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Nonrigid Molecules. Enthalpy and Entropy Differences between Rotational Isomers of (π -Cyclopentadienyl)(methylchlorosilyl)-dicarbonyliron^{1,2}

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The solution infrared spectrum of the title compound (I) has been thought³ to indicate rotational isomerization about the Fe-Si bond. This view was supported by the assignment of the CO stretching region of the spectrum to the individual rotational isomers.¹ In this paper are reported measurements of the enthalpy and entropy differences between these isomers.

Experimental Section

Samples of I were prepared by the method of Jetz and Graham.³ Spectroscopic samples were purified by slow sublimation onto a water-cooled probe at ~ 0.2 Torr. Infrared spectra were taken on a Perkin-Elmer 257 spectrophotometer using a Research and Industrial Instruments Model VLT-2 variable-temperature infrared cell. The path length was 1.0 mm, the solvent was *n*-hexane, and a variable-path-length cell containing *n*-hexane was placed in the reference beam and adjusted to provide a flat base line at machine ambient temperature. Since a weak *n*-hexane absorption at ~ 2025 cm^{-1} proved to be temperature sensitive, only the two lower energy CO stretching absorptions were used to calculate relative intensities. Replicate measurements were made at +25, +3, -25, and -75°. The results were analyzed by the method of Noack,⁴ using the band assignments proposed earlier.¹ The least-squares fit to Noack's equation was a line with gradient 0.81, intercept 1.36, and correlation coefficient 1.00. The gradient is probably an underestimate of the enthalpy change due to incomplete band separation.

Results and Discussion

The measured entropy difference between symmetric and unsymmetric isomers⁵ was 1.4 ± 0.5 eu. Its sign was such as to favor the unsymmetrical isomers. Since the symmetry number of each isomer is 5 and the other components of their partition functions should be similar in size, the calculated value is ~ 0 eu. However the infrared experiment is blind to the difference between the two unsymmetrical enantiomers, resulting in a statistical contribution of $R \ln 2$ (~ 1.4 eu) in their favor (compare ref 6, p 315). The agreement confirms the assignments¹ and the interpretation³ of the spectrum upon which they are based.

The measured enthalpy difference, of course, provides only a lower limit for the average potential barrier to rotation about the Fe-Si bond. Its value was found to be $0.8 (-0.1, +0.7)$ kcal mol⁻¹ in favor of the symmetrical isomer, which was the isomer with the

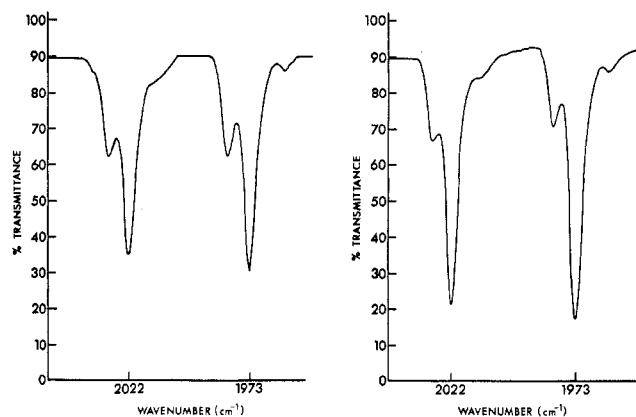


Figure 1.—Infrared transmittance of a *n*-hexane solution of (π -C₅H₅)Fe(CO)₂SiCl₂CH₃ at +25° (left) and -78° (right).

lower average CO stretching frequency. Thus the observed enthalpy difference cannot be due to differential Fe→Si π bonding between the isomers.

It is commonly accepted that the π^* orbitals of CO become partially occupied upon coordination to a metal. This electron density, being antibonding in character, must swell the van der Waals envelope of the ligand. Steric compression should therefore destabilize these orbitals, causing a decrease in their electron density and raising the vibrational frequency of the CO bond. Therefore the relative CO stretching frequencies of the isomers are consistent with the view that steric compression is responsible for most of the enthalpy difference between them. It follows that both the average CO stretching frequency difference and the enthalpy difference between isomers should decrease with increasing size of the group IV ligand atom in a related series of complexes. This result is consistent with the observation⁷ by Bryan, *et al.*, that intramolecular forces exercise very little constraint upon the conformation around the Fe-Sn bonds in the complexes (π -C₅H₅)Fe(CO)₂SnX₃ where X = phenyl, Cl, or Br.

