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) phen$Mo(CO)_2[P(OCH_3)_3]_2$[6] and $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$.[7]

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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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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 $M(4\text{-}Me(py))_4(SCN)_2$, (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 $M(4\text{-}Me(py))_4(SCN)_2$ 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 $Cu(4\text{-}Me(py))_2(SCN)_2$.

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

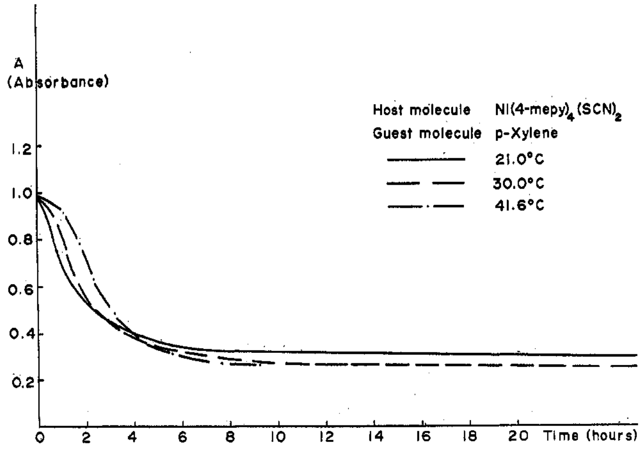

Figure 1.

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(1) G. Gawalek and H. G. Konnecke, *Rev. Chim. Acad. Repub. Pop. Roum.*, **7**, 875 (1962).

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

guest to host was measured for each of the clathrates formed and found to be 0.861 (21.0°), 0.899 (30.0°), and 0.935 (41.6°).

The results of the rate studies using benzene as a possible guest molecule are presented in Figure 2. The Mn(4-Me(py))$_4$(SCN)$_2$ and Cu(4-Me(py))$_2$(SCN)$_2$ complexes did not form clathrates with benzene under the conditions used. The results of using toluene (molecular volume 106.3 cm^3/mol) as a guest molecule verified earlier results in which it had been established that the iron, cobalt, and nickel complexes do form clathrates. New results in this laboratory indicate that no clathrate is formed with Cu(4-Me(py))$_2$(SCN)$_2$ and that the formation with Mn(4-Me(py))$_4$(SCN)$_2$ is very slow, requiring at least 16 hr by the suspension method (25.0°). Finally, in Figure 3 the results using *p*-xylene (molecular volume 123.3 cm^3/mol) as a possible guest molecule with all the complexes are shown. Again, the clathrate with Cu(4-Me(py))$_2$(SCN)$_2$ was not observed to form.

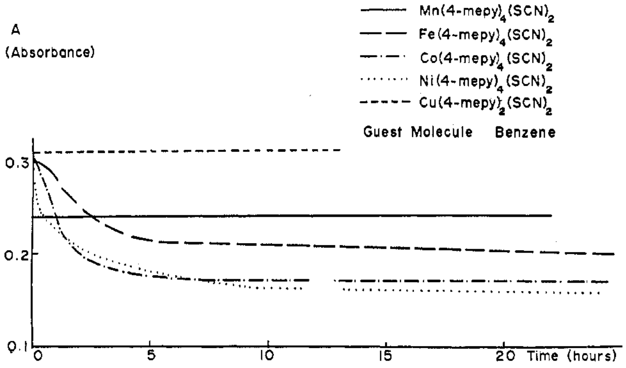

Figure 2.

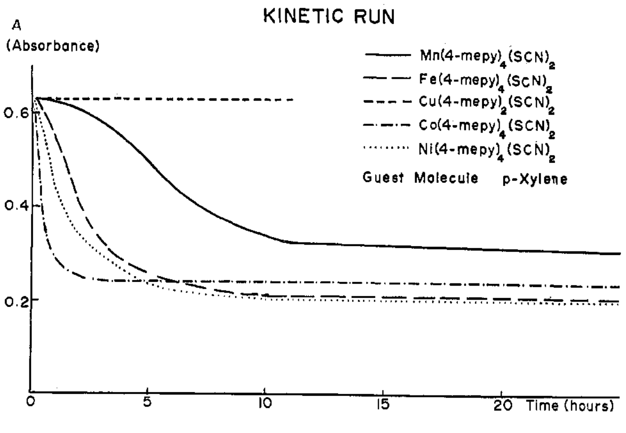

Figure 3.

The figures show that the time required for initiation of clathration (by the suspension method) varies from a few minutes to 16 hr with the notable exception of the manganese compound. Again, with the exception of the manganese compound, all reactions were found to be essentially complete after 6 hr. Increasing the temperature of the system did not change the rate significantly nor did it greatly change the guest to host ratio of the product.

