

probable reason why it has not been possible to fit the observed time dependence, viz. Figure 6, to rate law kinetics. The observation that, when the sample was ground, the crystalline substance assumed the behavior of a semisolid material indeed supports our assumption that rather loosely bound α -picoline molecules are present at room temperature.

An important factor that may be responsible for differences associated with the spin transition is the successive cracking of the crystallites, on the cycling of temperature, as a consequence of the crystallographic phase change. The cracking may produce the different shape of the hysteresis loop that has been observed for the crystalline substance (cf. Figures 2 and 3). Moreover, the cracking affects the relative intensity of X-ray diffraction peak profiles by changing the texture of the sample; thus it does not allow the estimation of the high-spin fraction from the area ratios.

Another observation of importance is the significant reduction in the width of the hysteresis loop and the almost continuous character that the spin transition assumes on grinding of the crystalline absorber. Simultaneously, the residual fraction of both the 5T_2 and 1A_1 phases increased considerably. In view of the above discussion, the number of defects will be increased on grinding of the material due to the surface effects and the migration of α -picoline molecules. This will result in a nonuniform environment for a large fraction of molecules and thus will give rise to a distribution of T_c values. In addition, a certain number of crystallites will have a size below the critical size as a result of grinding and thus will not be able to participate in the crystallographic phase

change and the associated spin transition. The observed reduction in the values of ΔT_c is thus arising due to a distribution of T_c^\uparrow and T_c^\downarrow values and an increase in the residual 5T_2 and 1A_1 fractions. The first-order nature of the transition is nonetheless maintained, evidence being the observed hysteresis. Similar results have been reported by Haddad et al.³² for the grinding and doping effects in the iron(III) complex $[\text{Fe}(\text{3-OCH}_3\text{SalEen})_2]\text{PF}_6$, where 3-OCH₃SalEen is the monoanion of ((ethylamino)ethyl)(3-methoxysalicylidene)amine and recently for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.²³ For these complexes, the residual fractions are a sensitive function of the extent of grinding.

The difference of ΔE_Q values for both spin phases that was found for the different sets of observations is not easy to understand. For the 5T_2 phase, the difference is quite pronounced in the higher temperature region, where fitting uncertainties are small. For the 1A_1 phase, the difference is much smaller and is confined to the region above T_c . We believe that the encountered differences may be another consequence of the structural relaxations that are associated with the migration of α -picoline molecules in the lattice.

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Iodine-127 Mössbauer Study of Some Phenyl-Iodine Compounds and the Alkane-Activating Manganese Porphyrin Complexes Containing Iodosylbenzene Ligands

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Iodine-127 Mössbauer spectra at 4.2 K have been obtained on several compounds that contain the phenyl-iodine moiety including the alkane-activating Mn porphyrin complexes containing iodosylbenzene ligands, $[\text{XMn}^{\text{IV}}\text{TPP}(\text{OIPh})_2]\text{O}$, X = Cl, Br (**1-Cl** and **1-Br**, respectively), that were recently purified and characterized. The relation of the ^{127}I Mössbauer parameters and the structural parameters of several iodine(III) compounds strongly implies that the observed positive quadrupole constants (2410–2507 MHz) and large asymmetry parameters (0.47–0.79) of these compounds reflect a disruption of the classical T-shape symmetry around I(III) by the proximity of a fourth ligand. The ^{127}I Mössbauer parameters for **1-Cl** and **1-Br** are similar to those of the other I(III) compounds, but quite distinct from those of I(I) or I(V) compounds. The iodine(III) in each of complexes **1** is coordinated by carbon, oxygen, and halogen atoms to give distorted T-shaped arrangements.