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Transition Metal π Complexes. I. Reactions of π -Cycloheptatrienyldicarbonyl Iodides of Molybdenum and Tungsten with Tertiary Phosphines and Phosphites

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Considerable interest has developed in recent years in the detection and interconversion of isomeric forms of transition metal organometallic carbonyls of the general types (π -ring)M(CO)_nL_{2-n}X or (π -ring)M(CO)_nLX. The existence of at least three general types of isomerism has been observed. Examples include cis-trans isomerism in π -C₅H₅Mo(CO)₂P(OC₆H₅)₃R (R = CH₃

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(1) Part II; for part I see J. Dalton, *Inorg. Chem.*, **10**, 1822 (1971).

(2) Experimental work from the laboratories of Professor F. G. A. Stone, Bristol, U. K., whom I thank for facilities and encouragement.

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

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(5) Newman projections of the isomers, along the Fe-Si bond axis, are reproduced in ref 3. There is one symmetric conformation, with a reflection plane bisecting the cyclopentadienyl and methyl groups, and two enantiomeric conformations with no nontrivial symmetry elements.

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TABLE I
 ANALYTICAL DATA AND PHYSICAL PROPERTIES FOR COMPOUNDS OF THE TYPE C_7H_7MCOI

L	Color	Mp, ^b °C	Yield, %	Purification ^d	Analyses, %					
					Carbon		Hydrogen		Phosphorus	
					Calcd	Found	Calcd	Found	Calcd	Found
M = Mo										
$P(OC_6H_5)_3^a$	Dark green	128–130	64	R, CH_2Cl_2 -heptane	43.97	44.37	3.29	3.08	4.20	4.27
$P(OCH_3)_3^e$	Green	130–131	77	R, CH_2Cl_2 -hexane	28.35	28.96	3.46	3.43	6.65	6.62
$P(OC_2H_5)_3^e$	Dark green	106–109	59	R, CH_2Cl_2 -heptane	33.09	32.91	4.36	4.26	6.09	5.89
$P(i-OC_3H_7)_3^e$	Dark green	101–103	45	R, heptane	37.11	37.01	5.13	4.96	5.63	5.48
$P(C_6H_5)_3$	Green	148–149 ^c	73	R, CH_2Cl_2 -heptane	51.67	50.88	3.68	3.64	5.12	5.33
$P(n-C_4H_9)_3^e$	Green	143–144	72	R, CH_2Cl_2 -heptane	44.13	43.92	6.30	6.25	5.69	5.42
M = W										
$P(OC_2H_5)_3$	Light green	78–80	8	C, CH_2Cl_2 -benzene (50:50)	28.21	29.00	3.73	3.77	5.20	5.30
$P(i-OC_3H_7)_3$	Light green	96–98	10	C, benzene-hexane (60:40)	31.99	31.12	4.43	4.37	4.85	4.65

^a CH_2Cl_2 adduct. ^b Darkens upon melting. ^c Darkens but does not melt below 300°. ^d R = recrystallization from solvents(s); C = elution fraction from a Florisil column. ^e Molecular weight was established by the parent ion peak in the mass spectrum.

 TABLE II
 INFRARED AND NMR DATA FOR COMPOUNDS OF THE TYPE C_7H_7MCOI

L	$\nu(CO)$, ^a cm^{-1}	$\nu(CO)$ intens ratio, high freq/low freq	Proton nmr spectra, ^c ppm	
			$\tau(C_7H_7)$ [$J(Ch-P)$, Hz]	$\tau(others)$ [J , Hz]
M = Mo				
$P(OC_6H_5)_3$	1973	...	5.50 d [2.7]	2.81 m (C_6H_5), 4.88 s (CH_2Cl_2)
$P(OCH_3)_3$	1960, ^b 1947	10/9.8	4.88 d [3.0]	6.47 d [11.0] (CH_3)
$P(OC_2H_5)_3$	1969, 1950	10/8.3	4.90 d [2.7]	6.11 q [7.0] (CH_2), 8.81 t [7.0] (CH_3)
$P(i-OC_3H_7)_3$	1970, 1948	10/10	4.96 d [3.2]	5.42 m (CH), 8.81 t [5.5] (CH_3) ^d
$P(C_6H_5)_3$	1950	...	5.15 d [2.1]	2.76 m (C_6H_5)
$P(n-C_4H_9)_3$	1944	...	5.04 d [2.1]	8.10–8.93 m (CH_2), 9.17 t [5.5] (CH_3)
M = W				
$P(OC_2H_5)_3$	1945, 1927	10/9.5	4.90 d [2.8]	6.08 q [7.0] (CH_2), 8.78 t [7.0] (CH_3)
$P(i-OC_3H_7)_3$	1947, 1926	8.2/10	4.94 d [2.6]	5.43 m (CH), 8.81 d [6.0] (CH_3), 8.75 d [6.0] (CH_3)

