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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

VIII *. DIACETYLFERROCENE–METAL HALIDE COMPLEXES

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Summary

Mössbauer parameters are reported for a series of diacetylferrocene (DAF) complexes with Lewis acids ($AlCl_3$, $SnCl_4$, $FeCl_3$, $TiCl_4$). All the complexes show a lowering of quadrupole splitting (QS) relative to uncomplexed DAF. The decreases in QS are discussed in terms of their stereochemistry and related to previous findings in the ferrocenyl ketone series. ^{119}Sn Mössbauer data are presented for $SnCl_4 \cdot DAF$.

Introduction

Ferrocene complexes with $HgCl_2$ [2] and $HAlCl_4$ [3] possess high values of quadrupole splitting (QS) as a result of Fe–Hg and Fe–H bonding. The large QS values associated with these compounds have led us to propose a bonding scheme in which the Fe atom donates charge to the Hg or H atoms via $d_{x^2-y^2}$ and d_{xy} orbitals (e_{2g}). Similar proposals have accounted for Mössbauer data obtained on a range of ferrocene carbenium ions [4,5]. In Mössbauer studies on ferrocenyl ketones [6] small QS values relative to ferrocene resulted. These are explained in terms of charge withdrawal from the ring-based orbitals, thus altering charge in $3d_{xz}$ and $3d_{yz}$ Fe orbitals and resulting in a modified electronic environment at the Fe nucleus. We have explained the low QS values of [1]ferrocenophanes [1] in terms of withdrawal of electrons from e_1 ligand-based orbitals by overlap with appropriate d orbitals on the bridging heteroatom. Since the degree of ring tilting is of particular relevance to these postulated bonding schemes, we have continued to examine the ferrocene literature for compounds in which ring tilt may be significant.

Diacetylferrocene has been reported to react with a number of metal chlorides to give adducts in which the carbonyl functions on the ferrocene moiety are bridged by

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the metal chloride [7,8]. Such complexes containing Al, Sn, and Ti have been characterised. We report here results of Mössbauer studies on these compounds as well as studies on a similar complex formed by reaction of diacetylferrocene with $FeCl_3$.

Results and discussion

Diacetylferrocene itself has a quadrupole splitting [9,10] of 2.15 mm s^{-1}. That this is smaller than the value for ferrocene is due to the acetyl groups withdrawing electron density from the ring-based orbitals (e_1) modifying the symmetry of the electron environment about the iron atom. To withdraw electron density in this fashion the acetyl groups have to be coplanar with the ferrocene rings, to ensure maximum overlap of π orbitals. In the parent molecule the acetyl moieties are nearly diametrically opposed [11].

In all the metal complexes studied, the *QS* values are smaller than those of diacetylferrocene (Table 1). The proposed structures of the Al and Sn adducts for the 1/1 M/Fe (M = Al, Sn) complexes have the metal (M) binding to both carbonyl oxygen atoms. Such bonding could displace the oxygen atoms from the plane of the cyclopentadienyl ring and would be expected to diminish π overlaps with the rings, effectively increasing electron density in the rings and manifesting itself as an increase in *QS* in the Mössbauer spectrum. However, this is not observed.

Assuming metal–oxygen distances of about 2.0 Å for a *cis* configuration, a ring tilt of about 5° would be necessary to accommodate the coordinated metal. Alternatively, the carbonyls could twist out of the Cp plane. A twist angle of about 10° would achieve the same stereochemistry about the metal as the above mentioned ring tilt. Comparison of the ν(C=O) bands for the monoacetyl- and diacetyl-$SnCl_4$ adducts is instructive. In the case of the former no ring tilt or carbonyl twist is necessary, and values of 1538 and 1563 cm^{-1} of the symmetric and antisymmetric carbonyl stretching frequency were observed indicating very substantial through-

TABLE 1

^{57}Fe MÖSSBAUER PARAMETERS FOR THE DIACETYL COMPLEXES AT 80 K

	Isomer shift (*IS*) (mm s^{-1})	*QS* (mm s^{-1})	ΔQS [a] (mm s^{-1})	Linewidth, half width at half height (mm s^{-1})
$Fe(CpCOCH_3)_2$	0.54(1)	2.15(1)	–	0.13(1)
(DAF)	0.53(1) [b]	2.15(1) [b]	–	
$AlCl_3 \cdot$DAF	0.51(1)	2.07(2)	0.08	0.16(1)
$SnCl_4 \cdot$DAF [c]	0.55(1)	2.08(1)	0.07	0.15(1)
$FeCl_3 \cdot DAF \cdot H_2O$	0.53(1)	2.10(1)	0.05	0.14(1)
	0.39(1)	c.a.0		0.28(1)
$TiCl_4 \cdot$DAF	0.52(1)	2.10(1)	0.05	0.14(1)
$2TiCl_4 \cdot$DAF	0.51(1)	2.04(1)	0.11	0.15(1)

[a] $\Delta QS = QS(\text{DAF}) - QS(\text{MCl}_n \cdot \text{DAF})$. [b] Ref. 9. [c] ^{119}Sn Mössbauer parameters for $SnCl_4 \cdot$DAF: *IS* 0.37(1) mm s^{-1}, *QS* 0.0 mm s^{-1}, relative to SnO_2.

conjugation to the tin atom. For the diacetyl complex both frequencies were increased (1544 and 1574 cm^{-1}) which supports the carbonyl twist effect, reducing the through-conjugation.

