which follow eq 5 at higher temperatures. This general behavior reveals the onset of another equilibrium (in addition to (1)) and has been observed previously.[3,5,6] Unlike previous cases, however, the direction of deviation of ΔF from linearity, at least down to $-40°$, indicates that the new, presumably associated, solute species are either diamagnetic or less, rather than more,[3,5,6] paramagnetic than the planar–tetrahedral equilibrium mixture at the same temperature. The cause of the unexpected line broadening at the lower temperatures is currently being investigated. Despite the uncertainty in solution composition at the lower temperatures, the linear variation of ΔF with temperature above room temperature is believed to provide substantial verification of the predominance, if not the exclusiveness, of the configurational equilibrium in the temperature ranges shown in Table VIII.

The thermodynamic data obtained allow the first quantitative comparison of the energetics of stabilization of tetrahedral nickel(II) by a series of bidentate ligand systems in solution. Using an R group (isopropyl), solvent ($CDCl_3$), and temperature (60°) common to all, the order of increasing stabilization of the tetrahedral form is pyrrole-2-aldimine (**3**, 8.5% tetrahedral) < salicylaldimine (**1**, X = 5-CH_3, 51% tetrahedral) < β-ketoamine (**2**, $R_\alpha = R_\gamma = CH_3$, ~100% tetrahedral). This order in chloroform solution is borne out by additional observations made at room temperature which also fortify the conclusion that in each group steric effects are mainly responsible for the destabilization of the planar form. With R = H the complexes of each group are wholly planar in solution. When R is increased in size to methyl, the tetrahedral form has been detected only in the β-ketoamine complex ($R_\alpha = R_\gamma = CH_3$) where it is present in barely detectable concentration (~2%).[6,11] With R = *n*-alkyl the tetrahedral form is present only in the β-ketoamine complexes ($R_\alpha = CH_3$, $R_\gamma = C_6H_5$, R = ethyl, propyl, butyl) and to an extent of 18–30%. In the absence of complete X-ray structural results on either the planar or tetrahedral forms of the pyrrole-2-aldimine or β-ketoamine complexes, it is not yet possible to detail the nature of the steric interactions stabilizing the two forms. A discussion of the stereochemistry of salicylaldimine complexes is given elsewhere.[18] The stabilization of the planar and tetrahedral structures of complexes of these three basic ligand systems with other divalent metals is being actively investigated.

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The Electronic Spectra of Some Six-Coordinate Complexes of Iron(II) with Heterocyclic Amines

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The preparations are reported of the compounds: $Fe(isoquinoline)_4X_2$ (X = Cl, Br, I), $Fe(\beta\text{-picoline})_4Br_2$, $Fe(\gamma\text{-picoline})_4Br_2$, FeL_2X_2 (L = 4-cyanopyridine, 3,5-dichloropyridine; X = Cl, Br), and $Fe(py)Cl_2$. The electronic spectra of these compounds and some previously known complexes with pyridine are in accord with tetragonally distorted octahedral structures. The splitting of the ^5E_g level is discussed in terms of the McClure theory.[1]

Introduction

There is relatively little information available concerning the electronic spectra of high-spin six-coordinate iron(II) complexes. In ligand fields of O_h symmetry the ^5D free ion ground state splits into a $^5T_{2g}$ ground state and a ^5E_g excited state. Accordingly, the spectra of such compounds should show one spin-allowed band, expected to be in the visible or near-infrared region.

It has been observed, however, that, even when the six ligands bonded to iron(II) are identical, *e.g.*, $Fe(H_2O)_6^{2+}$ or $Fe(NCSe)_6^{4-}$, this band often suffers appreciable broadening or is split into two maxima.[2–5] Such splittings can arise from a dynamic Jahn–Teller effect or from static, tetragonal (D_{4h}) or rhombic (D_{2h}) distortions of the primary coordination sphere. Cotton and Meyers have discussed the probable causes for the

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splittings observed for $Fe(H_2O)_6^{2+}$ in various environments.[4]

When the six ligands are not identical, *e.g.*, *trans*-FeL_4X_2, then a splitting of the ^5E_g level will be expected (E_g in $O_h \rightarrow A_{1g} + B_{1g}$ in D_{4h}), unless the ligand fields of L and X are fortuitously the same or the effective ligand field experienced by the metal ion has trigonal symmetry. Consequently, in mixed-ligand complexes observation of the splitting of the band due to $^5T_{2g} \rightarrow {}^5E_g$ can provide information concerning the asymmetry of the field.