^a Recorded in *n*-hexane unless noted otherwise. ^b Recorded in carbon disulfide. ^c Recorded in $CDCl_3$ with TMS as internal standard. Key: s, singlet; d, doublet; t, triplet; q, quintet; m, multiplet. ^d Run at 100 MHz; $\tau(CH_3)$ 8.79 [6.0], 8.71 [6.0].

or $C_6H_5CH_2$ ^{1,2} and $\pi-C_5H_5MoCO[PCH_3(C_6H_5)_2]_2Cl$,³ optical isomerism due to an asymmetric metal center in $\pi-C_5H_5FeCO[P(CH_3)_2C_6H_5]COCH_3$ ⁴ and $\pi-C_5H_5FeCO[P(C_6H_5)_3][CH_2Si(CH_3)_3]$,⁵ and conformational isomerism due to (1) different orientations of the π -allyl group in $\pi-C_5H_5Mo(CO)_2-\pi-C_3H_4R$ ($R = H, CH_3$),⁶ (2) restricted rotation about the Fe–Sn bond in $\pi-C_5H_5FeCO[P(C_6H_5)_3][Sn(C_6H_5)_3]$ ⁷ and the Fe–Si bond in $\pi-C_5H_5Fe(CO)_2(SiCl_2CH_3)$,⁸ or (3) restrictions within the phosphorus ligand as in $\pi-C_5H_5FeCO[P(OCH_3)_3]I$ ⁹ and its ruthenium analog.¹⁰ Furthermore, these complexes may exist in more than one isomeric form.^{1,5,7,9}

Cycloheptatrienyl(group VIb metal) carbonyl derivatives offer an opportunity to investigate the nature of isomerism in further detail. Even though numerous metal carbonyl complexes containing π -bonded carbocyclic rings such as cyclopentadienyl and benzene with a large variety of Lewis base ligands are known,¹¹

analogous π -cycloheptatrienyl chemistry is nonexistent with the exception of one compound, $\pi-C_7H_7MoCO-[P\{N(CH_3)_2\}_3]I$.¹² This paper describes reactions of $\pi-C_7H_7Mo(CO)_2I$ ($M = Mo, W$) with monodentate tertiary phosphines and phosphites yielding primarily monosubstituted complexes of the type $\pi-C_7H_7MCOI$, which in some cases appear to exist in two different isomeric conformations.

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were recorded in *n*-hexane or carbon disulfide solutions and potassium bromide pellets on a Model 621 Perkin-Elmer spectrometer. Proton nmr spectra were taken in chloroform-*d* on Varian Associates Model A-60 and HA-100 machines (Table II) with tetramethylsilane as an internal standard. Mass spectra were recorded on a Varian Associates Model CH7 spectrometer using a direct-inlet probe heated from 40 to 100°. Conductivity measurements were made on a $10^{-3} M$ nitrobenzene solutions using an Industrial Instruments conductivity bridge, Model RC 16B2, and a cell with platinum electrodes. Melting points were taken in open capillaries and are uncorrected. The organophosphines and organophosphites were obtained from Eastman, Aldrich, and M and T Chemical Co. and used without further purification. Florisil (60–100 mesh) used for chromatography was obtained from Fisher Scientific Co. The starting materials $C_7H_7Mo(CO)_2I$ ¹³ and $C_7H_7W(CO)_2I$ ¹⁴ were prepared from literature methods. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

A typical synthesis of the complexes discussed in this paper involves refluxing an equimolar mixture of $C_7H_7M(CO)_2I$ and ligand in 200 ml of benzene or toluene for 3–48 hr. Evaporation

- (1) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **91**, 1550 (1969).
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- (10) D. A. Brown, H. J. Lyons, and R. T. Sane, *ibid.*, **4**, 621 (1970).
- (11) (a) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 58 (1959); (b) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959); (c) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966); (d) R. L. Pruett, *Prep. Inorg. React.*, **2**, 187 (1965); (e) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

(12) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(13) D. J. Bertelli, Ph.D. Thesis, University of Washington, 1961.