The interaction of iodosylbenzene with Mn(III) porphyrins in nonpolar, relatively inert organic media leads to the production of at least five types of isolable high-valent Mn porphyrin complexes depending on the axial ligand and the reaction conditions.^{4–8} The most intriguing of these isolable

species are the $[\text{XMn}^{\text{IV}}\text{TPP}(\text{OIPh})_2]\text{O}$ (X = Cl or Br; TPP = tetraphenylporphinato dianion) complexes, **1**.⁷ These complexes are not only unique with regard to their chemical properties but also highly unusual with regard to some of their physical and structural properties.⁷ Complexes **1** are capable of replacing unactivated alkane C–H bonds with both C–O and C–X bonds (X = Cl or Br) at temperatures below 0 °C.⁹

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Table I. ¹²⁷I Mössbauer Data Recorded at 4.2 K

compd	δ, mm s ⁻¹	e ² q ¹²⁷ Q _g /h, MHz	η	Γ, mm s ⁻¹
C ₆ H ₅ I	-0.16 ± 0.02	-1706 ± 14	0.19 ± 0.02	1.52 ± 0.1
	-0.11 ± 0.04 ^a	-1840 ± 20 ^a		
C ₆ H ₅ IO	-0.51 ± 0.03	2410 ± 15	0.47 ± 0.01	2.08 ± 0.09
	-0.57 ± 0.05 ^a	2345 ± 20 ^a	0.60 ± 0.05	
C ₆ H ₅ IO ₂	-1.02 ± 0.03	1244 ± 30	0.18 ^b	3.0 ± 0.2
	-0.59 ± 0.25 ^a	1050 ± 30 ^a	0.18 ^a	
C ₆ H ₅ ICl ₂	-0.62 ± 0.05 ^a	2525 ± 30 ^a	0.70 ± 0.05 ^a	
C ₆ H ₅ I(O ₂ CCH ₃) ₂	-0.87 ± 0.01	2507 ± 6	0.79 ± 0.01	1.53 ± 0.04
1-Cl	-0.67 ± 0.03	2128 ± 20	0.68 ± 0.02	2.01 ± 0.11
1-Br	-0.71 ± 0.02	2215 ± 14	0.64 ± 0.01	1.78 ± 0.08
KI	0.0 ± 0.03			2.81 ± 0.13

^a Data of Ehrlich and Kaplan;¹³ the isomer shifts have been converted to KI as the reference zero, and therefore the errors quoted may be higher than indicated. ^b Value restricted to NQR result in computer fitting as in ref 12.

Both the Mn(IV) and the iodine centers are involved in the functionalization of alkanes.⁹ Complexes **1** are the only complexes in the literature that contain iodosylarene moieties as ligands.⁸ Although the magnetic and spectroscopic (NMR, IR, UV-vis) properties of both purified complexes, **1-Cl** and **1-Br**, strongly indicate the presence of Mn^{IV}TPP moieties antiferromagnetically coupled through a μ-oxo bridge, the coordination geometry about the iodine atom is uncertain.

Iodine-127 Mössbauer spectroscopy as a tool for studying the nature of iodine containing molecules has not been extensively investigated. Early work, largely of an exploratory nature, has been reviewed.¹⁰ Ehrlich and Kaplan have used this method to study the electron distribution in simple iodine-containing molecules^{11,12} and in iodobenzene and related polyvalent iodine derivatives.¹³ More recently we have reported data on the linear [X-I-Y]⁻ (X = F, Cl, Br, I) systems,¹⁴ on the four-coordinate [X₂IY₂]⁺ (X = Cl, Br, I; Y = F, Cl) systems,^{15,16} on some sulfur-iodine cations,¹⁷ and on the dimerization of the [I₂]⁺ cation.¹⁸ In these latter papers¹³⁻¹⁸ the Mössbauer results have been interpreted in terms of the structures of the compounds, where known.

Sufficient data now exist on compounds of known structure that we are able to use the method to investigate compounds whose structures have not been determined. In this paper we present some ¹²⁷I Mössbauer results for complexes **1**. Data for related phenyl-iodine molecules are included for comparison with earlier literature results and the structures of the compounds examined, where known.

Experimental Section

Iodobenzene and potassium iodide were reagent grade commercial samples and were used without purification. Iodobenzene dichloride,¹⁹ iodosylbenzene (iodosobenzene),²⁰ and iodoxybenzene²¹ were made by literature procedures. The thermally unstable complexes, **1-Cl** and **1-Br**, were prepared from the corresponding XMn^{III}TPP (X = Cl, Br) derivatives and iodosylbenzene as described elsewhere.⁷ ¹²⁷I Mössbauer spectra were recorded on equipment that has already been described.¹⁵ The spectra were computer fitted with a program which