Both crystal field and molecular orbital models have been advanced to relate, either quantitatively or qualitatively, the splittings of electronic spectral bands to ligand field asymmetry.[6] The method of McClure[1] relates the observed band splittings to the differences in the σ- and the π-antibonding energies experienced by the d orbitals of the metal ion in the complex. The application of this method to six-coordinate iron(II) complexes is of interest since it predicts that the splitting of the band due to $^5T_{2g} \rightarrow {}^5E_g$ is a function only of the difference in the σ-antibonding contributions of the ligands. Accordingly, we thought it worthwhile to measure the spectra of a series of six-coordinate iron(II) complexes in order to examine the value of the McClure theory in interpreting the results.

In view of the relative stability toward oxidation of $Fe(py)_4Cl_2$[7] and the fact that several other pyridine complexes of iron(II) have been reported by previous workers,[8] compounds with pyridine and some related ligands were chosen for the initial study. We report here the results of this work.

Experimental Section

Electronic Spectra.—These were obtained by the reflectance technique with a Beckman DK2 spectrometer, using finely powdered samples.

X-Ray Powder Photographs.—These were taken with an Enraf-Nonius Guinier-De Wolff No. II camera using iron radiation.

Preparation of Compounds. **$Fe(py)_4Cl_2$.**—This was prepared as described in ref 7.

$Fe(isoquinoline)_4X_2$, Where X = Cl, Br, or I, and $Fe(picoline)_4Br_2$, Where Picoline = β-or γ-Picoline.—These compounds were prepared by a method essentially similar to that used for $Fe(py)_4Cl_2$, whereby a concentrated aqueous solution of the iron(II) halide, which had been allowed to stand over iron powder, was added to an excess over the calculated quantity of the amine, either as the pure liquid or as a solution in a small volume of methanol. In every case the complex precipitated immediately and was filtered off, washed with acetone, and dried for a short time *in vacuo*.

$Fe(isoquinoline)_4Cl_2$.—This orange compound gave the following analysis. *Anal.* Calcd for $C_{36}H_{28}Cl_2FeN_4$: Cl, 11.03; Fe, 8.68; N, 8.71. Found: Cl, 10.72; Fe, 8.50; N, 8.68.

$Fe(isoquinoline)_4Br_2$.—This orange compound gave the following analysis. *Anal.* Calcd for $C_{36}H_{28}Br_2FeN_4$: C, 59.05; H, 3.85; Br, 21.82; Fe, 7.63; N, 7.65. Found: C, 59.04; H, 4.02; Br, 21.52; Fe, 7.40; N, 7.54.

$Fe(isoquinoline)_4I_2$.—This yellow compound gave the following analysis. *Anal.* Calcd for $C_{36}H_{28}FeI_2N_4$: C, 52.43; H, 3.42; I, 30.58; N, 6.80. Found: C, 52.01; H, 3.57; I, 30.20; N, 6.52.

$Fe(\beta\text{-picoline})_4Br_2$.—This yellow compound gave the following analysis. *Anal.* Calcd for $C_{24}H_{28}Br_2FeN_4$: Br, 27.17; Fe, 9.50. Found: Br, 27.00; Fe, 9.25.

$Fe(\gamma\text{-picoline})_4Br_2$.—This yellow compound gave the following analysis. *Anal.* Calcd for $C_{24}H_{28}Br_2FeN_4$: C, 49.00; H, 4.80; Br, 27.17; N, 9.53. Found: C, 48.79; H, 5.09; Br, 27.25; N, 9.32.

$Fe(py)Cl_2$.—This yellow-brown compound was obtained by heating $Fe(py)_4Cl_2$ to constant weight *in vacuo* at 96°. Weight loss: Calcd: 53.53. Found: 53.44. *Anal.* Calcd for $C_5H_5Cl_2FeN$: Cl, 34.43. Found: Cl, 33.98.