(14) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

of the solvent (25° (40 mm)) yields a dark green solid or oil. Recrystallization from mixed solvents or elution from a Florisil column (Table I) produces light to dark green crystals.

Complexes of the type $C_7H_7MoCOLI$ obtained only as oils or impure solids were $C_7H_7MoCO[As(C_6H_5)_3]I$ ($\nu(CO)$ 1941 cm^{-1} in CH_2Cl_2), $C_7H_7MoCO(C_6H_5N)I$ ($\nu(CO)$ 1947 cm^{-1} in CH_2Cl_2), $C_7H_7MoCO[P(n-OC_2H_5)_3]I$ ($\nu(CO)$ 1968, 1952 cm^{-1} in *n*-hexane), and $C_7H_7WCO[P(OCH_3)_3]I$ ($\nu(CO)$ 1922 cm^{-1} in CS_2).

Infrared Spectra (cm^{-1}) (KBr Pellets).—(A) $C_7H_7MoCOP-(OC_6H_5)_3I \cdot CH_2Cl_2$: 3048 (m), $\nu(CO)$ bands in Table II, 1586 (s), 1560 (sh), 1540 (sh), 1479 (s), 1452 (m), 1430 (m), 1244 (m), 1215 (s), 1180 (s), 1158 (s), 1068 (m), 1021 (s), 1004 (m), 976 (sh), 958 (m), 916 (s), 897 (s), 879 (s), 833 (m), 800 (s), 775 (s), 764 (s), 740 (s), 730 (s), 718 (s), 690 (s), 599 (m), 562 (m), 531 (m), 500 (s), 479 (s), 421 (m). (B) $C_7H_7MoCOP(OCH_3)_3I$: 3059 (sh), 3035 (sh), 3005 (sh), 2980 (m), 2941 (s), 2888 (sh), 2832 (m), $\nu(CO)$ bands in Table II, 1481 (m), 1460 (sh), 1450 (sh), 1431 (s), 1245 (m), 1173 (s), 1049 (s), 1001 (vs), 966 (sh), 939 (sh), 872 (w), 855 (w), 805 (s), 789 (s), 761 (s), 740 (s), 539 (m), 520 (s), 462 (m), 422 (m). (C) $C_7H_7MoCOP(OC_2H_5)_3I$: 3042 (m), 2978 (s), 2925 (m), 2900 (m), $\nu(CO)$ bands in Table II, 1485 (sh), 1475 (m), 1431 (s), 1387 (m), 1284 (w), 1240 (w), 1159 (s), 1092 (s), 1010 (vs), 939 (s), 865 (sh), 852 (m), 810 (s), 778 (s), 721 (s), 532 (s), 465 (m), 429 (m). (D) $C_7H_7MoCOP-(i-OC_3H_7)_3I$: 3040 (w), 2975 (s), 2929 (m), 2878 (w), $\nu(CO)$ bands in Table II, 1484 (w), 1461 (m), 1449 (m), 1431 (m), 1382 (s), 1370 (s), 1344 (m), 1244 (w), 1175 (m), 1139 (m), 1102 (s), 1043 (sh), 1001 (s), 966 (vs), 886 (s), 851 (m), 801 (s), 759 (s), 718 (m), 540 (s), 490 (m), 455 (w), 424 (m). (E) $C_7H_7MoP-(C_6H_5)_3I$: 3037 (s), $\nu(CO)$ bands in Table II, 1489 (m), 1477 (s), 1407 (m), 1430 (s), 1307 (w), 1270 (w), 1262 (w), 1240 (w), 1181 (m), 1104 (m), 1087 (s), 1068 (m), 1037 (m), 997 (m), 965 (w), 856 (m), 804 (s), 745 (s), 694 (s), 586 (m), 518 (sh), 509 (s), 497 (s). (F) $C_7H_7MoCOP(n-C_4H_9)_3I$: 3028 (w), 2952 (s), 2919 (s), 2891 (sh), 2854 (s), $\nu(CO)$ bands in Table II, 1476 (m), 1460 (sh), 1450 (s), 1430 (s), 1417 (m), 1378 (s), 1340 (m), 1300 (w), 1273 (w), 1226 (sh), 1209 (m), 1178 (m), 1090 (s), 1077 (m), 1048 (m), 1003 (w), 959 (m), 906 (s), 893 (sh), 851 (m), 804 (s), 769 (m), 734 (sh), 720 (m), 538 (s), 505 (sh), 458 (m), 424 (s). (G) $C_7H_7WCOP(OC_2H_5)_3I$: 3038 (w), 2976 (s), 2921 (m), 2899 (m), 2854 (sh), 2029 (w), $\nu(CO)$ bands in Table II, 1489 (m), 1474 (m), 1438 (m), 1428 (m), 1387 (s), 1364 (sh), 1283 (w), 1259 (m), 1159 (s), 1093 (s), 1009 (vs), 940 (s), 868 (m), 851 (m), 808 (s), 777 (s), 766 (sh), 723 (s), 532 (s), 464 (w), 443 (m). (H) $C_7H_7WCOP(i-OC_3H_7)_3I$: 3037 (w), 2975 (s), 2927 (m), 2817 (m), $\nu(CO)$ bands in Table II, 1488 (m), 1462 (m), 1448 (m), 1429 (m), 1384 (s), 1370 (s), 1345 (m), 1260 (m), 1245 (sh), 1176 (s), 1138 (s), 1104 (s), 1006 (s), 959 (vs), 887 (s), 880 (sh), 854 (m), 808 (s), 759 (s), 717 (s), 546 (s), 489 (m), 439 (m).

