$ were washed with ice-water and air-dried. The compound melts at 157°, is slightly soluble in water, but very soluble in ethanol and chloroform.

Anal. Calcd. for $IrC_{16}H_{40}S_4Cl_2NO_3$: Ir, 28.03; C, 28.02; H, 5.88; S, 18.71; Cl, 10.34; N, 2.04; O, 7.00. Found: Ir, 28.00; C, 28.41; H, 6.12; S, 18.50; Cl, 10.59; N, 2.12; O, 6.26 (by difference).

$[Ag(py)_2][Ir((C_2H_5)_2S)_2Cl_4]$.—An ethanol solution of $[Ag(py)_2]ClO_4$[19] was added in slight excess to a chloroform solution of the red isomer. The resulting pale orange crystalline precipitate was separated from the yellow filtrate (B), washed with ethanol and chloroform, and recrystallized from pyridine by addition of water. $[Ag(py)_2][Ir((C_2H_5)_2S)_2Cl_4]$ melts at 162°, is insoluble in water, ethanol, and chloroform, but soluble in pyridine (not analyzed).

$[Ir((C_2H_5)_2S)_4Cl_2]ClO_4$.—Filtrate B from the preceding preparation was evaporated at room temperature, and the residue was extracted with chloroform. The extract was similarly evaporated, and the yellow product was recrystallized several times from ethanol by addition of water. $[Ir((C_2H_5)_2S)_4Cl_2]ClO_4$ is insoluble in water, but very soluble in ethanol and chloroform. Since the compound explodes on ignition, it was not analyzed.

$[Ir((C_2H_5)_2S)_4Cl_2][B(C_6H_5)_4]$.—An ethanol solution of $Na[B(C_6H_5)_4]$ was added in slight excess to a chloroform solution of the red isomer. After 5 hr., the resulting yellow crystalline deposit was separated from the pale orange filtrate (C) and recrystallized from chloroform by addition of ethanol. Ethanol-washed, air-dried $[Ir((C_2H_5)_2S)_4Cl_2][B(C_6H_5)_4]$ melts at 182°, is insoluble in water and ethanol, slightly soluble in acetone, and very soluble in chloroform.

Anal. Calcd. for $IrC_{40}H_{60}S_4Cl_2B$: Ir, 20.40; C, 50.95; H, 6.42; S, 13.61; Cl, 7.52. Found: Ir, 19.31; C, 51.14; H, 6.24; S, 12.88; Cl, 7.30.

$NH_4[Ir((C_2H_5)_2S)_2Cl_4]$.—An ethanol solution of $AgNO_3$ was added in slight excess to filtrate C from the preceding preparation, and the precipitate of $Ag[Ir((C_2H_5)_2S)_2Cl_4]$ and $Ag[B(C_6H_5)_4]$ was collected by filtration and washed with water. Concentrated aqueous NH_3 was added to dissolve $Ag[Ir((C_2H_5)_2S)_2Cl_4]$, and the remaining $Ag[B(C_6H_5)_4]$ residue was removed by filtration. Silver was removed as Ag_2S from the pale orange filtrate by addition of aqueous $(NH_4)_2S$. Orange crystals of $NH_4[Ir((C_2H_5)_2S)_2Cl_4]$ were obtained by evaporating the filtrate at room temperature (not analyzed).

Similar attempts to prepare derivatives by metathesis of the red isomer with tetramethylammonium chloride, tetra-*n*-propylammonium iodide, and tris-(1,10-phenanthroline)-nickel(II) perchlorate[20] resulted only in regeneration of the original red isomer.

(6) **Synthesis of Red Isomer from Derivatives.**—Ethanol solutions of $[Ir((C_2H_5)_2S)_2Cl_4]$ and $[Ir((C_2H_5)_2S)_4Cl_2]NO_3$ were mixed. After 5 hr., the resulting red crystalline deposit was collected and recrystallized from chloroform by addition of benzene. The product was identical in melting point, solubilities, and absorption and n.m.r. spectra with the original red isomer prepared according to ref. 8.