$Fe(4\text{-cyanopyridine})_2Cl_2$.—Iron(II) chloride tetrahydrate (2.0 g, 0.01 mole) was dissolved in ethanol (10 ml), and the solution was allowed to stand over iron powder overnight. The solution was then filtered and 4-cyanopyridine (2.08 g, 0.02 mole) in ethanol (10 ml) was immediately added, slowly and with stirring. The orange-yellow precipitate was filtered off, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for $C_{12}H_8Cl_2FeN_4$: Cl, 21.16; Fe, 16.67. Found: Cl, 20.85; Fe, 16.85.

$Fe(4\text{-cyanopyridine})_2Br_2$.—This orange compound was prepared similarly to the chloro complex, except that the solution of iron(II) bromide was prepared from Analar reagent grade bromine and iron powder in ethanol. *Anal.* Calcd for $C_{12}H_8Br_2FeN_4$: Br, 37.70; Fe, 13.17. Found: Br, 37.25; Fe, 12.74.

$Fe(3,5\text{-dichloropyridine})_2X_2$ (X = Cl, Br).—These compounds were prepared as for their 4-cyanopyridine analogs. The *chloro complex* was pale yellow. *Anal.* Calcd for $C_{10}H_6Cl_6FeN_2$: Cl (anionic), 16.77; Fe, 13.12. Found: Cl (anionic), 16.50; Fe, 12.66. The *bromo complex* was yellow. *Anal.* Calcd for $C_{10}H_6Br_2Cl_4FeN_2$: C, 23.47; H, 1.18; Br, 31.23. Found: C, 23.20; H, 1.40; Br, 31.05. The preparations of the other compounds have been reported by previous workers.[8]

Results

The compounds we have studied are listed in Table I. No attempt has been made to carry out a comprehensive investigation of the types of complex which can be prepared from the iron(II) halides and the various heterocyclic amines. Instead, we have restricted the preparative aspect of this work to those compounds which have enabled us to examine the effects on the electronic spectra of varying the value of n in FeL_nX_2 and the identities of L and of X in complexes of constant stoichiometry. Attempts to isolate 4:1 com-

TABLE I

ELECTRONIC SPECTRAL RESULTS FOR THE COMPLEXES

Compd	Absorption max, cm^{-1}	$\delta\sigma$, cm^{-1}
$Fe(py)_4(NCS)_2$	11,250, ~9900 sh	500[b]
$Fe(py)_4(NCSe)_2$	11,200, ~9900 sh	500[b]
$Fe(py)_4Cl_2$	10,300, ~8550 sh	−650
$Fe(py)_4Br_2$	10,650, 7750	−1100
$Fe(isoquinoline)_4Cl_2$	10,950, ~9100 sh	−700
$Fe(isoquinoline)_4Br_2$	11,450, 7800	−1350
$Fe(isoquinoline)_4I_2$	11,750, ~5900[a]	−2200
$Fe(\beta\text{-picoline})_4Br_2$	11,000, 7500	−1300
$Fe(\gamma\text{-picoline})_4Br_2$	11,000, ~6700[a]	−1600
$Fe(py)_2Cl_2$	9,900, ~5850[a]	+1500
$Fe(py)_2Br_2$	9,550, ~5200[a]	+1650
$Fe(4\text{-cyanopyridine})_2Cl_2$	9,850, 6250	+1350
$Fe(4\text{-cyanopyridine})_2Br_2$	9,780, ~5850[a]	+1450
$Fe(3,5\text{-dichloropyridine})_2Cl_2$	9,350, 6300	+1150
$Fe(3,5\text{-dichloropyridine})_2Br_2$	9,050, 5875	+1200
$Fe(py)Cl_2$	8,370, ~5950[a]	+1800

[a] Approximate value due to the presence of vibrational bands.
[b] Sign unknown.

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(6) For references and a discussion of the crystal field model as applied to low-spin cobalt(III) complexes see: R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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plexes of 4-cyanopyridine and 3,5-dichloropyridine with iron(II) chloride or bromide gave impure products. However, the preparations of most of the compounds were relatively straightforward and merit little comment. The compound Fe(isoquinoline)$_4$I$_2$ is relatively stable, in contrast to the reported[9] instability of the pyridine complexes of iron(II) iodide.

