tetrachloroplatinate(II) (0.2 g; 0.5 mmol dissolved in 2–3 ml of water). The mixture was refluxed for 10 hr. The bright yellow solution was filtered from the potassium chloride and the filtrate was treated with an ethanol solution of sodium tetraphenylborate. The resulting granular, cream-colored material was collected on a filter, washed with ethanol, and finally recrystallized from an ethanol–acetone mixture. *Anal.* Calcd for $C_{53}H_{50}As_2BClPtS_2$: C, 55.72; H, 4.41; Cl, 3.10. Found: C, 55.58; H, 4.31; Cl, 3.29.

Pt(demethylated C_3).—The bright yellow solution that resulted from the reaction of the C_3 ligand and potassium tetrachloroplatinate(II) (as described above) was treated with ether to precipitate a yellow solid. This material was collected on a filter, dissolved in DMF (10 ml), and the solution was refluxed for 10 hr. The solution was concentrated until some yellow crystals separated. Ethanol (20 ml) was added and the mixture was stored overnight at 5°. The crystals were collected, washed with ethanol, and dried. *Anal.* Calcd for $C_{27}H_{24}As_2PtS_2$: C, 42.81; H, 3.19; S, 8.46. Found: C, 42.60; H, 3.13; S, 8.39.

Pt(demethylated C_2).—This complex was obtained by a procedure similar to that given above for Pt(demethylated C_3). *Anal.* Calcd for $C_{26}H_{22}As_2PtS_2$: C, 41.97; H, 2.98; S, 8.62. Found: C, 41.79; H, 3.05; S, 8.50.

$Pt(C_3)I_2$.—The Pt(demethylated C_3) complex was treated with excess methyl iodide and allowed to stand at room temperature overnight. The methyl iodide was then removed and the residue was recrystallized twice from dichloromethane. *Anal.* Calcd for $C_{29}H_{30}As_2I_2PtS_2$: C, 33.44; H, 2.90; I, 24.38. Found: C, 33.27; H, 2.71; I, 24.26.

$Pt(C_2)I_2$.—This compound was prepared by treatment of Pt(demethylated C_2) with methyl iodide as described above for $Pt(C_3)I_2$. *Anal.* Calcd for $C_{28}H_{28}As_2I_2PtS_2$: C, 32.73; H, 2.75; I, 24.70. Found: C, 32.04; H, 2.65; I, 25.02.

$Pt(dias)I_2$.—1,2-Bis(diphenylarsino)ethane (Strem Chemicals) (0.25 g; 0.5 mmol) was dissolved in a hot ethanol–chloroform mixture and to this was added an aqueous ethanol solution of potassium tetrachloroplatinate(II) (0.2 g; 0.5 mmol). The pinkish white precipitate was collected on a filter, washed with water and ethanol, and then digested with hot concentrated HCl–ethanol (1:1 volume ratio) for 2 hr. The solid was collected on a filter, washed with ethanol, suspended in ethanol–chloroform (1:1), and then stirred with ethanolic sodium iodide for 1 hr. The yellow material was recrystallized from a chloroform–ethanol mixture. *Anal.* Calcd for $C_{26}H_{24}As_2I_2Pt$: C, 33.01; H, 2.54; I, 26.88. Found: C, 32.88; H, 2.57; I, 26.98.

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A Novel Criterion for Carbonyl Stretching Band Assignment and Its Application to the Infrared Spectrum of (π-Cyclopentadienyl)(methyldichlorosilyl)dicarbonyliron[1,2]

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Received June 23, 1970

Cyclohexane solutions of the complex[3] $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_2CH_3$ show four strong infrared absorptions in the region of CO stretching vibrations. The expected number is 2, both of roughly equal intensity.[4] The extra bands were atrributed to the presence of rotational isomers I and II,[5] which differ by rotation through 120° about the Si–Fe bond.

Accordingly, the bands may be grouped into two pairs on the basis of their relative intensities. Thus the weaker pair (at[3] 2031 and 1983 cm^{-1}) arise from the less abundant isomer, while the pair at[3] 2022 and 1973 cm^{-1} arise from the more abundant one. However, none of the usual criteria allows the band pairs to be assigned to the individual isomers I and II. Therefore the following method was employed.