Interplanar distances for the more prominent X-ray reflections of both the complexes and clathrates were measured and they support the theory that there is a definite structural change during the formation of most clathrates. This has previously been referred to as $\alpha \rightarrow \beta$ by Hart and Smith[4] where α represents the lattice of the Werner complex and β the "empty" clathrate lattice. The data for the spacings in the *p*-xylene clathrate with the nickel complex agreed with previously published results in which the powder data were indexed on the basis of a tetragonal unit cell.[4,5] A comparison with our X-ray data suggests that the basic space group in all of the host structures studied is $I4_1/a$, as originally reported by Belitskus, *et al.*[5] In the case of the benzene clathrates with the iron and manganese complexes and toluene with the manganese complex, the clathrate interplanar spacings were found to be identical with those of the complex. This is probably due to the high mobility of the small guest molecules in these particular lattices. The experimental data on this series of clathrates indicated a size limitation on the molecular volume of a guest molecule which may be accommodated. For example, it would appear that the molecular volume of a guest molecule must be in the range 106–132 cm^3/mol if it is to form a clathrate with the host Mn(4-Me(py))$_4$(SCN)$_2$. On the other hand the complexes of iron, cobalt, and nickel will accommodate smaller guests, down to at least 88.8 cm^3/mol. Our findings are not completely in agreement with earlier, reported results. It has been reported that 4-ethyltoluene (molecular volume 139.8 cm^3/mol) forms a clathrate with the nickel complex.[3] We were unable to duplicate that result using the suspension method described in this paper. However, this may be due to a difference in the method of preparation (suspension *vs.* solution). Previous workers have reported that the guest content of clathrates does vary according to the method of preparation.[6]

The results obtained also indicated that the size of the guest molecule which can be accommodated increased in proportion to the increase in ionic radius of the central metal ion, from Ni^{2+} (0.69 Å) to Mn^{2+} (0.80 Å). In other words a clathrate was observed to form between benzene (88.8 cm^3/mol) and the nickel complex, whereas no clathrate was observed with benzene and the manganese complex. This result was quite surprising in light of the small change in radius.

Although Cu^{2+} has about the same ionic radius as Co^{2+}, we were unable to form clathrates using copper as the metal ion, and our analytical data suggest that the complex formed was actually Cu(4-Me(py))$_2$(SCN)$_2$. According to the work of Graddon, *et al.*,[7] compounds of the type ZnB$_2$X$_2$ predominate for zinc also, with B being a heterocyclic base and X a halogen. Our initial studies with zinc support this conclusion in that no clathrate formation has been observed with Zn^{2+} complexes. As possible guest molecules cyclopentane and cyclohexane both have a molecular volume in the range for clathration. However, neither was observed to form clathrates with the complexes investigated.

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(4) M. I. Hart, Jr., and N. O. Smith, *J. Amer. Chem. Soc.*, **84**, 1816 (1962).

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This finding would suggest that π-electron interactions are also an important factor in clathrate formation and recent findings in other laboratories[8] support the concept of a "sandwich-type" interaction in these Werner-type complex clathrates.

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Bis Adducts of Some Long-Chained Primary Alkyl- and Alkenylamines with the Acetylacetonates of Cobalt(II) and Nickel(II)

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Numerous preparations of adducts of N donors with metal β-diketonates have been reported.[1] Hashagen and Fackler[2] reported the preparation of bis adducts of some β-diketonates of cobalt(II) and nickel(II) with several primary amines, including *n*-propylamine and *n*-butylamine. The *n*-butylamine adduct of nickel(II) acetylacetonate was also prepared by Olszewski and Martin.[3] We were interested in seeing if the chain length of the coordinated amines could be extended beyond four carbon atoms to produce complexes of unusual dimensions; we were also interested in the effect of chain length on physical properties and in the effect of the presence of unsaturation in the hydrocarbon chain. We report the preparation of adducts of bis(acetylacetonato)cobalt(II) and -nickel(II) with primary alkylamines containing six, eight, eleven, thirteen, fourteen, and sixteen carbon atoms. We also report the preparation of adducts of the same metal chelates with unsaturated primary amines containing three, eleven, and eighteen carbon atoms; these amines include allylamine (1-amino-2-propene), undecenylamine (1-amino-10-hendecene), oleylamine (1-amino-9-octadecene), and linoleylamine (1-amino-8,11-octadecadiene).

Experimental Section

Preparation of the Adducts.—The bis acetylacetonates of cobalt(II) and nickel(II) were obtained from Alfa Inorganics. The amines were obtained from various commercial sources, except for undecenylamine, which was prepared by the Gabriel synthesis from undecylenyl bromide and potassium phthalimide followed by hydrolysis of the *N*-undecylenyl phthalimide.