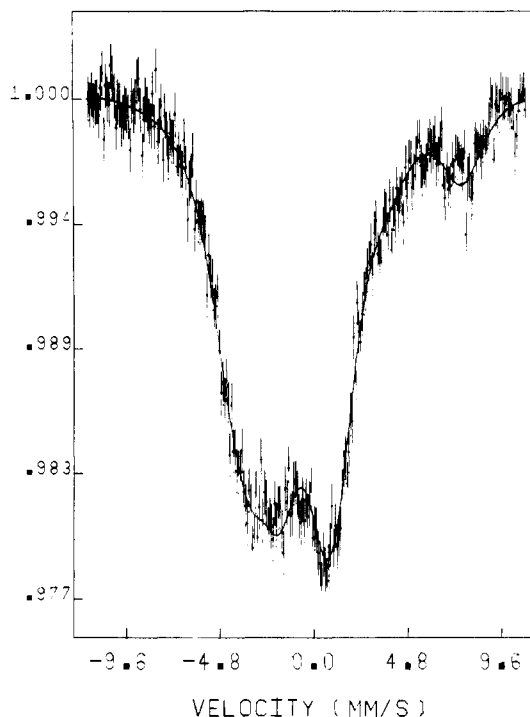


Figure 1. ¹²⁷I Mössbauer spectrum of C₆H₅I recorded at 4.2 K.

incorporated full transmission integral procedures.²² All isomer shifts are quoted with respect to KI as zero isomer shift.²³

Results and Discussion

There still remain a number of possibilities for the interaction between the iodosylbenzene moiety and the Mn porphyrin moiety in complexes **1** that are compatible with all previously reported spectral data.⁷ The iodosylbenzene unit could be bound to the Mn atom through the oxygen atom in a number of possible geometries or, less likely, bound to the Mn atom through the iodine atom. These possibilities each dictate different molecular environments for the iodine atom and hence different ¹²⁷I Mössbauer parameters. A change in iodine oxidation state and/or coordination number will affect the parameters; thus, it was necessary to record ¹²⁷I Mössbauer spectra for some phenyl derivatives of iodine in which the iodine oxidation states are different, as well as for complexes **1**. The data are summarized in Table I.

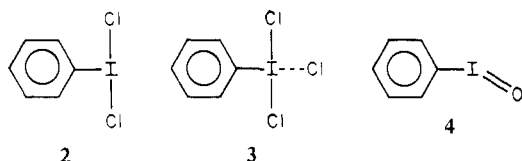
For comparison purposes we have included data reported by Ehrlich and Kaplan.¹³ In general the agreement between the earlier isomer shifts and ours is quite good. However for iodobenzene we find a much smaller quadrupole coupling

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constant than that reported earlier.¹³ The reason for this discrepancy is not apparent, since our spectrum, Figure 1, and the previously published¹³ spectrum appear to be the same. Perhaps the difference lies in the fitting procedures used. Our fitting method used full transmission integral procedures in the spectral analysis, and this has been demonstrated to be important in those cases where the various spectral lines are not completely resolved.²⁴ The previous workers do not appear to have used transmission integral procedures, and this could account for the differences between the two sets of data. It is obvious from this spectrum, Figure 1, and to be expected, that the quadrupole coupling constant is negative. This indicates that there has been a removal of p electrons from the iodine on forming the phenyl-iodine bond. For $C_6H_5IO_2$ we find a more negative isomer shift and a more positive quadrupole coupling constant than Ehrlich and Kaplan,¹³ though the differences can probably be attributed to the difficulties discussed above since the quadrupole coupling constant is small and the peaks are poorly resolved. It has been shown that there is only one type of iodine environment in $C_6H_5IO_2$ that has been described as being intermediate between AX_3E and AX_3E_2 .²⁵