The complexes formed by heterocyclic amines with the halides of several other divalent first series transition metal ions, especially Mn^{II}, Co^{II}, and Ni^{II}, have been well studied in recent years. X-Ray investigations have shown that M(py)$_4$X$_2$ compounds (M = Co, Ni; X = Cl, Br, NCS) are *trans*-octahedral,[10–12] and the other related ML$_4$X$_2$ compounds are also thought to have this structure. The X-ray powder photographs of Fe(py)$_4$(NCS)$_2$, Fe(isoquinoline)$_4$X$_2$ (X = Cl, I), Fe(β-picoline)$_4$Br$_2$, and Fe(γ-picoline)$_4$Br$_2$ are quite similar to those of their nickel(II) analogs, suggesting that these iron complexes are *trans*-octahedral. The similarity of their electronic spectra (see Table I) to those of the other FeL$_4$X$_2$ compounds indicates that the latter also have this type of structure.

With the related compounds of stoichiometry ML$_2$X$_2$ planar, tetrahedral, or polymeric octahedral structures may be obtained, depending on the identities of M, L, and X.[9,13,14] The powder photograph of Fe(py)$_2$Cl$_2$ is similar[9] to that of the violet form of Co(py)$_2$Cl$_2$, which has a polymeric octahedral structure with bridging chlorine atoms and pyridine molecules in *trans* positions.[15] Since the electronic spectra of the other FeL$_2$X$_2$ complexes listed in Table I closely resemble that of Fe(py)$_2$Cl$_2$, these also appear to be octahedral polymers. The spectra are quite different from those of the tetrahedral compounds Fe(quinoline)$_2$X$_2$ (X = Cl, Br).[16] The only 1:1 complex studied, Fe(py)Cl$_2$, most probably also has a polymeric, octahedral structure similar to those of other M(py)Cl$_2$ compounds.[14,17]

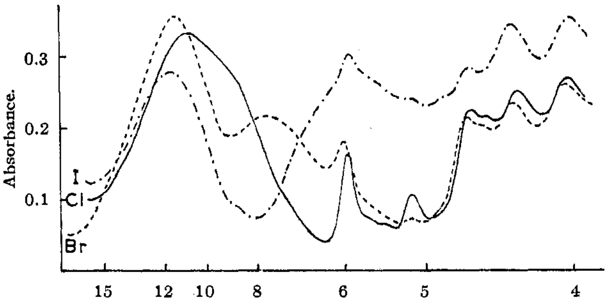

Figure 1.—Reflectance spectra of Fe(isoquinoline)$_4$X$_2$; X: Cl, ———; Br, ---------; I, —·—·—·.

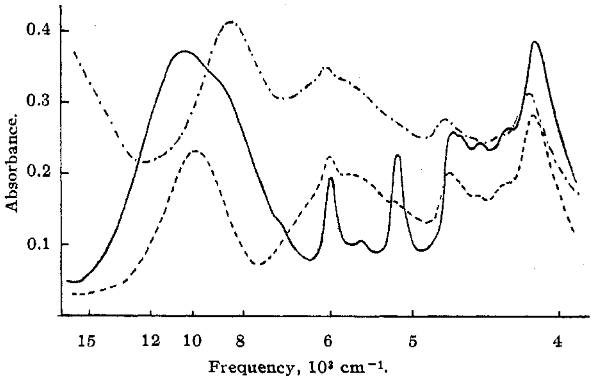

Figure 2.—Reflectance spectra of: Fe(py)$_4$Cl$_2$, ———; Fe(py)$_2$Cl$_2$, ---------; Fe(py)Cl$_2$, —·—·—·.

Spectra.—The spectra of all of the complexes have bands in the near-infrared region assignable as d–d transitions. The numerical results are given in Table I. The compounds Fe(py)$_4$(NCX)$_2$, X = S or Se, have one asymmetric band, consisting of a maximum at ~11,200 cm^{-1} and a pronounced shoulder at ~9900 cm^{-1}. The spectra of FeL$_4$Cl$_2$, where L = py or isoquinoline, resemble those of the complexes with NCX$^-$, but the whole band contour is moved to lower energy. The splitting of the electronic band for FeL$_4$Br$_2$ is greater than that for the chloro- and pseudo-halide complexes, and two bands are clearly resolved (Figure 1). (The figures are copies of the experimental spectra, to permit assessment of band resolution and also of the effects of the presence of vibrational bands.) The band splitting is even larger for Fe(isoquinoline)$_4$I$_2$ (Figure 1 and Table I).