The $AlCl_3$ and $SnCl_4$ complexes with diacetylferrocene both show similar *QS* values (2.07, 2.08 mm s^{-1}, respectively), representing a reduction of about 0.07 mm s^{-1} from the parent. This compares with the observed reduction of 0.05 mm s^{-1} for monoprotonated diacetylferrocene [6] where the proton is thought to hydrogen bond between the two carbonyl functions. For the extreme case where both carbonyls are protonated a massive decrease in *QS* has been observed to a value of 1.78 mm s^{-1} [6]. In view of the infrared evidence presented above, the reduction in *QS* in the $AlCl_3$ and $SnCl_4$ complexes is probably due to electron withdrawal via e_1 orbitals by the metal and not due to ring tilt effects. The comparatively small twist angle between the carbonyl and Cp planes would still allow substantial π overlap.

The formation of these compounds could involve the presence of both *cis* and *trans* oxygen at the Al and Sn atoms. The ^{119}Sn Mössbauer spectrum, however, shows no quadrupole splitting and so this would suggest the bonding of the oxygen is *cis*. A *trans* bonding would distort the ferrocene environment in such a way as to open the rings, and bring the chlorine substituents rather close to the Fe. Alternatively if the acetyl groups were staggered whilst maintaining parallel planar rings, steric crowding would still occur.

We have previously postulated that the lowering of *QS* for [1]ferrocenophanes was due to $d\pi$–$d\pi$ overlap of the e_1 ferrocene orbitals with the appropriate *d* orbitals on the hetero atom (P, Si) [1]. For the complexes described in this paper, the large Fe–metal distances preclude any such interaction.

In the case of titanium complexes, the 1/1 adduct is said to bind to only one carbonyl [7]. This material has a *QS* of 2.10 mm s^{-1} which compares well with that of protonated acetylferrocene [6]. In contrast the 2/1 adduct has a structure in which both carbonyls are bonded to a titanium atom and the two titanium atoms are linked by two chlorine bridges.

The *QS* for this material is 2.04 mm s^{-1} (ΔQS 0.11 mm s^{-1} Table 1) and is the result of electron withdrawal via both Ti atoms. The above structure can be achieved without perturbing the coplanarity of the Cp rings. The ΔQS is considerably lower than that for the diprotonated diacetylferrocene (ΔQS 0.36 mm s^{-1}) indicating much weaker charge withdrawal.

The last complex of the group is perhaps the most interesting of all. Usually when $FeCl_3$ is introduced into a solution containing ferrocene, oxidation of the ferrocene occurs and $[FeCl_3]^-$ is produced. Here, no such oxidation has occurred. Such behaviour has been reported for the reaction of diacetylferrocene with silver tetrafluoroborate [12].

For the $FeCl_3$ complex complete electron transfer does not occur. Either the Fe–Fe distance is too great, or the oxidation potential of the ferrocenyl iron is greater than that of the iron atom at the other site. For this complex a small *QS* is observed for the ferrocene site suggesting the Fe^{III} binds to diacetylferrocene in a similar manner to $SnCl_4$. The sixth position in the octahedral Fe^{III} environment is taken up by one water molecule. The line width of the Mössbauer spectrum for this Fe^{III} site is 0.279 mm s^{-1} which, though large, is much smaller than that of $FeCl_3 \cdot 6H_2O$.

It is apparent from the order of *QS* values that they are independent of Lewis acid strength [13,14]. The $AlCl_3$ and $SnCl_4$ adducts have identical *QS* values within experimental error and yet the acceptors themselves lie at opposite ends of the Lewis acidity range.

Experimental

The Mössbauer spectra were recorded and fitted using methods previously reported [1–6]. The microanalysis was performed by Manchester University Microanalytical Department.

$Fe(C_5H_4COCH_3)_2$ was prepared by the method reported by Rosenblum and Woodward [15]. All other reagents and solvents were used as supplied. $DAF \cdot SnCl_4$, $DAF \cdot AlCl_3$ $DAF \cdot TiCl_4$ and $DAF(TiCl_4)_2$ were prepared by the methods previously reported [7,8,16].

Preparation of DAF · FeCl₃

$Fe(C_5H_4COCH_3)_2$ (0.25 g, 0.93 mmol) was dissolved in 50 ml CCl_4 and placed in a 3-necked flask equipped with a dropping funnel and flushed with dry N_2. Anhydrous $FeCl_3$ (0.15 g, 0.93 mmol) was dissolved in 50 ml diethyl ether, flushed with N_2 and placed in the dropping funnel. The solution was then added over a period of five minutes to the stirred diacetylferrocene solution under N_2. A black precipitate was immediately produced. After a further fifteen minutes stirring, the flask was transferred to a dry box, the solution filtered, and the Mössbauer spectrum of a sample of the black powder isolated was obtained. The clear filtrate indicated a virtually quantitative reaction. The complex was extremely hygroscopic. $Fe(C_5H_5COCH_3)_2 \cdot FeCl_3 \cdot H_2O$. Found: C, 36.8; H, 3.5; Cl, 23.1; Fe, 24.25. $C_{14}H_{18}Cl_3Fe_2O_3$ calcd. C, 37.5; H, 3.6; Cl, 23.7; Fe, 24.9%.

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