(7) **Absorption, Reflectance, and Infrared Spectra.**—Absorption spectra in ethanol (220–400 mμ) or chloroform (300–1000 mμ) were measured with Beckman DK-2 and Cary 14 spectrophotometers. Reflectance spectra were measured against Al_2O_3 with a Beckman DU spectrophotometer provided with a standard reflectance attachment. Infrared spectra in chloroform or carbon disulfide solutions and KBr disks failed to show any characteristic differences between the yellow and red isomers.[21]

(8) **N.m.r. Spectra.**—Proton resonance spectra were obtained in deuteriochloroform solution at 25° on a Varian Associates Model A-60 high resolution spectrometer at 60 Mc. Eastman White Label diethyl sulfide was used without further purification. High temperature n.m.r. spectra of the red isomer were run at 75 and 100° on a Varian Model V-4300-2 spectrometer.

(9) **X-Ray Patterns.**—Powder patterns were obtained with iron-filtered Co Kα radiation, 0.5-mm. glass capillaries, and a Debye–Scherrer camera of 14.01-cm. diameter.

(10) **Optical Properties.**[22]—As a further means of characterizing the isomers, optical properties were determined by use of a Leitz SM-Pol polarizing microscope. The following data were obtained: Yellow isomer: sub-hedral crystals; no pleochroism; refractive indices, $\alpha = 1.683$, $\gamma = 1.701$; birefringence = 0.018,

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[16] If the current was stopped before the orange spot had reached the anode, oxidation with concentrated nitric acid of the orange portion of the paper also produced the violet color. The latter is believed to be due to an Ir(IV) compound, $[Ir((C_2H_5)_2S)_2Cl_4]$, whose preparation is described in the next section.

[17] M. Delépine, *Compt. rend.*, **175**, 1075, 1211 (1922); *Ann. chim.* (Paris), [9] **19**, 5 (1923); *Z. physik. Chem.*, **130**, 222 (1927); G. B. Kauffman, *Inorg. Syn.*, **7**, 220, 228 (1963).

[18] The authors wish to thank Dr. Kurt Eder, University of Geneva, Switzerland, for analyzing the derivatives.

[19] Prepared according to G. B. Kauffman and R. P. Pinnell, *Inorg. Syn.*, **6**, 6 (1960).

[20] G. B. Kauffman and L. T. Takahashi, *J. Chem. Educ.*, **39**, 481 (1962); *Inorg. Syn.*, **8**, in press.

[21] The authors are indebted to Dr. James V. Quagliano and Mr. Anthony Vinciguerra, Florida State University, for these measurements.

[22] The authors are indebted to Dr. Seymour Mack and Mr. Russell Harper, Dept. of Geology, Fresno State College, for these measurements.

second order; orientation, crystals are length-slow; anisotropic, biaxial positive; extinction angle = 40° with length of crystal. Red isomer: euhedral crystals; no pleochroism; refractive indices, $\alpha = 1.687$, $\gamma = 1.694$; birefringence = 0.007, first order; orientation, crystals are length-slow; anisotropic, biaxial negative; extinction angle = 19° with length of crystal.

Results and Discussion

(1) **Dipole Moments.**—Since Jensen's classic investigations of the configuration of *cis*- and *trans*-$[Pt(R_2S,Se)_2X_2]$[23] and $[Pt(R_3P,As,Sb)_2X_2]$,[24] dipole moments have been widely used in assigning structures to square-planar isomers. Unfortunately, insolubility in nonpolar solvents has prevented the widespread application of this method to octahedral complexes.

