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Mössbauer studies on ferrocene-containing cryptands and their metal complexes

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Abstract

⁵⁷Fe Mössbauer spectroscopy has been used to study a range of ferrocene-containing cryptands and macrocycles. The host-guest interactions for a series of metal cation complexes with a ferrocene-containing cryptand have been investigated. For group II cations, correlation between the ⁵⁷Fe isomer shift and the Fe–Mⁿ⁺ internuclear distance within the cryptate, has been observed.

Introduction

In recent years we have synthesised [1,2] a range of ferrocene-containing macrocycles and cryptands 1–6, whose structures are shown in Fig. 1. We have studied these compounds and their host-guest complexes with metal cations in solution by NMR spectroscopy [3], cyclic voltammetry [4], and electronic absorption spectroscopy [5]. In this paper we report the study of these compounds and some metal cation complexes in the solid state by use of ⁵⁷Fe Mössbauer spectroscopy.

Experimental

Mössbauer spectra were obtained at 80 K with a Cryophysics MS 103 microprocessor-controlled spectrometer operating in the constant acceleration mode. Samples were loaded under nitrogen. The spectrometer was calibrated by means of the metallic iron spectrum, and isomer shifts are quoted relative to iron metal. The source was ⁵⁷Co/Rh (25 mCi, Amersham International Plc.). Gamma photons were detected with an Ar/CH₄ proportional counter, and experimental spectra fitted by

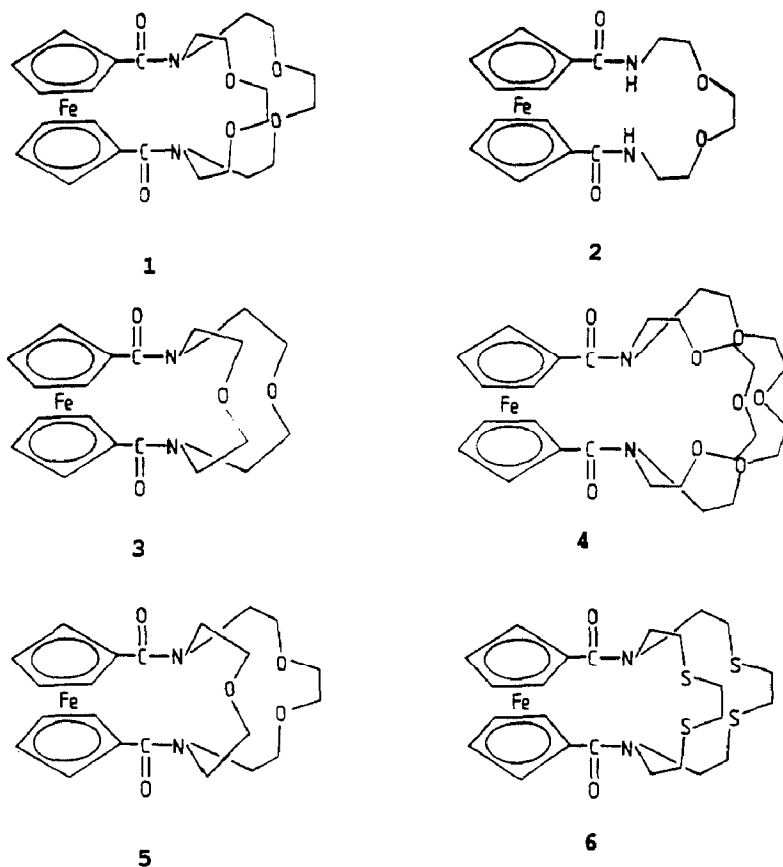


Fig. 1. Ferrocene-containing cryptands.

standard non-linear least squares procedures. A typical Mössbauer spectrum is shown in Fig. 2.

NMR spectra were recorded on a Bruker WM 250 instrument.

Synthesis

1,1'-(1,7,10,16-tetrathia-4,13-diazacyclooctadecane-4,13-diyl)dicarbonylferrocene (6). Solutions of 1,1'-bis(chlorocarbonyl)ferrocene (0.38 g) in benzene (100 ml) and

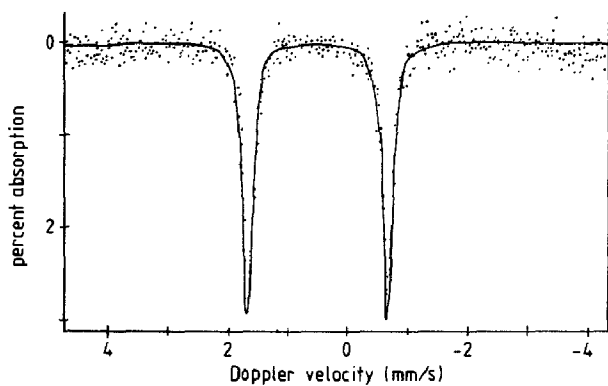


Fig. 2. The ^{57}Fe Mössbauer spectrum of the complex (Sr^{2+} (1)).