The two CO environments of isomer I are symmetrically identical since they are interchanged by a molecular symmetry element, the mirror plane.[5] Thus substitution of either position by $^{13}C^{16}O$ will produce identical satellite bands having about 2% of the intensity of the isotopically normal species in natural abundance. In contrast, the two CO environments of isomer II, which has no nontrivial symmetry elements,[5] will in principle be different from each other. Substitution of either position by $^{13}C^{16}O$ should produce a different spectrum in each case This would cause a splitting of the $^{13}C^{16}O$ satellite bands of isomer II, but not of isomer I, and provide a basis for distinguishing their spectra.

The previously published spectrum of the complex[3] reveals the expected splitting in the satellite of the 1983-cm^{-1} band but not in those accompanying the bands at 1973 and 2022 cm^{-1}. The latter absorption obscures the satellite of the 2031-cm^{-1} band. A sample of the complex was prepared by the method of Jetz and Graham.[3] Its infrared spectrum in cyclohexane solution agreed closely with that reported by those authors. In particular, the measured value of the splitting in the satellite of the 1983-cm^{-1} band was 4.2 ± 0.5 cm^{-1}. No splitting was observed in the satellites of the 2022- and 1973-cm^{-1} absorptions.

These observations confirm the original interpretation[3] of the spectrum, on which the present treatment is based, and allow the bands observed in this region to be fully assigned. In addition, the size of the splitting may be used as the third parameter necessary to evaluate all three approximate[4] CO force constants for isomer II. Those for isomer I may be calculated from the two CO frequencies of isotopically normal molecules (Table I).

TABLE I
ASSIGNMENTS OF CO STRETCHING FREQUENCIES AND APPROXIMATE CO FORCE CONSTANTS

	Isomer[a]	
	I	II
Assumed point symmetry	C_s	C_1
In-phase CO stretch, cm^{-1}	2022	2031
In-phase ^{13}CO stretch, cm^{-1}	2008	. . .
Out-of-phase CO stretch, cm^{-1}	1973	1983
Out-of-phase ^{13}CO stretch, cm^{-1}	1942	1959, 1954.5
k_i,[b] mdyn/Å	0.40	0.38
k (transoid to Cl), mdyn/Å	16.24	16.35
k (transoid to CH_3), mdyn/Å	. . .	16.45

[a] Reference 5. [b] I thank Dr. R. C. Dougherty for the use of a PDP8 computer to calculate the force constants.

The CO groups of isomer II may be transoid[5] to either a methyl group or a chlorine atom. The latter case

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(1) Work performed in the laboratories of Professor F. G. A. Stone, Bristol, U. K., whom I thank for facilities and encouragement.

(2) After this work was completed, a similar criterion was suggested by J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970). However the present work represents, to my knowledge, the first time that such a splitting has actually been observed and measured.

(3) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967).

(4) J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 2744 (1969), and references therein.

(5) Newman projections of the isomers, numbered as above, are reproduced in ref 3. Isomer I has the mirror plane of symmetry.

more closely resembles the situation of the CO groups in isomer I, which has a force constant lower than either of the two calculated for isomer II. Therefore the CO environment transoid to chlorine in isomer II is assigned the lower of the two force constants calculated for that isomer.

Thus the rotational asymmetry of the Fe–Si bond may be expressed numerically as the change in force constant accompanying its rotation, facilitating comparison with similar complexes. Such a comparison would provide a sensitive probe for investigating ligand influences upon the CO stretching frequencies of complexes of this type.[4]

Moreover the present approach provides a technique which is potentially useful in other cases of possible isomerism in dicarbonylmetal compounds. Examples might include (cis CO) phenMo(CO)$_2$[P(OCH$_3$)$_3$]$_2$[6] and (π-C$_5$H$_5$)Mo(CO)$_2$(π-C$_3$H$_5$).[7]

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[6] L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966); *J. Chem. Soc. A*, 317 (1966).

[7] R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

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Properties of Some Werner-Complex Clathrates Utilizing Tetrakis (4-methylpyridine)metal(II) Thiocyanate (Metal = Nickel, Cobalt, Iron, Manganese)

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Received August 18, 1970

Rate studies on the formation of Werner complex clathrates were first reported by Gawalek and Konnecke[1] and more recently by Minton and Smith.[2] These studies showed reaction times that varied from a few minutes to as much as 6 hr. Schaeffer, *et al.*,[3] had earlier described the clathration reaction as being characterized by very rapid formation—reaction times well under 1 min when the appropriate reagents are mixed.