It was hoped that the structure of the yellow and red isomers could be assigned by comparing their dipole moments. The values for the yellow isomer in several solvents were in fair agreement: 5.20, 5.23 D. (C_6H_6); 5.14, 5.17 D. (CCl_4); and 5.42 D. (CS_2). The moment of the red isomer, however, could not be determined since it proved to be an electrolyte. Because Ir–Cl and Ir–S bond moments are not known, the moment obtained for the yellow isomer does not permit a choice between the *cis* and *trans* structures.

(2) **Electrolytic Conductances.**[15]—The molar conductance, Λ_M (ohm^{-2} cm.^{2}), of the yellow isomer in chloroform was found to be 9.1×10^{-3}, a value essentially independent of concentration, whereas in nitrobenzene, the following Λ_M values were obtained: 1.54×10^{-2} (2.85×10^{-2} *M*), 3.35×10^{-2} (9.16×10^{-3} *M*), and 9.25×10^{-2} (1.83×10^{-3} *M*). The yellow isomer is thus a nonelectrolyte in these solvents. Molar conductances for the red isomer (2.85×10^{-2} to 7.32×10^{-5} *M*) in nitrobenzene varied from 16.54 to 23.70 ohm^{-1} cm.^{2}, which is in the range (18 to 30 ohm^{-1} cm.^{2}) typical of 1:1 electrolytes in this solvent.[25–27] Likely possibilities for the structure of the red isomer which would be electrolytes and still maintain the empirical formula $Ir((C_2H_5)_2S)_3Cl_3$ include $[Ir((C_2H_5)_2S)_6][IrCl_6]$ (I); $[Ir((C_2H_5)_2S)_5Cl][Ir((C_2H_5)_2S)Cl_5]$ (II); and $[Ir((C_2H_5)_2S)_4Cl_2][Ir((C_2H_5)_2S)_2Cl_4]$,[28,29] *cis-cis* (III), *cis-trans* (IV), *trans-cis* (V), and *trans-trans* (VI).

Further evidence for the electrolytic nature of the red isomer was obtained by electrophoresis experiments, which also showed the colors of the constituent ions and the oxidizable nature of the anion. The metathetical preparation and analysis of crystalline derivatives clearly established the structure of the red isomer as configurations III, IV, V, or VI. These structures were confirmed by the metathetical synthesis of the isomer from saline derivatives of its constituent ions.

(3) **Absorption and Reflectance Spectra.**—These data are shown in Table I. Comparison of these band positions with Yamatera's coefficients for band splittings of complexes of type MA_qB_{6-q} deviating slightly from octahedral symmetry[30–32] strongly suggests that the yellow isomer is *cis*-$[Ir((C_2H_5)_2S)_3Cl_3]$ without band splittings, whereas the relative intensities of the two components originating from the first spin-allowed transition in cubic symmetry suggests that the separated anion $[Ir((C_2H_5)_2S)_2Cl_4]^-$ has a *trans* configuration.[33] The positions of the spin-allowed and spin-forbidden transitions of the separated cation $[Ir((C_2H_5)_2S)_4Cl_2]^+$ are compatible only with a *trans* structure. Hence, the red isomer should be *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$, a formulation which may be favored by a high lattice energy. Since the red isomer consisting of the orange anion and lemon-yellow cation has been synthesized and isolated without isomerization from solutions of *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]NO_3$ and the dark violet $[Ir((C_2H_5)_2S)_2Cl_4]$, the Ir(IV)compound probably also has a *trans* configuration.