of triethylamine (0.35 ml) mixed with 1,7,10,16-tetrathia-4,13-diazacyclooctadecane (0.37 g; prepared as in ref. 6) in benzene (100 ml) were added dropwise separately and simultaneously during 2 h to vigorously stirred benzene (100 ml, 70 °C) under nitrogen. The mixture was stirred at 70 °C for a further 3 h, then allowed to cool, and the solids were removed by filtration. The orange filtrate was evaporated to dryness under reduced pressure to yield an orange semi-crystalline oil, which was chromatographed on silica with dichloromethane (98%)/methanol (2%) as eluent. The orange band was collected, evaporated to dryness under reduced pressure, and triturated with diethyl ether. The resultant orange powdery product was recrystallised from dichloromethane to yield the compound **6** (0.17 g, 25%, m.p. 223 °C). Found: C, 50.75; H, 5.80; N, 4.81. $C_{24}H_{32}N_2O_2S_4Fe$ calcd.: C, 51.06; H, 5.71; N, 4.96%. M^+ 564. δ ($CDCl_3$); 1H NMR, 2.89 (s, br, 16H, SCH_2), 3.74 (s, br, 8H, NCH_2), 4.44 (s, br, 4H, FcH) and 4.61 (s, br, 4H, FcH); ^{13}C NMR, 30.5 (br, SCH_2), 32.1 (br, SCH_2), 33.1 (SCH_2), 48.8 (br, NCH_2), 50.0 (br, NCH_2), 71.1 (FcC), 72.5 (FcC), 80.5 (ipso- FcC) and 170.0 ($C=O$).

1,1'-(1,7,10,13,19,22-hexaoxa-4,16-diazacyclotetracosane-4,16-diyldicarbonyl)ferrocene (4). The cryptand **4** was synthesised by a procedure analogous to that used for **6** above but from 1,7,10,13,19,22-hexaoxa-4,16-diazacyclotetracosane. Work up and purification as above gave the orange product **4** (16%, m.p. 136–139 °C). Found: C, 56.80; H, 6.86; N, 4.62. $C_{28}H_{40}N_2O_8Fe$ calcd.: C, 57.10; H, 6.85; N, 4.76%. M^+ 588. δ (toluene- d_8); ^{13}C NMR, 49.3 (NCH_2), 50.2 (NCH_2), 70.6 (OCH_2), 71.1 (OCH_2), 73.5 (FcC), 75.3 (FcC), 79.0 (ipso- FcC) and 169.7 ($C=O$).

Preparation of the cryptates. The cryptand **1** (200 mg, 0.4 mmol) was dissolved in dichloromethane (2 ml) and a solution of an alkaline earth metal perchlorate or transition metal tetrafluoroborate (0.4 mmol) in acetonitrile (1 ml) was added dropwise during 5 min. These operations were conducted under a rigorously dry atmosphere with solvents dried by standard procedures. The resultant solution was stirred for 30 min, after which diethyl ether was added to precipitate the complex. The dark orange powder was filtered off and recrystallised from acetonitrile/diethyl ether until satisfactory analyses for a 1/1 complex were achieved. Microanalytical data have been reported previously [3] for all the metal complexes studied, except for the manganese complex. For the 1/1 complex formed from **1** and $Mn(BF_4)_2$, the analysis was: Found C, 40.31; H, 4.77; N, 4.01. $C_{29}H_{32}FeN_2O_6$ calcd.: C, 39.54; H, 4.43; N, 3.84%. The cryptates are hygroscopic and were stored under nitrogen.

Results and discussion

All of the samples gave a well resolved quadrupole doublet in the Mössbauer spectrum, consistent with a distorted electronic environment around the ^{57}Fe nucleus. The isomer shift (IS) and quadrupole splitting (QS) data for the cryptands and macrocycle studied are given in Table 1. The variation in IS values through compounds **1–6** is not significant. Earlier studies [7] on bridged ferrocenes have suggested that both IS and QS parameters are sensitive to distortions within the ferrocene moiety, e.g. to changes in Fe–C bond distances. The crystal structures of **1** and **5** are known [8,9], and reveal cyclopentadienyl interplane ring tilt dihedral angles of 0.4 and 3.2° respectively. However the isomer shifts for the compounds **1** and **5** are the same. The variation in QS is perhaps more significant, but the QS values do not exhibit the suggested correlation with the variations in isomer shift [7].

Table 1

⁵⁷Fe Mossbauer data for the ferrocene-containing cryptands and their metal cryptates (at 80 K)

Compound	IS (mm s ⁻¹ , ±0.01)	QS (mm s ⁻¹ , ±0.02)
1	0.48	2.36
2	0.49	2.37
3	0.45	2.34
4	0.49	2.34
5	0.48	2.30
6	0.50	2.31
{Be ²⁺ (1)}	0.52	2.35
{Mg ²⁺ (1)}	0.52	2.33
{Ca ²⁺ (1)}	0.53	2.38
{Sr ²⁺ (1)}	0.55	2.39
{Ba ²⁺ (1)}	0.56	2.36
{Zn ²⁺ (1)}	0.58	2.34
{Mn ²⁺ (1)}	0.55	2.30

^a The Mn²⁺ cryptate is progressively oxidised in the γ -beam to yield a green product with a singlet Mössbauer absorption LS 0.31 mm s⁻¹, indicative of Fe³⁺. Although hygroscopic, the cryptate is not oxidised on contact with the atmosphere.