One of the purposes of the research reported here was to attempt a clarification for the wide variation in time reported for completion of the clathration reaction. Studies were carried out on the formation of a number of clathrates using Werner complexes of the type M(4-Me(py))$_4$(SCN)$_2$, (M = Ni, Co, Fe, Mn) as host and organic molecules as guests. The size of the guest molecule varied from benzene (molecular volume 88.8 cm^3/mol) to 4-methylstyrene (131.3 cm^3/mol).

Experimental Section

The complexes to be used as hosts in this study were prepared using the basic procedure of Schaeffer, *et al.*[3] However, it was found that a fivefold increase in the amount of water used was necessary in order to prevent coprecipitation of excess thiocyanate. The precipitates were air dried and then stored in a desiccator over solid potassium hydroxide. Removal of all moisture required approximately 1 week. A quantitative determination of the per cent of metal in each of the complexes was used as an indication of purity. For the kinetic rate studies it was found necessary to purify reagent grade heptane before using it as a suspension medium. Later spectral studies showed the purified heptane to be comparable with commercially available Spectroquality grade.

The kinetic rate studies were carried out in a constant-temperature bath capable of regulation to ±0.1°. All rate studies were carried out using the so-called suspension method.[3] Temperature measurements were made with a thermometer calibrated and certified by the United States National Bureau of Standards. The procedure followed in each of the rate determination runs was as follows. A 500-ml reaction flask containing 300 ml of purified heptane was placed in the constant-temperature bath and allowed to come to equilibrium. Ten milliliters of the guest component was then introduced and the solution stirred with a magnetic stirrer. After thermal equilibrium was again reached, the solid Werner complex was added. The complex was in a powder form which would pass a 325 mesh screen. Samples of the solution were withdrawn periodically by means of a filter stick and the progress of the clathration followed spectrophotometrically using a Beckman DB-G spectrophotometer operating in the ultraviolet region at preselected wavelengths (255 mμ for benzene, 263 mμ for toluene, 275 mμ for *p*-xylene). Each of the clathration studies was allowed to proceed for no less than 48 hr.

Samples of each of the complexes and of the materials obtained from the rate studies were used for powder diffraction X-ray patterns. The samples were prepared by mixing the solid material with a binder (either collodion or Vaseline) and extruding from a 0.5-mm diameter capillary. The patterns were run on a Siemens Kristalloflex-IV X-ray diffractometer using copper Kα radiation. A 2-radian camera was used and line measurements were made with a coincidence scale having an accuracy of ±0.01 mm.

The determination of the per cent metal in the complexes and clathrates followed standard analytical procedures. Manganese and nickel were determined gravimetrically, iron was determined volumetrically, and both copper and cobalt were determined electrolytically.

Results and Discussion

Analyses of the complexes M(4-Me(py))$_4$(SCN)$_2$ gave the following results for the per cent of metal ion. *Anal.* Calcd: Ni, 10.73; Mn, 9.90; Fe, 10.26; Co, 10.76; Cu, 19.03. Found: Ni, 10.66; Mn, 9.92; Fe, 10.55; Co, 10.66; Cu, 18.73. The calculated percentage of Cu is based on the complex Cu(4-Me(py))$_2$(SCN)$_2$.

Figure 1 shows the decrease in absorbance of the guest *p*-xylene as a function of time for the clathration reaction with the host Ni(4-Me(py))$_4$(SCN)$_2$. Runs were made at the three temperatures indicated and all were allowed to proceed for 48 hr. The mole ratio of

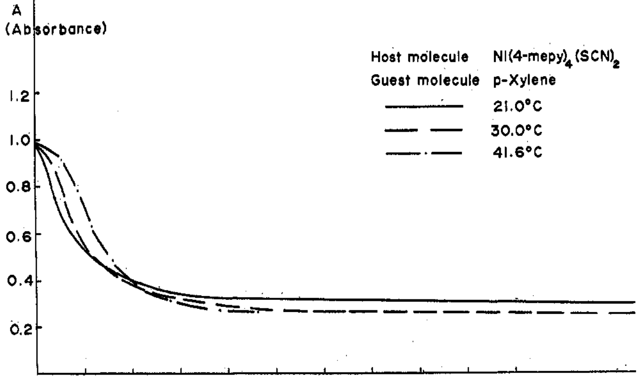

Figure 1.

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[3] W. D. Schaeffer, W. Dorsey, D. A. Skinner, and C. G. Christian, *J. Amer. Chem. Soc.*, **79**, 5870 (1957).