The wave numbers of spin-forbidden and spin-allowed $\gamma_5{}^6 \rightarrow \gamma_5{}^5\gamma_3$ transitions in analogous series of Ir–$(C_2H_5)_2S$ and Ir–py complexes are compared in Table II. One would extrapolate to values of *ca.* 31 and 35 kK., respectively, for the first spin-allowed transition in the hypothetical ions $Ir((C_2H_5)_2S)_6{}^{3+}$ and $Ir(py)_6{}^{3+}$. Since the extrapolated value for $Ir(H_2O)_6{}^{3+}$ is 31 kK., it appears that $(C_2H_5)_2S$ occupies a position similar to that of H_2O in the spectrochemical series[34,35]: $Cl^- < (C_2H_5O)_2PS_2^- < F^- < (C_2H_5)_2NCS_2^- < H_2O \sim py \sim NH_3 \sim SO_3^{2-}$. The arrangement of sulfur-containing ligands in this series can be understood if the spectrochemical parameter expresses the difference between the effects of σ-antibonding and π-antibonding on the partly filled shell. SO_3^{2-} with only one lone pair is thus σ-antibonding, whereas the thio anions have several lone pairs available and also show π-antibonding effects.[36] It is of interest that the thioether sulfur atom in $(NH_2CH_2CH_2)_2S$ has a position in the series somewhat to the right of H_2O.[36]

The spin-allowed transitions in the $(C_2H_5)_2S$ complexes measured here are stronger than in $IrCl_6{}^{3-}$ but

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[23] K. A. Jensen, *Z. anorg. allgem. Chem.*, **225**, 97, 115 (1935); **226**, 168 (1936).

[24] K. A. Jensen, *ibid.*, **229**, 225 (1936).

[25] E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947); G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, **1**, 239 (1962).

[26] Assuming the red isomer to be a 1:1 electrolyte, we obtained from cryoscopic measurements in nitrobenzene the degree of dissociation, $\alpha = 0.815$ at molality 1.95×10^{-2}; the incomplete dissociation may be due to ion-pair formation.

[27] A plot of Λ_M *vs.* $\sqrt{c}$ is linear, in agreement with the Debye–Hückel–Onsager prediction for a strong electrolyte. A similar plot for the red isomer in chloroform exhibits a minimum at $c =$ *ca.* 8×10^{-3} *M*, perhaps due to ion-pair formation.

[28] A precedent for this formulation occurs in the analogous case of $[Ir(R_3As)_3Cl_3]$, in which one of the two forms is monomeric, while the other is a "polymerization" isomer, $[Ir(R_3As)_4Cl_2][Ir(R_3As)_2Cl_4]$ (*cf.* F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N.S. Wales*, **79**, 121 (1946)).

[29] The preparation of the compound $NH_4[Ir((CH_3)_2S)_2Cl_4]$ is claimed by E. Kh. Fritsman and V. V. Krinitskiĭ (*Zh. Prikl. Khim.*, **11**, 1610 (1938)), but no details are given.

[30] H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

[31] D. S. McClure, in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 498.

[32] C. K. Jørgensen, *Solid State Phys.*, **13**, 375 (1962).

[33] *trans*-$[Rh(py)_2Cl_4]^-$ has a similar spectrum (*cf.* C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 151 (1957)).

[34] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 31 (1962).

[35] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publ. Co., Inc., Reading, Mass., 1962.