Results and Discussion

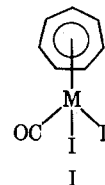
As part of a program to investigate metal carbonyls containing a variety of π -bonded carbocyclic rings, we have allowed benzene and toluene solutions of $\pi-C_7H_7M(CO)_2I$ ($M = Mo, W$) and various tertiary phosphines and phosphites to reflux for periods ranging from 3 to 48 hr (reaction times generally were longer for those systems with phosphine than for those with phosphite ligands and for tungsten than for molybdenum complexes) and have obtained primarily monosubstituted derivatives of the type $\pi-C_7H_7MCOLI$. In several phosphite reactions weak absorptions in the metal carbonyl region of the infrared spectra indicate the presence of additional products, possibly $[\pi-C_7H_7M(CO)_2L]^+I^-$, $[\pi-C_7H_7M(CO)_2]^+I^-$, or complexes similar to those obtained from reaction of cyclopentadienyl-iron carbonyl halides with tertiary phosphites, e.g., $[\pi-C_5H_5Fe(CO)_2P(O)(OC_2H_5)_2]^{15}$.

The derivatives are established to be monomeric from parent ion peaks in the mass spectra and to be nonsaline from conductivity measurements run in nitrobenzene.

The compounds synthesized in this investigation

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adopt a configuration (I) similar to that described for $\pi-C_7H_7Mo(CO)_2-\sigma-C_6F_6^{16}$ and are best envisioned as pseudooctahedral with the planar π -cycloheptatrienyl ring occupying three coordinate positions and the carbonyl, iodide, and phosphorus ligands the other three. However, because of the existence of isomeric forms,



minor deviations from this basic structure are possible.

Infrared and Nmr Spectra.—Even though these derivatives possess only one carbonyl functional group, each exhibits either a broad absorption line or two narrow lines in the $\nu(CO)$ region of the infrared spectrum (Table II). Since *cis-trans* isomerism is not possible in these molecules, this apparent anomaly must be attributed to conformational isomerism. Isomeric forms of similar molecules differing in the orientation of groups on a ligand relative to the ring, carbonyl(s), and other ligands^{7,8,17} or those with restrictions within the ligand itself^{9,10,17} have been previously observed. For phosphite derivatives of the type C_5H_5MCOLI , Brown, Lyons, and Manning⁹ favored the latter proposal based on the observance of two $\nu(CO)$ frequencies for all alkyl phosphites with the exception of one constrained phosphite, $P(OCH_2)_3CCH_3$.