The adducts with the saturated amines, and with allylamine, were prepared by addition of amine in excess of the calculated 2:1 molar ratio to hot benzene or toluene solutions of the metal acetylacetonate. A voluminous precipitate formed, which became a gelatinous mass upon cooling. The precipitate was filtered out by suction, washed with solvent, recrystallized from dimethylformamide, washed with *n*-pentane, and air dried. The allylamine complexes are obtained as fine needles. The complexes with saturated amines are obtained as fibrous, flaky solids. They are smooth and slippery to the touch and tend to pick up electrostatic charge from the air. The cobalt complexes are light orange and the nickel complexes light blue; the colors become paler as the chain length of the amine increases.

TABLE I

ADDUCTS OF TYPE $M(acac)_2(am)_2$[a]

Complex	Mp, °C	% C		% H		% N		μ_{eff},[b]
		Calcd	Found	Calcd	Found	Calcd	Found	BM
$Co(acac)_2(nha)_2$	139–140	57.49	57.56	9.66	10.06	6.10	5.84	4.8
$Co(acac)_2(noa)_2$	137–138	60.54	61.35	10.18	9.80	5.43	5.59	4.9
$Co(acac)_2(nua)_2$	132–133	64.07	63.95	10.78	10.52	4.67	4.67	4.8
$Co(acac)_2(trda)_2$	128–129	65.91	65.76	11.08	11.13	4.27	4.02	...
$Co(acac)_2(ttda)_2$	123–125	66.72	66.36	11.22	11.50	4.09	3.85	...
$Co(acac)_2(hda)_2$	122–123	68.15	65.26	11.44	11.01	3.78	3.39	4.8
$Co(acac)_2(aa)_2$	127–130	51.75	51.48	7.62	7.70	7.54	7.39	4.8
$Co(acac)_2(uena)_2$	116–118	64.50	63.44	10.15	10.12	4.70	4.63	...
$Co(acac)_2(ola)_2$	108–110	69.75	69.03	11.20	11.14	3.54	3.74	4.8
$Co(acac)_2(lla)_2$	106–107	70.10	70.05	10.74	10.62	3.55	3.54	...
$Ni(acac)_2(nha)_2$	150–152	57.42	58.45	9.67	9.86	6.10	6.20	3.3
$Ni(acac)_2(noa)_2$	148–150	60.57	60.80	10.19	9.92	5.43	5.25	3.4
$Ni(acac)_2(nua)_2$	149–151	64.09	64.83	10.78	11.43	4.67	4.34	3.4
$Ni(acac)_2(trda)_2$	148–149	65.93	65.36	11.09	11.31	4.27	4.45	...
$Ni(acac)_2(ttda)_2$	143–144	66.74	66.90	11.22	11.59	4.09	3.95	...
$Ni(acac)_2(hda)_2$	139–141	68.18	68.03	11.44	11.36	3.78	3.55	3.3
$Ni(acac)_2(aa)_2$	147–149	51.78	52.03	7.63	7.51	7.55	7.67	3.2
$Ni(acac)_2(uena)_2$	141–143	64.52	67.10	10.15	10.16	4.70	4.47	...
$Ni(acac)_2(ola)_2$	130–132	69.77	70.05	11.20	10.65	3.54	3.52	3.2
$Ni(acac)_2(lla)_2$	120–123	70.12	69.75	10.75	11.05	3.56	3.67	...

[a] Abbreviations: acac, acetylacetonate; am, amine; nha, *n*-hexylamine; noa, *n*-octylamine; nua, *n*-undecylamine; trda, *n*-tridecylamine; ttda, *n*-tetradecylamine; hda, *n*-hexadecylamine; aa, allylamine; uena, undecenylamine; ola, oleylamine; lla, linoleylamine. [b] Obtained for chloroform solutions 0.02–0.04 *M* in the complexes, at 298°K; error limits ±0.1 BM.

The adducts with the unsaturated amines other than allylamine were prepared in a similar manner, except that they were precipitated from dimethylformamide and recrystallized from ethyl acetate. These complexes are obtained as fine, somewhat sticky powders; otherwise, they are similar to the adducts with the saturated amines.

The complexes prepared are listed in Table I, along with melting points, analytical data, and magnetic moments. The analyses were obtained from Galbraith Laboratories.

Spectral and Magnetic Measurements.—Electronic spectra were taken on a Cary 14 recording spectrophotometer, Serial 244. Reflectance spectra in the visible and near-infrared regions were

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(1) For references prior to 1966, see the review article by J. P. Fackler, *Progr. Inorg. Chem.*, **7**, 361 (1966). For more recent work see, for example, P. E. Rakita, S. J. Kopperl, and J. P. Fackler, Jr., *J. Inorg. Nucl. Chem.*, **30**, 2139 (1968); M. K. Misra and D. V. Ramana Rao, *ibid.*, **31**, 3875 (1969); T. Shigematsu, T. Honjyo, M. Tabushi, and M. Matsui, *Bull. Chem. Soc. Jap.*, **43**, 793 (1970).

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(3) E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 1043 (1965).