[36] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

TABLE I

ABSORPTION AND REFLECTANCE SPECTRA OF YELLOW AND RED $[Ir((C_2H_5)_2S)_3Cl_3]$ AND DERIVATIVES

Compound	Wave length of band max.[a] λ, mμ	Wave no., σ (1 kK. = 1000 cm.$^{-1}$)	Molar extinction coeff. ε (per Ir atom)	Wave length of band max.[a] λ, reflectance, mμ	Band assignment
Yellow isomer *cis*-(1,2,3)$[Ir((C_2H_5)_2S)_3Cl_3]$	(450)	(22.2)	41	465	$^1\Gamma_1\gamma_5{}^6 \rightarrow {}^3\Gamma_4\gamma_5{}^5\gamma_3$
	(345)	(29.0)	(310)	(360)	$\rightarrow {}^1\Gamma_4$?
	313	32.0	404	...	$\rightarrow {}^1\Gamma_5$?
	238	42.0	19,300	...	$S \rightarrow \gamma_3 Ir$
Red isomer *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$	(500)	(20.0)	10	(520)	$^3\Gamma_4$ anion
	...	(23.8)	$\gg$10	(420)	$^1\Gamma_4$ (t_2) anion
	(360)	(27.8)	162	(360)	Anion + cation
	306	32.7	385	...	Cation
	240	41.7	22,000	...	$S \rightarrow \gamma_3 Ir$
trans-$[Ir((C_2H_5)_2S)_2Cl_4]^{-}$[b]	...	19.4	Weak	515[c]	$^1\Gamma_1\gamma_5{}^6 \rightarrow {}^3\Gamma_4\gamma_5{}^5\gamma_3$
	(413)	(24.2)	60	(415)[c]	$\rightarrow {}^1\Gamma_4$ (t_2)
	363	27.6	140	362[c]	$\rightarrow {}^1\Gamma_4$ (t_5)
	324	30.9	205	...	$\rightarrow {}^1\Gamma_5$
trans-$[Ir((C_2H_5)_2S)_4Cl_2]^{+}$[d]	(445)	(22.5)	18	(445)[e]	$^1\Gamma_1\gamma_5{}^6 \rightarrow {}^3\Gamma_4$
	(370)	(27.0)	110	(370)[e]	$\rightarrow {}^1\Gamma_4$ (t_5)
	(330)	(30.3)	330	...	?
	306	32.7	465	...	?
trans-$[Ir((C_2H_5)_2S)_2Cl_4]$	(725)	(13.8)	380	...	$S \rightarrow \gamma_5 Ir$
	662	15.1	700	...	
	561	17.8	3,980	...	S, Cl $\rightarrow \gamma_5 Ir$
	530	18.9	3,840	...	
	(450)	(22.2)	700	...	?
	359	27.9	1,280	...	?

[a] λ and σ values for shoulders are in parentheses. [b] This solution was prepared by dissolving ascorbic acid in a small amount of water, adding excess ethanol, then adding a drop of the resulting solution to a solution of the violet compound $[Ir((C_2H_5)_2S)_2Cl_4]$ in a 70% chloroform–30% ethanol mixture. The dilute solution of the reduction product $H[Ir((C_2H_5)_2S)_2Cl_4]$ was pink. [c] These reflectance spectra were obtained with $[Ag(py)_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$. [d] These spectra were obtained with an ethanol solution of *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]NO_3$. [e] These reflectance spectra were obtained with *trans*-$[Ir((C_2H_5)_2S)_4Cl_2][B(C_6H_5)_4]$.

weaker than in the inner complex $Ir(S_2P(OC_2H_5)_2)_3$.[36] However, it is not completely certain that the bands with ε ~400 in Table I might not be caused by electron transfer.

It has recently been possible to define optical electronegativities (x_{opt}) from the positions of the Laporte-allowed electron-transfer bands.[32,37] The band at 42 kK. (Table I) for Ir(III) would suggest $x_{opt} = 2.7$ for $(C_2H_5)_2S$, the same value obtained[36] for $(C_2H_5O)_2PS_2^-$. On the other hand, the electron-transfer bands observed for $[Ir((C_2H_5)_2S)_2Cl_4]$, when compared with the most recent measurements[38] for $IrCl_6^{2-}$, would tend to indicate that x_{opt} for $(C_2H_5)_2S$ is only *ca.* 0.1 unit below the value for Cl^- and hence as high as 2.9. There may be some connection between this deviation and the highly irregular behavior of O^{2-} as a ligand with strong π-antibonding effects on the partly filled shell.[32,37]

(4) **N.m.r. Spectra.**—Chemical shifts (Table III) are reported in c.p.s. relative to tetramethylsilane (1% by volume) and are believed accurate to ±0.3 c.p.s. Spin–spin coupling constants, accurate to ±0.05 c.p.s., were calculated by using the first- and second-order energy relations given by Pople, Schneider, and Bernstein.[39] Each value reported is, in general, the mean of three different spectral determinations.