The shift in band energy on replacing Cl by Br and then by I, in FeL$_4$X$_2$, is much greater for the lower energy component than for that at higher energy. In the case of Fe(isoquinoline)$_4$I$_2$ the exact position of the lower energy band is obscured somewhat by vibrational bands (Figure 1). However, because of the expanded energy scale of the spectrometer in this region and the relative sharpness and constancy of the vibrational bands, errors in assigning the band energies are not large and have little effect on the interpretation of the results as discussed below.

The near-infrared spectra of all of the compounds FeL$_2$X$_2$ contain two clearly resolved electronic bands. Comparison of the spectra of Fe(py)$_2$X$_2$ and Fe(py)$_4$X$_2$ (Figure 2) reveals that in the former the band separation is greater and the band energies are lower than in the latter compounds. Vibrational bands occur in the same region as the lower energy electronic band for some of the FeL$_2$X$_2$ complexes, and the comments made above for Fe(isoquinoline)$_4$I$_2$ apply here also.

Two electronic bands are also present in the spectrum of Fe(py)Cl$_2$, but the separation between them is less than that in Fe(py)$_2$Cl$_2$.

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Discussion

The spectral results show that in the compounds studied the ^5E_g level is appreciably split ($^5A_{1g} + {}^5B_{1g}$) and that, in most cases, the ligand fields depart markedly from O_h symmetry. According to the method of McClure,[1] the splitting of the ^5E_g level is equal to $^8/_3\delta\sigma$ for *trans*-disubstituted compounds FeA_4B_2, as for the compounds FeL_4X_2 and polymeric FeL_2X_2 listed in Table I, and $^4/_3\delta\sigma$ for monosubstituted compounds FeA_5B.[18] The $^5T_{2g}$ ground level will also be split (by $2\delta\pi$ for FeA_4B_2 and by $\delta\pi$ for FeA_5B). This should not affect the observed band splittings but would need to be taken into account in interpreting shifts in the absolute energies of the band components for the various compounds.

The $\delta\sigma$ values in Table I, calculated from the band splittings, are given to the nearest 50 cm^{-1}. In the case of the halide complexes the signs of $\delta\sigma$ have been indicated on the basis that the halide ions will have smaller σ-antibonding energies than the heterocyclic ligands. In other words, for the 4:1 complexes $^5B_{1g}$ lies above $^5A_{1g}$, while the reverse is true for the 2:1 compounds. The $\delta\sigma$ values obtained seem reasonable, when compared with that reported by McClure[1] for $Co(NH_3)_5Cl^{2+}$, bearing in mind the change in oxidation state and electronic configuration of the metal ion.

Several qualitative observations seem pertinent to the trends in the $\delta\sigma$ values. There is a marked increase in $|\delta\sigma|$ with change in halide ion for each of the series Fe(isoquinoline)$_4X_2$ (X = Cl, Br, I) and $Fe(py)_4X_2$ (X = Cl, Br). Two possible reasons for this are, firstly, that the σ-donor capacity of these anions toward Fe^{2+} decreases in the order Cl > Br > I, which agrees with the suggestions of McClure,[1] or, secondly, that a steric factor is operating. In $M(py)_4Br_2$ (M = Co, Ni) the planes of the pyridine rings lie at angles of 45–55° to the $M-N_4$ plane.[11] Any steric repulsion experienced by anions in the *trans*-octahedral sites will become greater with increasing size of the anion, and any lengthening in the M–X bond will increase $|\delta\sigma|$. It is, of course, possible that both factors are operating here.

The polymeric complexes $Fe(py)_2X_2$ (X = Cl, Br) may be regarded as FeB_4A_2 systems. On this basis, the values of $|\delta\sigma|$ for these compounds would be expected to equal those for the corresponding $Fe(py)_4X_2$ complexes, but they are in fact appreciably larger, especially for the chlorides. This indicates that the tetragonal distortions of the ligand fields are greater for $Fe(py)_2X_2$ than for the 4:1 compounds. More particularly, it suggests that the bridging halides form weaker σ bonds to the metal ions than when terminally bound. In agreement with this, metal–halogen bonds are usually longer for bridging than for terminal halides. Unfortunately, no bond lengths are known for the iron compounds we have studied, and such information is sparse for related complexes. However, it is known that the metal–donor atom bonds are longer in the polymeric form of $Co(py)_2Cl_2$ (Co–Cl = 2.49 A; Co–N = 2.14 A[15]) than in $Co(py)_4Cl_2$ (Co–Cl = 2.32 A; Co–N = 1.99 A[10]).