Apart from C_6H_5I , all of the other compounds in Table I have positive coupling constants. Positive quadrupole coupling constants have been observed for those compounds that have four ligands bonded to an iodine atom in a nearly planar arrangement.^{15,16} In these molecules there are two nonbonding pairs of electrons, one above and one below the plane of the atoms bonded to iodine. The quadrupole coupling constants reported here have values between those for species such as $[ICl_4^-]$ (3097 MHz), I_2Cl_6 (3028 MHz), and $[ICl_2^+][SbF_6^-]$ (3066 MHz)^{15,16} and those for $[(C_6H_5)_2IX]_2$ ($X = Cl$ (2044 MHz), Br (1970 MHz), I (1951 MHz)).¹⁶ These intermediate values are the result of there being only one phenyl group directly bonded to the iodine, rather than the four-halogen coordination, as in I_2Cl_6 , or the two-phenyl-two-halogen coordination, as in $[(C_6H_5)_2IX]_2$, the phenyl group being less effective at withdrawing electron density from the iodine than is a halogen atom. One might infer from these trends that the phenyl-iodine(III) compounds examined here have a similar geometrical arrangement, i.e., four ligands in a plane with nonbonding electron pairs above and below this plane. Ehrlich and Kaplan¹³ have interpreted their Mössbauer results for $C_6H_5ICl_2$ in terms of the T-shaped arrangement **2**, but it



is clear from the X-ray measurements²⁶ that there is an additional halogen contact to complete the trapezoidal coordination about iodine, as in **3**. This rather nicely accounts for the observed positive quadrupole coupling constant, with the large asymmetry parameter ($\eta = 0.7$) reflecting the different iodine-chlorine interactions.

The other iodine(III) compounds have quadrupole coupling constants of similar magnitudes and therefore, one might conclude, a similar iodine environment. Unfortunately this AX_4E_2 ($A = I$; $X = \text{ligand}$; $E = \text{nonbonding electron pair}$) type geometry²⁷ is not correct for $C_6H_5I(O_2CCH_3)_2$. Alcock et al.²⁸ have shown that phenyliodine(III) diacetate has a

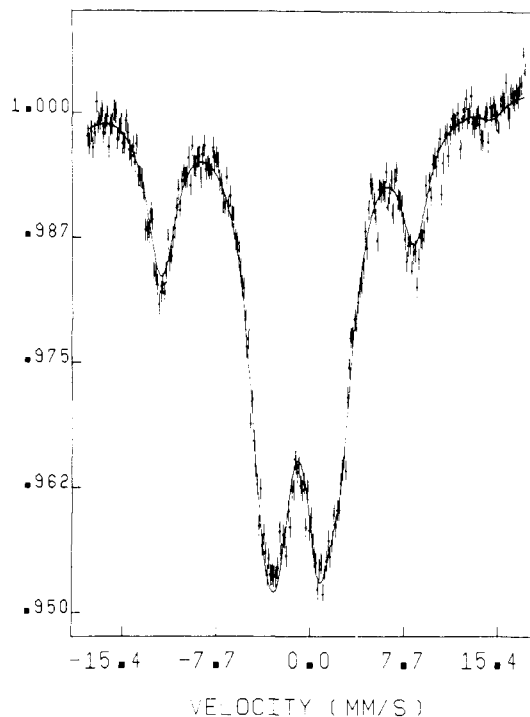


Figure 2. ^{127}I Mössbauer spectrum of $C_6H_5I(O_2CCH_3)_2$ at 4.2 K.

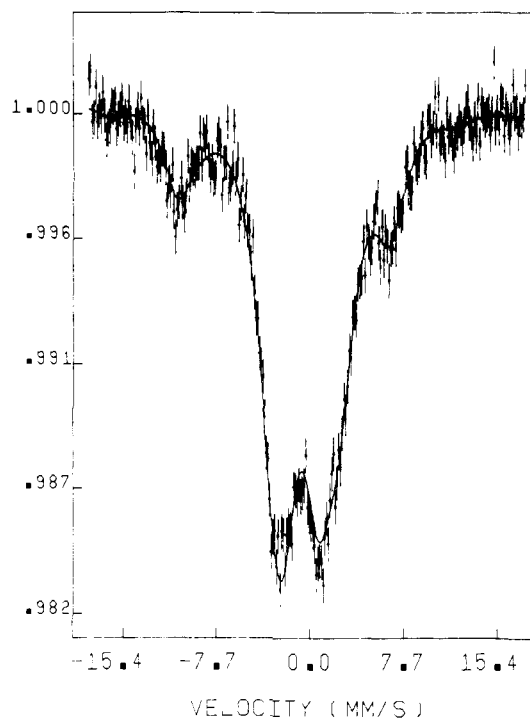


Figure 3. ^{127}I Mössbauer spectrum of **1-Br** at 4.2 K.