The n.m.r. spectrum of the ethyl group in the yellow and red isomers (Table III) consists of a triplet due to the methyl protons and a quartet due to the methylene protons. These spectra were compared with the spectrum of diethyl sulfide, which was found to be somewhat more complex, exhibiting some of the additional transitions reported[40] at 40 Mc. Since the complexity arises because the spin–spin coupling constant J is appreciable compared to the chemical shift between the methyl and methylene protons, the complexity is considerably reduced at 60 Mc. In the iridium complexes, the electron-withdrawing iridium(III) ion shifts the methyl and methylene resonances to lower field and increases the chemical shift δH_0 between the methyl and methylene protons. The decrease in the ratio $J/\delta H_0$ is apparently sufficient to render unresolved any remaining complexity. The rather large shifts in the resonances toward lower field upon coordination to iridium(III) are expected because of the large effective nuclear charge of a trivalent ion with electronic configuration d^6.[41] The J values reported here are in close agreement with the value of 7.42 ± 0.05 c.p.s. for $(C_2H_5)_2S$ reported by McGarvey and Slomp.[40]

As may be seen in Table III, the yellow isomer exhibits a single methyl triplet and a single methylene quartet; the red isomer shows two methyl triplets with intensity ratio 2:1 but only a single methylene quartet. The yellow isomer may be assigned the *cis* (1,2,3)

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TABLE II

WAVE NUMBERS OF $\gamma_5^6 \rightarrow \gamma_5^5\gamma_3$ TRANSITIONS IN Ir(III)–$(C_2H_5)_2S$ AND Ir(III)–PYRIDINE COMPLEXES

Complex	$^3\Gamma_4$	$^1\Gamma_4$	Complex	$^3\Gamma_4$	$^1\Gamma_4$
$[IrCl_6]^{3-}$	17.9	24.1	$[Ir(py)Cl_5]^{2-}$	18.5	(23.8)
			cis-$[Ir(py)_2Cl_4]^-$	21.6	...
trans-$[Ir((C_2H_5)_2S)_2Cl_4]^-$	19.4	(24.2, 27.6)	*trans*-$[Ir(py)_2Cl_4]^-$	19.4	(25.3)
cis-$[Ir((C_2H_5)_2S)_3Cl_3]$	(22.2)	(29.0)	*cis*-$[Ir(py)_3Cl_3]$	>23	...
			trans-$[Ir(py)_3Cl_3]$	23.1	...
trans-$[Ir((C_2H_5)_2S)_4Cl_2]^+$	(22.5)	(27.0)	*trans*-$[Ir(py)_4Cl_2]^+$	24.8	...

TABLE III

N.M.R. DATA FOR $[Ir((C_2H_5)_2S)_3Cl_3]$ ISOMERS AND DERIVATIVES

Compound	Concn.[a]	Chemical shifts, c.p.s.		*J*, spin–spin coupling const., c.p.s.
		$-CH_3$	$-CH_2-$	
$(C_2H_5)_2S$	14	−75.1	−152.5	7.40
Yellow $[Ir((C_2H_5)_2S)_3Cl_3]$	9	−86.0	−179.2	7.51
Red $[Ir((C_2H_5)_2S)_3Cl_3]$ (prepd. according to ref. 8)	12	−85.8 (1)[b] −89.7 (2)	−186.8	7.49 (anion) 7.44 (cation)
Red $[Ir((C_2H_5)_2S)_3Cl_3]$ (synthesized by metathesis)	*ca.* 10	−85.1 (1) −89.5 (2)	−186.3	
$[Ir((C_2H_5)_2S)_4Cl_2]NO_3$	25	−89.6	−186.2	7.35
$[Ir((C_2H_5)_2S)_4Cl_2]ClO_4$	15	−89.6	−186.3	7.34
$[Ir((C_2H_5)_2S)_4Cl_2][B(C_6H_5)_4]$	20	−78.1	−176.8	7.37
$[Ag(py)_2][Ir((C_2H_5)_2S)_2Cl_4]$	10[c]	−81.6	*ca.* −202 (very broad)	7.44