Although the $\delta\sigma$ values for the complexes FeL_2X_2 increase on replacing Cl by Br, the differences are much smaller than the changes observed for the similar process in the tetrakis complexes.

For a constant stoichiometry and anion, the values of $|\delta\sigma|$ appear to vary somewhat with the identity of L. For the complexes FeL_4Br_2 the order of decreasing $|\delta\sigma|$ is: L = γ-picoline > isoquinoline $\approx$ β-picoline > pyridine, while that for the 2:1 compounds is: L = pyridine > 4-cyanopyridine > 3,5-dichloropyridine.

Only one complex of the type $FeLX_2$ was examined, $Fe(py)Cl_2$. Its spectrum is in accord with a distorted octahedral structure. The band splitting (~2400 cm^{-1}) is appreciably less than that (~4000 cm^{-1}) for $Fe(py)_2Cl_2$. This is in reasonably good agreement with the predictions of the McClure theory that the splitting for a system FeA_5B will be half that of an analogous *trans*-FeA_4B_2 system. However, although we have treated $Fe(py)Cl_2$ as an FeA_5B species to calculate the $\delta\sigma$ value of 1800 cm^{-1} quoted in Table I, there is no detailed structural information available for the MLX_2 compounds of this type, and the halide bridges may not be equivalent.

The results for the compounds $Fe(py)_4(NCX)_2$ (X = S, Se) are more difficult to interpret in these terms. Pyridine and isothiocyanate lie close together in the one-dimensional spectrochemical series, having similar Δ values.[19] However, since Δ values are composed of both σ- and π-antibonding contributions,[1] a splitting of the ^5E_g level may be found for $Fe(py)_4(NCX)_2$ if $|\delta\sigma|$ is sufficiently large. The problem is that, although a splitting of ~1200 cm^{-1} is observed, the ion $Fe(NCSe)_6{}^{4-}$ has a very similar spectrum,[5] with a band maximum at 11,150 cm^{-1} and a shoulder at ~9760 cm^{-1}. If the difference in σ-antibonding energies between pyridine and the isothiocyanate ion is, in fact, rather small, then the ^5E_g level will be little split from this effect alone. However, it does appear that for six-coordinate Fe^{2+}, *e.g.*, $Fe(H_2O)_6{}^{2+}$, there is a general tendency for the degeneracy of the ^5E_g level to be lifted, if not by ligand field asymmetry then by Jahn–Teller effects dynamic[4] or otherwise.[20]

In summary, it appears that the McClure theory is of value in interpreting the spectra of the iron(II) halides with heterocyclic amines but that, in cases where the differences in the bonding parameters are likely to be small, other mechanisms for splitting the ^5E_g level may predominate.

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(18) Notations $\delta\sigma$ and $\delta\pi$ are as in ref 1.

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Transition Metal Complexes of a Constrained Phosphite Ester.
V. Metal Carbonyl Complexes of 2,8,9-Trioxa-1-phosphaadamantane[1-4]

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The preparation and characterization of metal carbonyl complexes of 2,8,9-trioxa-1-phosphaadamantane, $P(OCH)_3(CH_2)_3$, are described. Substitution products obtained from $Ni(CO)_4$ include compounds of the type $Ni(CO)_{4-x}[P(OCH)_3(CH_2)_3]_x$ where $x = 1, 2, 3$, or 4. Synthesis of the mono- and disubstituted complexes of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with $P(OCH)_3(CH_2)_3$ is also reported. A study of the carbonyl infrared stretching frequencies implies that $P(OCH)_3(CH_2)_3$ is equal to other phosphites in π-bonding ability. The proton nmr spectra of the compounds are discussed with special attention given to the disubstituted complexes. The proton nmr spectra of analogous disubstituted complexes of $P(OCH_2)_3CCH_3$ discussed previously by us (see ref 5) are more rigorously treated.