Similarly, for the metal cation complexes with **1**, the QS values display no discernable trend. It has been claimed previously [10] that for substituted ferrocenes a linear correlation exists between QS values and the redox potential of the Fe²⁺/Fe³⁺ couple. We have previously demonstrated unambiguously [4] a linear correlation between the redox couple for the complexes of **1** with the cations of Group II and the reciprocal of the ionic radius of the complexed cation. However, in the present study no correlation of QS values with ionic radius was evident. For the metal cation cryptates of **1**, the QS values are within experimental error the same as the QS value of **1** alone.

For all the complexes {M²⁺(**1**)}, the value of IS is larger than that for the free cryptand **1**. This may be rationalised in that coordination of the metal cation by **1** results in a decrease of *s*-electron density at the ⁵⁷Fe nucleus. We have shown previously [5], and IR studies have confirmed [3], that metal coordination by the cryptand **1** involves primarily the amide carbonyls. Carbonyl O-atom coordination to the metal cation centre results in net electron withdrawal from the ferrocene centre, and hence results in lower *s*-electron densities at the ⁵⁷Fe nucleus, i.e. in increased IS values.

Although changes between individual complexes are small, the values of IS for the complexes {M²⁺(**1**)} increase with increasing ionic radius of the Group II metal cations. The ionic radii for the series Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ are 27, 72, 100, 118 and 135 pm, respectively [11], and for the four larger cations a good linear correlation between the IS of the complex and the inverse of the ionic radius of the cation is seen. Previous studies [3] have indicated that for 1/1 stoichiometry the complexation is primarily through the carbonyls of the cryptand, and furthermore that these carbonyls rotate *cis* to hold the metal guest cation in the plane between the planes of the ferrocene rings. Thus model studies permit us to calculate the distance between the guest cation and the Fe nuclei centres, to yield a value *R* for the total inter-nuclear distance which takes into account both the guest cation radius and the molecular framework of the host within which it is held. For the complex

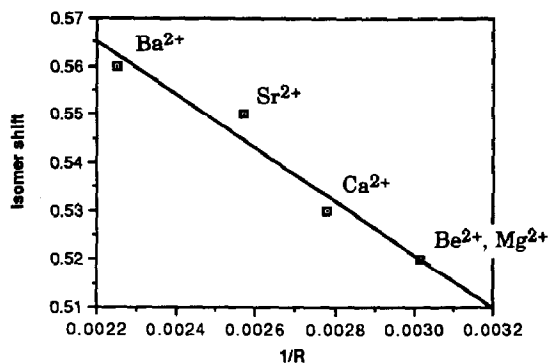


Fig. 3. Plot of ^{57}Fe isomer shift, IS (in mm s^{-1}), for the complex $\{\text{M}^{2+}(\mathbf{1})\}$ versus the reciprocal of the Fe- M^{2+} internuclear distance, R^{-1} (in pm^{-1}).

$\{\text{M}^{2+}(\mathbf{1})\}$ in the series Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} , the values for the total internuclear distances of Fe- M^{n+} , R , are 331.5, 331.5, 359.9, 388.9 and 444.2 pm, respectively. A plot of IS versus $1/R$ exhibits good linearity and is shown in Fig. 3.

The value of $1/R$ essentially reflects the electric potential experienced at the ^{57}Fe nucleus as a consequence of the proximity of the doubly charged coordinated cation. For the Group II metal cations, those of larger ionic radius consequently have lower charge densities. It can be seen that for higher values of R , the IS of the complex increases, i.e. there is a decrease in s -electron density at the ^{57}Fe nucleus. This may be ascribed to the interpenetration shielding effect of the Fe d -orbitals on the s -electron density at the ^{57}Fe nucleus. The greater the charge density in the complexed cation M^{2+} , the more polarised are the occupied Fe d -orbitals (d_{xy} , $d_{x^2-y^2}$) and the less shielding they afford the ^{57}Fe nucleus toward the Fe valence s -electrons. As a result, the isomer shift increases in the Group II series of complexes along with increasing cation ionic radius, and the IS value is largest for Ba^{2+} and smallest for Be^{2+} .

We have noted previously [5] that for the complexes $\{\text{M}^{2+}(\mathbf{1})\}$ in acetonitrile solution, the lowest energy $d-d$ visible absorption band centred at ca. 460 nm shows a trend toward increasing extinction coefficient with decreasing ionic radius of the Group II cations. This may reflect the increasing polarisation of the Fe centred d_{xy} , $d_{x^2-y^2}$ (HOMO) orbitals with increase in charge density in the complexed Group II metal cations. These UV/vis studies also permitted determination of complexation stoichiometries and their equilibrium constants. Parallel IR studies [3] confirmed these solution equilibria, and also demonstrated that in the solid state it is the complex of 1/1 host/guest stoichiometry that is present. The solid complexes for both the IR and these Mössbauer studies were prepared by the same procedure.

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