[a] Vol. % for $(C_2H_5)_2S$; g./100 ml. for complexes. [b] Numbers in parentheses indicate relative intensities. [c] Solvent was pyridine.

structure in which the diethyl sulfide groups are equivalent by a threefold axis. The n.m.r. data are also consistent with formulation I ($[Ir((C_2H_5)_2S)_6][IrCl_6]$), but this structure may be eliminated in view of conductance data and electrophoretic behavior.

For the red isomer, structure I, in which all $(C_2H_5)_2S$ groups are equivalent, is eliminated, as is structure II, which would require three different types of methyl triplets in intensity ratio 1:1:4. Structures III and IV, which would require three different types of $(C_2H_5)_2S$ groups in intensity ratio 1:1:1, may likewise be eliminated. The last two possibilities (V and VI), in which there is one type of $(C_2H_5)_2S$ group in the *trans* cation and one type in the *cis* or *trans* anion in intensity ratio 2:1, are in closest accord with the experimental data. In view of the *trans* structure established for $[Ir((C_2H_5)_2S)_2Cl_4]$ and $[Ir((C_2H_5)_2S)_2Cl_4]^-$ by absorption spectra, the red isomer is best formulated as the "polymerization" isomer, *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$.[42]

The red isomer which was synthesized from *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]NO_3$ and *trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$ is identical with original samples of the red isomer which were prepared according to ref. 8. The spectrum of the red isomer is essentially a superposition of the spectra of *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]NO_3$ and $[Ag(py)_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$ with a slight difference in the position of the anion resonance due to solvent effects or ion-pair interactions with the cation.

The nitrate and perchlorate gave nearly identical spectra, the lines coinciding with the methyl resonance of relative intensity (2) and the methylene resonance of the red isomer. The methyl resonance of intensity (2) is therefore due to the four $(C_2H_5)_2S$ groups of the cation as predicted previously on the basis of the intensity ratio. The *trans* configuration for the cation is confirmed since salts containing the cation give only one methyl and one methylene resonance. The spectrum of the tetraphenylborate is very similar, but the position of the lines is shifted upfield by *ca.* 10 c.p.s. This shift may be due to ring currents in the phenyl rings of the $[B(C_6H_5)_4]^-$ ion.

In the spectrum of $[Ag(py)_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$, a single methyl resonance, consistent with either the *cis* or *trans* configuration, was observed. For some unknown reason the methylene resonance of the anion is unusually broad and weak. As a result, in spectra of the red isomer, the methylene resonance of the anion is masked by the methylene resonance of the cation, and consequently only a single methylene quartet is observed.

The n.m.r. spectrum of the violet *trans*-$[Ir((C_2H_5)_2S)_2Cl_4]$ reveals a very broad tetramethylsilane and chloroform resonance. Moreover, the methyl and methylene resonances do not appear at all. The broadening indicates the presence of a paramagnetic ion, probably Ir(IV). A most puzzling feature is a broad band (line width *ca.* 34 c.p.s.) at *ca.* +440 c.p.s. relative to tetramethylsilane. This band is near the region in which protons bonded to metals in transition metal hydrides have appeared.[43] The infrared spectra, however, have shown no evidence for Ir–H bonding.

In early stages of this study, we considered for the red isomer the possibility of the monomeric *cis* structure with methyl groups made nonequivalent by restricted

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[42] The n.m.r. spectrum of the red isomer is also compatible with the *trans* (1,2,6) monomer since such a structure should have two equivalent $(C_2H_5)_2S$ groups (1,6 positions) and a third, different. In view of the conductance data, electrophoretic behavior, preparation of derivatives, synthesis from $[Ir((C_2H_5)_2S)_4Cl_2]NO_3$ and $[Ir((C_2H_5)_2S)_2Cl_4]$, and meager solubility in organic solvents, the ionic formulation is clearly indicated.