primary geometry about iodine of the familiar T shape, but there are additional oxygen contacts in the same plane, which results in a distorted pentagonal-bipyramidal arrangement with the nonbonding electron pairs at the apices. Alcock and co-workers²⁸ have described the two additional long iodine-oxygen interactions as arising from overlap of the $C-I \sigma^*$ orbital with two oxygen atoms in a three-center type of interaction. This different arrangement, to that of $C_6H_5ICl_2$, explains the more negative isomer shift and the much higher asymmetry parameter ($\eta = 0.81$) that we observe. This large η value has

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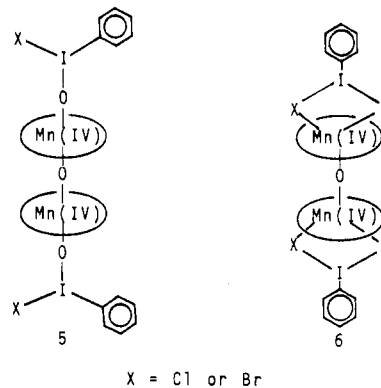
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a dramatic effect on the appearance of the Mössbauer spectrum (Figure 2), which is becoming more symmetrical; for $\eta = 1$, the spectrum would be symmetrical.¹⁰

The structure of iodosylbenzene, C_6H_5IO , has not been determined, but because of the positive value of the coupling constant, iodosylbenzene cannot have the angular structure **4**. There must be additional iodine-oxygen contacts that are sufficiently strong so that the nonbonding electron pairs on iodine are forced into positions perpendicular to the bonding interactions, as is found in $C_6H_5ICl_2$ and $C_6H_5I(O_2CCH_3)_2$. In these latter two cases, four and five bonding interactions are present, respectively, but we have recently reported a case, $[I_4^{2+}]$, where only three strong interactions to iodine are necessary to produce a positive quadrupole coupling constant.^{18,29} The smaller asymmetry parameter that we observe for C_6H_5IO , compared to that for $[I_4^{2+}]$, indicates a somewhat higher iodine axial symmetry.

Reaction of C_6H_5IO with the manganese porphyrins does not produce a dramatic change in the iodine Mössbauer parameters though the observed changes are significant. We can rule out oxidation of the iodine from the III to V state since in $C_6H_5IO_2$ the I(V) has a more negative isomer shift, a much smaller quadrupole coupling constant, and a very small asymmetry parameter compared to I in C_6H_5IO . A direct iodine-manganese interaction can be eliminated since this would utilize one of the iodine nonbonding electron pairs and the iodine environment would have to be described as being AX_3E ($A = I$; $X = \text{ligand}$; $E = \text{nonbonding electron pair}$). Such an iodine geometry would result in a negative sign for the quadrupole coupling constant rather than the positive sign that we observe. The iodosylbenzene-porphyrin complexes, **1**, then retain iodine coordination similar to that of the free iodosylbenzene. However, whereas in free C_6H_5IO the additional iodine interactions must be with oxygen, in the por-

phyrin complexes this is unlikely. The significantly smaller quadrupole coupling constants in the porphyrin complexes would be consistent with the replacement of a secondary I---O interaction in $[C_6H_5IO]_x$ by an I---X interaction. The lower electronegativity of X relative to that of O would reduce the mismatch between the electron density in the x - y plane and the z direction that contains the nonbonding electron pairs. One also notes an increase in the value of the asymmetry parameter on complexation, and again this can be rationalized in terms of the lower axial symmetry caused by replacement of an I---O interaction by an I---X contact. The ¹²⁷I Mössbauer and other spectral data are most compatible with a structure for the alkane-activating complexes (**1**) of **5**, although structures with seven-coordinate Mn atoms such as **6** cannot be ruled out.



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Registry No. **1-Cl**, 85185-72-4; **1-Br**, 85185-73-5; **2**, 932-72-9; **4**, 536-80-1; C_6H_5I , 591-50-4; $C_6H_5IO_2$, 696-33-3; $C_6H_5I(O_2CCH_3)_2$, 3240-34-4; KI, 7681-11-0; I, 14362-44-8.

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