TABLE II

EQUILIBRIUM CONSTANTS FOR 1:1 ADDITION COMPOUNDS WITH TIN(IV) CHLORIDE IN BENZENE SOLUTION

Donor	K_{11}, l./mole	ΔH, kcal./mole	ΔS,[a] cal./°K. mole
p-Chlorobenzonitrile	4.3 (20°); 3.6 (25°); 2.9 (30°); 2.2 (35°)	-7.1 ± 0.5	-15.0 ± 1.5
(in, 1,2-dichloroethane)	K_{11} at 30°, 2.9; K_{12} at 30°, 1.6	....	....
p-Methoxybenzonitrile	15.5 (30°); 10.9 (35°); 8.1 (40°)	-12.5 ± 1.0	-28.7 ± 3
9-Fluorenone	6.6 (30°); 5.4 (35°); 4.4 (40°)	-7.6 ± 0.3	-15.1 ± 1
Diisobutyl ketone	33.8 (30°); 23.7 (35°); 16.4 (40°)	-13.6 ± 1	-31.6 ± 3
Ethyl pivalate	4.2 (30°); 3.6 (35°); 3.1 (40°)	-5.6 ± 0.3	-9.4 ± 1

[a] ΔS computed from $(\Delta H - \Delta F)/T$, with ΔF in units of atm.$^{-1}$, for 30°.

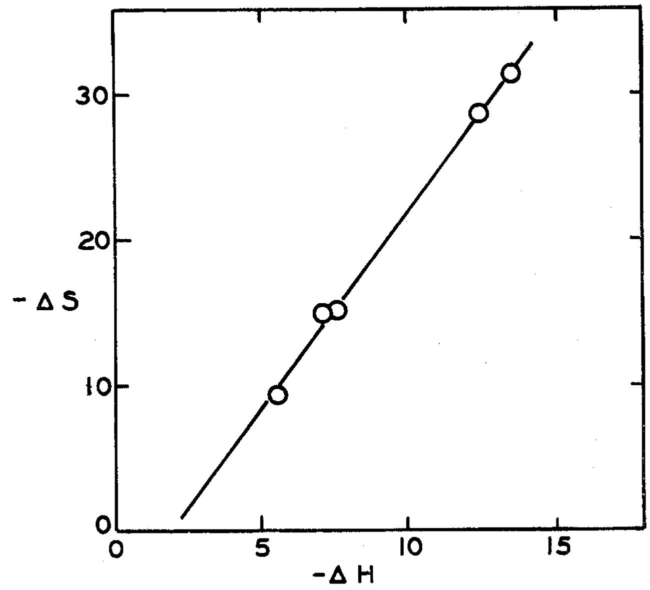

Fig. 1.—Enthalpy–entropy relationship for 1:1 tin(IV) chloride complexes.

the five donors involved in this study. They differ not only in that both nitrogen and oxygen donors are involved, but also in the degree to which adjacent portions of the donor molecule block the donor group. It seems evident that such steric interactions as do exist between donor and acceptor affect the strength of the donor–acceptor bond (and hence affect ΔH and ΔS) without introducing any special orientational requirements on complex formation, which would result in an abnormal enthalpy–entropy relationship. The larger ΔH value for the p-methoxybenzonitrile complex as compared with the p-chloro is in accord with earlier interpretations of intensity and frequency changes in the nitrile group absorptions.[6]

The results of this investigation, as well as of the previous study, establish the existence in solution of 1:1 addition compounds with tin(IV) chloride. It should be emphasized that the possibility of appreciable dimerization of the 1:1 compounds to form six-coordinate tin complexes is not consistent with the equilibrium constant data. The possibility remains that in benzene solution the solvent occupies a coordination position. This possibility, which is unlikely *a priori*, is apparently ruled out by the fact that the equilibrium constants obtained at 30° for the p-chlorobenzonitrile–tin(IV) chloride system in 1,2-dichloroethane are numerically equal to those obtained in benzene at 30°.[3] (The fact that K_{12} bears the same relationship to K_{11} in the two solvents is perhaps more significant than the equality of the corresponding K values.) The evidence, therefore, very strongly indicates a five-coordinate tin species in dilute solutions of tin(IV) chloride with donors.