Introduction

In a previous paper,[5] we reported metal carbonyl complexes of a bicyclic phosphite ester, 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$. A strong π-bonding ability for $P(OCH_2)_3CCH_3$ was inferred from the carbonyl absorptions of these complexes in the infrared region. The nmr spectra exhibited some very unusual features of phosphorus–phosphorus spin coupling. Although 2,8,9-trioxa-1-phosphaadamantane (hereafter referred to as $P(OCH)_3(CH_2)_3$) and $P(OCH_2)_3CCH_3$ are constrained structures wherein the electron pair on the bridgehead phosphorus is readily available for donation, $P(OCH)_3(CH_2)_3$ is slightly more bulky as shown in Figure 1. The increased steric requirements for $P(OCH)_3(CH_2)_3$ could lead to ligand–ligand repulsion effects in metal carbonyl complexes resulting in reduced ligand properties. On the other hand, the basicity of $P(OCH)_3(CH_2)_3$ has been found to be somewhat greater than $P(OCH_2)_3CCH_3$ from its higher dipole moment and its lower tendency to dissociate from the boron moiety in the boron trimethyl adduct.[6] It was of interest, therefore, to compare the ligand characteristics of $P(OCH)_3(CH_2)_3$ with those observed for $P(OCH_2)_3CCH_3$ in the same series of carbonyl complexes. Of interest also was the possible comparison of phosphorus–phosphorus spin–spin coupling in complexes of these ligands.

Experimental Section

Infrared spectra were obtained in Halocarbon oil and Nujol mulls and recorded on a Perkin-Elmer Model 21 double beam spectrometer using sodium chloride optics. In addition, the carbonyl region of the spectrum was observed for the compounds in dichloromethane solutions and Halocarbon oil mulls using a Beckman IR-7 spectrometer with sodium chloride grating optics. Proton nmr spectra were obtained in approximately 15% deuteriochlorofom or methylene chloride solutions on Varian Associates HR-60 and A-60 spectrometers. In cases where compounds exhibited low solubility, saturated solutions were used. Tetramethylsilane was used as an internal standard. Melting points were taken in capillaries and are uncorrected. Molecular weight determinations were made using a Mechrolab vapor pressure osmometer (Model 301-A) where compound solubilities permitted. Measurements were made over a concentration range of 0.025–0.01 *M* on chloroform solutions.

Carbon and hydrogen contents were determined by combustion. Nickel analyses were carried out by a standard procedure as the dimethylglyoxime complex.[7] Molybdenum[8] and tungsten[9] were determined gravimetrically as the 8-hydroxyquinoline complexes, chromium was determined spectrophotometrically using *sym*-diphenylcarbazide,[10] and iron was determined colorimetrically with 1,10-phenanthroline.[11] Yields of monosubstituted compounds were calculated on the basis of $P(OCH)_3(CH_2)_3$ and all others on the basis of metal carbonyl used.

Nickel tetracarbonyl and iron pentacarbonyl were purchased from A. D. Mackay, Inc., chromium hexacarbonyl was purchased from the Diamond Alkali Corp., and molybdenum and tungsten hexacarbonyl were gifts from the Climax Molybdenum Co. The phosphite ligand, $P(OCH)_3(CH_2)_3$ was prepared by a method described elsewhere.[12]

Two general methods were used in the preparation of the complexes of $P(OCH)_3(CH_2)_3$ (L) shown in Table I. In method A, a mixture of carbonyl, ligand, and 30 to 50 ml of solvent was brought to the desired temperature under a helium flush with magnetic stirring. After reaction for the indicated time interval, the solution was evaporated to one-fourth its volume under vacuum. Addition of 30 ml of pentane to the concentrated solution resulted in the formation of white crystals which were filtered, washed with 20 ml of pentane, and dried under vacuum. In method B, a mixture of carbonyl, ligand, and 100 ml of solvent was placed in a quartz tube. Irradiation with ultraviolet light (200-w Hanovia Model 654A) was carried out for the time indicated under a flush of helium with magnetic stirring. After evaporation of the solution to one-tenth its volume under vacuum, the product was isolated in the same manner as described in method A. Table I lists the amount of carbonyls and ligand,

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(1) Contribution No. 1781 from the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission and the Chemistry Department of Iowa State University.

(3) Presented before the Division of Inorganic Chemistry, at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(4) From a dissertation submitted by D. G. Hendricker to the Graduate College of Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1965.

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(8) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 508.

(9) Reference 8, p 567.

(10) Reference 8, p 791.

(11) D. E. Blair and H. Diehl, *Anal. Chem.*, **33**, 867 (1961).

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