Other than for the two triisopropyl phosphite complexes, the proton nmr spectra run at ambient temperatures displayed no unusual features. In each sample the signal for the seven equivalent cycloheptatrienyl protons was split into a doublet (1.8–3.2 Hz) by the phosphorus nucleus, and the spectrum of the ligand in the complex corresponded to that of the free phosphite or phosphine. However, the methyl resonances in the (triisopropyl phosphite)molybdenum derivative appeared not as the expected doublet but as a triplet when run at 60 MHz. When obtained at 100 MHz two doublets were observed thus confirming overlapping signals at 60 MHz and two different environments for the methyl groups. Further, two doublets were observed at 60 and 100 MHz for the tungsten complex. It seems plausible that the explanation for the nonequivalence of the methyl groups in the present instance is the same as that advanced to explain the nmr spectrum of $\pi-C_5H_5FeCO[P(CH_3)_2C_6H_5][COCH_3]$.⁴

The triphenyl phosphite complex crystallized as a methylene chloride adduct with the formulation supported by elemental analysis, two infrared absorptions between 690 and 740 cm^{-1} assigned to the carbon-chlorine stretching fundamentals, and an nmr resonance peak at τ 4.88. Consistent with previously reported results, the phosphite and molybdenum derivatives exhibit higher metal-carbonyl stretching frequencies than those of phosphines and tungsten.

Acknowledgment.—We are indebted to the Memphis State University Research Foundation for partial support of this work. We also wish to express our grati-

(16) M. D. Rausch, A. K. Ignatowicz, M. R. Churchill, and T. A. O'Brien, *J. Amer. Chem. Soc.*, **90**, 3242 (1968).

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tude to coworkers in the organic division for helpful suggestions and to Dr. Richard Cox of the University of Georgia for running proton nmr spectra on the HA-100

instrument. Our thanks are extended to M and T Chemical Co., Inc., Rahway, N. J., for a gift of triphenylphosphine.

Correspondence

On the Structure of Tetrakis(pyridine)iron(II) Chloride

Sir:

A recent article¹ reports a theoretical and experimental Mössbauer study of iron(II)-pyridine complexes. The conclusion reached from this work was that $\text{Fe}(\text{py})_4\text{Cl}_2$ had a cis octahedral structure whereas $\text{Fe}(\text{py})_4(\text{NCS})_2$ and $\text{Fe}(\text{py})_4\text{I}_2$ had trans octahedral structures. The conclusion regarding the structure of $\text{Fe}(\text{py})_4\text{Cl}_2$ cast doubts upon the validity of several spectroscopic studies of iron(II)-pyridine complexes^{2,3} which have all assumed that $\text{Fe}(\text{py})_4\text{Cl}_2$ had the same trans octahedral structure as an X-ray structural determination⁴ had shown $\text{Ni}(\text{py})_4\text{Cl}_2$ to possess.

(1) P. B. Merrithew, P. G. Rasmussen, and D. H. Vincent, *Inorg. Chem.*, **10**, 1401 (1971).

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(4) M. A. Porai-Koshits, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **10**, 117 (1954); see also *Struct. Rep.*, **18**, 750 (1954); **19**, 540 (1955).

In view of this contradiction we decided to pursue a limited crystallographic investigation in order to ascertain if $\text{Fe}(\text{py})_4\text{Cl}_2$ was isotypic with $\text{Ni}(\text{py})_4\text{Cl}_2$.

Single crystals of $\text{Fe}(\text{py})_4\text{Cl}_2$ were obtained by recrystallization from pyridine. Precession photographs showed the crystals to have tetragonal symmetry with systematic absences consistent with the space group $I4_1/acd$ (D_{4h}^{20}), which was the space group found for $\text{Ni}(\text{py})_4\text{Cl}_2$ and $\text{Co}(\text{py})_4\text{Cl}_2$.⁴ Lattice constants for $\text{Fe}(\text{py})_4\text{Cl}_2$ obtained from low-order powder lines are $a = 15.82$ and $c = 16.96$ Å, which may be compared with values of $a = 15.9$ and $c = 17.0$ Å for $\text{Ni}(\text{py})_4\text{Cl}_2$ and $a = 16.0$ and $c = 17.1$ Å for $\text{Co}(\text{py})_4\text{Cl}_2$. These results can be considered as strong evidence that the complexes $\text{Fe}(\text{py})_4\text{Cl}_2$, $\text{Co}(\text{py})_4\text{Cl}_2$, and $\text{Ni}(\text{py})_4\text{Cl}_2$ are, in fact, isotypic and $\text{Fe}(\text{py})_4\text{Cl}_2$ must be considered to have a trans octahedral structure.

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