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Synthesis of Anhydrous Metal Chlorides by Action of Carbon Tetrachloride on the Metal Sulfides

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The method of Knox and Tyree[2] for the conversion of metal oxides to anhydrous chlorides by action of CCl_4 at 400° in a bomb has been extended to permit replacement of metal oxides by metal sulfides. WS_2, WS_3, MoS_3, and Re_2S_7 give WCl_6, $MoCl_5$, and $ReCl_5$, respectively. The ore, FeS_2, and commercial grades of FeS and MoS_2 give $FeCl_3$ and $MoCl_5$, respectively. Acid-insoluble residues remain after treatment of these lower grades of sulfides.

Experimental

Materials.—Tungstic acid (Matheson Coleman and Bell) was converted to WS_2 or WS_3 by literature methods.[3-5] $Na_2MoO_4 \cdot 2H_2O$ (Merck) and rhenium metal (Department of Chemistry, Univ. of Tennessee) were converted to MoS_3 and Re_2S_7, respectively.[6,7] Iron pyrites, FeS_2 (Staley Consolidated Mine, Staley, N. C.), commercial FeS (Baker and Adamson), and MoS_2 (Climax Molybdenum Co.) were used without purification.

General Procedure.—The appropriate metal sulfide was sealed in a 100 to 130 ml. glass tube along with CCl_4. Eight ml. of

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[6] T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 4175 (1961).

[1] From work performed in partial fulfillment of requirements for the Ph.D. degree in chemistry at the University of North Carolina, Chapel Hill, N. C.

[2] K. Knox, S. Y. Tyree, Jr., *et al.*, *J. Am. Chem. Soc.*, **79**, 3358 (1957).

[3] E. Corleis, *Ann.*, **232**, 261 (1886).

[4] E. Corleis, *ibid.*, **232**, 257 (1886).

[5] E. Corleis, *ibid.*, **232**, 263 (1886).

[6] W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1932, p. 592.

[7] W. Geilmann and G. Lange, *Z. anal. Chem.*, **126**, 321 (1944).

CCl_4 was used for each 26 ml. of tube volume, *i.e.*, 32 to 40 ml. of CCl_4 was used.[2] The sealed glass tube was placed in a steel bomb into which was also added 8 ml. of CCl_4 for each 26 ml. of void space to balance the pressure in the tube. The temperature was held to 400° for a period ranging from 2 to 4 hr. Products were handled in a drybox.

Analysis.—Tungsten was determined gravimetrically as WO_3, chlorine as AgCl, and rhenium as $(C_6H_5)_4AsReO_4$. Iron was titrated with Ce(IV). Molybdenum was determined by reduction to Mo(III), oxidation with Fe(III), and back titration of the iron Fe(II) formed with Ce(IV).

Products. (a) **WCl_6.**—Five grams of WS_3 gave 6.8 g. of WCl_6 (85% yield) and 0.8 g. of WS_3 gave 0.8 g. of WCl_6 (70% yield).

Anal. Calcd. for WCl_6: W, 46.4; Cl, 53.6. Found: W, 45.9 ± 0.1; Cl, 53.4 ± 0.1; Cl/W, 6.05.

(b) **$MoCl_5$.**—About 2.6 g. of MoS_3 gave 2.8 g. (80% yield) of $MoCl_5$. The best yield was obtained when 1 g. of MoS_2 was allowed to react for 12 hr.; 3% acid-insoluble residue remained.

Anal. Calcd. for $MoCl_5$: Mo, 35.1; Cl, 64.9. Found: Mo, 35.1 ± 0.1; Cl, 64.7 ± 0.1; Cl/Mo, 4.97.

(c) **$ReCl_5$.**—About 1.5 g. of Re_2S_7 after 10 hr. heating in the bomb gave 1.5 g. of $ReCl_5$ (80% yield).

Anal. Calcd.: Re, 51.2; Cl, 48.8. Found: Re, 50.8 ± 0.2; Cl, 47.0 ± 0.1; Cl/Re, 4.86.