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rotation about the metal–sulfur bond. The n.m.r. spectrum of the red isomer, however, showed no change at 75°. After heating to 125°, the spectrum was run at 100°, at which temperature it most resembled that of the yellow isomer. Upon evaporation of the chloroform solvent, yellow crystals were obtained whose X-ray powder pattern and melting point were identical with that of the yellow isomer. It is apparent that the isomerization *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4] \rightarrow$ *cis*-$[Ir((C_2H_5)_2S)_3Cl_3]$ has occurred at elevated temperatures. This reaction appears similar to the conversion of $[Pt((CH_3)_2S)_4][PtCl_4]$ to the monomer $[Pt((CH_3)_2S)_2Cl_2]$.[44] It is interesting to note that in the present case only the *cis* isomer was obtained upon isomerization. Preferential formation of the *cis* isomer over the *trans* isomer may be due to stronger iridium–sulfur π-bonding in the *cis* isomer as suggested for the dichlorobis-(trialkylphosphine)-platinum(II) complexes.[45]

In view of the agreement between the results of the different approaches described in this paper, the authors feel that the structures of the yellow and red isomers of empirical formula $Ir((C_2H_5)_2S)_3Cl_3$ have been definitely established.[46] However, there is need for similar stereochemical investigations of other isomer pairs, especially those of type MA_3B_3, for which configurational assignments have been made on the basis of meager data. Although the configurations finally established in the present case differ from those originally predicted by us on the basis of chromatographic behavior the general rule that the more polar compound should be adsorbed more strongly by polar adsorbents than the less polar compound[4] is still valid. Since it was the discrepancy in elution order which led us to undertake this stereochemical study, the value of chromatographic behavior as a diagnostic tool in structure proof is thus underscored.

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[46] The preparation of a third isomer has been claimed by Fritsman and Krinitskiĭ (*cf.* ref. 29), but no details or properties are given. This compound may be the true *trans* monomer.

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On the Existence of Red Tungsten(III) and of Pentapotassium Tetradecachlorotritungstate(III) during the Reduction of Chlorotungstates with Tin

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Comparison of X-ray diffraction data indicates that the substance $K_5[W_3Cl_{14}]$ as reported by Laudise and Young is presumably a mixture of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ instead. This is strongly supported by the changes in absorption spectra observed during the decomposition of $K_2[W(OH)Cl_5]$ solutions. The wine-red color of these solutions is caused by superposition of the absorption spectra of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$. The same seems to apply to the red color observed during the reduction of chlorotungstates with tin, which has been attributed to a red tungsten(III) compound. Absorption and reflection spectra of both $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ are presented.

Tungstates(VI) when dissolved in 12 *M* hydrochloric acid are at first reduced electrochemically or chemically to a blue solution, which according to oximetric and coulometric measurements[2] contains tungsten(V). The absorption spectrum shows one band at 15,300 cm.$^{-1}$ with $\epsilon \sim 7$ presumably due to the presence of the monomeric species $[WOCl_5]^{2-}$.[3] One single spectral transition is indeed expected in the visible for the $(5d)^1$ system of tungsten(V) in an approximately cubic field of ligands. The appearance of the $[WOCl_5]^{2-}$ ion is supported by the fact that tungsten(V) oxychlorides have been crystallized from solutions reduced to the oxidation state +5 at a platinum cathode.[4]

Continued reduction produces intensely violet colored solutions, an absorption band at 19,100 cm.$^{-1}$ with $\epsilon \sim 600$ having been found by Jørgensen.[3] From these solutions a red compound has been obtained,[5] which has the apparent composition $K_2[W^{IV}(OH)Cl_5]$, whereas it was demonstrated distinctly by means of

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