(d) **$FeCl_3$.**—Four grams of FeS_2 gave 5.3 g. of $FeCl_3$ after 8 hr. heating in the bomb; 10% of acid-insoluble residue remained; Cl/Fe found, 3.02. Three grams of FeS gave 5.4 g. of $FeCl_3$ after 12 hr. heating in the bomb; 4% of an acid-insoluble residue remained; Cl/Fe found, 3.01.

Discussion

The advantages of this method are that: (1) Anhydrous metal chlorides are directly prepared from the sulfides, either synthetic or natural. (2) Under the conditions of the experiment usually the metal is converted to a single chloride rather than a mixture of chlorides and/or oxide chlorides. (3) Where sand is the only significant contaminant, as from certain ores, if the metal chloride is to be carried through further reaction steps, then no purification is indicated. However, if the pure metal chloride is the objective of the process it can be separated from the admixed solid usually by sublimation or extraction with an inert solvent, such as CCl_4, appropriate to the particular metal chloride. (4) It appears that many sulfides will prove to be as easily converted to the metal chlorides by this method as the corresponding oxides and some may, indeed, be more readily converted. (5) The more ready availability of some of the sulfides, *e.g.*, the MoS_2 used in this work, as compared to the oxides indicates inherent simplification of any process requiring ultimately the anhydrous chloride. (6) The method is a straightforward, single-step manipulation for solubilizing and extracting metals from their sulfide ores.

Correspondence

Infrared Spectral Evidence of π-Bonding in the $Fe(CN)_5NO^{-2}$ Ion

Sir:

Recently, Ballhausen and Gray[1] have derived a rule for octahedral distorted complexes of tetragonal symmetry (ML_5X), in which they state that almost all the π-bonding is axially directed and involves the metal d_{xz} and d_{yz} orbitals, the d_{xy} being approximately a nonbonding orbital. Following the above rule in the case of $M(CN)_5NO$ complexes, they arrived at the conclusion that the M–NO bond order was unusually high; there is strong M–NO π-bonding and therefore the pentacyanonitrosyls are not octahedral.

One of us[2] arrived at similar conclusions by measurements of the Mössbauer effect in the case of $Fe(CN)_5NO^{-2}$. Herington and Kynaston,[3] using infrared spectroscopy in the region of the antisymmetric stretching of the CN bond, have called attention to the striking difference existing between the nitroprusside and some other pentacyano complexes of iron. In the present work we have extended the infrared spectroscopic data to other $Fe(CN)_5X$ complexes in the region of the CN (ν_6) and MC (ν_7 and ν_8) stretching vibrations.

As can be seen in Table I, the frequencies of the CN and MC bands depend on the charge of the central ion and are independent of the charge of the X group with the exception of $Fe(CN)_5NO^{-2}$. All the spectra of Fe^{II} compounds exhibit a very strong and broad band at 2040–2060 cm.$^{-1}$ and those of Fe^{III} compounds a strong and narrow band at 2120–2130 cm.$^{-1}$ assigned to the antisymmetric stretching vibration of the CN group. On the other hand, in the spectra of Fe^{II} compounds there are two absorptions in the KBr region, one at 570–580 cm.$^{-1}$ and the other at 400–420 cm.$^{-1}$. These two absorptions are shifted to 495–535 and 390–400 cm.$^{-1}$, respectively, in the spectra of Fe^{III} compounds. It has been shown[4] that the higher of the two absorptions (ν_7) is mainly associated with MCN bending and the lower one (ν_8) with MC stretching. Although there is some mixing of the two modes in these vibrations, it is worth noting that the higher one shows the most marked shifts in passing from the Fe^{II} to the Fe^{III} pentacyano complexes, as might be expected of the vibration which is mainly associated with the stretching mode. Qualitatively, we also confirmed the previous observation that the intensity of the CN band in Fe^{II} complexes is about two times that in Fe^{III} complexes.

The position of the MC and CN stretching bands and the intensity of the latter can be explained on the basis of the ideas of Jones.[5] Investigating the hexacyanometal complexes, this author concludes that the

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(1) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).

(2) J. Danon, *J. Chem. Phys.*, **39**, 266 (1963).

(3) E. F. Herington and W. Kynaston, *J. Chem. Soc.*, 3555 (1955).

(4) L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

(5) L. H. Jones, Proceedings, 7th International Congress on Coordination Chemistry, Stockholm, 1962.